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Preparation of Biocomposites using Sawdust and Lignosulfonate with a Culture Liquid of Levan Producer *Azotobacter vinelandii* as a Bonding Agent

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The possibility of preparing molding-bioengineered materials, such as woodchip boards (WCB), from sawdust using technical lignosulfonate (LGS), a wood waste product, and a culture liquid (CL) of levan microbial polysaccharide producer by *Azotobacter vinelandii* D-08 is explored in this article. The parameters of the derived materials are comparable to those of traditional materials made from toxic phenol-formaldehyde resins. The various physical and mechanical characteristics of the materials depend on the quantity of the bonding agent used for the preparation. Adding a culture liquid increases the humidity resistance of the molding materials. Using electron microscopy and X-ray micro-tomography, it is clear that the structure of woodchip boards become more homogeneous without microcracks with the addition of CL. The strength of the best samples prepared was approximately 24 to 29 MPa with a density of 1170 to 1255 kg/m^3 and a swell on wetting of 6.7%. During hot pressing, noticeable changes were observed by Fourier transform infrared spectroscopy (FTIR) at frequencies typical of LGS sulfonic-acid groups, levan fructose fragments, and skeletal vibrations of a syringal/guaiacyl core in lignin and of C-H groups of hemicelluloses. This indicates the involvement of these functional groups in the process of binding wood particles with hot pressing.

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INTRODUCTION

A large number of various wood composites that possess good operational and consumer properties have been created (Thoemen *et al.* 2010; Burton *et al*. 2011). The broadest application of these composites is for preparing woodchip boards, which are widely used in the construction and furniture industries. Woodchip board technology is based on processing sawmill waste and other woodworking by-products, which saves huge amounts of wood. Despite sophisticated technology employed during the preparation of these materials from phenol-formaldehyde resins, phenol, formaldehyde, and other toxic substances are released into the air when used. This is the major factor that limits the use of woodchip boards in the construction industry. Therefore, decreasing the toxicity of woodchip boards is a critical issue (Carll 1986; Li *et al.* 2005; Carlborn and Matuana 2006).

Some known ways of decreasing the toxicity of woodchip boards are surfacing the boards with an insulation layer of finishing and coating materials; modifying the

bonding agent; developing alternate methods of board pressing; processing boards or particles with substances capable of forming stable connections with formaldehyde; and biologically modifying wood waste with micro-organisms and enzymes with follow-up pressing (Kadimaliev *et al.* 2001; Kadimaliev *et al.* 2004; Idirs *et al.* 2011; Varankina and Chubinskiy 2011; Zhang *et al.* 2011).

One of the most promising solutions to reduce the boards' toxicity problem is the replacement of synthetic resins with ecologically safe and inexpensive bio-binding materials. However, the high cost and low humidity resistance of these glues and the absence of application production-technology prevent their widespread introduction into pressed material preparation. Meanwhile, there are data in the literature indicating that it is possible to use composites derived from modified bio-organic waste and microbial polysaccharides as substitutes for glues of a natural origin. For example, it has been shown that modifying barmy waste creates adhesive properties and enables the material to be used as a bioglue for paper, fabric, and wood (Zhang *et al.* 2011; Kadimaliev *et al.* 2012, 2015). Microbial polysaccharides such as levan and dextran also possess adhesive properties. These polysaccharides can be derived by the cultivation of bacteria in a low-cost nutritional medium (Combie *et al.* 2004; Kang *et al.* 2009; Revin and Vedyashkina 2009; Revin *et al.* 2010; Shutova *et al.* 2010).

Among bio-organic wastes, lignosulfonates, which are generated in large quantities from the pulp and paper industry, are of special interest (Tretyakov and Petruhin 2012). Lignosulfonates (LGS) represent aromatic cores connected by propanoic fragments in long, nonpolar chains that include polymeric sulfonic-acid groups, as well as carbonyl, carboxyl, and hydroxyl functional groups. Such structures can induce the manifestation of surface-active and adhesive properties. At high temperatures, lignosulfonates are capable of participating in condensation polymerization reactions (Brovko *et al.* 2009; Dumitrescu *et al.* 2013; Akchurina 2014). These properties enable LGS to be used as a bonding agent in the production of various materials derived from vegetable waste (Laemsak and Okuma 2000; Privas and Navard 2013; Yuan *et al.* 2014). However, the technology to use LGS to derive woodchip boards possessing high durability and humidity resistance has not yet been developed. For this purpose, it is necessary to determine the conditions of the preparation and processing of source raw material (wood shavings) with lignosulfonate. Also the requirements of manufacturing molding-material pressing parameters, such as temperature, pressure, and duration of pressing (Lambuth 2003; Zhang *et al.* 2011), need to be evaluated.

It is known that wood consists of approximately 15% to 36% lignin, which gives cell-like walls a necessary hardness to enable the wood to resist blows, compression, and bending. Wood's degree of resistance to the influence of moisture and micro-organisms depends on the quantity of lignin present in it (Sarkanen and Ludwig 1981). Lignosulfonate structurally represents a phenylpropanol polymeric network (Gorodnov *et al.* 1976; Gavrilov 2004). In addition to the functional groups typical of lignin, the monomeric unit of phenylpropanol polymer has a sulfonic-acid group (SO_3H group), which provides the macromolecule with a hydrophilic nature. Thus, the introduction of a sulfonic-acid group to a macromolecule of lignin gives hydrophilic properties to a water-insoluble polymer. Lignosulfonate forms colloidal solutions in water and is inclined to thermopolymerization (Savitsky *et al.* 2012; Akchurina 2014). It is also known that macromolecules of lignosulfonates possess unregulated, branched spirals with various degrees of compaction. The low molecular weight fractions can have a linear structure. This structure, in the form of polyaromatic chains that include functional groups, defines

the oil and water sensitive character of lignosulfonates and their surface, adsorption and adhesion activity. The surface activity is shown at high concentrations of LGS (Wu *et al*. 2010; Vishtal and Kraslawski 2011; Peng and Zhang 2012; Savitsky *et al.* 2012; Privas and Navard 2013; Yuan *et al.* 2014).

The purpose of this work was to investigate the possibility of using lignosulfonate (LGS) and a culture liquid with levan (CL) as bio-bonding agents in the manufacturing of pressed biocomposites from wood waste.

EXPERIMENTAL

Materials

A CL containing polysaccharide levan was derived by cultivating an *Azotobacter vinelandii* D-08 strain with a nutritional medium containing food production waste, such as molasses (Romodanovsky sugar factory, Russia), grain stillage (Kemlyansky Alcohol plant, Russia), and milk whey (Saransk Milk Factory, Russia) in a ratio of 5:2:3, and adding 10% of a seed material (bacteria mother solution). Biosynthesis was carried out in a temperature-controlled environmental shaker (Inkubator ES 20/60, BioSan, Riga, Latvia) in conical flasks for 72 h at 250 rpm and a temperature of 28 °C. The derived culture liquid was mixed with an antiseptic solution (1% of fumarole acid) for the purpose of preventing microflora and other sour processes from developing in the bonding agent. The quantity of levan was determined by weight using the ethanol sedimentation method. The amount of protein was determined by the Bradford method (Bradford 1976) based on the amount of biomass by weight. The viscosity of the culture liquid was determined by a Gotech VT-04F viscometer (Gotech Testing Machines Inc., Taiwan), and the humidity of the sawdust and molding material was determined by an MS-70 thermo-hydraulic analyzer (A.N.D., Japan). The density of the boards was determined by an H-300S automatic densitometer (Hildebrand Pruf und Messtechnik GmbH, Germany, State Standard 10634-88 1991). We used lignosulfonate (JSC Solikamskbumprom, Russia) as a component for bio-binding.

Methods

To make the biocomposites, a portion of sawdust having 4 to 7 mm (length), 1 to 2 mm (width), and 0.5 to 1.5 mm (thickness) was used. To make the molding materials, the wood filler was mixed in precise ratios with technical lignosulfonate (LGS) powder and the CL that contained the polysaccharide levan. The derived molding material was loaded into a compression mold (5 × 15 cm) and was then cold-pressed. Following this, hot-pressing was carried out on a Gotech 7014-H hydraulic press (Gotech Testing Machines Inc., Taiwan), at a temperature of 100 to 180 °C and a pressure of 3 to 5 MPa per 1 mm of board thickness. The pressing time was 30 s per 1 mm of board thickness. All samples thus prepared were cooled at room temperature during 24 hours to reach the highest physicomechanical properties. Physicomechanical properties were defined according to the standard 10632-89 (2007). Flexural strength was defined according to standard 10635-88 (1989) on a Gotech AI-7000M universal testing machine (Gotech Testing Machines Inc., Taiwan).

The distribution of the sawdust and bonding agent in the woodchip boards was determined with a Hitachi Tabletop SEM TM 300 multipurpose raster super microscope (Hitachi, Tokyo, Japan) and by computer X-ray micro-tomography with a SkyScan-1172

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microtomograph (Bruker, Brussels, Belgium). The results of the microphotographs' reconstruction were analyzed with the CTan, CTvol, CTvox, and CTviewer programs. For the detection of chemical and structural changes in the chemical components of the boards after pressing, FTIR analysis was performed. The woodchip boards were crushed and mixed with KBr and the FTIR spectra were recorded in the range of 4000 to 800 cm^{-1} on an IR-Fourier Shimadzu IRPrestige-21 spectrometer (Shimadzu Co., Tokyo, Japan). IR spectra were recorded with a resolution of 4 cm^{-1}.

RESULTS AND DISCUSSION

At the initial stage of this work, it was necessary to choose a ratio of LGS to sawdust at which the derived biocomposites would possess optimum physical and mechanical characteristics. Taking into account earlier studies and scientific data (Semochkin and Pashkov 2002; Kadimaliev *et al.* 2012; Privas and Navard 2013; Yuan *et al.* 2014; Kadimaliev *et al.* 2015), the following ratios of LGS to sawdust were chosen: 30:70; 50:50; 60:40; and 70:30 g/g. For monitoring, we used biocomposites derived without the addition of LGS as a control sample. Pressing was performed at 140 °C and 39.2 MPa for 10 min. The results are shown in Table 1.

Table 1. The Main Physical and Mechanical Parameters of the Biocomposites with the Addition of Lignosulfonate as a Bonding Agent Derived by Hot Flat Pressing at 140 °C and 39.2 MPa for 10 min

The used ratio of lignosulfonate and sawdust (g/g)	Density (kg/m^3)	Ultimate strength (MPa)	Swelling thickness (%)
Monitoring (0 g LGS + 100 g sawdust)	1087.5 ± 23.9	3.1 ± 1.0	Did not pass the test
(30 g LGS + 70 g sawdust)	1446.0 ± 33.6	30.9 ± 3.5	57.5 ± 11.5
(50 g LGS + 50 g sawdust)	1493.4 ± 6.3	34.8 ± 3.3	65.1 ± 11.7
(60 g LGS + 40 g sawdust)	1076.4 ± 4.8	16.3 ± 1.3	77.0 ± 6.8
(70 g LGS + 30 g sawdust)	966.5 ± 24.9	18.1 ± 2.2	Did not pass the test

As can be seen in Table 1, the addition of LGS led to an increase in the strength of the biocomposites as compared to the control biocomposite (0 g LGS + 100 g sawdust) at all used LGS:sawdust ratios. However, when the proportion of LGS component increased in samples, the humidity resistance and the durability of materials decreased.

During the hot-pressing of molding materials, a high percentage of LGS "boiling" with foaming, which complicated the exit of water vapor and gases, was visually observed and had a negative impact on the processes of bonding between the sawdust and LGS. At lower concentrations, LGS shows more adsorption and adhesion activity (Zaynullin *et al.* 1985). Consequently, a high concentration of LGS in molding materials increases water absorption (swelling in water) and reduces the strength and density of the biocomposites. Based on these and our data, which will be considered in further studies, a 50:50 ratio of LGS to sawdust was chosen.

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One of the factors influencing the physical and mechanical parameters is the molding conditions. Therefore, the pressure, temperature, and duration of molding was changed at the next stage. The results are presented in Tables 2 and 3.

Table 2. Density and Ultimate Strengths of Biocomposites without (Control Specimens) and with the Addition of LGS as a Bonding Agent Derived by Hot Flat Pressing

The molding conditions			Density (kg/m^3)		Ultimate strength (MPa)	
Temperature (°C);	Pressure (MPa);	Time of molding (min)	Without bonding agent addition (monitoring)	With bonding agent	Without bonding agent addition (monitoring)	With bonding agent
100	39,2	10	1032.4±16,0	1409.7±13,0	2.3±0,3	14.0±2,2
120			1068.4±13,3	1417.4±25,0	2.9±0,2	17.4±1,2
140			1087.5±23,9	1493.4±6,3	3.1±1,0	34.8±8,3
160			1165.3±27,7	1468.0±3,1	3.6±0,9	35.1±1,6
180	26,1		1166.1±28,9	1468.3±5,9	2.8±0,4	23.9±1,9
		5	1100.4±8,2	1455.3±3,8	1.8±0,2	19.8±1,6

Table 3. Swelling Thickness of Biocomposites with the Addition of LGS as a Bonding Agent in a 1:1 Ratio with Sawdust (50:50 g/g) Derived by Hot Flat Pressing

The used molding conditions: temperature (°C); pressure (MPa); time of molding (min)	Swelling thickness (%)
100; 39.2; 10	Did not pass the test
120; 39.2; 10	Did not pass the test
140; 39.2; 10	54.1 ± 11.7
160; 39.2; 10	34.6 ± 3.5
180; 26.1; 5	45.8 ± 5.9
180; 26.1; 10	57.9 ± 7.6

From the obtained data (Tables 2 and 3), it is clear that the pressure, temperature, and duration of molding considerably influenced the strength of the resulting biocomposites. A temperature increase from 100 to 160 °C with a pressure of 39.2 MPa and a molding duration of 10 min led to an increased strength of the boards. At higher temperatures, even with lower pressure and a shorter duration, strength loss was observed. However, testing the boards for humidity resistance showed that changing the molding conditions did not increase the humidity resistance to the level recommended by the standards (State Standard 10632-2007 (2007)). Most likely, this is because at high temperatures and pressures there is partial destruction and depolymerization of LGS and a loss of adhesion properties (Ahmed-Haras *et al.* 2013). Consequently, the strength and humidity resistance of the boards decreased.
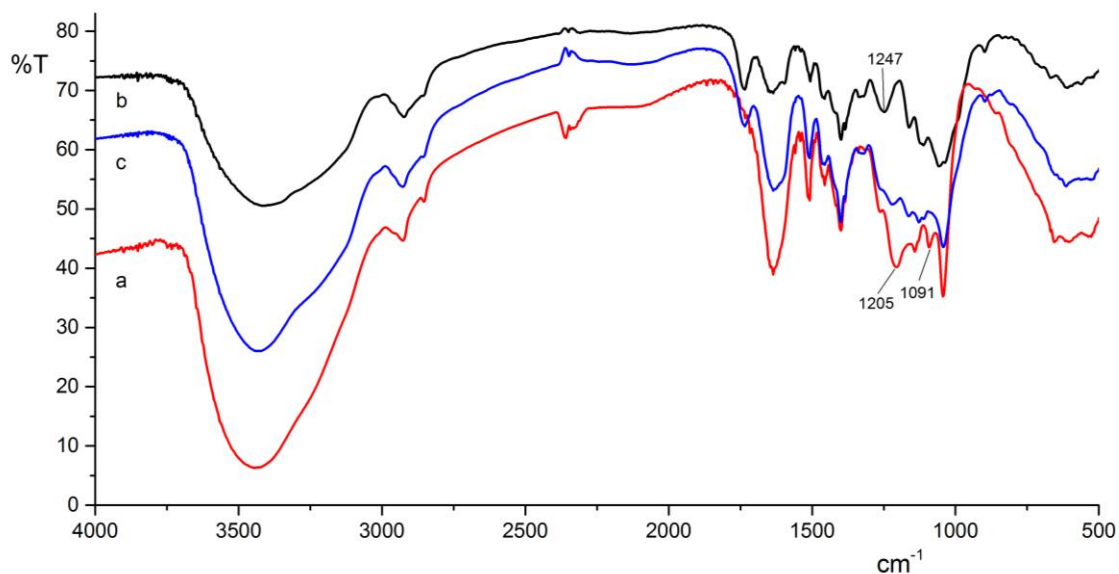
Fig. 1. FTIR spectra of the initial LGS, sawdust, and biocomposite sample derived using LGS as a bonding agent: a – LGS; b – biocomposite without LGS; c – biocomposite with LGS

In Fig. 1, the FTIR spectra of the initial LGS, sawdust, and biocomposite sample derived using LGS as a bonding agent (50:50) are shown. As can be seen in Fig. 1a, the IR spectra of LGS comprised the following absorption bands: 655, 1043, and 1205 cm^{-1} (SO_3 groups); 1020 cm^{-1} (OH groups); 3440 cm^{-1} (OH – phenol groups), 1091 cm^{-1} (OH - groups of alcohols); 1450 and 1508 cm^{-1} (replaced benzene ring of lignin); 1635 cm^{-1} (vibrations of carboxyl group and -C=C bond in the benzene ring); 1400 cm^{-1} (belonging to CH_3); and 2926 and 2860 cm^{-1} (aliphatic bonds) (Mohamad Ibrahim *et al.* 2003; Savitsky *et al.* 2012; Ahmed-Haras *et al.* 2013; Klapiszewski *et al.* 2013; Yuan *et al.* 2014).

In the FTIR spectra of the control sample (Fig. 1b) derived from pressing sawdust without LGS, the following absorption bands were observed: 3600 to 3000 cm^{-1}, caused by valence vibrations of OH-groups involved in hydrogen bonding in cellulose, lignin, and hemicellulose (Bazarnova *et al.* 2002; Fengel and Wegener 2003; Kadimaliev *et al.* 2015); 2920 and 2850 cm^{-1} of CH valence vibrations of methyl and methylene groups in lignin (Bazarnova *et al.* 2002; Fengel and Wegener 2003); 1734 cm^{-1} of C=O vibration in the ester group of hemicelluloses (uronic acids) (Bazarnova *et al.* 2002; Muller *et al.* 2009); 1635 cm^{-1} adsorption of O-H groups and conjugated C-O bonds or carbonyl and carboxyl groups in lignin (Pandey and Pitman 2003); 1400 cm^{-1} vibrations of CH_3 groups of lignin; 1247 cm^{-1} skeletal vibrations of a syringal and guaiacyl core in lignin and of C-H groups of hemicelluloses; and 1043 cm^{-1} that of aromatic C-H bonds (Bazarnova *et al.* 2002; Pandey and Pitman 2003).

The FTIR spectra of the test samples derived by molding sawdust with LGS differed from the FTIR spectra of the control sample and LGS (Fig. 1c). In the FTIR spectra of the test sample we observed a decrease in absorption intensity and a shift of the LGS stretching in the area of 1205 cm^{-1} (SO_3H groups) and in the area of 1091 cm^{-1} (OH - groups of alcohols). In the FTIR spectra of the control sample, an absorption peak in the area of 1247 cm^{-1}, caused by skeletal vibrations of syringal and guaiacyl cores in lignin and of the C-H groups of hemicelluloses, turns into a shoulder peak. During hot pressing,

there is a softening of lignin and LGS, a partial destruction of β-O-4–bonds between lignin monomers, degradation of benzene rings, and a reaction of demethylation and oxidation (Bazarnova *et al.* 1997, Garrote *et al.* 2001; Sivonen *et al.* 2002). This indicates that the sulfonic-acid groups of LGS are involved in the process of bonding between wood particles and LGS. Taking into account these changes, it is possible to believe that during hot-pressing, there is penetration of sulfonic-acid groups of LGS into the aromatic cores of a macromolecule of lignin of wood particles; thus, LGS probably bonds to wood particles because of weak interactions or by purely mechanical means (Semochkin and Pashkov 2002) rather than chemical bonding.

Various options are available in the literature to increase the humidity resistance of biocomposites derived from LGS. A number of authors suggest carrying out a preliminary modification of the LGS and sawdust by oxidation, adding other materials along with LGS, or using other polymers that have adhesive properties to both wood particles and LGS (Liu and Li 2006; Hu *et al.* 2011; Hu and Guo 2013; Klapiszewski *et al.* 2013; Yuan *et al.* 2014) for this purpose. However, these methods demand a great amount of preliminary work and are labor-intensive. Because of this, there is particular interest in microbial polysaccharides in general and levan in particular, which possesses good adhesive properties because of the existence of reactive groups; these materials can fulfill the role of the bonding agent between LGS and wood particles and increase the humidity resistance of biocomposites (Combie 2003; Combie *et al.* 2004; Haag *et al.* 2004; Haag *et al.* 2006). To test this concept, a culture liquid (CL) containing levan at a concentration of 14.5 g/L and a viscosity of 0.4 dPa•s in various ratios was added before molding with LGS. The content of the proteins in CL made up 2.80 mg/mL of the biomass of 13.54 g/L. The parameters of molding followed the above-stated procedures. The obtained data are presented in Table 4.

Table 4. Physical and Mechanical Parameters of Biocomposites derived at 160 °C and 39.2 MPa for 10 min

Ratio of molding components - sawdust: lignosulfonate: levan containing bonding agent	Density (kg/m^3)	Flexural strength (MPa)	Swelling thickness (%)
10 : 1 : 4	1251.0 ± 2.7	24.2 ± 1.3	6.7 ± 3.5
10 : 2.5 : 2.5	1201.0 ± 3.8	24.6 ± 0.8	13.3 ± 1.1
10 :4 : 1	1170.0 ± 2.5	29.8 ± 1.7	13.9 ± 2.3

From Table 4 it is clear that the addition of CL slightly reduced the strength of the bioplastics, and they conformed to the standards (State Standard 10634 - 1988 1991; State Standard 10632-2007 2007). At the same time, the derived samples with the addition of CL exceeded the samples with LGS in humidity resistance almost two-fold and conformed to the standard. The main substance of CL possessing adhesion properties is polysaccharide levan. However, the role of extracellular proteins and bacteria biomass could not be neglected.

In Fig. 2, the FTIR spectra of the initial LGS, sawdust, and specimens of biocomposite derived using LGS and CL as bonding agents are presented.
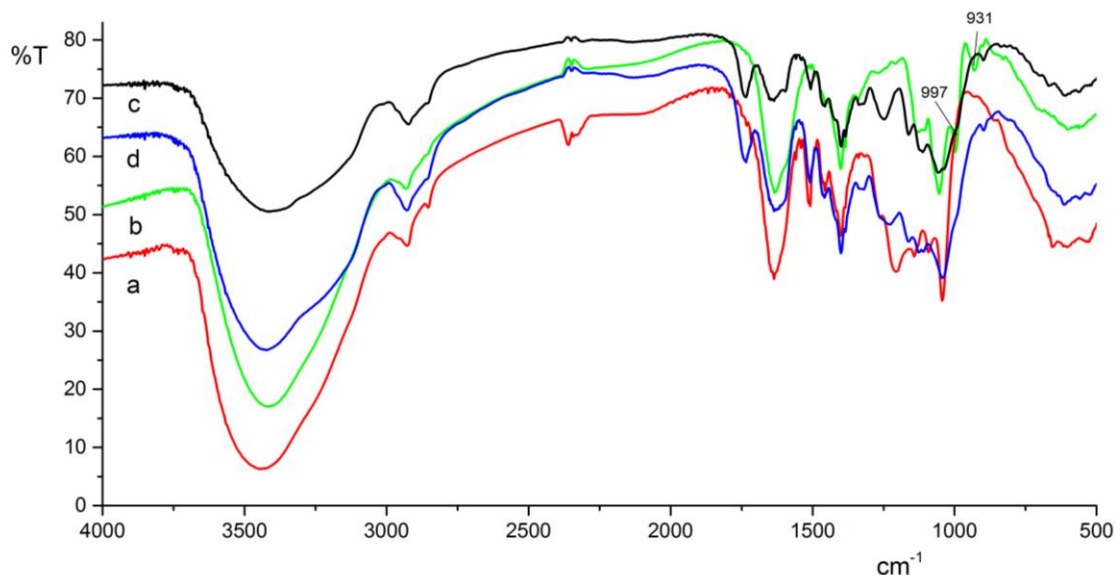
Fig. 2. FTIR spectra of the initial LGS, sawdust, and biocomposite sample derived using LGS and CL as bonding agents: a - LGS; b - CL; c - biocomposite without bonding agent; d - biocomposite with LGS and CL

As can be seen in Fig. 2, in the IR spectra of CL, there are absorption peaks in the area of 931 and 997 cm^{-1}, which are typical for those of fructose from which the levan molecule (Grube *et al.* 2002; Abdel-Fattash *et al.* 2005) is synthesized. During hot-pressing, the absorption intensity at these frequencies sharply decreases and turns into a shoulder peak, which can indicate the involvement of fructose molecules in bonding between biocomposite components (Yang *et al.* 2007). In LGS, changes occur in the same areas as when pressing without CL.

According to the available scientific data, levan consists of fructose fragments packed into spherical structures and, unlike other polysaccharides, does not significantly swell in water and is capable of forming crystals (Ananthalakshmy and Gunasekaran 1999). It is likely that the increase in the humidity resistance of the materials derived with the use of CL is because levan microcrystals infiltrate the micropores of cellulose during pressing and reduce water absorption.

For the structural analysis of the materials derived with the use of a biological bonding agent in the form of LGS mixed with CL containing polysaccharide levan, scanning X-ray micro-tomography (Wieland *et al.* 2013, Charwat-Pessler *et al.* 2014) and scanning electron microscopy (SEM) were used. In the samples in which a bonding agent was not used, there were a large number of microcracks penetrating the whole sample (Fig. 3a). These cracks apparently were one of the causes of destruction of the materials in water.

Samples that used LGS as a binding agent also had a small number of pores and holes (Fig. 3b). In the microstructure of the lignocellulose material derived by using the combined binder in the form of LGS and CL containing polysaccharide levan, microcracks, pores, holes, and defects are rarely observed (Fig. 3c).
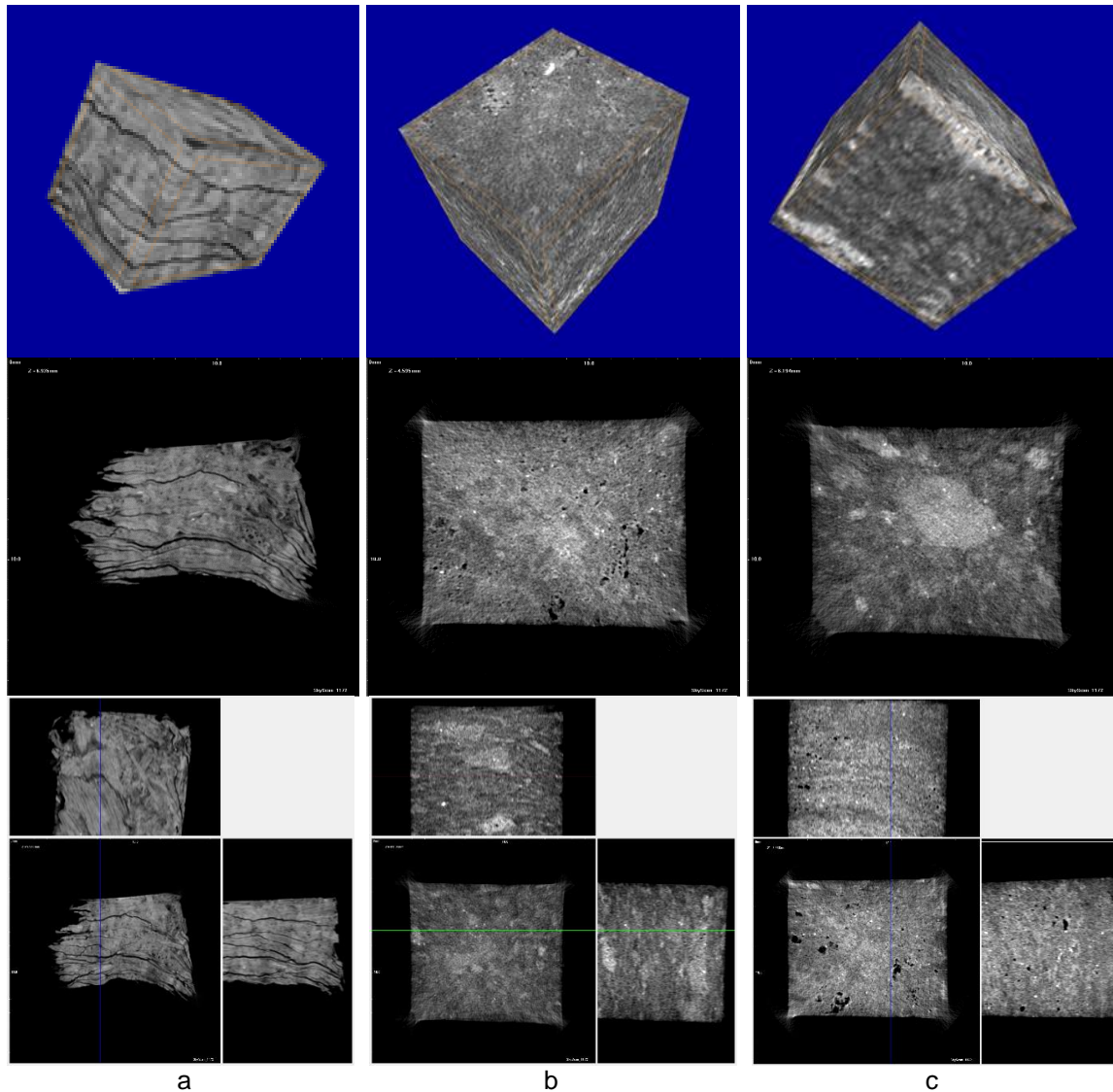
Fig. 3. X-ray micro-tomographies of biocomposites derived at 160 °C and 39.2 MPa for 10 min: a – without the addition of a bonding agent; b – with the addition of LGS; c – with the addition of LGS and CL containing levan

For additional comparative morphological analysis on the processes of agglomeration of wood particles with synthetic and biological binding, SEM (scanning electron microscopy) analysis was performed. In Fig. 4a, the samples derived without the use of a bonding agent are shown. The process of adhesion was not observed, except for some agglomeration of wood particles caused by the temperature and pressure of molding and the partial destruction of the lignocellulose filling. This is visible because of the existence of multiple diagonal microcracks, which are seen on virtually the whole surface of the material.
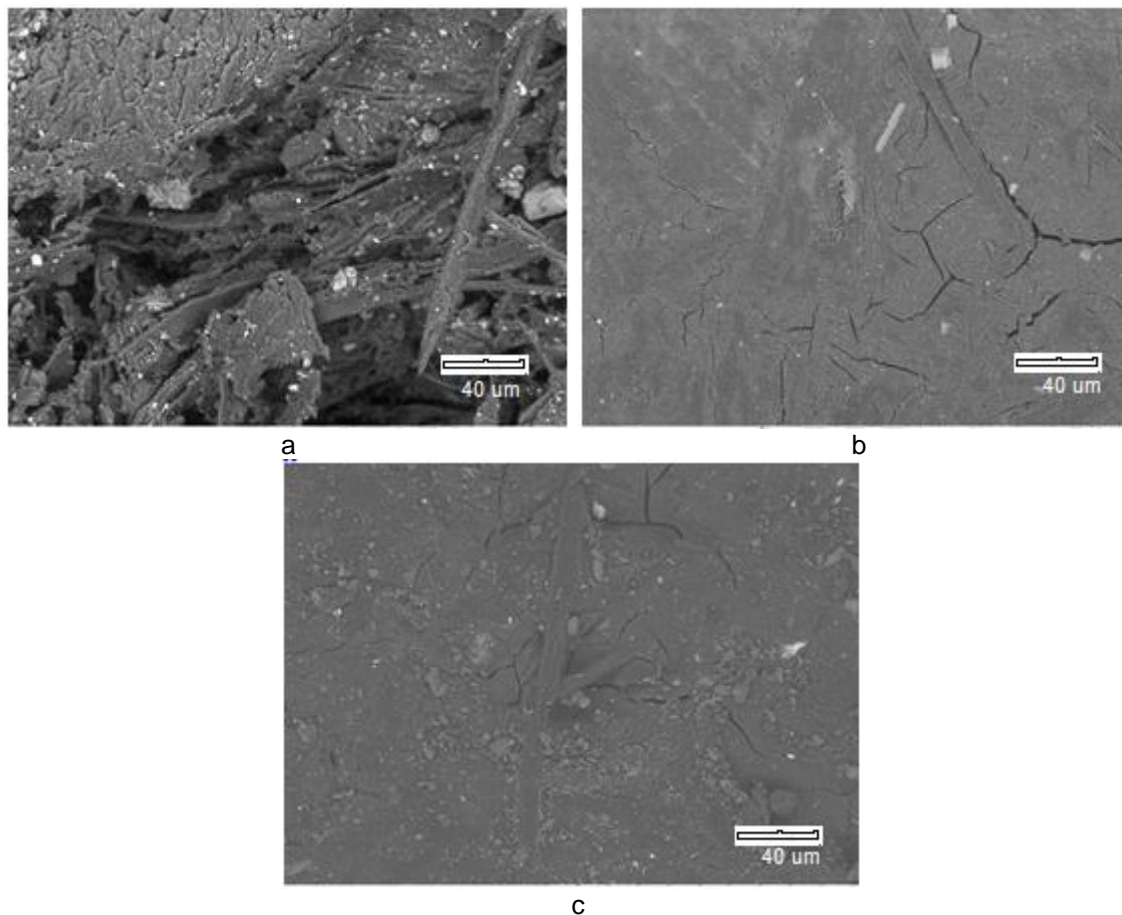
Fig. 4. Scanning electronic microscopy (SEM) of the biocomposites derived at 160 °C and 39.2 MPa for 10 min: a – without a bounding agent; b – with LGS; c – with LGS and CL containing levan

Small gaps and holes and a rather unequal distribution of wood particles were observed. The microstructure of the bioplastics derived from LGS became more homogeneous (Fig. 4b), and the morphology and agglomeration of the particles were similar to those of the sample derived using the mixture of LGS and CL components as biobinders (Fig. 2c).

CONCLUSIONS

1. The use of lignosulfonate as the bonding agent enables the preparation of pressed biocomposites that are in comparable strength to the boards made with phenol-formaldehyde resins. However, their humidity resistance (swelling in water) does not conform to the standard.

2. During the cultivation of *Azotobacter vinelandii* D-08 on organic waste, the polysaccharide levan possessing bonding properties is formed.

3. The use of lignosulfonate and a culture liquid containing levan increases the humidity resistance of biocomposites, maintaining their strength and humidity resistance.

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