Obtaining lined environmentally friendly wood-based panels

V E Tsvetkov¹, M Yu Ekimova² and O P Machneva¹
¹Mytishchi branch of the Bauman Moscow State Technical University, Moscow region, Mytishchi, 141005, Russia
²Scientific and testing center 4 GCMP, Astrakhan region, Znamensk, 416540, Russia
E-mail: natali-26.05@mail.ru, mashula111@yandex.ru

Abstract. This paper considered manufacturing of faced wood-based panels based on a carbamide-formaldehyde oligomer modified with a mixture of low molecular weight polyoxyymethylene glycols. For facing material, we propose paper-resin films obtained by impregnating textured decorative papers with an amino-formaldehyde oligomer modified with salts of polyfunctional acids.

Keywords: urea-formaldehyde oligomer, paraformaldehyde, amino-formaldehyde oligomer, impregnation, manufacturing mode, alkali-free catalysis, modifier.

1. Introduction

Currently, the main task of the woodworking industry and the production of panel in particular is to manufacture high-quality structural materials meeting all the strength, operational and environmental requirements.

It is known that the requirements of current standards for wood-based materials manufactured with synthetic binders allow some reduction in strength and water-resistant properties, but remain adamant in terms of environmental safety. It is important to remember that the strength of the materials does not have to be very high, but it must be sufficient under certain operating conditions of the wood material. These requirements also apply to the water resistance of the boards.

Obtaining environmentally friendly wood-based panels seems to be entirely feasible thanks to a number of measures carried out both the stages of synthesizing the binder and at the stage of manufacturing wood-based panel materials and their lining. So, it is essential to rigorously observe the necessary manufacturing regimes at each stage of production, since each stage is significant in its own way.

The production of lined chipboards is one of the most promising and rapidly developing branches of the woodworking industry, since these boards have a fairly wide range of applications due to their availability. For more than half a century, they have been successfully used to make affordable and sufficiently high-quality furniture for various purposes, in packaging production, in transport buildings, carriage and shipbuilding, in interior and exterior decoration of premises, in the formation and reconstruction of facilities in the agriculture. Lined chipboards are of great interest for the furniture industry because of the variety of decorative surfaces. This fact boosts the range of products and results in economic benefits to the furniture manufacturers.

Speaking about the advantages of lined wood-based panels, it is important to note that the manufacturers of these versatile materials are currently still facing an severe problem of reducing their toxicity, from the synthesis of binders to the polymers used for lining the panels.

Amino-formaldehyde oligomers are mainly used to make composite wood-based panel materials. Currently, these substances must satisfy stringent environmental safety requirements and ensure a sufficient margin of safety of finished product and, preferably, good water resistance. In the literature, the issue of resistance of polymer material to prolonged exposure to aggressive media has not been thoroughly studied. Usually, researchers limit the studies to investigation of the strength under operating loads and temperature resistance [1-5].

Amino-formaldehyde oligomers have enjoyed widespread use as the main binder in the preparation of wood-based panels [6]. The cause of their popularity is due to their certain advantages over other synthetic oligomers. These advantages include: high adhesion, high curing rate, low viscosity at a sufficiently high concentration, high storage stability (properties remain almost constant for a long time),
colorlessness, good miscibility with water, low cost and availability of raw materials. Cured aminoformaldehyde oligomers have no color and they also have limited resistance to environmental influences.

The disadvantages of such oligomers include low water and heat resistance, and slightly increased toxicity.

Other disadvantages can be handled by improving the process parameters of the polycondensation of melamine and urea with formaldehyde and chemical modification both directly during the synthesis, as well as the modification of the finished oligomer [7].

2. Experimental study

In the study, we propose to use a mixture of low molecular weight polyoxymethylene glycols for the chemical modification of amino-formaldehyde polymers. The glycols are formed as a result of storage in formalin tanks at an ambient temperature below 10 °C. A mixture of low molecular weight polyoxymethylene glycols has other names: paraformaldehyde, paraform (PF) [8-12]. This toxic substance is a slurry or powder (in a dried state) of white color, but it can also have a slightly yellowish shade, 90-95% consists of formaldehyde and water (up to 5%). Gradually, paraformaldehyde accumulates and is compacted in tanks, where formalin was originally stored before its stratification. After that the tanks can no longer be operated, since the extraction of paraformaldehyde is a rather laborious task. Also, it is known that this product does not dissolve in almost any substance, which greatly complicates its processing and disposal.

From the chemical perspective, the formation of paraformaldehyde is a very interesting process associated with the course of the polycondensation reaction of glycols with the formation of polyoxymethylene glycols at a temperature below 10 °C according to the following scheme

$$ \text{CH}_2\text{O} + \text{H}_2\text{O} \leftrightarrow \text{HOCH}_2\text{OH}; $$

$$ n\text{HOCH}_2\text{OH} \leftrightarrow \text{HO(CHOH)}_n\text{H} + (n-1) \text{H}_2\text{O}, \text{where } n = 3 \ldots 100. $$

When stored in formalin tanks, there processes happen slowly. The general formula combining a mixture of low molecular weight polyoxymethylene glycols is HO(CH$_2$O)$_n$H [1, 8-12].

To stabilize the properties of process formalin a certain amount of methyl alcohol is added. Methanol-free solutions of formaldehyde can retain their stability only above a certain temperature limit of saturation, which is in direct proportion to the concentration of the solution (formalin). With a decrease in the saturation limit, spontaneous formation of a mixture of solid polyoxymethylene glycols (POM) with different molecular weights begins.

Earlier it was proved [8-12] that paraformaldehyde can be successfully used for synthesizing aminoformaldehyde resins, as a modifying additive, while containing formaldehyde in its composition, which made it possible to replace part of formalin with paraformaldehyde. When paraformaldehyde is added during the synthesis of amino-formaldehyde polymers in the form of a powder or slurry, synthetic resins are obtained that do not need further evacuation, which excludes the formation of wastewater at the enterprise, thus, the environmental situation does not deteriorate. But, at the same time, it is not always possible to introduce paraformaldehyde into the synthesis in the form of a powder or gruel. This is often due to the laboriousness of extracting this product from the tanks. Therefore, a number of effective solvents have been developed that allow the use of dissolved paraformaldehyde in the synthesis of polymers, which greatly facilitates the modification process. Nevertheless, finished polymers have to be vacuum dried.

In the studies [11-15], the effect of modification at the stage of synthesis of amino-formaldehyde polymers was fully confirmed, as indicated by the data in Tables 1-3.

| Indicator name | Paraformaldehyde content depending on the amount of formalin, % |
|----------------|------------------------------------------------------------|
| 0              | 10             | 15           | 20            |
Refractive index | 1.466…1.470  
---|---
pH | 7.5…8.5  
Polymer viscosity according to VZ-4, s | 51…62  
Polymer concentration (dry residue), % | 63±2  
Gelling time (curing) with NH4Cl: | 63±2  
- at 100°C, s | 49…57  
- at 20°C, h | ≥ 11  
Polymer compatibility with water, mL/ mL | 1:1…1:2  
Free formaldehyde content, % | 0.41  
Methynol groups’ content, % | 18.0  
Lifetime, days | under 30

| Indicator name | Paraformaldehyde content depending on the amount of formalin, % |
|---|---|
| Refractive index | 1.467…1.470  
pH | 7.85…8.4  
Polymer viscosity according to VZ-4, s | 51…62  
Polymer concentration (dry residue), % | 63±2  
Gelling time (curing) with NH4Cl: | 63±2  
- at 100 oC, s | 49…57  
- at 20 oC, h | ≥ 11  
Polymer compatibility with water, mL/ mL | 1:1…1:2  
Free formaldehyde content, % | 0.41  
Methynol groups’ content, % | 18.0  
Lifetime, days | under 30

Tables 1 and 2 show that a slight increase in the para-formaldehyde content in the polymer leads to a decrease in the free formaldehyde content without a decrease in other important properties. Therefore, the effect of modifying amino-formaldehyde polymers with paraformaldehyde has been confirmed. Also, the optimal amount of modifying paraformaldehyde was found to be 15%, since it is with this amount of modifier that polymers have minimal toxicity and high physicochemical properties.

Three-layer chipboards were prepared using the obtained polymers modified in an amount of 15% paraformaldehyde. The quality indicators of the panels are presented in Table 3.

In the manufacture of plates, conventional woodworking industry press regimes were used: pressing temperature - 180 °C; pressing pressure - 2 MPa; holding time in a hot press - 0.35 min / mm; binder consumption - 12% board thickness - 16 mm; panel density - 750 kg / m3; the moisture content of the chips before resinification was 2%. The properties of the obtained slabs were compared the requirements of GOST 10632-2014.

Table 3. Physico-mechanical properties of chipboards based on amino-formaldehyde polymers

| Indicator names | Panel properties |
|---|---|
| | GOST 10632-2014 | 15% of the paraformaldehyde solution | 15% of the “dry” paraformaldehyde solution |
| Board strength for: | | | |
| - static bending, MPa | 11 | 16.9 | 19.2 |
| - tension perpendicular to the board face, MPa | 0.35 | 0.38 | 0.60 |
Swelling across the panel, %
Free formaldehyde content, mg / 100 g absolutely dry board

|                |          |          |
|----------------|----------|----------|
| Swelling       | 22.5     | 20.9     |
| Free formaldehyde | E1      | 6.8      |
| content        | 6.04     | 6.04     |

Analysis of results from Table 3 also confirmed the positive effect of paraformaldehyde not only on the properties of binders, but also on finished chipboard. Table 3 also shows that the obtained plates significantly exceed the standard values in terms of strength indicators. In terms of toxicity class, they clearly belong to toxicity class E1, which is important and necessary [16-20].

The next stage of obtaining low-toxicity boards is lining the boards with paper-resin films. To produce the films, we propose to use amino-formaldehyde resins modified with polyfunctional acid salts as an impregnating agent. This product performs a complex action in polymer synthesis, being both a modifier and a catalyst for the favorable course of the polycondensation reaction of aminopolymers. The quality of the finished lined chipboard is influenced by the properties of the impregnating oligomers, on the basis of which this product is manufactured.

In the synthesis of amino-oligomers, alkali, in particular NaOH, is used to neutralize formalin. It is known that the oxidation-reduction reaction of Cannizzaro occurs in this case. During the reaction, reduction of one formaldehyde molecule with the simultaneous oxidation of another takes place:

\[
2\text{CH}_2\text{O} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCOOH}
\]

As a result of the Cannizzaro reaction, the pH of the reaction mixture (determined by adding caustic soda) gradually decreases, especially quickly in the presence of compounds that play the role of a catalyst [17-19].

Studies have been carried out on the use of a modifier-catalyst in the synthesis of amino-oligomers, which prevents the Cannizzaro reaction from proceeding. The modifier catalyst is a polyfunctional citric acid salt [7, 13].

Table 4 shows the formulation of the impregnating oligomer.

| Table 4. Impregnating composition formulation |
|---------------------------------------------|
| Component name                             | MFSP-30 |
| Urea-formaldehyde concentrate (UFC), mass part | 80      |
| Melamine, mass part                        | 75      |
| Modifier-catalyst, mass part                | 2.5     |
| Diethylene glycol, mass part                | 20      |
| Distilled water, mass part                  | 80      |
| Caustic soda, 33% solution, mass part       | To reach the required pH level |

The properties of the impregnating amino oligomer were determined, the main quality indicators of which are given in Table 5 in comparison with the known analogue.

| Table 5. Properties of the impregnating amino oligomer and a known analog |
|---------------------------------------------|
| Oligomer property                          | MFO-30 | Known analogue |
| Dry residue content at 105°C, %            | 59     | 58±1           |
| Hydrogen indicator, units pH               | 9.8    | 9.0            |
| Conditional viscosity according to VZ at 20°C, sec | 14.0  | 16.5           |
| Miscibility of resin with water, ml / ml   | 1:2.5  | 1:2            |
| Free formaldehyde content, %              | 0.2    | 0.5            |
| Penetration time (paper impregnation), sec | 1.6    | 4.8            |
The analysis of the properties of the considered oligomers showed that the introduction of 1% of a modifier-catalyst enables the synthesis of impregnating oligomers at a constant pH value. The synthesized amino oligomers were used to impregnate decorative papers to line the chipboards. As the base resin, an oligomer of the MFPS brand with a melamine content of 35% was chosen, on the basis of which the formula of the impregnating composition was developed. Table 6 shows this formula.

**Table 6. Impregnating composition formulation**

| Components                                              | Component quantity |
|---------------------------------------------------------|--------------------|
| Impregnating resin (amino oligomer), mass part          | 1.0                |
| Oligo-S30Y hardener, mass part                          | 0.35               |
| Oligo-SM2 release agent, mass part                      | 0.10               |

Table 7 shows the properties of the paper-resin films.

**Table 7. Properties of paper-resin films**

| Property name                                         | MFO-30 | Initial variant of MFPS |
|-------------------------------------------------------|--------|-------------------------|
| Resin content, %                                      | 58.5   | 60.3                    |
| Volatile substance content, %                         | 5.9    | 5.9                     |
| Content of water-soluble fractions, %                 | 71.8   | 69.3                    |
| Spreadability, %                                      | 6.6    | 4.8                     |

Table 7 shows the properties of paper-resin films obtained by impregnation of texture papers intended for lining boards. From Table 7, it is seen that films based on modified oligomers have the best properties.

Lining of the 16 mm thick chipboard was done with the following process regimes:

- Pressing temperature – 195°C;
- Pressing time – 20 s;
- Pressing pressure – 2.3 MPa.

Physico-mechanical properties of lined wood-based panels are given in Table 8.

**Table 8. Physico-mechanical properties of lined wood-based panels**

| Property name                                                                 | MFO-30 | Initial variant of MFPS |
|--------------------------------------------------------------------------------|--------|-------------------------|
| Static bending strength, MPa                                                  | 20.2   | 20.7                    |
| 24 hours swelling in cold water, %                                           | 21.9   | 21.4                    |
| Acid test (on the 5 point scale)                                             | 5      | 4                       |
| Resistivity at normal separation of the lining from the face of the lined panels, MPa. | 0.8    | 0.6                     |
| Scratching resistance, μm                                                    | 76     | 76                      |
| Hydrothermal resistance                                                      | 2      | 2                       |
| Free formaldehyde emission, mg/m³                                             | 0.008  | 0.02                    |
3. Conclusions
The conducted investigation and its positive results allow one to conclude that the proposed comprehensive approach of manufacturing lined wood-based panels by using modified amino oligomers to making and lining panels allows producing low-toxicity, eco-friendly, high-strength and water-resistant materials. All the obtained components (the modified polymers and the panel) meet the requirements of Russian and international standards.

References
[1] Petrova A P and Malysheva G V 2017 Adhesives, adhesive binders, adhesive prepreg (Moscow: VIAM) p 472
[2] Nelyub V A and Borodulin A S 2018 Properties of epoxy materials used for production of glass-reinforced plastics by winding method Polymer Science – Series D 11(2) pp 147-53
[3] Borodulin A S, Kharaev A M, Kalinnikov A N, Bazheva R C, Kvashin V A, Beshtoev B Z 2019 Synthesis and performance characteristics of superstructure polyethers Key Engineering Materials 816 pp 307-311
[4] Nelyub V A 2018 Adhesive-Strength Evaluation via the Pull-Out Method in a Binder—Elementary-Filament System at Various Treatments of Filaments Polymer Science - Series D 11(3) pp 263-266
[5] Yangyang C and Malysheva G 2019 Method for determining the rational regimes of curing determining the rational regimes of curing products from polymer composite materials Materials Today: Proc. 11 pp 128-33
[6] Virpsha Z and Brzezinski J 1972 Amino resins Moscow: Chemistry 344 p
[7] Ekimova M Yu, Tsvetkov V E and Machneva O P 2020 Amino-formaldehyde oligomers modified with salts of polyfunctional acids Klei. Germetiki. Tekhnologii 6 pp 37-40
[8] Valeeva A T et al 2019 Universal binders for wood materials Science without borders 1(29) pp 10-5
[9] Enikolopyan N S and Wolfson S A 1968 Chemistry and technology of polyformaldehyde Moscow: Khimia 280 p
[10] Machneva O P, Tsvetkov V E and Ekimova M Yu 2018 Polyhydric alcohols as modifiers of urea-formaldehyde resins Klei. Germetiki. Tekhnologii 12 pp 15-8
[11] Zueva M Yu et al 2015 Method for the manufacture of urea-formaldehyde oligomer Patent RU2537620C2, 01/10/2015. Application No. 2013119168/05 dated 04/25/2013
[12] Zueva M Yu et al 2014 Method for the manufacture of urea-formaldehyde oligomer Patent for invention RU2534550C1, 11/27/2014. Application No. 2013119174/05 dated 04/25/2013
[13] Zueva M Yu et al 2014 Method for the manufacture of impregnating oligomers Invention patent RU No. 2535226C1, December 10, 2014. Application No. 2013119171/05 dated 25.04.2013
[14] Zueva M Yu et al 2012 Method for the manufacture of impregnating oligomers Invention patent RU2446193C1, 27.03.2012. Application No. 2010139821/05 from 29.09.2010
[15] Zueva M Yu et al 2014 Method of manufacturing non-toxic particle boards Invention patent RU2527524C1, 09/10/2014. Application No. 2013119166/13 dated 04/25/2013
[16] Zueva M Yu et al 2014 Method for the manufacture of urea-formaldehyde oligomer Invention patent RU2527786C1, 09/10/2014. Application No. 2013119163/05 dated 04/25/2013
[17] Tsvetkov V E and Ekimova M Yu 2011 Synthesis and properties of modified melamine-formaldehyde oligomers Klei. Germetiki. Tekhnologii 1 pp 16-9
[18] Tsvetkov V E and Ekimova M Yu 2011 Influence of the amount of melamine on the synthesis and properties of modified impregnating oligomers Klei. Germetiki. Tekhnologii 12 pp 23-6
[19] Tsvetkov V E, Zueva M Yu and Machneva O P 2011 Investigation of the effect of surfactants on the surface tension of modified impregnating oligomers Bulletin of the Moscow State University of Forest – Forestry Bulletin 5 pp 135-7
[20] GOST 10632-2014 Chipboards. Specifications [Electronic resource]. URL: http://docs.cntd.ru/document/1200110850 (date of access: 03/15/2021)