Original scientific paper
UDK: 674.81.028:678.632.01

MODIFICATION OF PHENOL-FORMALDEHYDE RESIN BY WASTE PRODUCTS OF SULFITE-CELLULOSE PRODUCTION

Dmitry Rusakov, Galina Varankina, Anatolii Chubinskii

Saint – Petersburg Forest Technical University, Russia,
Department of materials technology, designs and constructions of wood
e-mail: dima-ru25@mail.ru, varagalina@yandex.ru, a.n.chubinsky@gmail.com

ABSTRACT

Reducing the toxicity of plywood to the level corresponding to the requirements of European Standard (EN 717-2) is one of the main problems of plywood production. This problem has been solved by creating new types of resins and glues on their basis and justification of the chemical processes occurring in the interaction of lignosulfonates with phenol-formaldehyde resin grade SFF-3013, which was the purpose of the work. The factional chemical composition of the organic substance of sulphite lye is considered as a feedstock for the production of lignosulfonate. The structure of polymer chain of lignosulfonate is taken into consideration. The charts of co-operation of lignosulfonate are presented with phenol and formaldehyde. Due to the astringent, glueings and superficially active properties, lignosulfonate is used in production of plywood, as addition to resin. The influence of the modifier of lignosulfonate is an experimental research on maintenance of free formaldehyde in the prepared products. The introduction in the adhesive compositions based on phenolic resin products sulphite pulp production, improves the technological properties of adhesives; it accelerates the process of curing the adhesive bonding strength to increase and reduce the free formaldehyde content in the final product.

Key words:, Plywood, resin, phenol - formaldehyde, lignosulfonate

1. INTRODUCTION

Phenol-formaldehyde resins are used in the production of plywood, plywood and wood-based panels, as well as other glued products that operate under high humidity conditions. They are modified (Brutian et al, 2010); (Varankina and Chubinskii, 2014), when it is necessary to obtain a low content of toxic substances, to increase strength, adhesion reliability, heat and frost resistance, water resistance and weathering resistance of wood materials.

In this regard, one of the principal tasks of the industry is the search for new resin modifiers, which will make it possible to obtain products from wood with the necessary operational properties. Earlier in (Chubinskii et al, 2011); (Varankina et al, 2016); (Chubinskii et al, 2017), it was found that the by-products of sulfate cellulose, in particular pectol, can be effective fillers for phenol-formaldehyde resins. There are reasons to believe that the effective modifiers may be products of sulphite pulp production, in particular lignosulfonate.

Reducing the toxicity of plywood (Varankina and Chubinskii, 2013); (Varankina and Vysotskii, 1997); (Chauzov and Varankina, 2014); (Varankina et al, 2016); (Rusakov et al, 2017); (Varankina et al, 2017) to the level corresponding to the requirements of the European Standard (EN 717-2) is one of the main problems of plywood production. This problem is solved by creating new types of resins and adhesives based on them and substantiating the chemical processes occurring during the interaction of lignosulfonates with the phenol-formaldehyde resin, which was the goal of the work done at the St. Petersburg State Forestry University and the Bratsk State University .

2. MATERIAL AND METHODS

Tests were conducted in accordance with GOST-27678 (definition of free formaldehyde in finished products). To substantiate the decrease in toxicity of finished products on a phenol-formaldehyde resin modified with lignosulfonates, a multifactorial experiment was carried out to glue pine wood veneer with thickness of 2.0 and 2.2 mm. The study was focused on the content of lignosulfonates in the resin, the durability of the adhesive composition and the consumption of the glue.

The quality of plywood was estimated by the content of free formaldehyde in the finished product (m, mg / 100 g abs dry plywood).

The processing of the experimental results was carried out by methods of mathematical statistics.

It is rather difficult to describe lignosulfonates, since they are a polydisperse system, the ratio of unstable fractions, which can have a significant effect on the colloidal chemical properties. However, it seems possible to determine the main regularities.

The macromolecule of lignosulphonates forms a nonlinear structure approximating the character of globular polymers. A feature of such structures is their compactness and flexibility, even with a large molecular mass and a relatively low content of bound water. In this macromolecule, particles of lngnus sulfonates with different degrees of dispersion are connected with each other by transverse bonds, the main of which is the C_β-O-C_4 bond; in addition, the presence of hydrogen bonds is allowed. The higher the molecular mass of these particles, the higher is the possibility of formation after appropriate modification of the three-dimensional structure.

During sulphite cooking processes, labile α-ether bonds break up and substitution of benzyl alcohol hydroxy groups for strongly polar sulfonic acid groups. New carbon-carbon bonds appear at the same time. By chemical nature, industrial lignosulfonates are anionic water-soluble polymers with a wide range of molecular weight (MM) values of 2000-100000.

The action of lignosulfonates of sulfite liquor and sulphite-yeast mash is caused by the interaction of lignosulfonates in the process of concentration at a temperature above 100°C with amino acids and oligomers of protein nature present in the sulfite-yeast bougie. The resulting condensation products remain soluble and have increased surface activity.

Surfactant components of bisulfite brewing high yield pulp along with lignosulfonates are oligomeric carbohydrates, especially those containing carboxyl groups (for example, polyuronides) - consisting of carbonyl and hydroxyl groups.

At elevated temperature, lignosulfonate reacts readily with phenols of the resorcinol series, forming high-molecular condensed products. Phenol "crosslinks" the structural units of lignosulfonate, with the benzyl alcohol groups participating in this reaction [Rusakov, 2016], the approximate reaction is shown in Figure 1.

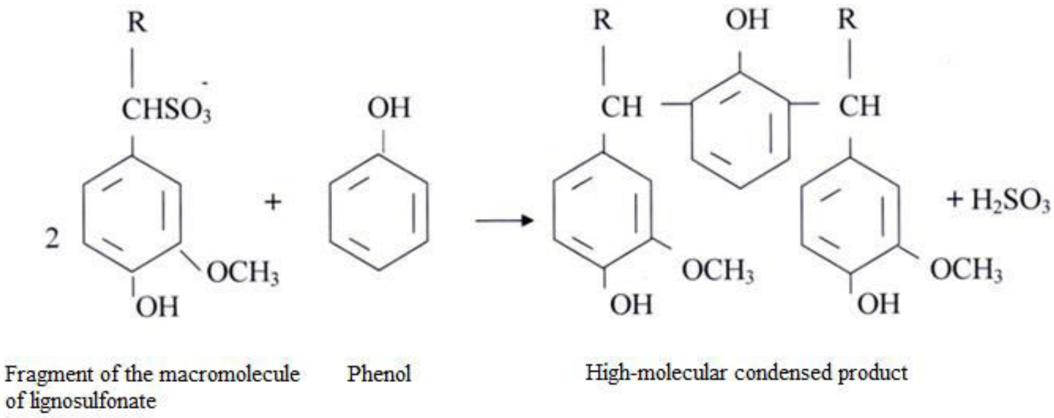

Figure 1. *An approximate reaction of phenol with the structural unit of lignosulfonate*

This ensures a high activity of the complex, despite the reduced degree of polymerization of lignosulfonates compared to the alkali of sulphite varieties.

Polycondensation of phenol with formaldehyde reacts A-groups of lignosulfonate, but B-groups can react, so phenolization reaction competes with sulfonation reaction, as phenolization of lignosulfonate occurs more easily than simple condensation.

It has been established (Rusakov, 2016) that the condensation reaction of phenol and formaldehyde with 10% lignosulfonate or sulfate lignin proceeds to form a phenol-formaldehyde resin with a greater proportion of bridged methylene and ethylene fragments. The chain is broken as a result of the reactions of copolycondensation of fragments of the lignin macromolecule with the growing phenol-formaldehyde chain. The resulting product is a mixture of the resulting copolymer, fragments of a highly destructed lignin macromolecule, as well as carbohydrates and extractives.

3. RESULTS AND DISCUSSION

To substantiate the decrease in the content of free formaldehyde in finished products, a multifactor experiment on gluing plywood was carried out in the conditions of the company "Ilim Bratsk DOK". Glued plywood was tested for content of free formaldehyde in the finished product. The dependence of the content of free formaldehyde in plywood on the duration of aging of the adhesive composition, the content of lignosulfonate in the resin, and the consumption of the adhesive (Figure 2,3) is described by the regression equation (1):

$$m = 3{,}181 - 0{,}014\ n - 0{,}0295\ \tau + 0{,}0082\ R \quad (1)$$
$$\text{at } 5\% \le n \le 15\%;\ 2 \text{ hours} \le \tau \le 10 \text{ hours};\ 120 \text{ g / m}^2 \le R \le 140 \text{ g / m}^2$$

where m – content of free formaldehyde in plywood, mg / 100 g abs. dry plywood; n – content of lignosulfonates in the resin,%; τ – duration of adhesive composition, hour; R – consumption of glue, g / m^2.

Analyzing the results of the study (Figure 1,2), we can conclude that the introduction of lignosulfonate in phenol-formaldehyde resin significantly reduces the content of free formaldehyde in the finished product.

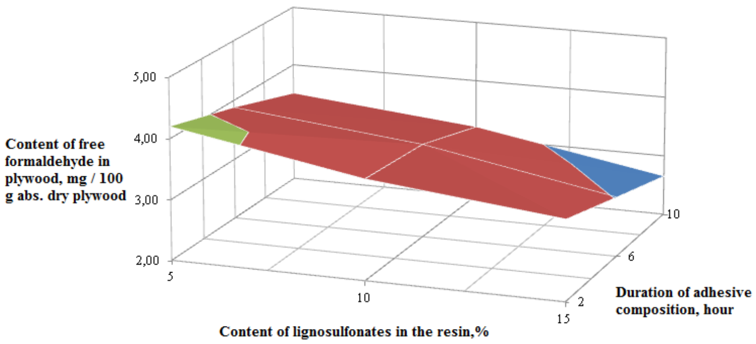

Figure 2. *Dependence of free formaldehyde content in plywood on the content of lignosulfonates in the resin and the duration of aging of the adhesive composition.*

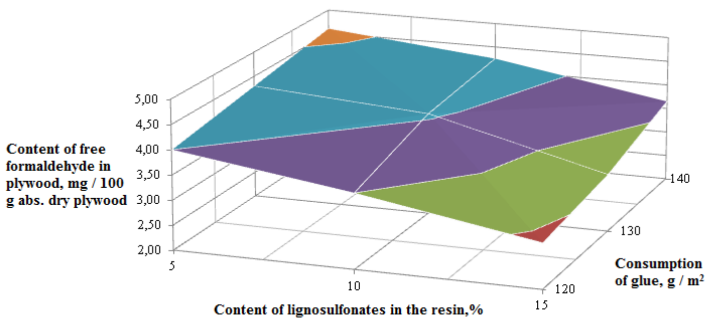

Figure 3. *Dependence of free formaldehyde content in plywood on the content of lignosulfonates in the resin and the consumption of glue.*

4. CONCLUSIONS

The introduction of adhesive products based on phenolic resins products of sulfite-cellulose production, allows improving the technological properties of adhesives and reducing the content of free formaldehyde in finished products.

Due to their astringent, adhesive and surface active properties, lignosulfonates are used in production of plywood, heat-insulating and finishing plates as an additive in the binder. Mixing in the process of manufacturing the modified resin with 5-15% of technical lignosulfonates allows to obtain a combined binder. It was found that lignosulfonates significantly reduce the content of formaldehyde in the finished product from 4.80 to 2.10 mg / 100 g abs. dry plywood; the condensation reaction of phenol and formaldehyde with lignosulfonate proceeds to form a phenol-formaldehyde resin with a greater proportion of bridged methylene and ethylene fragments. The chain is broken as a result of the reactions of copolycondensation of fragments of the lignosulfonate macromolecule with the growing phenol-formaldehyde chain.

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