Monitoring hardeners of low toxic urea-formaldehyde resins

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Abstract. According to European standards, the most stringent standards for the content of formaldehyde belong to the emission class E 0.5. The hardening of resins with different formaldehyde content is different and it has not yet been sufficiently studied. The production of the woodworking industry face difficulty in the use of low toxic urea-formaldehyde resins. On the one hand, life and standards require environmentally friendly products, on the other hand, the use of low-toxic resins leads to a large percentage of defects in the production process, reduced productivity and deterioration of the strength properties of the finished product. The polycondensation reaction of low-toxic resins using a classical hardener-ammonium chloride is slower in comparison with resins with a high content of formaldehyde, that is, performance is reduced. The paper examines the influence of various hardeners on the physical and chemical properties of the glue (gelatinization time, viability, pH of liquid and cured adhesives). All the studied preparations can be used as a hardener of low-toxic urea-formaldehyde resin, but its content should be adjusted taking into account the physical and chemical parameters of the initial state of the resins and production conditions.

1. Introduction

European standards for glued wood materials regulate the content of free formaldehyde in it. The standards provide for 3 classes of formaldehyde emission E 0.5, E1, E2. The curing of resins with different formaldehyde content is different and has not yet been sufficiently studied. The paper provides a comparative assessment of hardeners of urea-formaldehyde resins in terms of its influence on the physical and chemical properties of working solutions (gelatinization time at 100°C, pH of liquid and cured glue). Various chemicals can be used as a hardener for low-toxic urea-formaldehyde resins during hot pressing: ammonium chloride, ammonium silicofluoride, ammonium sulphate, zinc chloride and other acidic salts. Insufficient amount of hardener or its excess leads to deterioration of properties of adhesive solutions and as a result to deterioration of strength of the glued compositions.

The main component of adhesives used by the woodworking industry in Russia are urea-formaldehyde resins (UFR). This popularity is due to the availability and cheapness, good adhesion to wood and wood materials, and high strength of the adhesive connection. Formalin is used as the starting material for producing synthetic resins. The main cause of formaldehyde emission from wood boards and wood materials is the presence of free formaldehyde remaining after polycondensation of synthetic resins. Formaldehyde is toxic and is classified as a dangerous substance for humans, irritating the mucous membrane, causing coughing, allergic reactions, etc. [1, 2]. Therefore, the special attention is paid to reducing the amount of this substance in the manufacture of materials containing...
formaldehyde. To ensure competitiveness, products must meet the emission class E 0.5 and contain no more than 4 mg/100 g of free formaldehyde on a completely dry plate. [3, 4].

To fulfill this condition, it is necessary to use low-toxic UFR synthesized with a reduced molar ratio of carbamide to formaldehyde (C:F). The reduction of free formaldehyde in resins is achieved by reducing the mole ratio (C:F) before 1:1.3;1:2.15; 1:1.2; 1:1.1. The content of free formaldehyde in resins is 0.19; 0.13; 0.12; 0.1%, and the emission of formaldehyde from wood glued materials, respectively 20...26; 16...20; 13...16; 5...9 mg/100 g on a completely dry plate [5].

The process of hardening resins with different molar ratios goes in different directions [6, 7].

The amount of free formaldehyde in the UFR plays an important role in the speed of the hardening reaction. The low-toxic UFR with a reduced formaldehyde content of 0.01-0.05% [8] are poorly cured by the classical hardener - ammonium chloride, while cracks and fractures are observed in the cured adhesive joint [9].

The hardeners are used to speed up the hardening of UFR, which occurs as a result of cross-linking resin molecules during condensation. The crosslinking reaction of urea resins in an alkaline environment practically does not occur, and in an acidic environment occurs the sooner the higher the acidity.

The polycondensation reaction will occur more intensively in an acidic environment. Therefore, acidic substances are used as hardeners, such as hydrochloric, sulfuric, acetic, oxalic, lactic acids, Petrov’s contact, as well as ammonium salts of strong acids. The hardening speed of the UFR is affected by the nature and quantity of the hardener, and the hardening conditions. For example, for hot gluing, the pH of the liquid glue should be in the range of 6-5. 5, for cold gluing 3-5.

A review of the literature shows that there are recommendations for the use of various hardeners, including combined ones[10, 11, 12].

The most common hardener of urea-formaldehyde resins when bonding with heating is ammonium chloride. It reacts with free or weakly bound formaldehyde, which leads to a decrease in the pH of the medium. In production, the pH of the medium is affected by the type of hardener, its quantity, and the acidity of wood particles, slowing or speeding up the process of gelatinization of the binder.

Ammonium chloride has its disadvantages [9, 10] and therefore the search for more effective hardeners remains an urgent task.

The purpose of the work is to monitor hardeners of the low-toxic UFR and study its influence on physical and chemical properties.

2. Experimental part

In the course of the study, the low-toxic UFR of the KF-MT-15 brand was used. The physical and chemical parameters of the resin are shown in table 1.

Previously, we studied ammonium chloride (NH4Cl) and ammonium silicofluoride (NH4)2(SiF6) as hardeners of UFR [13, 14].

The effect of ammonium chloride on the resin:

\[ 4 \text{NH}_{4}\text{Cl} + 6 \text{CH}_2\text{O} \rightarrow 4 \text{HCl} + (\text{CH}_2)\text{N}_2 + 6 \text{H}_2\text{O} \]

Ammonium chloride (NH4Cl) reacts with free formaldehyde, which is found in UFR in greater or lesser amount according to the above scheme with the formation of hydrochloric methylamine and formic acid.

The gelatinization of the adhesive and then a rapid transition to a solid state occurs upon reaching the acidity of the medium (pH 2.5 - 4.0).

In the manufacture of wood particle board, especially for construction purposes, antiseptics (sodium fluoride, sodium pentachlorophenolate, HMBB-3324, HMR-221 preparations, etc.) are also used in addition to hardener. Therefore, it is necessary to find a chemical that would simultaneously possess the properties of both a hardener (without the presence of chlorine in it) and an antiseptic. Based on exploratory experiments, we have found that one of the antiseptics used in wood preservation technology ammonium silicofluoride (ASF), chemical formula (NH4)2(SiF6) could be this chemical.
We assumed that the chemistry of ammonium silicofluoride as a hardener of urea-formaldehyde resins may be the following: in the first stage, a hydrolysis reaction may occur with the formation of fluorsilicic acid:

\[(\text{NH}_4)_2\text{[SiF}_6\text{]} + 2 \text{HOH} \rightarrow \text{H}_2\text{[SiF}_6\text{]} + 2\text{NH}_4\text{OH}\]

In the second stage, ammonia water is partially resolved into ammonia and water, and partially interacts with free formaldehyde forming hexamine and water:

\[2 \text{NH}_4\text{OH} + \text{CH}_2\text{O} \rightarrow (\text{CH}_2)_6\text{N}_4 + \text{H}_2\text{O}\]

\[\text{NH}_4\text{OH} \rightarrow \text{NH}_3 + \text{H}_2\text{O}\]

Table 1. Physical and chemical parameters of urea-formaldehyde resin.

| Indicator                                      | Standards for resin of the following brands |
|------------------------------------------------|---------------------------------------------|
| Mass fraction of dry residue, %                | 66 ± 2                                      |
| Mass fraction of free formaldehyde, %, not more than | 0.15                                        |
| Conventional viscosity according to VZ-246    |                                             |
| Nozzle diameter of 4 mm                        | 50-80                                       |
| Nozzle diameter of 6 mm                        | 40-60                                       |
| Concentration of hydrogen ions, pH             | 7.5-8.5                                     |
| Duration of gelatinization at 100°C, s         | 50-70                                       |
| Miscibility of the resin with water at 20 ±1°C in a ratio by volume 1:2 | 1:2-1:10                                   |
| Ultimate split strength on the adhesive layer of plywood after soaking the specimens in water for 24 hours, MPa, not less than | 1.6                                         |

It is also proposed to use sulfuric acid, nitric acid, ammonium phosphoric acid, and aluminum sulfuric acid as a hardener for the low-toxic UFR [15]. The authors found that the low-toxic UFR are well combined with combined hardeners: aluminum sulfuric acid and ammonium chloride, ammonium nitric acid and aluminum sulfuric acid. Our research is aimed at studying the physical and chemical properties of the glue using a combined hardener-aluminum sulfate and ammonium chloride.

Aluminum sulphate (\(\text{Al}_2(\text{SO}_4)_3\)) is a complex inorganic substance, a white salt with a gray, blue or pink hue, with a density of 1.62-2.67 g / cm³. Hygroscopic. It is quickly dissolved in water, melts at a temperature of + 7000 C. Aluminum sulfate is mostly harmless to the human body. But working with it requires the use of protective equipment (gloves, glasses, respirator), as well as strict compliance with all safety techniques for working with chemical reagents. The result of electrolytic dissociation is that the salts form poorly soluble phases. In an aqueous solution, hydrogen ions accumulate, and the solution becomes acidic.

The determination of the pH of liquid resins and adhesive solutions was performed by the potentiometric method with a pH meter of 150 M according to the standard method.
of the pH of cured adhesives was also performed with a pH meter of the pH 150 M mark, only after holding the crushed cured glue in distilled water at a ratio of glue to water of 1: 10 for a day.

The viability of adhesives was determined by measuring the viscosity using a VZ-4 viscometer at certain time intervals.

3. Results and discussion

At the first stage, the optimal ratio of aluminum sulphate and ammonium chloride in the combined hardener was determined. To do this, we prepared several recipes for adhesives that differ in the percentage of components included in it. The glue recipes are shown in table 2.

| Table 2. Hardener composition. |
|-------------------------------|------------------|------------------|------------------|------------------|------------------|
| Hardener components            | The composition of the hardener, % |
| Hardener components            | 1                | 2                | 3                | 4                | 5                |
| Ammoniumchloride               | 100              | 75               | 50               | 25               | 0                |
| Aluminiumsulphate              | 0                | 25               | 50               | 75               | 100              |

The amount of hardener introduced into the resin was 1 % of the resin weight. The results of the study are shown in graphs 1 and 2.

As can be seen from the graph (figure 1), aluminum sulfate has a higher reactivity and the gelatinization time with its use is 1.5 times less than with ammonium chloride. The use of these two hardening agents in combination allows to reduce the time of gelation. The greater the proportion of aluminum sulphate, the shorter the gelatinization time.

The same trend is observed when measuring the pH of liquid glue (figure 2). The more aluminum sulfcuric acid is contained in the composition of the combined hardener, the higher the acidity of the liquid glue. The dependence of the pH of the cured glue on the hardener composition (figure 2) is reversed, lower pH values have a hardener with a large amount of ammonium chloride. Thus, with a content of 25% aluminum sulfate, the pH is 3.2, and at 75 % it is already 3.8.
Analyzing the graphs (figure 1-2), we can say that the use of a combined hardener based on ammonium chloride and aluminum sulfate allows you to reduce the pH of the adhesive solution and reduce the gelatinization time. The graphs show that the optimal ratio of components in the combined hardener is 25% ammonium chloride and 75% aluminum sulfate. At the same time, pH is 5.5 and the gelatinization time is 57 seconds. Using «pure» aluminum sulphate as a hardener can lead to premature hardening of the adhesive.

Since aluminum sulfate has a higher reactivity, it is necessary to check how the combined hardener affects the viability of the glue.

The graph (figure 3) shows that when using ammonium chloride, the pot life of the glue (reaching a viscosity of 300 c) is 9.5 hours. When using aluminum sulphate-3.3 hours, and when combined-8 hours, which is quite enough in the bonding technology.

After determining the optimal composition of the combined hardener, experiments were conducted on the effect of the amount of combined hardener on the controlled parameters (gelatinization time,
pH of the liquid and cured glue). The amount of hardener varied from 0.25 to 4 percent. The results are shown in figures 4-6.

In order to evaluate the effectiveness of using a combined hardener, the same graphs show dependencies when using previously studied hardeners - silicofluoride and ammonium chloride.

As you can see from the graph (figure 4), with an increase in the amount of hardener to 1.5%, the gelatinization time decreases. A further increase in the content of the hardening agent does not affect the gelatinization time. If we compare the effect on the gelatinization time of the hardener type, we can state the same character of the curves. However, the gelatinization time of 60 seconds is achieved by different hardener amounts. So, when using ammonium silicofluoride, you need 3%, ammonium chloride-1.5%, and combined-0.5% hardener.

From the graph (figure 5), we can see that when adding a combined hardener, the pH of the UFR decreases to 5.48 and when increasing the hardener amount, it practically does not change. While adding silicofluoride and ammonium chloride, the pH of the resin also decreases, and then gradually increases with the increase in the amount of hardener. Moreover, a more acidic environment is observed when using a combined hardener (pH=5.5), less acidic when using ammonium chloride (pH=6.4).

While analyzing dependencies (figure 6), the situation is reversed. The lowest pH value has a cured adhesive using ammonium chloride (pH=2.5), and the highest with a combined hardener (pH=3.2).
Figure 5. The pH of the liquid glue depends on the hardener type and amount.

Figure 6. The pH of the cured adhesive depends on the hardener type and amount.

4. Conclusions
The search for effective low-toxicity hardening agents for UFR led to the following conclusions:
1. Aluminum sulphate has a higher reactivity than ammonium chloride. Its use as a hardener is limited due to the low viability of the resulting adhesives.
2. The use of ammonium chloride and aluminum sulphate in combination reduces the gelatinization time and ensures sufficient viability of the adhesive. The optimal ratio of components is 25% ammonium chloride and 75% aluminum sulphate.

3. Comparing the studied hardeners (ammonium chloride, ammonium silicofluoride and a combination of ammonium chloride and aluminum sulphate), we found that the percentage of the combined hardener to achieve a gelatinization time of 60°C is minimal and is 0.5%, for ammonium chloride 1.5% and ammonium silicofluoride 3%.

4. All the studied preparations can be used as a hardener of the low-toxic UFR, but its content should be adjusted taking into account the physical and chemical parameters of the initial state of the resins and production conditions.

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