Modified Phenol Formaldehyde Reactive Oligomers

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Abstract. Polymeric heat-insulating materials based on casting phenolic foams have low thermal conductivity, reduced fire hazard, high operating temperatures, low cost of the starting components, and biostability. Due to these properties, they are superior in technical and economic indicators to mineral and other polymeric heat-insulating materials used in the construction industry. Low strength, tendency to smoldering, and high toxicity are significant limiting factors for the wider use of thermal insulation materials based on phenol formaldehyde oligomers. Modification of phenol-formaldehyde oligomers can improve the operational properties of materials and products based on them. One way is to introduce chemically active modified additives into the feedstock. As such compounds, metal chlorides of variable valence (FeCl₃) and sodium hexafluorosilicate (Na₂[SiF₆]) were used in the work. It was established by studies that iron (III) salts of 2.0–2.6 wt.% are most effective in reducing toxicity. The simultaneous introduction of sodium hexafluorosilicate in an amount of 0.5 wt.% Allows to reduce the material consumption of products based on phenol formaldehyde oligomers.

1. Introduction

Modern technologies in the construction industry impose certain requirements on the materials used. Building materials must be energy efficient, environmentally friendly and competitive.

Providing modern requirements for energy efficiency to buildings and structures under construction, as well as reducing heat loss during the transit of heat carriers through pipelines, is practically impossible today without involving the appropriate materials for heat-insulating purposes.

The most effective building thermal insulation materials are polymeric materials. The first technologies for the industrial synthesis of polymer materials were created in Germany in the mid-twentieth century [1]. Currently, heat-insulating materials on polymer binders are increasingly used. This is due to such characteristics as the temperature interval of operation, chemical resistance, water resistance. The area of application is limited by a high tendency to burning with the release of toxic products, high smoke-forming ability, and relatively low positive operating temperatures.

For the production of thermal insulation works in the construction industry, materials and products based on phenol-formaldehyde resins, polystyrene foam, polyurethane foam, and polyethylene foam are used. Expanded polystyrene has high heat-insulating characteristics, water resistance. A serious limiting factor of its application is fire hazard and low positive operating temperature. The authors of [2] showed that, during combustion, the cellular structure of the material is destroyed and a monolithic polymer melt is formed, the oxygen index for both the foamed thermoplastic and the original polymer (d = 40-100kg / m³) is 18%.
A significant amount in the market of thermal insulation materials is occupied by polyurethane foams and products based on them. Polyurethane foams are distinguished by high heat-insulating properties, manufacturability of the production of heat-insulating work directly on the construction site by spraying, and the simplicity of the technology for manufacturing products and structures in the factory [3-6].

The limited use of polyurethane foams as effective thermal insulation materials is associated with the high cost of products based on it, due to the lack of a domestic production base of one of the main components of the production of polyurethane foams - isocyanates, the need of which is provided by import.

Phenol foams have proven themselves well. Gas-filled foam foams have low coefficients of thermal conductivity: at 20 °C 0.032-0.043 W/(m·K), high biostability, low water absorption, heat and frost resistance [7,8].

In this regard, there is an increase in the production of phenol-formaldehyde resole oligomers for pouring phenol foams. To improve the properties, work is underway on the modification of phenol foams to increase their thermal and fire resistance. In [9], the results on increasing the heat resistance of foam phenol foams using kaolin and fiberglass are presented. Phenol foams and flame retardants based on dicyandiamide [10], ammonium polyphosphates, pentaerythritol and zinc oxide increase fire resistance [11]. The authors of [12] conducted studies on the variation of the coefficient of thermal expansion in a wide temperature range (77–293 K). The coefficients of thermal expansion of foam foams, as well as other polymers, are almost independent of temperature, which expands the scope of their application. In [13], the authors presented a heat-insulating material with improved characteristics.

The main obstacle to the use of foams is the release of free phenol and formaldehyde in the production and operation of products based on them. In [14–16], methods for reducing the toxicity of phenol formaldehyde oligomers are presented.

The purpose of this study is to find ways to reduce the toxicity of phenol foams.

2. Materials and methods
Phenol foams FRP-1 was chosen as the object of study. Heat-insulating products of foam-plastic of FRP-1 is a resoles foam, which is obtained by the casting method. The production technology is based on mixing two components with further pouring the mixture into the mold cavity and subsequent curing, accompanied by an increase in the temperature of the system to 100 °C. Components for producing casting resoles phenol foams FRP-1: FRV-1A, VAG-3. FRV-1A (TU 6-05-1104-78) - resoles prepolymer, homogeneous mixture of FRV-1 prepolymer with plasticizer and aluminum powder. FRV-1 is a polydisperse mixture of the primary polycondensation products of phenol with formaldehyde in the presence of a strong base catalyst (NaOH). VAG-3 (TU-6-05-1116-88) is a condensation product of sulfophenolurea with formaldehyde, as well as phosphoric acid.

As a result of the processes of polycondensation and simultaneous foaming with hydrogen of the cured mass, a developed porous-cellular structure with a cell diameter of 0.1-0.3 mm is formed. The residual amounts of unbound monomers of phenol (hazard class II) and formaldehyde (hazard class II) during emission can enter the environment, having a significant toxic effect on humans, accumulating in the body [17]. To reduce the concentration of unbound phenol and formaldehyde, the authors of [18] proposed such approaches as the use of modifying additives that bind phenol monomers, the addition of sorbents, such as zeolites, and the development of resin synthesis methods with the reduction or replacement of a part of phenol in the composition of the raw material.

The properties of phenol-formaldehyde foam directly depend on the characteristics of the feedstock and the modifiers introduced into its composition [19-22]. Due to the nature of the phenol foams, particular effectiveness in modifying the properties can be achieved by making composites based on the phenol formaldehyde oligomer [23-26].

A reduction in the released phenol monomers can be achieved by the addition of complexing agents to phenol-formaldehyde resins capable of binding free phenol monomers to heavy less volatile...
complex compounds. Known methods for the formation of such bonds, lowering the concentration of emitted phenol monomers, the introduction of fluoride aluminum compounds or tin chlorides in the raw material [14].

It is possible to reduce the toxic substances released from products by reducing the mass fraction of the solid polymer matrix in the material and replacing it with a large amount of the gaseous phase. This effect can be achieved by adding a polycondensation process to the initial component mixture of catalysts, intensifying the reaction of the formation of the polymer chain and allowing to obtain products of lower density. For these purposes, fluoride compounds may be added to the feed.

In addition, a decrease in the material consumption of products can be achieved by introducing an additional gas-forming component, which contributes to an increase in the porosity of the manufactured product and a decrease in the density of the material. An increase in the evolution of the gas phase in the process of manufacturing a material or product can be achieved both by changing the content of aluminum powder contained in FRP-1A and by adding an additional blowing agent, for example, low-boiling liquids (pentane, trichlorofluoromethane and others).

In this study, a comprehensive approach to reducing toxicity was chosen, combining the method of binding phenol to nonvolatile complexes with a complexing agent represented by iron (III) chloride (FeCl₃) while reducing the material consumption of products by adding a catalyst represented by sodium hexafluorosilicate (Na₂[SiF₆]).

The use of iron (III) chloride allows the binding of free phenol monomers to non-volatile complexes of iron phenolates, reducing the potential danger of phenol-formaldehyde foam.

The use of polycondensation catalysts can compensate for a possible decrease in the reactivity of the casting mixture and, if possible, even increase it, which will also help reduce the toxicity of the manufactured product.

During the study, tests were conducted to determine the effectiveness of using various concentrations of sodium hexafluorosilicate on the rate of foaming of products and their average density. The measurements of the foaming rate of the products were carried out according to the standard method in accordance with TU 6-05-1104-78 "Resin phenol-formaldehyde expandable brand FRV-1A". The compressive strength of the samples was determined at 10% linear deformation by an AS-102 hydraulic press (Hungary) on cubic samples of size 50x50x50 mm. The determination of the amount of residual phenolic monomers was carried out by gas chromatography in accordance with GOST 11235-2017 “Phenol-formaldehyde resins. Methods for the determination of free phenol”.

3. Results
At the first stage of work, the optimal composition of the modified composition was experimentally determined. For modification, the chemical additive sodium hexafluorosilicate was used. Model
compositions with a modifier content of 0.25 were prepared; 0.5; 0.75; 1.0; and 1.25 wt.%, respectively. For each composition, the average density, compressive strength, and foaming ratio were determined. The data are presented in Figure 1. The curve shows that the optimal composition is 0.5% sodium hexafluorosilicate based on the weight of the FRV-1A oligomer. The rate of foaming has a maximum value of 31.5, the compressive strength and density are minimal.

![Graph showing the effect of sodium hexafluorosilicate on the properties of the phenol-formaldehyde composition.](image)

**Figure 1.** The effect of sodium hexafluorosilicate on the properties of the phenol-formaldehyde composition.

Sodium hexafluorosilicate acts as a catalyst for foaming and curing processes. The optimal is the introduction of additives in a concentration of 0.5 wt.% By weight of phenol-formaldehyde resins of the type FPV-1A. The increase in additives accelerates the process of gas formation in the raw material mixture. This phenomenon negatively affects the polycondensation process, the appearance of strong shrinkage of products.

Compositions containing additives of less than 0.5 wt.% Have insufficient compressive strength, less foaming.
The second stage of the work was the selection of optimal concentrations of iron (III) chloride in order to reduce the concentration of free phenol in the finished foam. FeCl$_3$ was introduced into the prepared composition in increments of 0.4 wt. % to a maximum of 3.2 wt.%. In addition to the free phenol content, mean density values for each sample were determined. The data are presented in Figure 2.

![Figure 2](image)

**Figure 2.** The effect of iron (III) chloride on the properties of phenol foams.

An analysis of the results showed that at a concentration of iron (III) chloride of 1.8 - 3.2 wt.%, the content of free phenol is very low and was below the detection limit by gas chromatography. The decrease in free phenol monomers occurs due to its binding to complex compounds. An iron (III) cation acts as a complexing agent. Effectively the introduction of a chemical additive in an amount of 2.0-2.6 wt. %.

Thus, the results of the studies showed that the introduction of the chemical additives FeCl$_3$, Na$_2$[SiF$_6$] into the feed mixture of phenol-formaldehyde oligomer allows one to obtain modified compositions of the optimal composition with a low free phenol content and improved properties, which leads to a decrease in the material consumption of products obtained on the basis of phenolic binders. Recommended amounts of modifying additives are 0.5 wt.% Na$_2$[SiF$_6$], 2.0 - 2.6 wt. % FeCl$_3$.

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