forests

MDPI

Article

The Application of Oak Bark Powder as a Filler for Melamine-Urea-Formaldehyde Adhesive in Plywood Manufacturing

Radosław Mirski, Jakub Kawalerczyk *, Dorota Dziurka, Joanna Siuda and Marek Wieruszewski

Department of Wood-Based Materials, Faculty of Forestry and Wood Technology,
Poznań University of Life Sciences, Wojska Polskiego 38/42, 60-627 Poznań, Poland;
rmirski@up.poznan.pl (R.M.); dorota.dziurka@up.poznan.pl (D.D.); joanna.siuda@up.poznan.pl (J.S.);
marek.wieruszewski@up.poznan.pl (M.W.)
* Correspondence: jakub.kawalerczyk@up.poznan.pl

Received: 5 November 2020; Accepted: 24 November 2020; Published: 25 November 2020

Abstract: The woodworking industry generates a great amount of bark which has not yet found a wider industrial application. None of the previously conducted research has considered oak bark application (which is one of the most often processed wood species in Poland) as a filler for wood adhesives. Moreover, no studies have determined the properties of bark containing melamine-urea-formaldehyde resin (MUF), which increasingly replaces pure urea-formaldehyde adhesives. Thus, the aim of the study was to determine the possibility of grinded oak bark application as a filler for MUF adhesive in plywood manufacturing. The chemical composition of oak bark was evaluated. Properties of liquid resins, such as viscosity, gel time, pH, and solid content, were determined. Chemical interaction between the filler and resin was assessed with using Fourier-transform infrared (FTIR) spectroscopy. Plywood panels manufactured using MUF adhesive filled with different bark concentrations (10%, 15%, 20%, 25%) were tested in terms of such properties as formaldehyde release and bonding quality. Studies have shown an improvement in liquid resin properties. The course of FTIR spectra did not explain the chemical interaction between the polymer and the filler. The addition of oak bark at a concentration of 15% made it possible to produce plywood panels characterized by reduced formaldehyde release and improved bonding quality.

Keywords: oak bark; filler; plywood; melamine-urea-formaldehyde adhesive

1. Introduction

The compositions of adhesive mixtures in plywood production must contain proper additives, usually called fillers or extenders [1]. In practice, the difference between a filler and an extender is that an extender usually refers to proteinaceous or amylaceous substances. The aim of the filler introduction can be to adjust the rheological properties of an adhesive, to reduce the costs of raw material, to limit the resin penetration into the porous veneer surface, or to reduce the formaldehyde (HCHO) emissions, etc. [2–4]. In general, fillers are nonvolatile, insoluble substances which can be divided into lignocellulosic (furfural residues, nutshell, rice husk, coconut shell) and inorganic (attapulgite clay, bentonite clay, sepiolite) substances [5,6]. Moreover, the concept of using bark particles as a filler has become increasingly investigated in recent years.

In the production process, the woodworking industry generates considerable amounts of various types of waste, such as shreds, sawdust, bark, etc. [7]. Pasztory et al. [8] estimated that the annual global amount of produced bark is approximately 359,111,200 m^3. Most of this resource is used for landscaping or utilized as a fuel. The great potential of bark in many applications results from its high content of various organic compounds, such as tannins, mainly ellagitannins, and gallotannins. Moreover, bark is also a source of catechin, gallocatechin, flavonoids, proanthocyanidin [9–12]. The recycling of wood waste has a great potential in wood-based materials manufacturing [13].

Many ongoing studies are studying the possibility of manufacturing environmentally friendly boards. Tudor et al. [14] highlighted the possibility of manufacturing a decorative board characterized by lowered formaldehyde release based on larch bark. Sahin and Arslan [15] concluded that red pine bark is a suitable material for particleboard production. In their opinion, the continuing research on using forest residues in wood-based materials production can mitigate raw wood shortages. Medved et al. [16] determined the possibility of using spruce and pine bark as materials for particleboard manufacturing. Studies have shown that the substitution of wood particles with bark significantly lowered the formaldehyde release. Moreover, bark can also be used for manufacturing bark-based thermal insulation and sound insulation panels [17,18].

The replacement of wheat or rye flour with bark in the adhesive formulation has recently become an interesting idea for waste management. According to Sellers [19], on the West Coast of the United States, alder bark has been applied as a filler in plywood production since around 1962. Réh et al. [20] investigated the possibility of using beech bark as an additive for urea-formaldehyde (UF) resin. Studies have shown that the introduction of a maximum share of the bark particles caused a decrease in heat transfer by 11% during the plywood pressing process. According to authors, the more water is absorbed by the bark particles, the less water can penetrate the veneer. Consequently, their thermal conductivity decreases. Moreover, the addition of a proper amount of bark resulted in the possibility of obtaining plywood panels characterized by good mechanical properties and bonding quality exceeding the value required by the standard. The formaldehyde emissions significantly decreased in comparison with the variant with the technical flour applied as the extender. Ružiak et al. [21] confirmed that the incorporation of beech bark can reduce the harmful HCHO emissions and improve the mechanical properties of manufactured plywood. The authors also pointed out that this kind of research can make it possible to find an effective way to utilize woodworking industry waste. The partial replacement of wheat flour with chestnut and fir bark powders also resulted in the decrease of free formaldehyde content and the increase in plywood's mechanical properties [22]. Furthermore, Marbun et al. [23] studied the effect of benuang (*Octomeles sumatrana BN*) and duabanga (*Duabanga moluccana DB*) barks as the filler for phenol-formaldehyde resin (PF) in glulam production. On the basis of the presented results, it was concluded that the bark of both species can be effectively used as a modifier of PF adhesive. The experimental fillers made it possible to obtain glulams with high bonding strength and low delamination. Polymeric diphenylmethane diisocynate (pMDI) adhesives have been steadily gaining popularity in wood bonding due to their moisture tolerance and fast cure [24,25]. Polymeric diphenylmethane diisocynate bonds filled with western red cedar bark showed a comparable dry shear strength and improved wet shear strength compared with nonmodified pMDI. Moreover, the experimental bark-filled adhesive formed more consistent and thicker bond lines [26].

As outlined above, the disintegrated bark has a good potential to be applied as an environmentally friendly, inexpensive filler in plywood production. Despite a number of studies concerning the use of bark as a filler for UF, PF, and pMDI adhesives, no studies have examined the effect on the properties of MUF bond lines in plywood manufacturing. MUF adhesives increasingly replace pure UF adhesives, especially in applications for kitchen, floor, and structural purposes. Moreover, no studies have concerned the incorporation of oak bark. However, according to Wieruszewski and Mikołajczak [27], oak wood is listed among the most often processed wood species in Poland. The aim of the current study was to investigate the effect of the addition of oak bark particles to MUF resin on the properties of manufactured plywood.

2. Materials and Methods

2.1. Materials

A commercially available MUF resin was purchased from AkzoNobel (Amsterdam, Netherlands) with the following characteristics: Viscosity of 1000–2500 mPa × s, solids content of 64% to 69%, pH from 9.5 to 10.7, density of 1.27 g/m^3, and gel time of 63 s at 100 °C. Ammonium nitrate (20 wt%) was used as a catalyst. The reference variant (prepared for comparison purpose according to industrial formulations) contained a rye flour, which was obtained from the market, as an extender. The experimental variants contained powder obtained from the bark. The oak (*Quercus robur* L.) bark was purchased from a local sawmill processing oak timber. Plywood was produced using birch (*Betula* L.) veneer sheets with the dimensions of 320 × 320 mm, average thickness of 1.5 mm, average density of 583 kg/m^3, and moisture content of 5% ± 1%.

2.2. Methods

The oak bark provided for this experiment was washed with distilled water to get rid of dirt and mineral particles and was then dried in laboratory oven at 60 °C to a moisture content (MC) of 2 ± 1%. After reaching the assumed MC, the bark was grinded with the use of laboratory mill and sieved with mechanical sieve shaker to obtain a dimensional fraction retained on the screen with a mesh size of 0.315 × 0.315 mm^2, which was selected by the authors as the most effective one in a previously conducted research [28].

The investigations of bark chemical characteristics were conducted in accordance with the widely used methodology. Acid-insoluble lignin content was determined according to the T 222 om-06 standard TAPPI method [29], using 72% sulphuric acid to hydrolyze and solubilize carbohydrates. Extractives soluble in alcohol were determined according to TAPPI method T 204 cm-97 [30]. The determination of cellulose content was conducted using Seifert's method with a mixture of 1,4-dioxane, hydrochloric acid and acetyloacetone [31]. The holocellulose content was determined according to the chlorite method using $NaClO_2$ as a reagent [31]. The acidity was measured using an extract solution made of 100 mL of distilled water boiled with the addition of 3 g of the bark for 30 min [32]. The analyses were repeated in triplicate.

The additives were introduced to the resin in different amounts depending on the variant (Table 1). The reference adhesive mixture containing rye flour as the extender was prepared according to industrial formulations.

Table 1. Compositions of adhesive mixtures.

Variant Label	**Quantity (pbw * per 100 g of Solid MUF Resin)**			
	Oak Bark	**Rye Flour**	**Water**	**Total Solution Weight of Catalyst**
RF-15	0	15	10	3
OB-10	10	0	10	3
OB-15	15	0	10	3
OB-20	20	0	10	3
OB-25	25	0	10	3

* pbw—Parts by weight.

Both reference and bark containing mixtures were stirred mechanically (200 rpm, 60 s) until the proper homogenization level was achieved.

The viscosity and its changes were investigated for 6 h right after mixture preparation with a Brookfield DV-II + Pro viscometer (Middleboro, MA, USA) using spindle no. 5 at 50 rpm. For comparison purposes, the changes in viscosity were also determined for the MUF resin with the addition of the catalyst. The value of the adhesive mixture's pH was determined according to EN 1242 [33], gel time was measured at a temperature of 100 °C according to Polish standard PN-C-89352-3 [34], and solid content was measured according to EN 827 [35].

In order to assess the possible chemical interactions between oak bark and the MUF adhesive, the Fourier-transform infrared spectroscopy (FTIR) was carried out. The bark-filled resin was cured in laboratory oven at 140 °C and grinded using a laboratory mill. The obtained powder, with a dimensional fraction of 0.125×0.125 mm^2, was mixed with KBr at a 1/200 mg ratio. Spectra was registered using a Bruker FT-IR IFS 66/s spectrometer (Bruker, Ettlingen, Germany) with the Fourier transform range of 500–4000 cm^{-1} at the resolution of 4 cm^{-1}, registering 16 scans. The same preparations were conducted for the pure MUF resin without any filler/extender and for the oak bark itself.

Three-layer plywood was produced under laboratory conditions. The adhesive-containing additives were applied on the surface of the external veneer in the spread rate of 170 g/m^2 right after the resin preparation. The time between the application and the pressing was 10 min. The pressing process was conducted for 4 min at 140 °C with the unit pressure of 1.3 MPa. Three replicate panels were manufactured for all the test groups.

The formaldehyde release was measured by means of Flask method according to EN 717-3 [36], which is a commonly used, low-cost methodology suitable for uncoated wood-based boards [22]. The measurements were conducted initially and after 8 weeks of samples conditioning. In order to determine plywood's bonding quality, the shear strength test was carried out using a Tinus Olsen H10KT testing machine according to EN 314-1 [37]. Samples prepared, as shown in Figure 1, were conditioned for 2 weeks before testing (20 ± 2 °C and 65 ± 1% relative humidity).

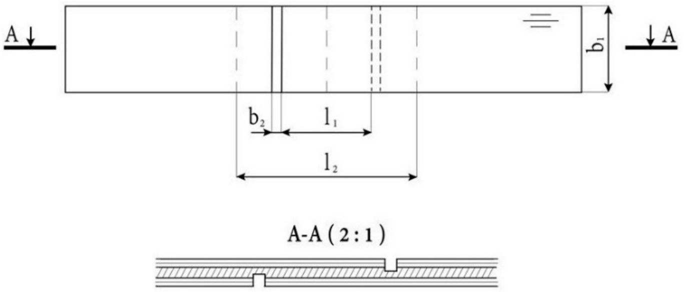


Figure 1. Method of sample preparation for shear strength testing according to EN 314-1 [38] (b_1—25 ± 0.5 mm; b_2—2.5 ± 0.5 mm; l_1—25 ± 0.5 mm; l_2—minimum distance between the grips of the testing machine—50 mm).

Samples were tested after 24 h of soaking in water (20 ± 3 °C) and after pretreatment including boiling in water for 6 h and cooling in water for 1 h (20 ± 3 °C). The assessments of bonding quality involved 12 samples of each variant.

The obtained results were subjected to a multivariate statistical analysis ANOVA. Moreover, the Tukey test on the significance level of $\alpha = 0.05$ was carried out in order to distinguish homogeneous groups using Statistica 13.0 software (StatSoft Inc., Tulsa, OK, USA).

3. Results and Discussion

The overall chemical composition of bark, including main components such as lignin, cellulose, holocellulose, and extractives, is summarized in Table 2.

Table 2. Chemical composition of oak bark (mean value ± standard deviation).

	Lignin (%)	**Extractives (%)**	**Cellulose (%)**	**Holocellulose (%)**	**pH**
Oak bark	50.27 ± 2.17	12.70 ± 0.57	31.60 ± 0.37	45.76 ± 1.26	5.04 ± 0.01

The sum of main constituents exceeded 100% because the presented values were calculated in relation to the wood dry matter due from the imperfection of wet methods, which are commonly used to determine the compositions of lignocellulosic materials [38]. The acidity of oak bark is beneficial, since a pH value of about 4–5 is required to obtain an optimal pressing time for amino resins [2]. In comparison with chemical composition of the mature heartwood of oak (*Quercus* sp.), the bark is characterized by significantly higher lignin and extractive content. Furthermore, wood contains more cellulose and holocellulose than bark [39]. The majority of extractives are phenolic substances characterized by the ability to react with HCHO [40]. Moreover, there are some indicators that lignin also can chemically interact with the formaldehyde [41]. Hence, both the pH and chemical composition makes oak bark a suitable material for application as a filler for MUF resin in plywood manufacturing.

Gel time, solid content, and pH are extensively used as industrial methods for the quality control of amino resins [42]. Table 3 presents the values of the investigated properties.

Table 3. Properties of adhesives mixtures (mean value ± standard deviation).

Variant Label	Gel Time (s)	Solid Content (%)	pH
RF-15	81 ± 1	68.23 ± 0.02	7.7 ± 0.1
OB-10	75 ± 2	65.91 ± 0.06	6.8 ± 0.2
OB-15	71 ± 1	68.38 ± 0.07	6.4 ± 0.1
OB-20	69 ± 1	71.12 ± 0.03	6.4 ± 0.1
OB-25	68 ± 3	72.42 ± 0.06	6.3 ± 0.2

On the basis of the presented results, it was found that the MUF resin was characterized by a longer gel time than pure UF resin [28], which confirms observations by Zhang et al. [43] that the addition of melamine has an adverse effect on UF resin curing behavior. However, the addition of oak bark had a positive effect on the gel time. The shortening of curing time probably resulted from the acidity of the introduced bark powder since, in the case of amino resin, a polycondensation process significantly depends on the pH level [44]. The water extracts of the added rye flour had a pH level of 7.01 ± 0.01, which is a significantly higher value than when it comes to the oak bark. Solid contents were comparable in variants containing the same amounts of fillers or extenders regardless of their type. The increased solid content in the variants labeled as OB-20 and OB-25 resulted from the increased share of filling particles in the adhesives and can also lead to gel time reduction. Overall, the introduction of oak bark powder led to improvement in the liquid resin's properties. The shortening of gel time is particularly important from the technological point of view, since a pressing cycle should be as short as possible to reduce the energy consumption [45,46].

Viscosity is an essential parameter in plywood manufacturing [47]. The time-viscosity dependences of the reference mixture and the bark-containing ones are shown in Figure 2.

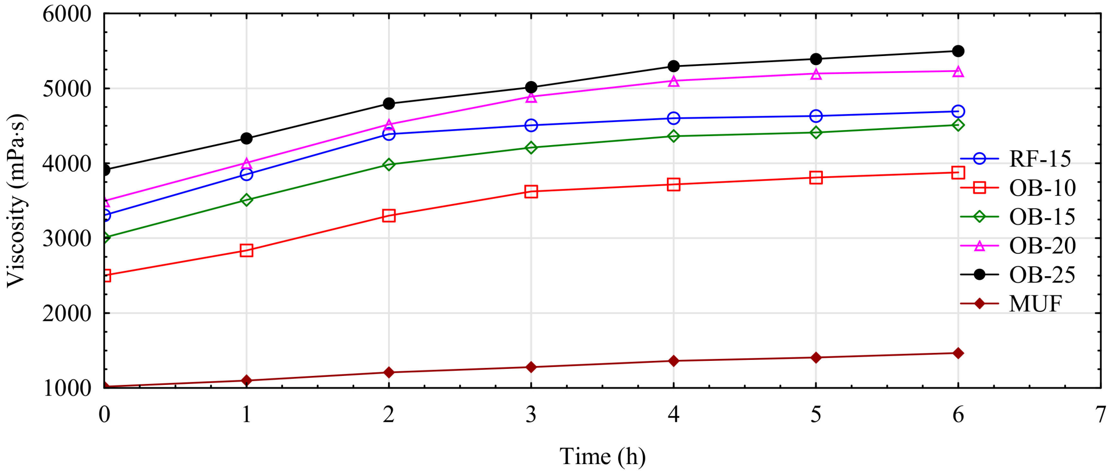


Figure 2. Changes in viscosity measured for 6 h.

The course of a viscosity changes can be considered as similar to linear regardless of the additive type. The viscosity values were constantly increasing during the measurements because of the progressive polycondensation reactions. The mixtures containing the fillers or the extenders reached much higher values since the additives accelerated the resin curing time and they continuously absorbed water during the measurements. When compared to the variants containing the filler/extender concentration of 15%, the viscosity of the pure MUF adhesive was characterized by about 2000 mPa × s and 3000 mPa × s lower values initially and after 6 hours, respectively. The variant labeled as OB-15 reached a comparable value to the reference mixture, as in the case of studies concerning both birch and beech bark additions to the UF resin [20,28]. The variant containing oak bark was characterized by decreased viscosity by 9% and 4% measured initially and after 6 hours, respectively, in comparison with a mixture filled with the same amount of the rye flour extender. The molecules of the proteins contained in the composition of rye flour link with each other to form the webs and, consequently, increase the viscosity slightly more effectively than the oak bark [5]. As the amount of the introduced bark particles increased to 20 pbw and 25 pbw, the viscosity also increased when compared to the reference formulation. However, all of the prepared mixtures, regardless of the additive type and their concentration, obtained rheological properties, which resulted in easy application on the veneer surface. The easy application means that the adhesive can be evenly spread and it does not flow into the cavities of the wavy veneer during the application. An improper level of viscosity can considerably affect the bonding quality of plywood [48]. The resin, having unsuitable rheological properties, penetrates into a porous surface of the veneer during both the application and the pressing. Consequently, the amount of adhesive remaining on the veneer is insufficient to ensure a high strength of the bond lines [19]. Moreover, viscosity levels that are too high indicate a lack of water, which participates in crosslinking reactions. This can lead to a significant shortening in the resin's pot life [20]. In addition to the influence on mechanical properties, Li et al. [49] stated the hypothesis that an unsuitable viscosity level can also affect the formaldehyde release. According to the authors, low viscosity makes it easier for resin to penetrate into the cell lumens, which increases the formaldehyde emissions.

Figure 3 presents the FTIR spectra of A—oak bark, B—MUF resin with the addition of oak bark (OB-15), and C—pure MUF resin. The spectra of bark containing adhesives had the same course regardless of the amount of the introduced additive. The FTIR spectroscopy was carried out in order to determine the chemical bonding between the filler and the polymer matrix. Since the transmittance spectra of modified and nonmodified resins mostly revealed the functional groups of MUF resin, the study did not clearly explain the interaction between the bark particles and the adhesive.

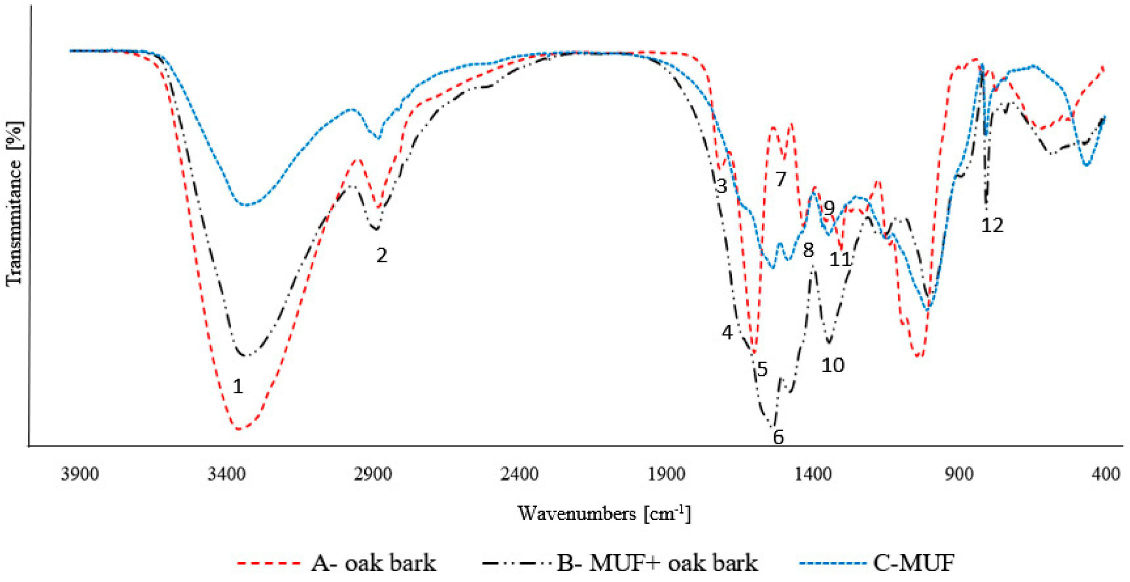


Figure 3. Fourier-transform inrafred (FTIR) spectra of oak bark, modified resin and nonmodified resin.

A peak around 3400 cm^{-1} (Figure 3, 1), corresponding to OH vibration groups, was observed in each of the three spectra. Moreover, in the frame of the B and C spectra, the peak also corresponded to the stretching vibration of the N-H bonds [50]. A band at 2926–2932 cm^{-1} (Figure 3, 2) was detectable for A, B, and C spectra and corresponded to C-H stretching vibrations. The oak bark spectra was a source of many peaks because of its complex chemical composition. As a result, the spectra labeled as A showed C=O stretching vibrations at 1736 cm^{-1} (Figure 3, 3) [51], which can be attributed to hemicellulose [52–55]. Sample A presented peaks at 1619 cm^{-1} (Figure 3, 5) and 1516 cm^{-1} (Figure 3, 7), which corresponded to C=O stretching attributed to lignin and C=C aromatic skeletal stretching of the lignin, respectively [52–54]. The peaks attributed to lignin and hemicellulose, namely C=C, the C-H bond, and O-H in the plane deformation, were observed at 1448 cm^{-1} (Figure 3, 8) [52–54,56–58]. The bands at 1371 cm^{-1} (Figure 3, 9) and 1317 cm^{-1} (Figure 3, 11) were recognized as characteristic cellulose peaks attributed to the C-H deformation vibration and CH_2 rocking vibration [53,54,57–59]. A very weak peak at 1650 cm^{-1} (Figure 3, 4) corresponded to the scissoring mode of NH_2. The peak present in spectra B and C, where the MUF resin was applied. The band at 1555 cm^{-1} (Figure 3, 6) was only detected in the sample where the MUF resin was used (spectra B and C). According to Luo et al. [50], this band was caused by secondary amides (-CONH-). The B and C sample peak at 1359 cm^{-1} (Figure 3, 10) was assigned to the C-N stretching of CH_2-N [52]. Bands from triazine ring of melamine occurred at 812 cm^{-1} (Figure 3, 12) [50,60].

Formaldehyde is the simplest aldehyde classified as a known carcinogen [61]. Due to increasing public awareness, legislation concerning the permissible amount of formaldehyde has become stricter. Applied resins are the main sources of HCHO release from wood-based materials, such as fiberboard, particleboard, and plywood. Since formaldehyde-containing wood adhesives are sources of a great amount of formaldehyde emissions, there are many ongoing studies concerning their modification to reduce the harmful emissions [62,63]. The results of formaldehyde release, tested initially and after 8 weeks of samples conditioning, are presented in Figure 4.

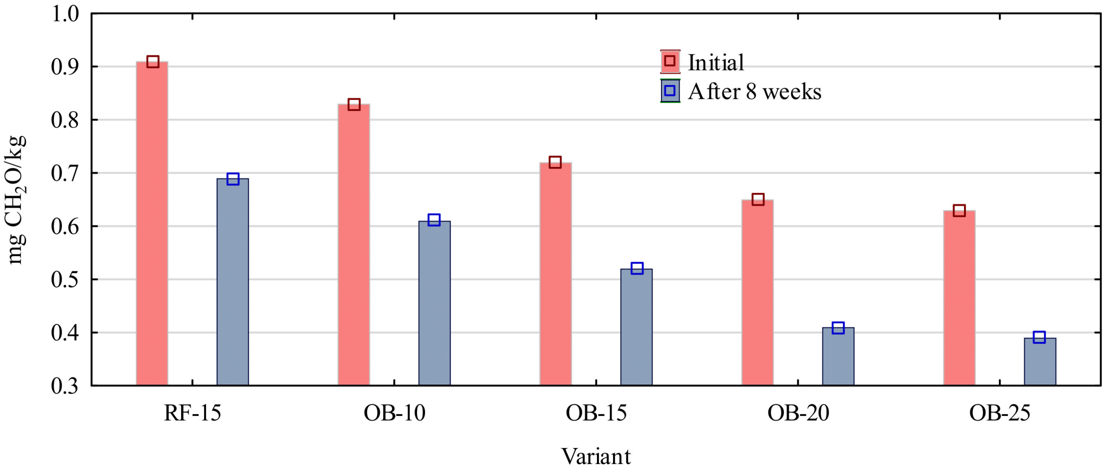
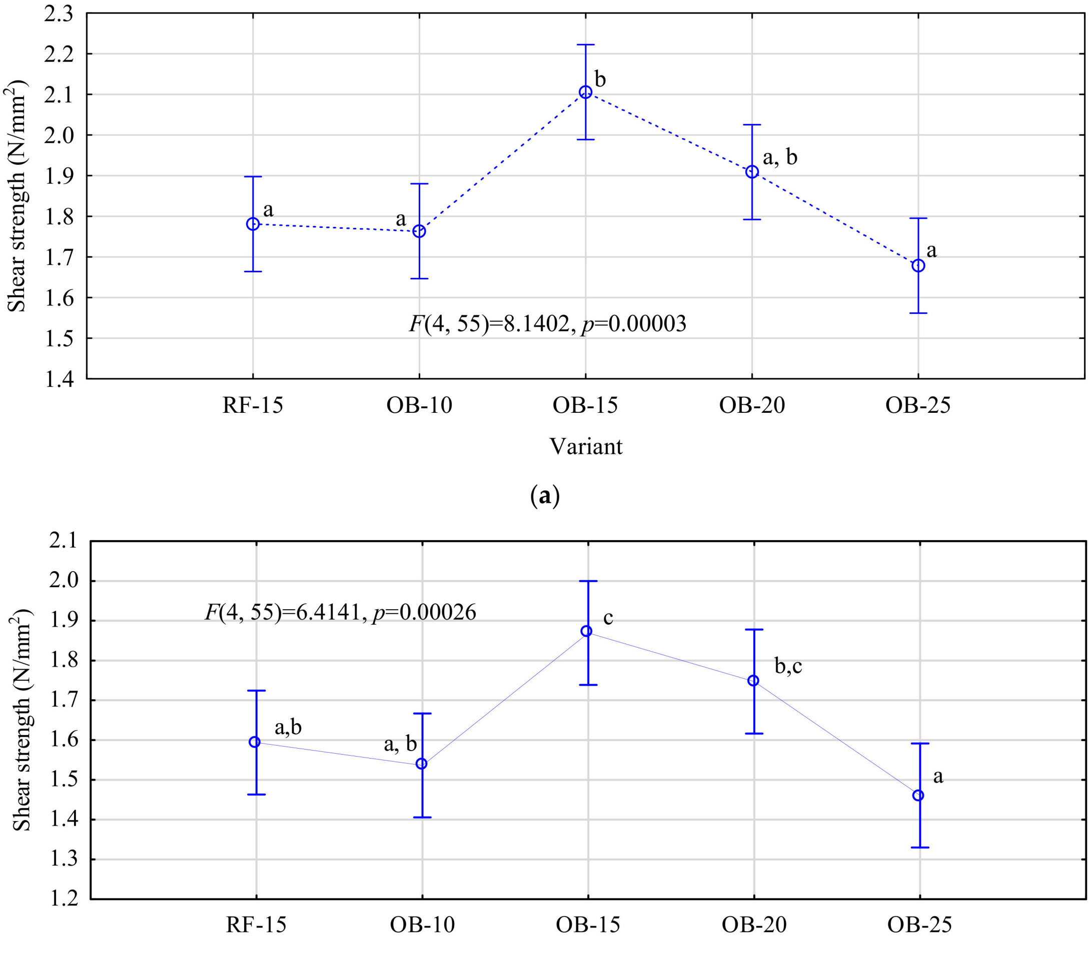


Figure 4. Formaldehyde release from plywood.

The formaldehyde emissions, initially measured and after 8 weeks, experienced a 9% and 31% decrease in comparison with the reference variant, respectively. The results of measurements conducted after 8 weeks of samples conditioning revealed the same tendency. The reduction in the amount of HCHO emissions arises from the high amount of tannins in the bark's chemical composition. Condensed polyflavonoid tannins can easily undergo reactions with formaldehyde under acidic and alkaline conditions due to their phenolic nature [64]. Formaldehyde reacts with tannins and produces a polymerization through the methylene bridge linkages to reactive positions of the flavonoid molecules [28]. Moreover, in addition to the polyflavonoids, lignin is also capable of reacting with formaldehyde in the acidic medium. According to Van Der Klashorst and Strauss [65], the formed benzylic alcohols react with a lignin model compound and form methylene-linked dimers. The ability of bark to reduce the formaldehyde release makes it a suitable material for application as a bio-based scavenger. The addition of beech bark resulted in a 46%–74% decrease in HCHO emissions [20], the introduction of birch bark led to a 17% reduction [28], and the application of fir and chestnut bark caused a decrease of approximately 11% [22]. However, it is hard to compare the effect of various bark species since the formaldehyde release depends strongly on the pressing parameters and the type of applied resin.

The results of the shear strength test, which is a commonly used indicator of adhesive behavior in plywood [66], are presented in Figure 5.



(**a**)

(**b**)

Figure 5. Shear strength of plywood tested (**a**) after soaking and (**b**) after boiling; (a,b,c letters mark homogenous groups in the HSD Tukey test; F(x,y) = z,p where: *F*—Roland Fisher's test method, x—number of degrees of freedom, y—number of tests, z—value of F test, *p*—probability level).

Studies have shown that the effect of oak bark addition on the bonding quality of manufactured plywood depends on the share of filling additives. The variant containing the least amount of bark was characterized by shear strength levels similar to the reference plywood, probably because the viscosity level was too low. The most notable reinforcing effect (18%) was observed in the case of the OB-15 variant. Further, the addition of 20 pbw of oak bark also resulted in a slight but statistically significant increase when compared to the reference plywood. The improvement was probably caused by a chemical reaction between the tannins and formaldehyde. Radical groups of tannins react with methylol groups and formaldehyde, which consequently leads to the increase of crosslinked structure [67].

However, the addition of 25 pbw led to a deterioration in bonding quality. The oak bark added in that major amount absorbs most of the water which participates in forming a three-dimensional crosslinking network structure [20]. Moreover, levels of viscosity that are too high may indicate the occurrence of agglomerates made of filling particles. The fillers act as carriers of stress along the glue line, and concentrations of stress at certain points can lead to a weakening of bonding strength [66]. The shear strength of all manufactured plywood, regardless of the additive quantity and type, exceeded the value of 1.0 N/mm^2 required by EN 314-2 [68]. Furthermore, the obtained results correspond with the results of previous research on the introduction of beech, fir, chestnut, and walnut bark to UF adhesives [20,22].

4. Conclusions

- The chemical composition of oak bark makes it a suitable material for application as a filler for MUF adhesive.
- The addition of oak bark considerably affected the properties of the MUF resin by influencing the time-viscosity dependence, reducing the gel time, and decreasing the pH. The bark-containing adhesive mixture was characterized by slightly lower viscosity in comparison with the variant containing the rye flour at the same concentration. Hence, the oak bark introduction had a positive effect on the liquid resin properties.
- The FTIR spectroscopy did not explain the chemical interaction between the MUF adhesive and the oak bark.
- Since the free formaldehyde content is an important health and environmental issue, it is beneficial that the introduction of oak bark to the adhesive mixture led to a significant reduction in the amount of harmful emissions released from the plywood.
- Adding the proper amount of oak bark (15 g) to the MUF adhesive mixture resulted in the improvement of bonding quality in comparison with adding the adhesive prepared with the rye flour as the extender.
- In summary, we found that oak bark, which is considered to be unused woodworking industry waste, has the potential to become a filler for MUF resins and, simultaneously, a bio-based formaldehyde scavenger.

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

Funding: This research was funded by the National Centre for Research and Development, BIOSTRATEG3/344303/14/NCBR/2018. The authors are grateful for the support of the Ministry of Science and Higher Education program “Regional Initiative of Excellence” in the years 2019–2022, Project No. 005/RID/2018/19.

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

References

1. Kawalerczyk, J.; Dziurka, D.; Mirski, R.; Trociński, A. Flour Fillers with Urea-Formaldehyde Resin in Plywood. *BioResources* **2019**, *14*, 6727–6735. [CrossRef]
2. Bekhta, P.; Sedliačik, J.; Kačík, F.; Noshchenko, G.; Kleinová, A. Lignocellulosic waste fibers and their application as a component of urea-formaldehyde adhesive composition in the manufacture of plywood. *Eur. J. Wood Wood Prod.* **2019**, *77*, 495–508. [CrossRef]
3. Dukarska, D.; Czarnecki, R. Fumed silica as a filler for MUPF resin in the process of manufacturing water-resistant plywood. *Eur. J. Wood Wood Prod.* **2016**, *74*, 5–14. [CrossRef]
4. Sellers, T.; Miller, G.D.; Smith, W. Tool wear properties of five extender/fillers in adhesive mixes for plywood. *For. Prod. J.* **2005**, *55*, 27–31.

5. Hogger, E.M.; van Herwijnen, H.W.G.; Moser, J.; Kantner, W.; Konnerth, J. Systematic assessment of wheat extenders in condensation resins for plywood production: Part I—Physico-chemical adhesive properties. *J. Adhes.* **2020**, 1–19. [CrossRef]
6. Kawalerczyk, J.; Dziurka, D.; Mirski, R.; Szentner, K. Properties of Plywood Produced with Urea-Formaldehyde Adhesive Modified with Nanocellulose and Microcellulose. *Drvna Industrija* **2020**, *71*, 61–67. [CrossRef]
7. Cichy, W. Combustion of plywood waste in a low-power boiler. *Drewno* **2012**, *55*, 21–36.
8. Pasztory, Z.; Mohácsiné, I.R.; Gorbacheva, G.; Börcsök, Z. The utilization of tree bark. *BioResources* **2016**, *11*, 7859–7888. [CrossRef]
9. Fernández de Simón, B.; Cadahía, E.; Conde, E.; García-Vallejo, M.C. Low molecular weight phenolic compounds in Spanish oak woods. *J. Agric. Food Chem.* **1996**, *44*, 1507–1511. [CrossRef]
10. Jordão, A.M.; Ricardo-da-Silva, J.M.; Laureano, O. Ellagitannins from Portuguese oak wood (*Quercus pyrenaica* Willd.) used in cooperage: Influence of geographical origin, coarseness of the grain and toasting level. *Holzforschung* **2007**, *61*, 155–160. [CrossRef]
11. Scalbert, A.; Monties, B.; Favre, J.-M. Polyphenols of Quercus robur: Adult tree and in vitro grown calli and shoots. *Phytochemistry* **1988**, *27*, 3483–3488. [CrossRef]
12. Skrypnik, L.; Grigorev, N.; Michailov, D.; Antipina, M.; Danilova, M.; Pungin, A. Comparative study on radical scavenging activity and phenolic compounds content in water bark extracts of alder (*Alnus glutinosa* (L.) Gaertn.), oak (*Quercus robur* L.) and pine (Pinus sylvestris L.). *Eur. J. Wood Wood Prod.* **2019**, *77*, 879–890. [CrossRef]
13. Ihnat, V.; Lübke, H.; Balbercak, J.; Kuňa, V. Size reduction downcycling of waste wood. Review. *Wood Res.* **2020**, *65*, 205–220. [CrossRef]
14. 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]
15. Sahin, T.H.; Arslan, B.M. Weathering performance of particleboards manufactured from blends of forest residues with Red pine (*Pinus brutia*) wood. *Maderas. Cienc. Y Tecnol.* **2011**, *13*, 337–346. [CrossRef]
16. Medved, S.; Gajšek, U.; Tudor, E.M.; Barbu, M.C.; Antonović, A. Efficiency of bark for reduction of formaldehyde emission from particleboards. *Wood Res.* **2019**, *64*, 307–316.
17. Tudor, E.M.; Dettendorfer, A.; Kain, G.; Barbu, M.C.; Réh, R.; Krišťák, L'. Sound-Absorption Coefficient of Bark-Based Insulation Panels. *Polymers* **2020**, *12*, 1012. [CrossRef]
18. Pásztory, Z.; Mohácsiné, I.R.; Börcsök, Z. Investigation of thermal insulation panels made of black locust tree bark. *Constr. Build. Mater.* **2017**, *147*, 733–735. [CrossRef]
19. Sellers, T. *Plywood and Adhesive Technology*; CRC Press: Boca Raton, CA, USA, 1985; ISBN 978-0-8247-7407-3.
20. Réh, R.; Igaz, R.; Krišťák, L'.; Ružiak, I.; Gajtanska, M.; Božíková, M.; Kučerka, M. Functionality of beech bark in adhesive mixtures used in plywood and its effect on the stability associated with material systems. *Materials* **2019**, *12*, 1298. [CrossRef]
21. Ružiak, I.; Igaz, R.; Krišťák, L.; Réh, R.; Mitterpach, J.; Očkajová, A.; Kučerka, M. Influence of urea-formaldehyde adhesive modification with beech bark on chosen properties of plywood. *BioResources* **2017**, *12*, 3250–3264. [CrossRef]
22. Aydin, I.; Demirkir, C.; Colak, S.; Colakoglu, G. Utilization of bark flours as additive in plywood manufacturing. *Eur. J. Wood Wood Prod.* **2017**, *75*, 63–69. [CrossRef]
23. Marbun, S.D.; Wahyudi, I.; Suryana, J.; Nawawi, D.S. Bonding strength of benuang and duabanga glulams using their barks as phenol formaldehyde-filler. *Appl. Adhes. Sci.* **2020**, *8*, 1–12. [CrossRef]
24. Dziurka, D.; Mirski, R. Properties of Liquid and Polycondensed UF Resin Modified with pMDI. *Drvna Industrija* **2014**, *65*, 115–119. [CrossRef]
25. Mirski, R.; Derkowski, A.; Dziurka, D.; Wieruszewski, M.; Dukarska, D. Effects of Chip Type on the Properties of Chip–Sawdust Boards Glued with Polymeric Diphenyl Methane Diisocyanate. *Materials* **2020**, *13*, 1329. [CrossRef]
26. Chen, H.; Yan, N. Application of Western red cedar (Thuja plicata) tree bark as a functional filler in pMDI wood adhesives. *Ind. Crop. Prod.* **2018**, *113*, 1–9. [CrossRef]
27. Wieruszewski, M.; Mikołajczak, E. The influence of selected factors on the share of by-products in sawmill processing. *Ann. Wars. Univ. Life Sci. SGGW. For. Wood Technol.* **2018**, *104*, 540–548.

28. Mirski, R.; Kawalerczyk, J.; Dziurka, D.; Wieruszewski, M.; Trociński, A. Effects of Using Bark Particles with Various Dimensions as a Filler for Urea-formaldehyde Resin in Plywood. *BioResources* **2020**, *15*, 1692–1701.
29. Technical Association of the Pulp and Paper Industry. *Acid Insoluble Lignin in Wood and Pulp, T 222 cm-06*; Technical Association of the Pulp and Paper Industry: New York, NY, USA, 2006; p. 5.
30. Technical Association of the Pulp and Paper Industry. *Solvent Extractives of Wood and Pulp, T 204 cm-97*; Technical Association of the Pulp and Paper Industry: New York, NY, USA, 2007; p. 12.
31. Browning, B.L. *The Chemistry of Wood*; Interscience Publishers: New York, NY, USA, 1967.
32. Nemli, G.; Ayan, E.; Ay, N.; Tiryaki, S. Utilization potential of waste wood subjected to insect and fungi degradation for particleboard manufacturing. *Eur. J. Wood Wood Prod.* **2018**, *76*, 759–766. [CrossRef]
33. *EN 1245. Adhesives—Determination of pH*; European Committee for Standardization: Brussels, Belgium, 2011.
34. *PN-C-89352-3. Kleje-Kleje do Drewna-Metody Badań—Oznaczanie Czasu Żelowania*; Polish Committee for Standardization: Warsaw, Poland, 1996.
35. *EN 827. Adhesives: Determination of Conventional Solids Content and Constant Mass Solids Content*; European Committee for Standardization: Brussels, Belgium, 2005.
36. *EN 717-3. Wood-Based Panels–Determination of Formaldehyde Release–Part 3: Formaldehyde Release by the Flask Method*; European Committee for Standardization: Brussels, Belgium, 1996.
37. *EN 314-1. Plywood–Bond quality–Test Methods*; European Committee for Standardization: Brussels, Belgium, 2004.
38. Kusiak, W.; Majka, J.; Ratajczak, I.; Górska, M.; Zborowska, M. Evaluation of Environmental Impact on Selected Properties of Lime (*Tilia Cordata* Mill.) Wood. *Forests* **2020**, *11*, 746. [CrossRef]
39. Babiński, L.; Fabisiak, E.; Zborowska, M.; Michalska, D.; Prądzyński, W. Changes in oak wood buried in waterlogged peat: Shrinkage as a complementary indicator of the wood degradation rate. *Eur. J. Wood Wood Prod.* **2019**, *77*, 691–703. [CrossRef]
40. Tanase, C.; Mocan, A.; Coșarcă, S.; Gavan, A.; Nicolescu, A.; Gheldiu, A.-M.; Vodnar, D.C.; Muntean, D.-L.; Crișan, O. Biological and chemical insights of beech (*Fagus sylvatica* L.) bark: A source of bioactive compounds with functional properties. *Antioxidants* **2019**, *8*, 417. [CrossRef] [PubMed]
41. Malutan, T.; Nicu, R.; Popa, V.I. Contribution to the study of hydroxymetylation reaction of alkali lignin. *BioResources* **2008**, *3*, 13–20.
42. Gonçalves, M.; Paiva, N.T.; Ferra, J.M.; Martins, J.; Magalhães, F.D.; Carvalho, L. Chemical composition of melamine-urea-formaldehyde (MUF) resins assessed by near-infrared (NIR) spectroscopy. *Int. J. Adhes. Adhes.* **2019**, *93*, 102327. [CrossRef]
43. Zhang, J.; Wang, X.; Zhang, S.; Gao, Q.; Li, J. Effects of melamine addition stage on the performance and curing behavior of melamine-urea-formaldehyde (MUF) resin. *BioResources* **2013**, *8*, 5500–5514. [CrossRef]
44. Lei, H.; Frazier, C.E. Curing behavior of melamine-urea-formaldehyde (MUF) resin adhesive. *Int. J. Adhes. Adhes.* **2015**, *62*, 40–44. [CrossRef]
45. Mirski, R.; Dziurka, D.; Łęcka, J. Potential of shortening pressing time or reducing pressing temperature for plywood resinated with PF resin modified using alcohols and esters. *Eur. J. Wood Wood Prod.* **2011**, *69*, 317–323. [CrossRef]
46. Kawalerczyk, J.; Siuda, J.; Mirski, R.; Dziurka, D. Hemp Flour as a Formaldehyde Scavenger for Melamine-Urea-Formaldehyde Adhesive in Plywood Production. *BioResources* **2020**, *15*, 4052–4064. [CrossRef]
47. Kawalerczyk, J.; Dziurka, D.; Mirski, R.; Siuda, J. The reduction of adhesive application in plywood manufacturing by using nanocellulose-reinforced urea-formaldehyde resin. *J. Appl. Polym. Sci.* **2020**, e49834. [CrossRef]
48. Hong, M.-K.; Park, B.-D. Effect of urea-formaldehyde resin adhesive viscosity on plywood adhesion. *J. Korean Wood Sci. Technol.* **2017**, *45*, 223–231. [CrossRef]
49. Li, X.; Li, J.; Li, J.; Gao, Q. Effect of Sepiolite Filler in Malamine-Urea-Formaldehyde Resin on the Properties of Three-ply Plywood. *BioResources* **2015**, *10*, 6624–6634. [CrossRef]
50. Luo, J.; Zhang, J.; Luo, J.; Li, J.; Gao, Q. Effect of Melamine Allocation Proportion on Chemical Structures and Properties of Melamine-Urea-Formaldehyde Resins. *BioResources* **2015**, *10*, 3265–3276. [CrossRef]
51. Suzuki, T.; Deguchi, K.; Kimura, Y.; Funaki, M.; Yamada, T. Hydrogasification of wood for high heating-value gas production X: Effect of pretreatment of Japanese oak bark by HNO_3 oxidation on subsequent iron-catalyzed hydrogasification. *J. Wood Sci.* **1999**, *45*, 76–83. [CrossRef]

52. Naumann, A.; Navarro-González, M.; Peddireddi, S.; Kües, U.; Polle, A. Fourier transform infrared microscopy and imaging: Detection of fungi in wood. *Fungal Genet. Biol.* **2005**, *42*, 829–835. [CrossRef] [PubMed]
53. Ozgenc, O.; Durmaz, S.; Kuştaş, S. Chemical analysis of tree barks using ATR-FTIR spectroscopy and conventional techniques. *BioResources* **2017**, *12*, 9143–9151. [CrossRef]
54. Pandey, K.K. A study of chemical structure of soft and hardwood and wood polymers by FTIR spectroscopy. *J. Appl. Polym. Sci.* **1999**, *71*, 1969–1975. [CrossRef]
55. Popescu, C.-M.; Popescu, M.-C.; Vasile, C. Characterization of fungal degraded lime wood by FT-IR and 2D IR correlation spectroscopy. *Microchem. J.* **2010**, *95*, 377–387. [CrossRef]
56. Mohebby, B. Attenuated total reflection infrared spectroscopy of white-rot decayed beech wood. *Int. Biodeterior. Biodegrad.* **2005**, *55*, 247–251. [CrossRef]
57. Özgenç, Ö.; Durmaz, S.; Boyaci, I.H.; Eksi-Kocak, H. Determination of chemical changes in heat-treated wood using ATR-FTIR and FT Raman spectrometry. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* **2017**, *171*, 395–400. [CrossRef]
58. Pandey, K.K.; Pitman, A.J. FTIR studies of the changes in wood chemistry following decay by brown-rot and white-rot fungi. *Int. Biodeterior. Biodegrad.* **2003**, *52*, 151–160. [CrossRef]
59. Durmaz, S.; Özgenç, Ö.; Boyacı, İ.H.; Yıldız, Ü.C.; Erişir, E. Examination of the chemical changes in spruce wood degraded by brown-rot fungi using FT-IR and FT-Raman spectroscopy. *Vib. Spectrosc.* **2016**, *85*, 202–207. [CrossRef]
60. Reimschuessel, H.K.; McDevitt, N.T. Infrared spectra of some 1, 3, 5-triazine derivatives. *J. Am. Chem. Soc.* **1960**, *82*, 3756–3762. [CrossRef]
61. Salem, M.Z.M.; Böhm, M. Understanding of formaldehyde emissions from solid wood: An overview. *BioResources* **2013**, *8*, 4775–4790. [CrossRef]
62. Antov, P.; Jivkov, V.; Savov, V.; Simeonova, R.; Yavorov, N. Structural Application of Eco-Friendly Composites from Recycled Wood Fibres with Magnesium Lignosulfonate. *Appl. Sci.* **2020**, *10*, 7526. [CrossRef]
63. Antov, P.; Mantanis, G.I.; Savov, V. Development of Wood Composites from Recycled Fibres with Magnesium Lignosulfonate. *Forests* **2020**, *11*, 613. [CrossRef]
64. Jahanshaei, S.; Tabarsa, T.; Asghari, J. Eco-friendly tannin-phenol formaldehyde resin for producing wood composites. *Pigment Resin Technol.* **2012**. [CrossRef]
65. Van Der Klashorst, G.H.; Strauss, H.F. Polymerization of lignin model compounds with formaldehyde in acidic aqueous medium. *J. Polym. Sci. Part A Polym. Chem.* **1986**, *24*, 2143–2169. [CrossRef]
66. Kawalerczyk, J.; Dziurka, D.; Mirski, R.; Siuda, J.; Szentner, K. The Effect of Nanocellulose Addition to Phenol-formaldehyde Adhesive in Water-resistant Plywood Manufacturing. *BioResources* **2020**, *15*, 5388–5401. [CrossRef]
67. Gangi, M.; Tabarsa, T.; Sepahvand, S.; Asghari, J. Reduction of formaldehyde emission from plywood. *J. Adhes. Sci. Technol.* **2013**, *27*, 1407–1417. [CrossRef]
68. *EN 314-2. Plywood-Bond Quality-Requirements*; European Committee for Standardization: Brussels, Belgium, 1993.