Статья поступила в редакцию: 05.06.2026
Статья принята к публикации: 16.06.2026
Статья опубликована: 28.08.2026

УДК 674.8+678.5

Current state of polymer binders used in particleboard production: a review

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Современное состояние полимерных связующих материалов, используемых в производстве ДСП: обзор

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Abstract

The article presents the results of research on the influence of reactive compounds on the hardening process of both modified and unmodified carbamide-formaldehyde resin derivatives, and determines the optimal hardening regimes for their application in the production of wood-plastic tile materials.

Increasing requirements for the strength, performance, and durability of wood-plastic boards necessitate the modification of carbamide-formaldehyde resins using physical and chemical methods. This modification is aimed at improving the adhesive, physical-mechanical, and technological properties of the binder.

As a result of studying the physicochemical properties of unmodified and modified resins, it was established that an increase in the content of modifying additives is accompanied by an increase in the concentration of chlorine ions in the resin. In this case, the hardening time changes in the following sequence: polyvinyl chloride → epichlorohydrin → benzyl chloride. It has been established that introducing a modifier in an amount exceeding 10 % of the resin mass is inappropriate, as it leads to a significant increase in its hardening time and a deterioration of the process's technological indicators.

Аннотация

В статье представлены результаты исследований влияния реактивных соединений на процесс отверждения как модифицированных, так и немодифицированных производных карбамидоформальдегидной смолы, а также определены оптимальные режимы отверждения для их применения в производстве древесно-пластиковых плиток.

Повышение требований к прочности, эксплуатационным характеристикам и долговечности древесно-пластиковых плит обуславливает необходимость модификации карбамидоформальдегидных смол физико-химическими методами. Эта модификация направлена на улучшение адгезионных, физико-механических и технологических свойств связующего.

В результате изучения физико-химических свойств немодифицированных и модифицированных смол установлено, что увеличение содержания модифицирующих добавок сопровождается увеличением концентрации хлорид-ионов в смоле. При этом время отверждения изменяется в следующей последовательности: поливинилхлорид → эпихлоргидрин → бензилхлорид. Установлено, что введение модификатора в количестве, превышающем 10 % от массы смолы, нецелесообразно, поскольку это приводит к значительному увеличению времени ее отверждения и ухудшению технологических показателей процесса.

Библиографическое описание: Современное состояние полимерных связующих материалов, используемых в производстве ДСП: обзор // Universum: технические науки : электрон. научн. журн. Ходжаева Д.Н. [и др.]. 2026. 8(149). URL: https://7universum.com/ru/tech/archive/item/23053

For citation: Current state of polymer binders used in particleboard production: a review // Universum: Technical Sciences : electronic scientific journal. Khodjaeva D.N. et al. 2026. No. 8(149). Available at: https://7universum.com/ru/tech/archive/item/23053

Keywords: polymer, urea-formaldehyde resin, modification, reactive compounds, benzene chloride, epichlorohydrin, polyvinyl chloride, gossypol resin, lignin, composite wood-plastic plate material.

Ключевые слова: полимер, карбамидоформальдегидная смола, модификация, реакционноспособные соединения, хлористый бензол, эпихлоргидрин, поливинилхлорид, госсиполовая смола, лигнин, композиционный древесно-пластиковый плитный материал.

Introduction

Wood-plastic materials are among the most dynamically developing types of woodworking industry products and hold one of the leading positions in the world in terms of production growth rates. Their widespread use is due to a number of valuable properties, including high uniformity of structure and characteristics across the entire volume of the material, size stability under changing humidity conditions, as well as good operational performance.

An additional advantage is the technological ease of manufacturing products of various shapes and configurations, including large-format sheet materials. The possibility of using affordable polymer binders and using single-year plant stems as raw materials expands the raw material base of production and contributes to the wider implementation of wood-plastic materials in various industrial sectors. [3; 7; 10; 13].

Research object. To study and analyze the states of polymer binders used in the production of particleboard (PB) and wood-plastic materials and boards (WPMB), we examined phenol-formaldehyde, urea-formaldehyde, and other polymer resins in this article.

Study results and their analysis. Let us consider the phenol-formaldehyde and urea-formaldehyde resins widely used in the production of PB and WPMB [4; 8; 9].

Phenol-formaldehyde resins are the primary component of adhesive compositions, possessing a complex of valuable properties and found wide application in various industrial sectors. Establishing the relationship between composition, structure, and properties is one of the key tasks of the modern stage in the development of adhesive material production technologies. Solving this task will allow for the purposeful development of composite materials and adhesive compositions with a specified set of properties, including increased heat resistance and weather resistance, as well as significantly simplify and intensify the technological process and improve the quality of finished products. [2].

These resins are used as a binding component in the production of filled press compositions with various fillers (cellulose, glass fiber, wood flour), wood-fiber and wood-wool boards, adhesives, and impregnating and filling compositions (for plywood, woven, and fiber-filled materials).

Phenol-formaldehyde resin is a substance of synthetic origin and is used for the manufacture of wood shavings. Phenol-formaldehyde resin ensures high stability and strength of adhesive compounds under the influence of hot and warm water, which is why it is classified as a highly water-resistant resin [1].

Phenol-formaldehyde resin is most widely used in the manufacture and bonding of WSB. Such resin hardens quite quickly and possesses very high adhesive strength and a light color. When gluing wood shavings, low-toxic SFJ-3014 grade resin is used, which complies with the accepted standard (GOST 20907-75*).

Table 1.

Physicochemical properties of SFJ-3014 phenol-formaldehyde resin

Name	Indicators
Content of non-volatile substances (dry residue), %	46-52
Viscosity according to VZ-4, s	17-90
Alkaline content, %	6.5 – 7.5
Free phenol content, %, not more than	0.10
Free formaldehyde content, %, not more than	0.15
After boiling in water for one hour, the strength limit of the plywood layer during cracking is -MPa, at least.	1.5

Phenol-formaldehyde resins are obtained by the polycondensation of phenol with formaldehyde. Phenol-formaldehyde resins of the resole type are formed at an equimolar reactant ratio or in the presence of excess formaldehyde under alkaline catalysis, whereas novolac resins are obtained in the presence of excess phenol under acidic conditions. The hardening process, i.e., the transformation into resite, occurs slowly at normal temperatures from 6 months to 1 year; at elevated temperatures, the hardening rate increases significantly. In the presence of acid catalysts, solution resins harden at a higher rate and at room temperature.

Resins in the resite stage are insoluble, insoluble, and possess fairly high heat resistance. At temperatures above 280 °C, they begin to decompose gradually. The study of the thermal destruction of phenol-formaldehyde resins showed that at these temperatures, the formation of diphenyl oxide bonds occurs, increasing the degree of system adhesion. During thermo-oxidative destruction, primarily, the oxidation of methylene groups to carboxyl groups occurs, which at a temperature of about 200 °C are capable of interacting to form heat-resistant polymers [11].

Novolac resin molecules do not contain methyl groups, and therefore are unable to undergo polycondensation reactions and do not form spatial structures. Novolac resins can be converted into an insoluble and non-melting state by treating them with formaldehyde, paraffin, and hexamethylene tetramine. Novolac resins are most often hardened using hexamethylene tetramine at elevated temperatures. Some characteristics of phenol-formaldehyde resins are shown in Table 2 [12].

Table 2.

Characteristics of phenol-formaldehyde resins

Name	Trade name	Molecular mass	Melting point, °C	Density, kg/m^3	Content of me thyl groups, %
p-third-Butylphenolformaldehyde resin	Phenofor B	500-600	65-80	1100	≥12
p-third-Octylphenol formaldehyde resin	Phenofor O	900-1200	75-90	1040	≥9
Bromethylated p-tert-butylphenolfor-mal-dehyde resin	Fenofor BB	1000-1400	60-80	-	≥10

To obtain adhesives, phenol-formaldehyde resins of the resolution type with a molecular weight of 700–1000 are primarily used. Novolactic phenol-formaldehyde resins are used significantly less frequently, primarily in modified adhesives. Resins from cresols and substituted phenols are of less interest for producing adhesives.

Phenol-formaldehyde resin is a transparent and homogeneous liquid in appearance, ranging from dark cherry-brown to red-brown, within the same color batch, without mechanical impurities. However, at a temperature of 100…105 °C, the hardening degree of SFJ-3014 grade resin is insufficient. At the same time, it possesses high alkalinity, which is associated with the conditions for synthesizing low-viscosity resins. Therefore, to manufacture slabs with increased water and atmospheric resistance suitable for use in elements of standard low-rise house construction, it is necessary to enhance the technological properties of the resin.

By modifying SFJ-3014 grade resin using aluminum sulfate, the deepening and acceleration of the hardening process are achieved, and water resistance is increased.

It should be noted that phenol-formaldehyde resin is not produced in our republic due to the lack of raw materials for obtaining phenol. Furthermore, it is very expensive and, accordingly, scarce; therefore, it will be necessary to purchase this product in foreign currency.

But the main disadvantage of phenol-formaldehyde resin is its toxicity.

Phenol-formaldehyde resins can have harmful effects on the skin, causing dermatitis and eczema [13]. Uncured phenol-formaldehyde resin can contain up to 11 % free phenol.

When phenol-formaldehyde resins are rejected in plastic (phenoplastics), the sewing of oligomeric resin fragments occurs with the participation of free phenol contained within it, while the content of phenol incorporated into the phenoplastic decreases to trace amounts; the sanitary regulations of the Russian Federation regulate the permissible quantities of phenol and formaldehyde migration for products made of phenoplastics; specifically, for products in contact with food products, for phenol – 0.05 mg/l, for formaldehyde – 0.1 mg/l.

Therefore, as noted above, it is necessary to modify the phenol-formaldehyde resin or replace it with another, less toxic resin, i.e., urea-formaldehyde (carbamide).

It should be noted that in our republic, urea-formaldehyde resin is primarily used as a polymer binder in the production of wood-plastic tile materials.

Urea-formaldehyde resin (M-resol type fixative) is a product of polycondensation of urea and formaldehyde in the presence of a catalyst.

It is colorless and easily stains into any color in mass.

The first products of urea condensation with formaldehyde (carbamide resins) were obtained as early as 1896, but the production of urea aldehyde resins was only established in 1920–1921.

Urea-formaldehyde resins are used as binders in the production of wood shavings, wood fiber boards, plywood, and adhesives in the manufacture of furniture, carpentry structures, etc.

Products of carbamide condensation with formaldehyde are very common adhesives for bonding wood, plywood, and other wooden materials.

Conclusion

Thus, the results of the analysis show that wood-sheet and wood-plastic slabs manufactured using non-modified urea-formaldehyde resin are characterized by insufficiently high physicochemical and operational indicators, limited durability, and in some cases do not fully meet the requirements of current standards.

In this regard, modifying urea-formaldehyde resin using physicochemical methods to enhance its adhesive, physicochemical, and technological properties is a pressing task. The implementation of this approach will allow for the production of wood-plastic slabs with improved strength characteristics, increased resistance to external influences, and a longer service life.

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