Application of lignin in production wood-polymer composites

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Abstract. The rational use of wood cannot be imagined without the use of synthetic resins and adhesives, on the basis of which all the main types of wood composite materials are made. The use of synthetic resins provides: production of high-quality glued products with an increased service life due to strength properties; reducing the material consumption of manufactured products and more complete use of low-grade raw materials; improve the fire, bio - and chemical resistance of manufactured materials. Due to the lower consumption of raw materials for the manufacture of glued parts, their cost is usually lower than that of solid wood parts. The international market of adhesives is represented by a wide range, in which 63% are synthetic adhesives. When wood is processed at pulp and paper enterprises, 40-50 million tons of alkaline lignin, 5 million tons of lignosulfonate, 3.5 million tons of technical hydrolytic lignin are produced annually in the world. In the future, the volume of industrial processing of wood will increase by 50-60% and therefore the issue of disposal of such waste is the most important task. Lignins in the form of various large-tonnage wastes are an environmental and technological problem for many chemical industry enterprises and adjacent residential areas.

1 Introduction

The problem of integrated wood processing is becoming increasingly urgent every year due to the need to protect the environment and the constant increase in prices for both plant resources and products of chemical wood processing.

Ilim Group is implementing one of the largest projects in the history of the timber industry complex in Eastern Siberia, which will ensure the qualitative use of the region's resource potential. Ilim Group is the largest investor in the Russian forest industry. As part of the investment program, the company is implementing a large-scale project "Big Bratsk", which involves the construction of a new modern cellulose line on the basis of an already operating enterprise. In 2012, the world's largest pulp production will be created in Bratsk. Total annual production will exceed 1 million tons. The production process will be carried out by sulphate heat treatment. [1-3].

Unlike the other alkaline, soda production method, where only sodium hydroxide is used, the sulphate process allows to obtain cellulose with greater mechanical strength. The main stage of this thermochemical process, sulphate treatment is the processing of wood

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chips with an aqueous solution containing sodium hydroxide and sulphide. Cellulose produced by the sulphate method is called sulphate pulp. The advantage of the method is the possibility of using almost all wood species in it, and the regeneration of chemicals makes the process cost-effective. [4].

In the process of sulphate heat treatment, in addition to the cellulose itself, a lot of wastes and by-products are formed, from which fodder yeast, sulphate soap, phytosterol, tall oil, rosin, sulfur compounds, methanol, turpentine and such large-tonnage waste as tall lignin are obtained. The scheme for obtaining it is as follows. In the process of sulphate heat treatment, part of the extractive substances of the wood goes into the thermal lye. When the sludge of the spent (black) lye the extractives that have passed into it (salts of resin and fatty acids) float up, forming a layer of so-called sulphate soap, and separate. Next is the decomposition of sulfate soap with sulfuric acid in order to highlight the tall oil. As a result of this treatment, the product is exfoliated and is easily divided into three layers: the top one, which is crude tall oil; medium, so-called tall lignin; bottom - sodium bisulfite solution. [5-7].

Tall lignin is a composition of the components of tall oil (resin, fatty acids and neutral substances - ALS), lignin, mineral salts (sodium bisulfate) and water; pH is shifted to acidic values; The product contains about 1% cellulose fiber.

Sulfate tall lignin is a solution of sodium salts, characterized by high density and chemical resistance. Dry sulphate lignin is a brown powder. The particle size of lignin varies in a wide range from 10 (or less) μm to 5 μm . It consists of individual porous spherical particles and their complexes with a specific surface up to 20. [8].

Sulfate lignin has a density of 1300. It is soluble in aqueous solutions of ammonia and alkali metal hydroxides, as well as in dioxane, ethylene glycol, pyridine, furfural, dimethyl sulfoxide. Heat treatment of sulphate lignin causes its decomposition with the formation of volatile substances, starting with a temperature of 190 °C. Sulfate lignin is classified as a practically non-toxic product, is used in the form of a wet paste, not dusty and not flammable.

The composition of tar acids tall lignin is shown in Table 1. The composition of fatty acids of tall lignin is shown in Table 2.

Table 1. The composition of tar acids tall lignin, %.

Pimar	6-13
Sandarin	2-3
Polustrovaya	1.5-3.5
Isopinar	6-13
Abietic	56-64
Dehydroabietic	11-18
Neoabietic	1.5-2.5

Table 2. The composition of fatty acids of tall lignin, %.

Palmitic	2.5-3.5
Palmitoleic	1.5-2.5
Stearic	0.5-1.0
Oleic	18-21
Isolienic	1.5-4.5
Lilolevaya	32-37
Isolienic	8.0-11.0
Linolenic	6.0-8.0
Genomekozanovaya	5.0-8.0
Begenovaya	1.0-1.5

Only in the Bratsk branch of the Ilim group, the existing pulp production facilities produce more than 10 thousand tons of tall lignin. In varying degrees, the enterprises producing it themselves are engaged in the utilization of lignin, but hydrolyzed lignin, sulfate lignin and lignosulfonates are present in the market as commercial products. There are no international or Russian standards for technical lignins and they are supplied according to various plant specifications. Under normal conditions, lignin is poorly soluble in water and organic solvents. In chemical technologies and in the environment, lignin can participate in a wide variety of chemical reactions and transformations. Lignin exhibits plastic properties at elevated pressure and temperature, especially in the wet state, which allows its use in wood composites.

This paper presents the results of a study on the use of sulphate tall lignin as one of the components of the sizing composition for the production of fibreboard.

Alkaline lignin additive (SCHDL), which is a solution of tall lignin in ammonia, was used. The work was performed under laboratory conditions of the current production of wet fibreboard.

To assess the impact of research variables on the output parameters (quality parameters of fiberboard) it was planned to develop a regression model that provides the ability to control technological regimes.

Table 3 presents variable factors in natural and code designation, their levels and intervals of variation.

Table 3. Main factors and levels of their variation.

Name factor	Code mark	Lower level	Basic level	Upper level	Variation interval
Mass fraction of resin, wt.h.	X₁	0.1	0.6	1.1	0.5
Paraffin mass fraction, wt.h	X₂	0.2	0.5	0.8	0.3
Mass fraction of the entered SCHDL in the composition, wt.h.	X₃	0.5	2	3.5	1.5

The quality parameters of the finished product were taken as output values when conducting a multifactor experiment (according to the second-order B-plan):

Y_1 - tensile strength of hardboard at static bending, MPa;

Y_2 - thickness swelling, %.

The results of the experiments were processed by the method of variation statistics.

The experiment planning matrix for the second-order B-composition plan in normalized and natural notation and the results of the experiments are shown in Table 4.

Table 4. Matrix planning and experimental results

No experience	X_1 , wt.h.		X_2 , wt.h.		X_3 , wt.h.		Y_1 , σ_{bend} , MPa	Y_2 , h, %
1	-1	0.1	-1	0.2	-1	0.5	34	22.2
2	+1	1.1	-1	0.2	-1	0.5	42	12.5
3	-1	0.1	+1	0.8	-1	0.5	35	15.4

4	+1	1.1	+1	0.8	-1	0.5	39	21.6
5	-1	0.1	-1	0.2	+1	3.5	41	11.1
6	+1	1.1	-1	0.2	+1	3.5	45	12.9
7	-1	0.1	+1	0.8	+1	3.5	40	12.9
8	+1	1.1	+1	0.8	+1	3.5	47	12.5
9	-1	0.1	0	0.5	0	2	40	14.2
10	+1	1.1	0	0.5	0	2	43	12.8
11	0	0.6	-1	0.2	0	2	41	11.1
12	0	0.6	+1	0.8	0	2	42	12.5
13	0	0.6	0	0.5	-1	0.5	40	15.9
14	0	0.6	0	0.5	+1	3.5	43	12.9

As a result of processing the experimental data after assessing the significance of the regression coefficients and checking the adequacy of the equation for the response functions to describe the pressing process, they are as follows:

- dependence of the strength of DVP during static bending on variable factors is described by the equation in the normalized values of the variables:

$$Y_1 = 42.1 + 2.6X_1 + 2.6X_3 - 0.5X_1^2 - 0.56X_2^2 + 0.375X_2X_3 \quad (1)$$

- the dependence of the thickness of the hardboard on the thickness of the variable factors is described by the equation in the normalized values of the variables:

$$Y_2 = 14.28 - 1.15X_1 - 1.73X_3 - 2.58X_2^2 + 1.42X_3^2 + 2.71X_1X_2 - 1.11X_2X_3 \quad (2)$$

The dependence of the tensile strength of hardboard at static bending on the amount of resin introduced into the composition presented in Fig.1.

Fig. 1. The dependence of the tensile strength of hardboard at static bending on the amount of resin introduced into the composition.

The dependence of the tensile strength of hardboard at static bending on the amount of resin introduced into the composition is expressed as a parabolic dependence. With the introduction of the resin composition from 0.1 to 1.1 wt.h. an increase in the strength of fiberboard with a static bend from 42 to 44.5 MPa.

The dependence of the tensile strength of hardboard at static bending on the amount of paraffin introduced into the composition presented in Fig.2.

Fig. 2. The dependence of the tensile strength of hardboard at static bending on the amount of paraffin introduced onto the composition.

The dependence of the tensile strength of hardboard at static bending on the amount of paraffin introduced into the composition is expressed in the form of a quadratic nonlinear dependence. With the introduction of paraffin composition from 0.2 to 0.8 wt.h. there is a slight decrease in the index of the strength of fiberboard with static bending from 42.1 to 41.7 MPa.

The dependence of the tensile strength of hardboard in static bending on the number of injected into the composition SCHDL presented in Fig.3.

Fig.3. The dependence of the tensile strength of hardboard at static bending on the number of injected into the composition SCHDL.

The dependence of the tensile strength of hardboard at static bending on the amount of resin introduced into the composition is expressed as a direct linear relationship. With the introduction of the composition SCHD with 0.5 to 3.5 wt.h. an increase in the strength of hardboard at static bending from 43 to 52 MPa is observed.

The dependence of the swelling of hardboard thickness on the amount of resin introduced into the composition presented in Fig.4.

Fig.4. The dependence of the swelling of hardboard thickness on the amount of resin introduced into the composition.

The dependence of the thickness of the hardboard on the amount of resin introduced into the composition is expressed as a direct linear relationship. With the introduction of the resin composition from 0.1 to 1.1 wt.h. there is a slight decrease in fiberboard swelling from 14 to 13%.

The dependence of the swelling of hardboard thickness on the amount of paraffin injected into the composition presented in Fig.5.

Fig.5. The dependence of the swelling of hardboard thickness on the amount of paraffin injected into the composition.

The dependence of the expansion of fiberboard thickness on the amount of resin introduced into the composition is expressed in the form of a quadratic nonlinear dependence. With the introduction of paraffin composition from 0.2 to 0.8 wt.h. there is a decrease in the rate of fiberboard swelling from 14.5 to 12.5%.

The dependence of the expansion of fiberboard thickness in the number entered in the composition SCHDL presented in Fig.6.

Fig.6. The dependence of the expansion of fiberboard thickness in the number entered in the composition SCHDL.

The dependence of the thickness of the fiberboard on the thickness of the number entered in the composition SCHDL is expressed in the form of a quadratic nonlinear dependence. With the introduction of the composition SCHDL from 0.5 to 3.5 wt.h. there is an increase in the rate of fiberboard swelling from 11.5 to 21.5%.

According to the obtained mathematical models, response surfaces were constructed characterizing the mutual influence of variable factors.

The dependence of the tensile strength of hardboard at static bending on the amount of resin and paraffin introduced into the composition when the amount of SCHDL is 2 wt.h. presented in Fig.7.

Fig.7. The dependence of the tensile strength of hardboard at static bending on the amount of resin and paraffin introduced into the composition when the amount of SCHDL is 2 wt.h.

The dependence of the tensile strength of hardboard at static bending on the amount of paraffin and SCHDL introduced into the composition with the amount of resin introduced into the composition, 0.6 wt.h. presented in Fig.8.

$$Y=42,1+2,6*Y+0,375*X*Y-0,56*X^2$$

Fig.8. The dependence of the tensile strength of hardboard at static bending on the amount of paraffin and SCHDL introduced into the composition with the amount of resin introduced into the composition, 0.6 wt.h.

2 Conclusions

1. On the basis of experimental and theoretical studies, the possibility has been established of the integrated use of the by-products of wood-chemical production, which reduces the urgency of environmental problems.
2. The possibility of using lignin for the production of fibreboard wet method has been established. Lignin is introduced into the sizing composition in the form of an alkaline solution (SCHDL).
3. The optimum ratios of the components of the fiberboard composition were determined:
 - hardening additive 0.4-0.6% by weight of a.s.v;
 - alkaline lignin additive - 1.5-2.5% by weight of a.s.s.
 - hydrophobic additive - not more than 0.5% by weight of a.s.s.;
 - wood fiber - the rest.
4. It was determined that the physicomechanical characteristics of wood-fiber plates, when using SCHDL, comply with the requirements of GOST 4586 "Fiber boards. Technical conditions "for plates of brand T.

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