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Modification of Phenol- and Carbamide-Formaldehyde Resins by Cellulose By-products

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Abstract—To improve their properties, phenol- and carbamide-formaldehyde adhesives were modified by cellulose by-products. It has been shown that the introduction of pectol into phenol-formaldehyde resin of SFZh-3013 grade and products of sulfite-cellulose production into adhesive compositions based on carbamide-formaldehyde resins increases the plywood gluing strength and curing rate.

Keywords: veneer, plywood, pectol, lignosulfonates, modification, phenol- and carbamide-formaldehyde adhesives, bonding strength

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INTRODUCTION

Complex and effective use of wood resources is impossible without the development of production of wood-plate materials. To increase the efficiency of production and the competitiveness of wood-based composite materials, special attention should be paid to improving adhesive compositions that reduce the duration of gluing and increase the bond strength while reducing the consumption of the main glue components.

Currently, for bonding plywood and wood boards, carbamide-formaldehyde and phenol-formaldehyde binders are widely used to make glued materials with high physical and mechanical properties. Due to the industry's need for modern adhesives, one of the promising areas of scientific research is the creation of new multifunctional composite materials using natural raw materials and secondary resources.

The pulp industry is the largest chemical processor of wood. However, the final main product, cellulose, contains only about half of the substance of processed wood, the rest being by-products [1, 2].

Modification of synthetic resins and adhesives is the main and most effective way of giving them the required properties [1–7]. In most cases, low-molecular compounds that have some reactive functional groups and change the physical nature of resins and adhesives are used in the modification. Modification of phenol- and carbamide-formaldehyde resins with reactive compounds can provide these synthetic oligomers with a number of positive technological properties after curing.

The purpose of this work was to improve the properties of phenol- and carbamide-formaldehyde adhesives by modifying them with cellulose by-products.

MATERIALS AND METHODS

Based on the analysis of the chemical composition and properties of cellulose by-products, pectol was chosen as a modifier for phenol-formaldehyde resins.

Pectol is a solution of pece in light tallow oil in a 2 : 1 ratio and contains resin and fatty acids (isopimaric, oleic, linolenic), which undergo an esterification reaction with formaldehyde to form esters. Mono- and dimethylolphenols, which are some of the condensation products of phenol-formaldehyde resins, also undergo esterification and additional reactions with acids along double bonds with formaldehyde to form multinuclear alkaline polymers.

Effective modifiers of carbamide-formaldehyde resins can be products of sulphite-cellulose production, lignosulfonates in particular [3–5]. The widespread industrial use of water-soluble derivatives of lignin, lignosulfonates, is associated with the valuable colloidal-chemical properties of these polyelectrolytes, in particular, with the presence of surface activity. Lignosulfonates are an anionic polymer containing methoxy, phenolic, hydroxyl, carbonyl, carboxyl, and sulfo groups in sodium form. In this case, sodium lignosulfonate is a high-molecular substance with characteristic acid properties.

To develop the technology for gluing plywood, a multifactorial experiment was carried out using sam-

Table 1. A methodological grid for conducting experiments on veneer gluing using modified phenol-formaldehyde glue

Experiment objectives	Constant factors		Varying factors		Output parameter	Number	Number of repetitions	Number	Total number
	name	value	name	value					
Investigation of dependences of the glue-curing time and the strength of plywood on the amount of pectol in SFZh-3013 resin	Resin grade Veneer breed Ambient temperature, °C Thickness of plywood, mm Glue viscosity, s Concentration of resin, wt % Pressing pressure, MPa	SFZh-3013 Pine 20 9.0 82 41 1.45	Pectol content in resin, wt % Duration of pressing, min Temperature of press plates, °C	5 10 15 6.5 7.5 8.5 108 115 122	Strength at static bending along fibers of outer layers, MPa, not less than Ultimate strength at shearing along the adhesive layer of plywood after boiling in water for 1 h, MPa, not less than	14 14	3 3	4 4	168 168

Table 2. A methodological grid for conducting experiments on veneer gluing using modified carbamide-formaldehyde glue

Experiment objectives	Constant factors		Varying factors		Output parameter	Number	Number of repetitions	Number	Total number
	name	value	name	value					
Investigation of dependences of the duration of curing and the strength of plywood on the amount of lignosulfonates in the glue based on KF-MT-15 resin	Resin grade Veneer species Ambient temperature, °C Thickness of plywood, mm Glue viscosity, s Concentration of resin, wt % Pressing pressure, MPa	KF-MT-15 Birch 20 6.5 100 66 1.6	Content of lignosulfonates in resin, wt % Temperature of press plates, °C	5 10 15 125 130 135	Ultimate strength at static bending along fibers of outer layers, MPa, not less than Ultimate strength at shearing along the adhesive layer of plywood after soaking the samples in water for 24 h, MPa, not less than	14 14	3 3	4 4	168 168

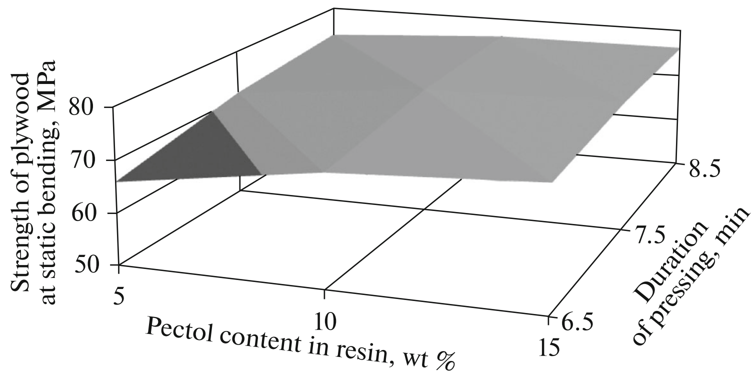


Fig. 1. The dependence of the strength of plywood at static bending on the content of pectol in SFZh-3013 resin and the duration of pressing.

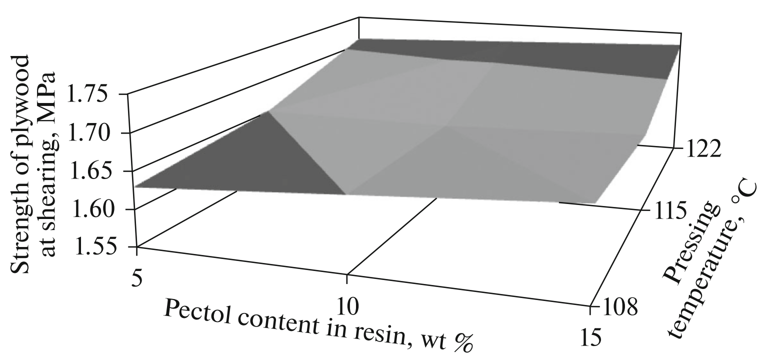


Fig. 2. The dependence of the strength of plywood at shearing along the fibers on the content of pectol in the SFZh-3013 resin and the pressing temperature.

ples of pine veneer (2.0 and 2.2 mm in thickness) with application of the pectol-modified phenol-formaldehyde glue based on SFZh-3013 resin and using samples from birch veneer (1.15 and 1.8 mm in thickness) in the case of carbamide-formaldehyde glue based on KF-MT-15 resin modified by technical lignosulfonates. The content of modifiers in the resin and the duration and temperature of pressing were studied. The experimental conditions are given in generalized methodological grids (Tables 1, 2). Tests of plywood were carried out in accordance with *GOST* (State Standard) *20907* and *9624*. The strength of the glued joint at static bending and the strength at shearing along the adhesive layer were determined.

RESULTS AND DISCUSSION

Based on the results of testing the coniferous plywood, regression equations (1) and (2) are obtained that adequately describe the dependence of the strength of plywood on the influencing factors (Figs. 1, 2): the content of pectol in the resin and the duration and temperature of pressing.

$$\sigma_{\text{bend}} = 74.78 + 1.231n + 1.478t - 0.125T - 0.1204n^2 - 0.727t^2 - 0.607nt, \quad (1)$$

$$\sigma_{\text{shear}} = 1.29 - 0.016n + 0.011t - 0.003T + 0.013n^2 + 0.049t^2 + 0.018nt - 0.001nT - 0.004tT, \quad (2)$$

where σ_{bend} is the ultimate strength at static bending, MPa; σ_{shear} is the ultimate strength at shearing along the adhesive layer, MPa; n is the content of pectol in the resin, %; t is the duration of pressing, min; and T is the pressing temperature, °C.

The limits of the changes in the parameters studied were determined earlier [1, 2]: $5\% \le n \le 15\%$. $6.5 \le t \le 8.5$ min, and $108 \le T \le 122$°C.

Analyzing the results of the study (see Figs. 1, 2), it can be concluded that the introduction of pectol into

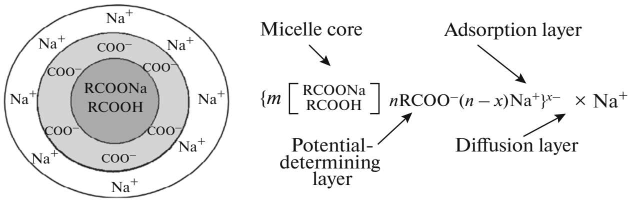


Fig. 3. The structure of the micelle of unsaponified tallow pece: n is the number of potential-determining ions, x is the number of counterions in the diffuse part of the layer, and m is the number of RCOONa and RCOOH molecules contained in the micelle aggregate.

phenol-formaldehyde resin of SFZh-3013 grade leads to increases in the strength and rate of the glue-curing process and, hence, the productivity of the press equipment.

Fatty acids $C_nH_{2n+1}COONa$, which are part of the unsaponified tallow pece, are characterized by high surface activity and dissociate, forming aggregates (micelles): ionogenic, polar groups (COO^-) face outward, and the hydrocarbon part (C_nH_{2n+1}) is directed into the micelle (Fig. 3).

Acceleration of the curing process of phenol-formaldehyde resins is possible due to the replacement of the hydroxyl groups of the phenol-formaldehyde resin for the sodium cations of the micelle of the unsaponified tallow pece with an increase in the alkaline medium of the glue:

$$C_nH_{2n+1}COONa \rightarrow Na^+ + C_nH_{2n+1}COO^-.$$

It can be supposed that the micelles are embedded in the molecule of the phenol-formaldehyde resin polymer, forming a spatially branched structure, which leads to the formation of an alkaline polymer with a new set of properties that accelerate the glue-curing process and increase the bonding strength.

At the next stage of the research, we obtained the results of a multifactor experiment on gluing plywood made of birch veneer with carbamide-formaldehyde glue modified with lignosulfonates and based on KF-MT-15 resin.

As a result of mathematical-statistical processing of the experimental data, regression equations (3) and (4) were obtained, which adequately describe the dependence of the strength of plywood on the influencing factors: the content of lignosulfonates in the resin and the pressing temperature:

$$\sigma_{\text{bend}} = 104.93 - 0.3346n - 0.2156T + 0.0427n^2 + 0.0003T^2 - 0.0129nT, \quad (3)$$

$$\sigma_{\text{shear}} = 2.0998 + 0.0032n - 0.0041T + 0.00187n^2 - 0.00016nT, \quad (4)$$

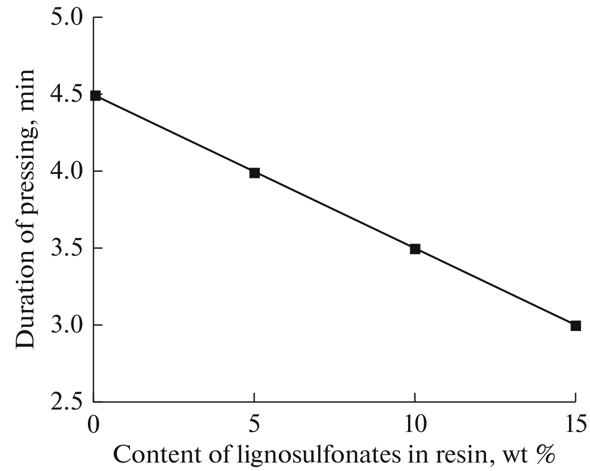


Fig. 4. The dependence of the duration of pressing of plywood on the content of lignosulfonates in KF-MT-15 resin.

where σ_{bend} is the strength at static bending, MPa; σ_{shear} is the strength at shearing along the adhesive layer, MPa; n is the content of lignosulfonates in the resin, wt %; and T is the temperature of the press plates, °C. The limits of change of the investigated parameters were determined earlier [3]: $5\% \le n \le 15\%$ and $125 \le T \le 135°C$.

Experiments have shown [3] that when 10 wt % of lignosulfonates are introduced (during the acid-condensation stage in the process of cooking the carbamide-formaldehyde resin), the duration of the plywood-gluing process on the basis of this binder decreases.

The dependence of the duration of plywood pressing on the content of lignosulfonates in the resin is described by regression equation (5):

$$\tau = -0.2n + 5.5 \text{ at } 5\% \le n \le 15\%, \quad (5)$$

where τ is the duration of plywood pressing, min, and n is the content of lignosulfones in resin, wt %.

A graphical interpretation of the dependence of the duration of plywood pressing on the content of lignosulfonates in the resin is shown in Fig. 4.

Analyzing Fig. 4, it can be concluded that the introduction of lignosulfonates in the carbamide-formaldehyde resin during its synthesis increases the reactivity of the ready-made glue and reduces the duration of its curing. In the case of the introduction of lignosulfonates in the carbamide-formaldehyde resin during its synthesis, the curing process of the glue is accelerated and, hence, so is the degree of its curing. Confirmation of this is found in the infrared absorption spectra, which showed the presence of changes in the structure corresponding to the minimum gelation time [3].

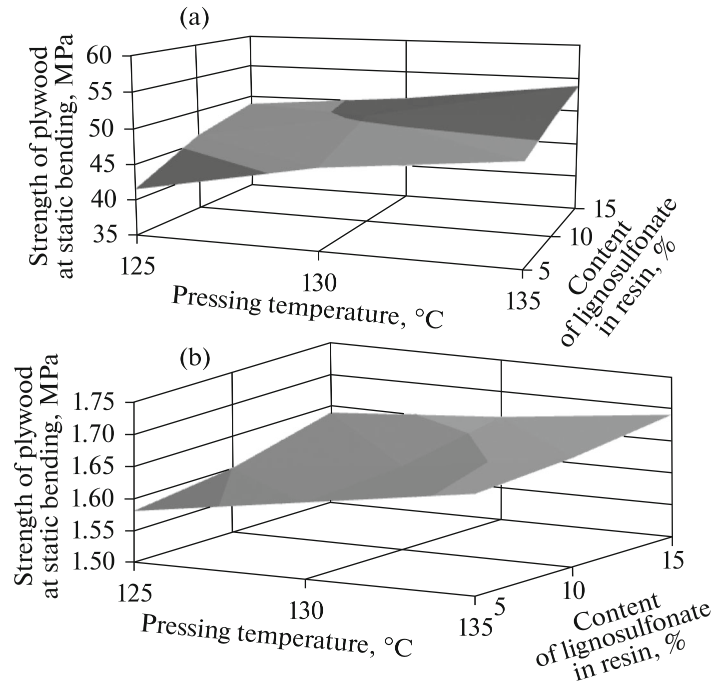
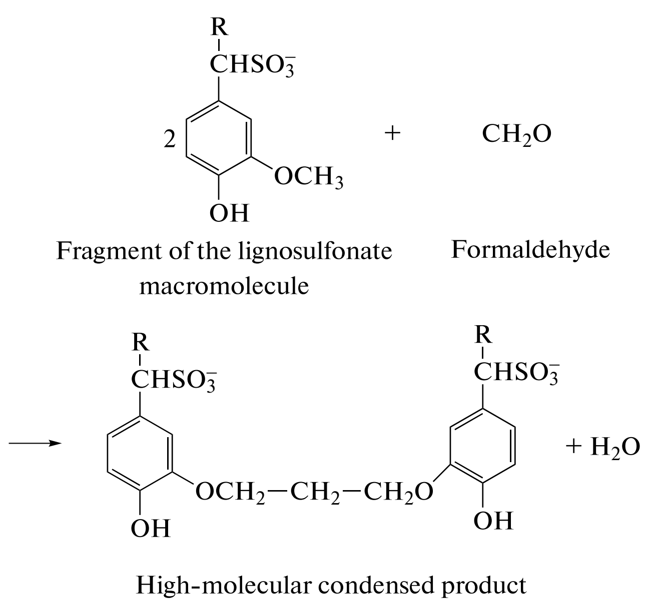


Fig. 5. The dependence of the strength of plywood at (a) bending and (b) shearing on the content of lignosulfonates in KF-MT-15 resin and the temperature of pressing.

Acceleration of the curing process of the carbamide-formaldehyde glue modified with lignosulfonates occurs due to the "acidic nature" of lignosulfonates (pH < 4), which facilitates the interaction of lignosulfonates with formaldehyde in the acidic-condensation stage during the process of cooking the carbamide-formaldehyde resin:



The graphical dependence of the strength at bending and shearing on the influencing factors is shown in Fig. 5. Analyzing the results of the study, it can be concluded that technical lignosulfonates, due to their adhesive and surface-active properties, have the ability to increase the strength of the glued plywood joint due to the chemical interaction of ligno-sulfonates with formaldehyde.

CONCLUSIONS

(1) Introduction of relatively cheap by-products of pulp and paper production into adhesive compositions based on phenol- and carbamide-formaldehyde resins makes it possible not only to improve the properties of adhesives and to reduce the cost of finished products, but also to utilize the waste of the industry, thereby solving the important problems in the field of ecology.

(2) With the introduction of pectol into the phenol-formaldehyde resin of the SFZh-3013 grade, the strength of the plywood gluing and the glue-curing process increase and, hence, the productivity of the press equipment does so as well.

(3) Introduction of products of sulfite-cellulose production into adhesive compositions based on carbamide-formaldehyde resins makes it possible to improve the technological properties of adhesives, namely, to accelerate the glue-curing process and to increase the strength of the glued plywood joint.

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