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BARK LIQUEFACTION FOR USE IN THREE-LAYER PARTICLEBOARD BONDING


The aim of this study was to evaluate the usefulness of liquefied bark products for panel manufacturing. The research was carried out with the use of waste bark, obtained from a local wood-processing company. Bark fractions were further processed by means of liquefaction. The liquefaction reaction was carried out at elevated temperature using a mixture of solvents from the polyhydroxy alcohol group. Three-layer particleboards based on the liquefied bark were produced. Standard physicochemical and mechanical properties of the boards, such as bending strength, modulus of elasticity, tensile strength and formaldehyde content, were determined. The parameters of the particleboards complied with the requirements of the PN EN 312:2011 standard for interior-general-use boards of type P2 used for indoor equipment elements. It was demonstrated that when melamine-urea-formaldehyde resin was substituted with liquefied bark to an amount of 20%, there was no increase in the formaldehyde content of the boards. All test results were compared with those for standard particleboard bonded with unmodified melamine-urea-formaldehyde adhesive resin.

Keywords: bark, biomass liquefaction, liquefied bark, bio-based adhesives, three-layer particleboard

Introduction

The generation of wood waste is an inseparable part of the processes of wood harvesting, processing and use. Wood waste, both industrial (created during wood processing, primarily in the sawmilling and furniture industries) and post-consumer (originating from used wood products), are regarded on the one hand as a burden on the environment, and on the other as a considerable raw material base.

In 2015 the estimated supply of wood by-products in Poland was 13.0 million m³ (which was more than 32% compared with wood removals) and further growth is anticipated. Potential resources of wood by-products (together with their imports) were estimated at 14.8 million m³, of which bark accounted for 13.1% [Szostak et al. 2016]. Of the total volume of industrial raw material

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used for further processing in Poland in 2016, the potential quantity of bark totalled 3,761,700 m³, of which approximately 2,877,000 m³ was softwood bark and approximately 884,000 m³ was hardwood bark (on the assumption that bark accounts for 10% of gross harvested industrial softwood and 12% of gross harvested industrial hardwood) [Bidzińska et al. 2017]. Approximately 59% of the bark produced in the wood sector is used for energy purposes, and approximately 41% for other purposes, for example in agriculture, horticulture, tanning, and the production of wood accessories [Szostak et al. 2016].

Many scientific centres worldwide are conducting research on new applications of bark. There are many literature reports on its use as, for instance, a bioindicator of environmental quality [Chrzan 2015], a biosorbent of heavy metals [Şen et al. 2015], a corrosion inhibitor for carbon steel [Mendonça Santos et al. 2017], a coating layer for flooring tiles [Tudor et al. 2018], a feedstock in pulp production and biorefinery [Neiva et al. 2016, 2018], and an ingredient of wood adhesives [Feng et al. 2015; Rużiak et al. 2017; Chen and Yan 2018]. However, because of its heterogeneous structure, diverse chemical composition, low strength and dark colour, the valorisation of bark remains a challenge [Feng et al. 2013].

One of the promising applications of waste biomass, including bark, is its liquefaction. Recently, this subject has attracted significant scientific interest [Huang and Yuan 2015; Jiang et al. 2018], which may result from the fact that liquefied wood has a wide spectrum of potential applications. In the manufacture of composite wood products, much importance attaches to the possibility of producing environmentally friendly adhesives, based on renewable natural raw materials, which are an alternative to the commonly used synthetic resins originating from petrochemicals. Moreover, panels manufactured with liquefied wood have recently been evaluated by a prototype expert system developed for quality control and traceability of particleboards. Panels based on liquefied wood were 100% correctly classified at the first level of the expert system with broad classes representing different particleboard manufacturers [Sandak et al. 2018]. Liquefaction has been tested on various lignocellulosic raw materials, including waste materials, such as wood packaging waste [Yuan and Ma 2013], cork [Esteves et al. 2017], moso bamboo [Li et al. 2018] and others.

This study focuses on the liquefaction of bark as a common by-product of roundwood processing. The aim of the study was to convert bark residues by means of liquefaction and to evaluate the usefulness of liquefied bark products for panel manufacturing.

Materials and methods

Tests were carried out on waste bark from the debarking of felled trees, obtained from a local wood-processing company. The bark was cut using a Pallmann flaker with knife position 0.9 mm. Before the liquefaction process, the waste

material was sorted and its fractional composition, bulk density, buffer capacity, and formaldehyde content determined [Janiszewska et al. 2016a]. The bark fraction ≤ 0.5 mm and ≥ 0.25 mm was selected as optimal for liquefaction experiments. The samples were dried at 103°C for 24 h before use. The bark fractions were then liquefied, as previously described by Janiszewska et al. [2016b, 2016c].

300 g of solvent and the catalyst *p*-toluenesulfonic acid (3% by weight of the liquefying agent) were poured into a three-neck reaction flask, equipped with a mechanical stirrer, a reversing cooler and a thermometer. The solvent was a polyhydroxy alcohol mixture containing glycerine and propylene glycol (G-PG) in the weight ratio 1:2. Glycerine and propylene glycol were purchased from Chempur, and *p*-toluenesulfonic acid (monohydrate 98%) from Alfa-Aesar. All chemicals and solvents were of synthesis grade and were therefore used without further purification.

50 g of the selected bark fraction was added gradually, with continuous stirring. The liquefaction reaction was carried out at a temperature of $120 \pm 10^\circ\text{C}$ for 2 h. Subsequently, the reaction mixture was cooled and solid residues were drained in vacuum conditions, by bathing them in a mixture of dioxane-water solvents in the ratio 4:1 (vol.). Finally the solvents were evaporated using a vacuum evaporator, thus obtaining a ready product in the form of a black liquid. The liquefied bark was then used as a component of the adhesive mass used for gluing the particleboards. The bonding agent for board production was a mixture of an industrial melamine-urea-formaldehyde (MUF) resin (80%) and liquefied bark (20% relative to the dry weight of the resin). The MUF resin had the following parameters: gelation time (at 100°C) 90 s with 2% hardener and 88 s with 3%, viscosity 288 mPa·s, pH 7.8, dry mass content 68.8%, melamine addition 4%. The viscosity of the adhesive composite was in the range 600-620 mPa·s. Due to the strong acidity (pH < 1) of the liquefied bark, 1M NaOH and 25% ammonium hydroxide were used to neutralise the composite. These solutions were treated both as an additive to the adhesive mixture (30%) and as an agent modifying the liquefied wood itself (30% in the case of NaOH, 1% in the case of ammonium hydroxide).

Urea-ammonium nitrate solution (46%) was used as a hardener in a quantity of 3% of the dry weight of the resin for the inner layer of the board and 2% for the outer layers. The viscosity of the adhesive composition was determined according to the PN-EN 12092:2004 standard (Rheotec RC01/02 rotary viscosimeter, measurement temperature 23°C), the pH according to PN-EN 1245:2011 (Schott TitroLine Alpha Plus titrator, measurement temperature 23°C), and the gelation time at 100°C according to PN-C-89352-3:1996.

Boards were produced using standard pine particles. The particles were sorted using an Allgaier vibration screening machine with a set of screens with mesh diameters 8, 2, 1 and 0.5 mm. The particle fraction ≤ 8 mm and ≥ 1 mm was designated for the inner layer of the particleboards, and particles <1 mm for the

outer layers. To characterise the wood material, its fractional composition was examined and a dimensional analysis of the inner layer particles was performed.

Determination of the fractional composition of particles took place after the sorting process. The analysis concerned the 8/1 particle fraction and the <1 mm microparticle fraction dried to a moisture content of approximately 8%. Tests were carried out using a Fritsch screening machine with the following sets of screens: 8.0, 4.0, 2.0, 1.0, 0.50, 0.25 and <0.25 mm for 8/1 fraction particles, and 1.0, 0.8, 0.5, 0.4, 0.315, 0.08 and <0.08 mm for microparticles. Using the quartering method, an adequate amount of the raw material was taken randomly from a given portion of particles (approximately 200 g of particles from the 8/1 fraction and approximately 30 g of microparticles). The sorting time was 15 minutes. Then the quantity of material from each screen was weighed. These operations were repeated three times for each tested portion of the raw material.

Approximately 200 pieces of raw material were taken randomly from a given particle portion in order to perform the dimensional analysis.

Three-layer particleboards with dimensions of 550 × 500 × 12 mm were produced, with a 20% content of liquefied bark. Pressing was performed at 210°C. The pressing time coefficient was 8.0 s/mm, and the resination rate was 10% for the outer layers and 8.5% for the inner layer. A 0.4% addition of paraffin emulsion in a concentration of 65% was used. The nominal density of the panels was 660 kg/m³. The board mat was moulded manually in a frame placed on aluminium sheets, pressed in an oil-heated one-shelf hydraulic press, using spacers. The pressed boards were conditioned for 2 days at 20°C and at 65% relative humidity. Two boards of each variant type were produced.

Table 1 lists the variant types of manufactured boards.

Table 1. Manufacturing variants of liquefied bark-based (LB) panels

Board code	Liquefied bark content (%)	Type of modifying agent	Content of modifying agent
ST	0	–	–
LB_1	20	1M NaOH	30% as adhesive additive
LB_2	20	1M NaOH	30% as LB modifier
LB_3	20	25% NH ₄ OH	1% in relation to liquefied wood

Standard physico-mechanical properties of the panels were determined according to the following standards: PN-EN 323:1999 for board density, PN-EN 322:1999 for moisture content, PN-EN 310:1994 for modulus of elasticity in bending and bending strength, and PN-EN 319:1999 for tensile strength. The formaldehyde content in the boards was determined by the perforator method according to PN-EN ISO 12460-5:2016-02. All test results were compared with

those for standard particleboard (ST) bonded with melamine-urea-formaldehyde adhesive resin which had not been modified with liquefied bark.

Results and discussion

Table 2 gives the characteristics of the raw wood material used for particleboard production.

Table 2. Characteristics of raw wood material used for particleboard production

Parameter	Particle fraction 8/1	
	Length	
	<i>x</i>	18.7
	<i>s</i>	9.2
	<i>n</i>	203
Average particle dimensions mm	Width	
	<i>x</i>	1.8
	<i>s</i>	1.0
	<i>n</i>	203
	Thickness	
	<i>x</i>	0.7
	<i>s</i>	0.2
	<i>n</i>	203
Slenderness coefficient	26.7	
Flatness coefficient	2.6	
Width coefficient	10.4	
Moisture content %	8.0	

x – mean value, *s* – standard deviation, *n* – number of samples taken for the test.

Results of the screen analysis of raw wood materials are presented in figure 1.

In the case of the inner layer the particle fraction 8/2 accounted for approximately 26% of the tested raw material, and the fraction 2/1 for more than 52%. The boards were produced using a mixture of those fractions, with a 68.5% content of the 8/2 fraction and 31.5% of the 2/1 fraction. The outer layers were composed of the fractions 1/0.5 and <0.5mm in the ratio 53.1% to 46.8%.

The results of the tests of the strength properties of boards produced with and without the use of liquefied bark are compared in table 3.

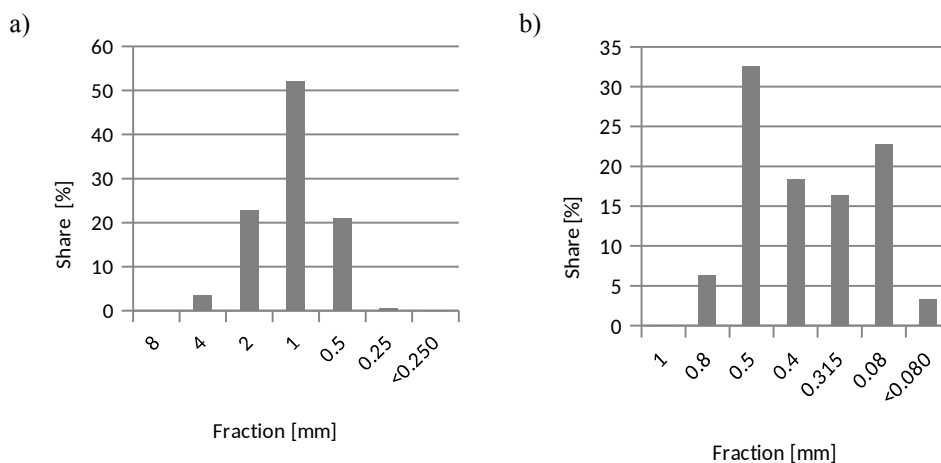


Fig. 1. Fractional composition of particles in a – the inner layer and b – outer layers

The average density of the samples tested for static bending strength, modulus of elasticity and perpendicular tensile strength was in the range 630-660 kg/m³ and was approximately equal to its assumed value. This meant that the influence of density on the above-mentioned parameters could be ignored. On the other hand, the moisture content of the boards was in the range 7.5-9.0%. It was shown, based on the initial tests, that replacing melamine-urea-formaldehyde resin with liquefied pine bark to an amount of 20% caused deterioration in the strength properties of the boards compared with standard particleboard produced without any content of liquefied waste material. The decrease was by approximately 10-20% in the case of modulus of elasticity, 22-29% for bending strength, and 25% for tensile strength. Results for particular versions of the produced boards fall within the limits defined in the PN-EN 312:2011 standard and fulfil the requirements for interior-general-use boards of type P2 used for indoor equipment elements (including furniture). It should be noted that in the case of tensile strength, the values were close to the lower limit allowed by the standard. The strength properties might have been affected by the strong acidic reaction of liquefied wood, and by the high acid buffer capacity of the bark. Literature data indicate that as the acid buffer capacity of the particles increases, the strength of the boards decreases [Frąckowiak 2005]. It was also found that replacing 20% of the melamine-urea-formaldehyde resin with liquefied bark did not lead to any increase in the formaldehyde content of the boards. The initial tests suggested that the formaldehyde content was reduced by more than 10%; however, further research is needed to arrive at firm conclusions.

Table 3. Properties of liquefied bark-based (LB) panels

Tested property	Value	Measure unit	Board code		
			ST	LB_1	LB_2
Bending strength	<i>x</i>		15.5	12.1	11.7
	<i>s</i>	N/mm ²	1.6	0.7	0.7
	<i>v</i>	%	10.5	5.8	6.0
	<i>n</i>	pcs	14	12	11
Modulus of elasticity	<i>x</i>		2622	2362	2205
	<i>s</i>	N/mm ²	155	192	173
	<i>v</i>	%	5.9	8.1	7.9
	<i>n</i>	pcs	13	13	13
Sample density for bending strength and modulus of elasticity tests	<i>x</i>		630	654	646
	<i>s</i>	kg/m ³	16	18	15
	<i>v</i>	%	2.6	2.7	2.4
	<i>n</i>	pcs	14	14	16
Tensile strength	<i>x</i>		0.52	0.39	0.40
	<i>s</i>	N/mm ²	0.03	0.01	0.02
	<i>v</i>	%	6.3	3.7	4.7
	<i>n</i>	pcs	16	14	13
Sample density for tensile strength test	<i>x</i>	kg/m ³	660	659	658
	<i>s</i>		7	7	7
	<i>v</i>	%	1.0	1.1	1.1
	<i>n</i>	pcs	16	16	16
Formaldehyde content	at the moment of test	mg/100g dry board	5.2	3.7	3.4
	after conversion to 6.5%	mg/100g dry board	5.7	5.0	4.6
Moisture content	%		5.8	3.9	3.8

x – mean value, *s* – standard deviation, *v* – coefficient of variation, *n* – number of samples taken for the test.

Conclusions

Based on initial research on bark liquefaction, it was shown that this process may be an effective means of utilisation of bark. Nevertheless, as regards the use of liquefied bark as an adhesive for particleboard production, further research is needed to optimise the composition of the adhesive and to obtain desired parameters for technological usefulness: adequate viscosity, pH, gelation time, and pot-life. Future research should be focused on fine-tuning the formula for

the manufacture of particleboards with the use of liquefied bark. Research is currently being conducted within the framework of the LIDER programme.

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List of standards

- PN-EN 12092:2004** Adhesives. Determination of viscosity
- PN-EN 1245:2011** Adhesives. Determination of pH
- PN-C-89352-3:1996** Kleje – Oznaczenie czasu żelowania (Adhesives. Determination of gel time)
- PN-EN 310:1994** Wood-based panels. Determination of modulus of elasticity in bending and of bending strength
- PN-EN 319:1999** Particleboards and fibreboards. Determination of tensile strength perpendicular to the plane of the board
- PN-EN 323:1999** Wood-based panels. Determination of density
- PN EN 322:1999** Wood-based panels. Determination of moisture content
- PN-EN ISO 12460-5:2016-02** Wood-based panels. Determination of formaldehyde content
- PN-EN 312:2011** Chipboard. Technical requirements

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