Modification of urea- and phenol-formaldehyde adhesives by natural fillers for the production of plywood

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Abstract. For the manufacture of plywood and chipboard are used urea-formaldehyde and phenol-formaldehyde hot curing adhesives. When it is necessary to reduce the content of toxic substances, to increase the strength and reliability of gluing, other properties of adhesive bonding heat urea and phenol-formaldehyde resins are modified. Urea-formaldehyde and phenol-formaldehyde resins were used for research. Urea-formaldehyde resin was modified with technical lignosulfonates with particle sizes of 0.01-0.2 mm, shungites with particle sizes of 0.2-0.8 mm, black shales with particle sizes of 0.005-0.2 mm and aluminosilicates with particle sizes of 0.2 - 0.8 mm. Phenol-formaldehyde resin was modified with pectol, black shales with particle sizes of 0.005-0.2, technical lignosulfonates with particle sizes of 0.01-0.2, and cold sludge from aluminum production with particle sizes of 0.01-0.2. A comparative analysis revealed that all the modifiers under study improve the physicochemical parameters of urea-formaldehyde and phenol-formaldehyde resins, increase the performance properties of glued materials from wood. Plywood was tested for shear strength over the adhesive layer and for the content of free formaldehyde in accordance with Russian standards. Modification of urea and phenol-formaldehyde resins with the proposed substances increases the strength of plywood, at the same time reducing the free formaldehyde content in products.

1. Introduction

In the wood processing industry is widely used variety of glue and which are made on the basis of synthetic substances.

For gluing plywood and particle boards, both urea-formaldehyde and phenol-formaldehyde are used, and a large number of works are devoted to improving them [1-12].

When it is necessary to reduce the content of toxic substances, to increase the strength, reliability of bonding, heat and frost resistance, water and weather resistance of wood materials, urea and phenol-formaldehyde resins modify [1,3,4,6,7].

By modifying is meant a targeted change in the structure or composition of a polymer, including the introduction of chemical additives in the binder in order to improve the technological or operational properties.

That is why, the direction of research on the properties of modified urea - and phenol-formaldehyde glue is relevant, and that was the purpose of the present study, performed at the St. Petersburg State Forestry University.
2. Methods of research
The study used: a) urea-formaldehyde resin, into which the modifiers were introduced: technical lignosulfonates with particle sizes of 0.01-0.2 mm, shungites with particle sizes of 0.2, 0.8 mm, black slates with particle sizes of 0.005 - 0.2 mm, aluminosilicates with particle sizes of 0.2 - 0.8 mm; b) phenol-formaldehyde resin, in which modifiers pectols were introduced, black shales with a particle size of 0.005 - 0.2 mm, technical lignosulfonates with particle sizes of 0.01 - 0.2 mm, cold sludge (CS) with particle sizes of 0.01 - 0.2 mm. The chemical composition of these products is presented in Table 1,2.

**Table 1. Chemical composition of modifiers.**

|                  | C    | O    | S    | Na   | Ca   | K    | Mg   | Прочие |
|------------------|------|------|------|------|------|------|------|---------|
| SiO₂             | 33,9 | 46,8 | 9,5  | 5,7  | -    | 0,18 | 0,80 | 3,12    |
| The chemical composition of pectols (%,) |
| SiO₂             | 54,5 | 0,02 | 0,79 | 4,62 | 0,28 | 0,64 | 4,28 | 1,15    |
| Fe₂O₃            | 4,62 | 0,28 | 0,64 | 0,64 | 0,64 | 0,64 | 0,64 | 0,64    |
| Al₂O₃            | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 | 1,50 | 1,50    |
| CaO              | 5,00 | 5,00 | 5,00 | 5,00 | 5,00 | 5,00 | 5,00 | 5,00    |
| MgO              | 4,80 | 4,80 | 4,80 | 4,80 | 4,80 | 4,80 | 4,80 | 4,80    |
| Na₂O             | 8,46 | 8,46 | 8,46 | 8,46 | 8,46 | 8,46 | 8,46 | 8,46    |
| K₂O              | 21,8 | 21,8 | 21,8 | 21,8 | 21,8 | 21,8 | 21,8 | 21,8    |
| C                | 0,02 | 0,02 | 0,02 | 0,02 | 0,02 | 0,02 | 0,02 | 0,02    |
| C₇O₃             | 0,03 | 0,03 | 0,03 | 0,03 | 0,03 | 0,03 | 0,03 | 0,03    |

**Table 2. Chemical composition of modifiers.**

|                  | Fatty and resin acids | Neutral and oxidized substances | Minerals |
|------------------|-----------------------|---------------------------------|----------|
|                  | Content, % of dry matter | 50-52 | 48-51 | 0-2 |
| The chemical composition of pectols (%,) |
| SiO₂             | 47,5 | 9,3 | 9,3 | 13,4 | 9,9 | 9,9 | 2,1 | 2,1 | 9,3 |
| Fe₂O₃            | 12,9 | 12,9 | 31,8 | 13,5 | 13,5 | 3,2 | 3,2 | 12,9 |
| Al₂O₃            | 51,5 | 51,5 | 51,5 | 51,5 | 51,5 | 51,5 | 51,5 | 51,5 |
| CaO              | 48,5 | 48,5 | 48,5 | 48,5 | 48,5 | 48,5 | 48,5 | 48,5 |
| MgO              | 24,5 | 24,5 | 24,5 | 24,5 | 24,5 | 24,5 | 24,5 | 24,5 |
| Na₂O             | 28,5 | 28,5 | 28,5 | 28,5 | 28,5 | 28,5 | 28,5 | 28,5 |
| K₂O              | 12,5 | 12,5 | 12,5 | 12,5 | 12,5 | 12,5 | 12,5 | 12,5 |
| FeO              | 12,5 | 12,5 | 12,5 | 12,5 | 12,5 | 12,5 | 12,5 | 12,5 |
| SO₃              | 20,5 | 20,5 | 20,5 | 20,5 | 20,5 | 20,5 | 20,5 | 20,5 |
| C₄H₅O₅            | 0,03 | 0,03 | 0,03 | 0,03 | 0,03 | 0,03 | 0,03 | 0,03 |

Lignosulfonates are a polydisperse system, an unstable ratio of fractions in which can have a significant impact on colloid-chemical properties. It is established that the condensation reaction of phenol and formaldehyde with 10% lignosulphonate or sulphate lignin proceeds with the formation of a phenol-formaldehyde resin with a greater proportion of bridge methylene and ethylene. Chain breakage occurs as a result of copolycondensation reactions of fragments of a lignin macromolecule with a growing phenol-formaldehyde chain. The resulting product is a mixture of the copolymer obtained, fragments of a highly destructed lignin macromolecule, as well as carbohydrates and extractive substances.

Shungite is a dark gray carbonaceous substance with significant porosity. Due to the uniqueness of the structure and composition of schungite, this breed has sorption, catalytic, bactericidal properties, biological activity, the ability to absorb and neutralize high-frequency electromagnetic radiation. Shungites have selective sorption properties. Their selectivity is due to the fact that only hydrocarbon molecules can freely pass through the “entrance windows” into the internal cavities of such sorbents. This sieve effect is explained by the difference in critical diameters of hydrocarbon molecules of various classes. Shungites are molecular sieves and can be used to separate substances at the molecular level. To penetrate into the adsorption cavity, the critical diameter of the molecules of
the adsorbed substance must be less than or equal to the size of the “entrance windows” of shungite. Shungites have fairly wide "entrance windows" and adsorb most of the components of complex mixtures, including all types of hydrocarbons. The mixture of shungite sorbents with a resin leads to a decrease in the surface porosity of shungite.

Black shale is an effective reactive modifier with the ability to accelerate the curing process with phenol - urea-formaldehyde adhesives.

Aluminosilicates are natural and synthetic silicates containing aluminum and silicon atoms in complex anions. The introduction of aluminosilicates into the resin makes it possible to improve the physicochemical, technological, and operational properties of the adhesive; reduce adhesive consumption and reduce the cost of finished products; affect the viscosity of the adhesive; reduce the depth of penetration and shrinkage of the adhesive; prevent glue from seeping onto outer surfaces of veneer sheets; increase the strength of adhesive bonding.

Pectol is a solution of tall oil pitch in light tall oil at a ratio of 2:1 and in this case it is called Pectol-L. Traditionally, pectol is used in the pulp and paper industry as a component for sizing bag paper and cardboard, as well as a means to increase the stickiness in the formulation of rubber. Pitch and fatty acids that make up pectol react with formaldehyde, it can enter into addition reactions by double bonds of fatty and resin acids and possibly participates in their esterification (ester production). The condensation products of phenol-formaldehyde resins contain mono- and dimethylolphenols, which can also undergo esterification reactions with acids and double bonding. Oleic, linoleic, and linolenic acids, which are found in tall products, can enter into the same reactions via double bonds.

Cold sludge slime fine powder that precipitates in settling tanks when sulfuric acid is inverted with an aqueous prehydrolyzate or hydrolyzate when preparing fodder yeast. SHO is a complex in composition amorphous, polydisperse, polyfunctional copolymer, consisting of 90% of the structural fragments of lignin. This is a low molecular weight component of lignin, which contains methoxyl groups of 7.0-10.2%, carbonyl groups of 3.5-7.1%, carboxyl groups of 1.5-2.0%, phenolic hydroxyls of 3.2-5.6%. By reducing the molecular weight and the content of reactive functional groups (carboxyl, phenolic hydroxyls), it is assumed that SHO will more actively enter into chemical reactions in the process of obtaining modified phenol-formaldehyde resin than sulphate lignin, hydrolysis lignin, ligno-containing substance of “caramel” type.

In the course of the research, the mass fraction of dry residue, the conditional viscosity of the adhesive 1 h after the introduction of the modifier, the duration of gelatinization at 100 °C (for urea-formaldehyde adhesives), the viability of the adhesive and the duration of curing (for phenol-formaldehyde adhesives), formaldehyde emission.

The quality of plywood was evaluated by the content of free formaldehyde in the finished product by the perforator standard method, physical and mechanical properties of plywood were evaluated by the indicator of the shear strength of adhesive bond.

3. The results of the study and analysis of the first
Properties of urea-formaldehyde glue, are presented in Table 3. Results of the experimental study show that all modifiers used for urea-formaldehyde adhesives can reduce adhesive cure time (Table 3).

Table 3. Properties of urea formaldehyde glue.

| Modifier        | Mass content of modifier, % | Mass fraction of dry residue, % | Relative viscosity of the glue 1 hour after production, with | Adhesive cure time at 100 °C, s |
|-----------------|----------------------------|-------------------------------|------------------------------------------------------------|-------------------------------|
| Without modifier (according to GOST 14231-88) | 0                          | 67                            | 60                                                         | 65                            |
| Lignosulfonates | 5-15                       | 72                            | 70-75                                                      | 42-55                         |
| Shungites       | 2.5 -15                    | 73.8                          | 49 -85                                                     | 3 8 -55                       |
The results of experimental studies show that all modifiers used for phenol-formaldehyde adhesives can reduce the duration of the curing process of the adhesive (Table 4).

### Table 4. Properties of phenol-formaldehyde glue.

| Modifier         | Mass content of filler, % | Relative viscosity of the glue 1 hour after production, with | The viability of the adhesive, h | The duration of the curing process, with |
|------------------|---------------------------|------------------------------------------------------------|---------------------------------|--------------------------------------|
| Without modifier | 0                         | 49                                                         | -                               | 579                                  |
| Pektol           | 5-15                      | 82                                                         | 10-12                           | 450                                  |
| Black slates     | 5-10                      | 73-75                                                      | 6-8                             | 471                                  |
| Lignosulfonates  | 5-15                      | 70-75                                                      | 8-10                            | 485                                  |
| Cold sludge      | 5-25                      | 65-85                                                      | 5                               | 505                                  |

Comparative analysis revealed that none of the investigated modifiers does not deteriorate the physicochemical properties of urea- and phenol formaldehyde resins, increasing adhesive performance properties of the compounds.

To substantiate the modes of bonding and increase the strength of the finished product, multifactorial experiments on gluing plywood were conducted. Gluing was carried out under the conditions of the existing plywood production in accordance with the technological regulations adopted at the enterprise. Glued plywood was tested for strength when splicing on the adhesive layer.

As a result of the experiment, dependencies were obtained, showing that with an increase in the content of the proposed modifiers in the established range, the strength of plywood in the glue also increases (Figure 1, 2).

To substantiate the reduction of free formaldehyde content in finished products, a multifactorial experiment was performed on gluing plywood under the conditions of an operating enterprise. Glued plywood was tested for the content of free formaldehyde in the finished product.

The dependence of the content of free formaldehyde in plywood on the number of modifiers in the adhesive composition is shown in Figure 3, 4.

### 4. Conclusions

Introduction to urea- and phenol formaldehyde adhesives resins by-products of pulp and paper production, helps to improve the technological properties of adhesives, namely to accelerate the adhesive curing process and increase the bonding strength in the finished product.

Introduction to urea- and phenol formaldehyde resins of the proposed modifiers increases the strength of plywood, while reducing the content of free formaldehyde in the finished product.
Figure 1. The dependence of shear strength of plywood on the adhesive layer on the mass content of the modifier for urea-formaldehyde adhesives.

Figure 2. The dependence of shear strength of plywood on the adhesive layer on the mass content of the modifier for phenol-formaldehyde adhesives.
Figure 3. The dependence of the content of free formaldehyde on the mass content of the modifier for urea-formaldehyde adhesives.

Figure 4. The dependence of the content of free formaldehyde on the mass content of the modifier for phenol-formaldehyde adhesives.
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