Periodica Polytechnica Chemical Engineering, 67(3), pp. 386–395, 2023

Usage of the New Modifier-curing Agent in Plywood Technology: The Influence to Urea-formaldehyde Resin Curing and Formaldehyde Emission

Daniil Ivanov[1*], Mariya Ekaterincheva[1], Aleksey Kalashnikov[2], Ksenya Baca[3], Anton Mazur[4]

[1] Department of Wood and Cellulose Composite Technology, Institute of Chemical Wood Biomass Processing and Technospheric Safety, Saint Petersburg State Forest Technical University, Institutskiy per. 5, 194021 St. Petersburg, Russia
[2] Parfinskiy Plywood Mill LCC, Ulitsa Kirova 52, 175130 Parfino, Novgorod Oblast, Russia
[3] FANPLAST JSC, Dnepropetrovskaya Ulitsa 8, 191119 St. Petersburg, Russia
[4] Magnetic Resonance Research Centre, Research Park, Saint-Petersburg State University, University Enbankment 7/9, 198504 St. Petersburg, Russia
[*] Corresponding author, e-mail: ivanov.d.v.spb@74.ru

Received: 19 October 2022, Accepted: 28 March 2023, Published online: 08 June 2023

Abstract

One of the urgent scientific and technical objectives in the technologies of plywood and wood boards is the search for ways to reduce of hot pressing time without increasing the formaldehyde emission from finished products. To solve this problem was developed the new modifier-curing agent MC-4SF, is mainly a product of interaction of citric acid with urea and ammonia. Compared to traditional ammonium salts, the modifier-curing agent combines the properties of both direct and latent catalysts. Determination of the composition of residual methylol groups in the aqueous extracts obtained by treating the resin cured at 100 °C showed that the modifier-curing agent provides relatively high hydrolytic stability of the UF-polymer during extraction. Spectra of solid-state ^{13}C NMR showed that in resins cured with MC-4SF increased the compound of methylene bridges compared to resins cured with standard catalysts. It is possible that the amino groups of urea (or its derivatives) included in the modifier-curing agent, react with the methylol groups of UF oligomers, fitting urea into the structure of the resulting polymer. Thus explains the increased hydrolytic stability and reduced toxicity of the cured resin. Manufacturing tests of nine-layer plywood made with a modifier-curing agent showed that replacing ammonium sulfate with MC-4SF allows a significant reduction in pressing time at 110 °C without loss of quality of the finished product. With the same pressing time, it was possible to increase the line shear strength by 14% and to reduce formaldehyde emission by 45%.

Keywords

plywood, urea-formaldehyde resin, curing agents, modifier-curing agent

1 Introduction

Currently, the main process of determining plywood formation is cures of synthetic, thermoset resins by the polycondensations mechanism. The urea-formaldehyde (UF) resin, which cures when it gets heated during hot pressing – is the most popular resin in Russian Federation. The curing time has a strong influence on the pressing duration and properties of finished products. The reduction of hot pressing duration in turn allows increasing of capacity of industrial line. Basically, an acid catalyst is used to speed up the polycondensation in UF oligomers.

As a rule, it's customary to highlight latent and direct catalysts, which are fundamentally different in their mechanism of action (reaction). Direct catalysts are providing acidic of resin after combining with resin, these catalysts are usually represented acids or strongly acidic salts (oxalic, citric, phosphoric acids, salts of amides, etc.). The main disadvantage of direct catalysts is the inability to provide a gradual decrease in the pH of the resin over time. At low content (usually not more than 0.4–1.0 wt.% based on solid resin) they will not provide required reactivity of UF resin, at the same time an increased amount of acid leads to a significant decrease in the pot-life of the resin or even to its cold curing [1].

In contrast with direct curing agents, latent catalysts slightly acidify the resin after combining with resin, but in high temperature they are providing pH value, which

Cite this article as: Ivanov, D., Ekaterincheva, M., Kalashnikov, A., Baca, K., Mazur, A. "Usage of the New Modifier-curing Agent in Plywood Technology: The Influence to Urea-formaldehyde Resin Curing and Formaldehyde Emission", Periodica Polytechnica Chemical Engineering, 67(3), pp. 386–395, 2023. https://doi.org/10.3311/PPch.21369

necessary for faster curing process. Latent catalysts are ammonium salts (ammonium chloride, sulfate, nitrate etc.), their latent action is possible because of their ability to react with free formaldehyde which contains in UF resin. According to one of the hypotheses, the reaction products are hexamethylenetetramine and mineral acid, which decreases pH of the resin [2, 3]. When resin gets heated, the reaction going faster, acid is formed in high yield, and the resin cures in a short time (40–80 s), when it's getting colder the reaction speed getting lower, and the glue cures in a few hours (no less than 4 h). This process determines the faster curing of the resin by hot pressing and its high pot-life of the previous technological stages.

A typical outcome of ammonium salts as latent curing agents is the presence of the so-called limit of effectiveness, when increasing the content of the catalyst ceases providing an acceleration of resin curing [4–6]. This limit depends on the type of curing agent, resin brand (the different UF resins type made by a one or other company and sold under a particular may has different properties), curing temperature, etc. Generally, the most difficulties are seen when the UF resin is low in free formaldehyde, in which case the effectiveness of the ammonium salts will not be sufficient for the necessary curing speed. Ammonium persulfate [7–9], aluminum sulfate and chloride [10, 11], ferric chloride [7] are known as more effective catalysts. Their disadvantage is a significant decrease in the pot-life of the resin with a comparable curing time. A simpler solution to accelerate resin curing is to use combined catalysts, which consist of different latent catalysts or latent and direct catalysts.

The work of Kantieva et al. [12] showed that the curing agent consisting of 75% aluminum sulfate and 25% ammonium chloride provides a 30–40% accelerated curing of UF resin, while its pot-life decreases slightly (from 10 to 8 hours). The patent of Andersen and Brehmer [13] disclosed the possibility of combining ammonium dihydrogen phosphate with aluminum chloride. Liu et al. [14] showed the possibility of combining ammonium chloride with citric and oxalic acids. The articles of Španić et al. [15, 16] explored the use of tartaric acid in combination with ammonium sulfate, the authors claim that the use of such a solution can accelerate the curing of UF resin and reduce the pressing time of particleboards by up to 20%. However, decreasing the duration of hot pressing always leads to an increase in the toxicity of the finished products. Formaldehyde, which is formed during UF resin curing, cannot escape from the pressed material in time and remains in its structure.

It is necessary to compensate for the negative impact from the reduction of hot pressing time. Combinations of latent catalysts with formaldehyde scavengers are known [17]. The work of Ivanov et al. [18] showed the effect of guanylurea sulfate as a UF resin modifier, in combing with ammonium sulfate, it accelerates resin curing and reduces the toxicity of medium density fiberboard (MDF). We found that the amide salts, which have an acidic reaction, act as direct catalysts that can interact with the methylol groups of UF oligomers during curing and incorporate into the resulting polymer structure. Similar results were obtained in work of Kotova et al. [19], where the authors showed the ability of diphthalic and dimaleic acid amides to accelerate the curing of UF resin and reduce its toxicity. We further developed a modifier-curing agent that combines the properties of direct and latent catalysts and can replace ammonium salts in the formulation of glue from UF resin. The product was named MC (modifier-curing agent), is a composition whose main components are adducts resulting from the interaction of citric acid, urea and ammonia. In research [20] we have shown that the modifier-curing agent synthesized at a molar ratio of citric acid: urea: ammonia – 1 : 1.5 : 1.5, can replace ammonium sulfate in particleboards, and at the same time, allows to reduce the pressing time to 20–30% without increasing toxicity.

Depending on the type of finished product (particleboard, MDF, plywood), resin brand, composition options (plywood glue or wood boards adhesive) we must use different modifier-curing agents, which differ in formulation and physicochemical properties. The aim of this work was to investigate the brand MC-4SF (modifier-curing agent fourth series, super-fast for curing UF with low free formaldehyde content under conditions of plywood technology.

2 Materials and methods

2.1 Materials

The low-toxicity UF resin was produced by one of the Russian manufacturers. The resin characteristics are given in (Table 1).

Aqueous solutions of ammonium sulfate and ammonium chloride with a concentration of 20% were used as curing agents. We also used MC-4SF modifier-curing agent, which is mainly a product of interaction of citric acid, urea and ammonia. The properties of the modifier-curing agent are presented in (Table 2).

Table 1 Properties of commercial UF resin

The appellation of the parameter	The value of the parameter
Mass fraction of solid resin, %	66.3
Free formaldehyde content, %	0.05
Conditional viscosity according to the viscometer with a nozzle diameter of 4 mm, s	50–70
Concentration of hydrogen ions, pH	7.63
Gel time with the addition of 1% ammonium chloride:	
at 100 °C, s	101
at 20 ± 1 °C, h	8

Table 2 Properties of modifier-curing agent MC-4SF

The appellation of the parameter	The value of the parameter
Appearance	transparent liquid without mechanical impurities
Mass fraction of the dry residue, %	60
pH (the hydrogen index)	2.4
Nitrogen content, %	15.6
The content of amino groups, %	11.0

2.2 Methods

2.2.1 Curing time of UF resin (at 100 ± 1 °C)

Compositions (resin + water + curing agent) were prepared in such a way that the mass fraction of solid resin in all cases was 55%. 10 g of commercial resin was weighed with an accuracy of 0.02 g, the calculated amount of distilled water and curing agent solutions were added. The tubes with the compositions were heated in a water bath, continuously stirring. The time from the immersion of the test tube in boiling water to the compositions loss of fluidity is considered to be the duration of curing.

2.2.2 Pot-life of UF resin (at 20 ± 1 °C)

Compositions (resin + water + curing agent) was prepared in the same way as for determining the curing time, and kept at room temperature (20 °C). For the time of gelatinization is taken as the time of adding of the curing agent into the resin to the moment of loss of fluidity of the compositions.

2.2.3 Change of UF resin pH-value and conditional viscosity in time

A viscometer with a nozzle diameter of 4 mm and a laboratory pH-millivoltmeter pH-410 were used for the test. The compositions (resin + water + curing agent) were prepared in such a way that the mass fraction of solid resin in all cases was 55%. For this purpose, 130 g of resin was weighed, a calculated amount of distilled water and curing agents' solutions were added to the resin. The compositions were mixed on a magnetic stirrer. The viscosity and pH were determined every hour.

2.2.4 UF resin curing depth (chemical analysis)

The reactivity of a mixture of UF resin and curing agent's solutions with different resin formulations was established by determining the amount of methylol groups and free formaldehyde in the cured compositions. The compositions (resin + water + curing agent) are cured, prepared in such a way that the mass fraction of solid resin in all cases is 55%.

To prepare the compositions, a volume of commercial resin of about 10 g, taken with an accuracy of 0.02 g, was transferred to a glass with a volume of 50 cm^3 and diluted with a calculated amount of distilled water. The calculated mass of the curing agents' solutions was added to the diluted resin. About 0.5 g of the prepared composition was applied to air-dry filter paper, pre-weighted to an accuracy of 0.1 mg. In total, 5 samples were prepared so that the estimated total weight of composition (resin + water + curing agent) on filter was about 2.5 g. The mass of each filter was determined together with the binder applied to it with an accuracy of 0.1 mg, after which the filters were placed in a specially made tripod, making sure that they did not touch. Then heat treatment was carried out for 3 min at 110 °C. The cured compositions were placed in a glass with a capacity of 250 cm^3 and filled with 150 cm^3 of water heated to 45–50 °C. Extraction was carried out for 30 min at a temperature of 40–45 °C, after which the contents of the glass were filtered into a measuring flask with a capacity of 250 cm^3, a glass of 100 cm^3 distilled water was washed and the contents of the flask were brought to the mark. In the resulting mixture, the content of free formaldehyde was determined by photometric method using acetylacetone [21] and the content of methylol groups by iodometric titration [22]. The amount of free formaldehyde in the composition (y, %) was calculated according to Eq. (1):

$$y = \left(2C \times 250/50 \times m_c\right) \times 100, \tag{1}$$

where 2 is the coefficient that takes into account the dilution; C – the mass of formaldehyde in a solution of 50 cm^3, g; m_c – total mass of the cured composition, g.

The total content of free formaldehyde and methylol groups (x, %) was calculated by Eq. (2):

$$\begin{aligned} x &= \left(0.0015 \times 250 \times 10\left(V_1 - V_2\right) \times K\right)/m_c \\ &= \left(3.75\left(V_1 - V_2\right) \times K\right)/m_c, \end{aligned} \tag{2}$$

where V_1 – the volume of 0.1 N sodium thiosulfate solution consumed for titration in the "control" experiment, cm^3; V_2 – the volume of 0.1 N sodium thiosulfate solution consumed for titration in the "working" experiment, cm^3; K – correction coefficient.

The content of methylol groups in the cured compositions (z, %) was found as follows in Eq. (3):

$$z = (31.03/30.03)(x - y) = 1.033(x - y), \tag{3}$$

where 31.03 and 30.03 are the molar weight of the methylol group and formaldehyde, respectively.

2.2.5 Solid state ^{13}C NMR spectroscopy

Different versions of composition (resin + water + curing agent) were prepared and cured at 100 °C for 3 min. The cured compositions were conditioned at room temperature for 30 min. Then the compositions were crushed and sifted using a sieve with a diameter of holes 0.5 mm. The powders which passed through the sieve and remained on the pallet were taken.

^{13}C solid-state NMR spectroscopy were used for instrumental analysis of the structure of the cured compositions. NMR spectra were obtained using a BRUKER AVANCE III WB 400 spectrometer; the zirconium oxide 4 mm rotor of the device rotated at a frequency of 4.1 kHz; CP/MAS pulse sequence ^{13}C {^{1}H} was used; relaxation delay – 2 s; contact time – 2 ms; number of pulses – 2048.

2.2.6 Preparation of plywood samples

Experimental-factory production of specimens of plywood at the production site of one of the Russian factories was carried out (the test certificate is available at the university). The total output was 3.5 m^3. Nine-layer plywood with a size of 1525 × 1525 × 12 mm was made from peeling birch veneer thickness 1.2 mm and moisture content 8%. The birch (*Betula pendula*) used at the factory grows in the North-West of Russia.

Flat hot pressing was carried out in a fifteen-stories periodically press according to the parameters adopted at the factory. Temperature of heating plates are 110 °C, a pressure of 1.5–1.8 MPa (the pressure changed randomly in this range), pressing duration of 3, 4, 5, 6 minutes. The glue consumption rate was 111–117 g/m^2.

In the preparation of glue, in addition to curing agents, kaolin was used as a bulking agent and urea as a formaldehyde scavenger. The compositions of plywood glue are presented in Table 3.

Table 3 Glue formulations used to make plywood

Component	Compositions of plywood glue		
	C1	C2	C3**
UF resin	100	100	100
MC-4SF*	4.5	3.4	–
Ammonium sulfate	–	–	2.0
Kaolin	7.0	7.0	7.0
Urea	0.7	0.7	0.7

* When compounding the glue, the components was calculated based on commercial resin, i.e., the content solid MO-4SF based on solid resin was 4 and 3% for composition 1 and 2 respectively.
** Control samples (plywood which usually manufactured at the factory) were made according to composition 3 (C3).

Plywood was tested according to Russian State Standards (GOST). Moisture content determined according to GOST 9621–72 [23], glue-line wet shear strength when shear along the glue layer according to GOST 9624–2009 [24]. The emission of formaldehyde was determined by the gas analytical method according to GOST 32155–2013 [25].

3 Results and analyses

According to the data of Table 4, classic curing agents have a clear efficiency limit. So, increase the amount of ammonium chloride from 1 to 3% allows reducing curing

Table 4 UF resin properties with different catalysts

Content, %	Curing time, s	pH	Pot-life, h
	Ammonium chloride		
1	101 ± 1	7.08	More than 8
2	79 ± 1	7.05	
3	74 ± 2	7.02	
4	71 ± 2	7.00	
5	70 ± 1	6.98	
6	69 ± 1	6.98	
	Ammonium sulfate		
1	106 ± 1	7.16	More than 8
2	88 ± 1	7.13	
3	78 ± 1	7.10	
4	77 ± 1	7.09	
5	76 ± 1	7.08	
6	75 ± 1	7.08	
	MC-4SF		
1	167 ± 1	6.04	6.0
2	96 ± 1	5.50	5.5
3	82 ± 1	5.11	5.0
4	71 ± 1	4.85	4.5
5	62 ± 1	4.79	4.0
6	60 ± 1	4.63	3.5

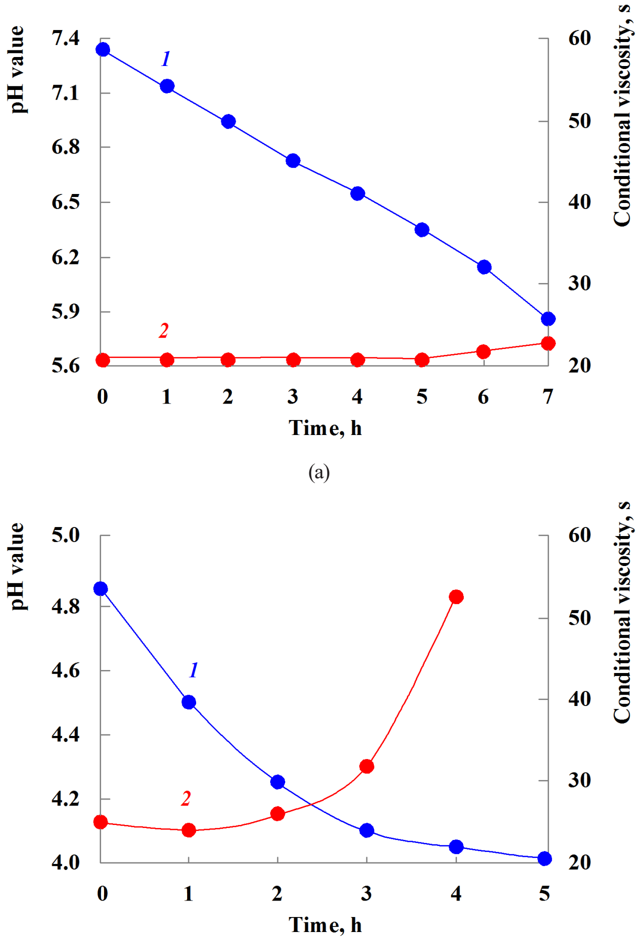
time from 101 to 74 s (by 27%). Further increase of curing agent consumption not appropriate; increase from 3 to 6% allows reducing curing time from 74 to 69 s (only by 7%). Efficiency limit of ammonium sulfate even lower that chloride.

Action of MC-4SF differs from traditional curing agents; it much inferior even ammonium sulfate at low amount (curing time 167 s), however at increase mass fraction to 4% modifier-curing agent surpasses sulfate ammonium and compares to chloride. At amount of 6% MC-4SF cures the resin by 13% faster than ammonium chloride. One of the features of modifier-curing agent is ability of greatly acidify resin; so, 1% MC-4SF provides pH value 6.08. and 1% ammonium chloride only 7.04. Herewith increased amount of modifier-curing agent to 6% leads to decrease pH to 4.63 while increased amount of ammonium chloride only to 6.98.

The characteristics of MC-4SF as a curing agent are shown more clearly in Fig. 1. After adding 3% ammonium sulfate in the UF resin, the pH value decreases slightly (from 7.8 to 6.8), but over the next 8 h the acidity gradually increases (to a pH value of 5.9).

Since MC-4SF is more acidic, it's more effective in reducing the pH value immediately after addition to the resin (up to 4.85 for 4% modifier-curing agent), thereby exhibiting the properties of direct curing catalysts. At the same time, the modifier-curing agent acts as a latent catalyst; after 3 h the pH value becomes 4.1 and the conditional viscosity begins to increase sharply. In the next 0.5 h the viscosity increases so much that the resin can no longer pass through the viscosimeter nozzle; in another 0.5 h the resin loses its fluidity and cures. In this way, MC-4SF has the properties of both direct and latent curing agent.

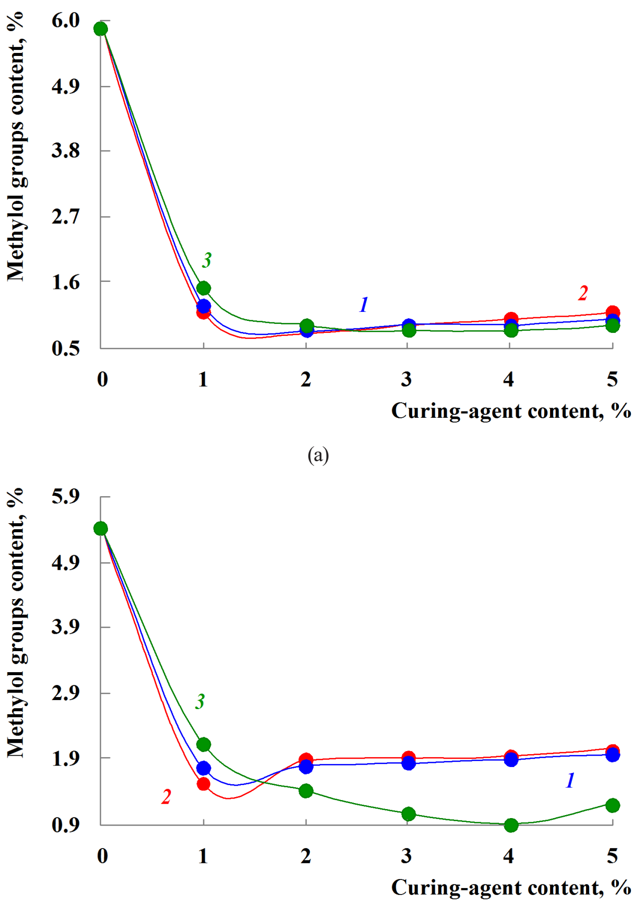
Fig. 2 shows the effect of the researched curing agents on the curing depth of the UF resin. After curing at 110 °C the minimum content of methylol groups is 0.8%; for ammonium sulfate and ammonium chloride this value is reached at a mass fraction of curing agents of 2%,



(a)

(b)

Fig. 1 Change of 1 – pH value and 2 – conditional viscosity of the UF resin with different curing-agent: (a) resin with 3% ammonium sulfate; (b) resin with 4% MC-4SF



(a)

(b)

Fig. 2 The effect of the amount curing agent on the methylol groups content in UF-resin cured at (a) 110 °C and (b) 100 °C: 1 – resin with ammonium sulfate; 2 – resin with ammonium chloride; 3 – resin with MC-4SF for MC-4SF 3% (Fig. 2 (a)). A further increase in the curing agents' consumption leads to an increase in the content of residual methylol groups, probably due to hydrolysis of the cured resin during extraction. Perhaps acids, which are formed as a result of curing agents action speed up hydrolysis and reduce UF resin hydrolytic stability. This assumption is partly by the results of other researches. So, the work of Nuryawan et al. [26] showed that cured UF resin is highly vulnerable to hydrolysis in the presence of hydrochloric acid. The article of Gagina et al. [27] showed that the hydrolysis degradations of the polymer are accompanied by an increase of methylol groups compounds.

UF resin, which is cured at 100 °C has a lower hydrolytic stability when classic curing agent usage (Fig. 2 (b)). So, increase of ammonium sulfate or chloride content from 2 to 5% leads to increase of methylol groups amount respectively at 12 to 30%. Probably at a relatively low temperature (100 °C) the sufficient number of bonds between UF oligomers does not have time to form that leads to increased availability of vulnerable to hydrolysis bond and functional groups. Wherein MC-4SF retains its effectiveness; at content 4% modifier-curing agent provides a content of methylol groups 0.8% – minimum amount, which ensure by ammonium sulfate and chloride at 110 °C. Relatively high resin hydrolytic stability in case of MC-4SF usage can be explained:

- comparative weakness of citric acid as a hydrolysis catalyst;
- high efficiency MC-4SF as a curing agent compared ammonium sulfate or chloride;
- modifier-curing agent amino groups reaction with methylol groups of UF oligomers and water resistance methylen bridges formation.

None of this assumption is not correct. Anyhow using MC-4SF increased of classic curing agents leads to increase of UF resin hydrolytic stability.

More information was received by usage of ^{13}C NMR spectroscopy (Fig. 3). Noteworthy, that spectrums all of the researched samples have signals that is usual and unusual for UF-resin. Chemical shifts in area 116–120 and 198–204 ppm (may refer to carbon atoms with double bond and aldehyde group respectively [28]) not typical for UF resins. Probably, the appearance of these signals is associated with the use of original chemical compounds in the synthesis. We will not examine the new signals in detail because their appearance is unique and related to the know-how of the resin developers. Besides, in area new signals are not detected any changes which associated with usage of MC-4SF.

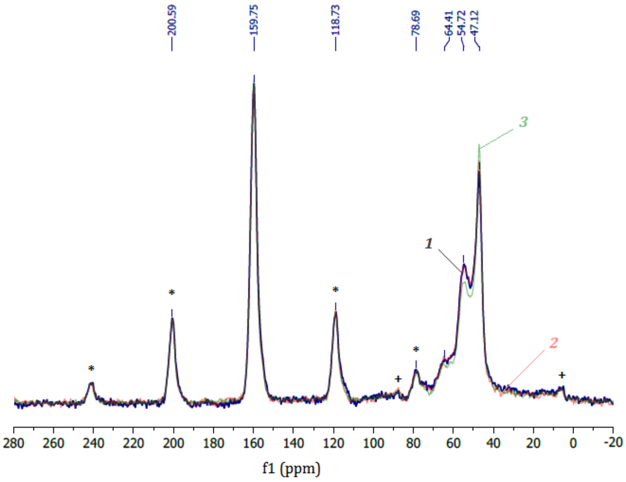


Fig. 3 Solid-state ^{13}C NMR spectra of cured UF resin: 1 – UF resin cured of ammonium sulfate; 2 – UF resin cured of ammonium chloride; 3 – UF resin cured of MC-4SF, * – SSB for carbonil groups; + – SSB for methylene groups

When considering the rest of the spectrum, it should be noted that signals which discovered in cured polymer in appearance agree to the signals that is typical for resin [29, 30]. The polymer is characterized by broad stripes, with each other in some areas [31], so we considered the peak maxima to identify the atoms. It is also important that the usage of MC-4SF instead of ammonium sulfate or chloride doesn't lead to qualitative changes in the cured resin. Only the amount of one or the other atoms differs, which we were expressing through peaks area (Table 5).

Compared with UF resin cured by classical catalysts, in the polymer which formed at MC-4SF usage increase the amount of type I methylene bridges and carbonil groups, decreases of type II methylene bridges (Table 5), amount of methylol groups and methylene ether bridges comparable. This result allows to suppose of chemical activity of MC-4SF components towards UF oligomers.

As has been said before MC-4SF contains urea or its derivatives, which has free amino groups. If we consider only a pure urea as a source of amino groups, then after adding the modifier-curing agent to the resin, the molar ratio F/U shifts downward. In [32–35], the resin synthesis showed that a decrease in the molar ratio leads to an increase in the number of methylene bridges in UF oligomers, and this pattern is true for reactions in both alkaline and acidic environments. It is noteworthy that mostly increase amount just methylene bridges type I, that is in reactions involved mainly the terminal methylol groups.

Table 5 Structures and chemical shift of cured UF resin in typical part

Grope	Shift, ppm	Peak maximum, ppm	Carbon content, %		
			glue with ammonium sulfate	glue with ammonium chloride	glue with MC-4SF
$–NH–CH_2–NH–$ *	40–52	47.12	27.07	27.59	29.26
$–NH–CH_2–NH<$ **	52–61	54.72	21.71	21.90	20.52
$–NH–CH_2OH$	62–70	64.41	10.60	10.80	9.83
$>N–CH_2–O–CH_2–N<$	72–80	72.37	5.94	5.70	5.48
$>C=O$	152–167	159.75	34.67	34.03	34.90

* Type I methylene bridges; ** Type II methylene bridges

In our case the formation of new methylen bridges can only be explained by the reaction of urea with UF oligomers during resin cured, herewith increased of amount bridges type I and reduce of amount bridges type II indicating that urea amino groups react mainly with terminal methylol groups of oligomers.

The fact that urea does not block the methylol groups, but includes into the structure of the cured resin, is evidenced by the remaining hydrolytic stability of the polymer, which was proven during a chemical experiment. This conclusion is consistent with the results of research of Chung and Maciel [36], where it was shown that methylen cross-bonds are more susceptible to hydrolysis than linear ones. According to the data of chemical analysis and NMR spectrums we can assume that UF resin, which cured of MC-4SF has structure shown in Fig. 4.

Manufacturing tests of nine-layer plywood (Table 6) showed that the replacement of ammonium sulfate with a modifier-curing agent can significantly reduce the pressing time. Thus, MC-4SF has greater efficiency compared to traditional curing agents. With an equal pressing time (6 min), plywood made of glue with MC-4SF (composition 1 – C1) significantly exceeds plywood made of glue with ammonium sulfate (composition 3 – C3) in its specifications. Thus, the use of MC-4SF as a curing agent in an amount of 4.5% relative to commercial resin allows to increase the glue-line wet shear strength when shear along the third glue layer by 14% (from 2.61 MPa for samples from C3 glue to 3.03 MPa for samples from C1 glue) and reduce the formaldehyde emission by 45% (from 0.280 mg/m^2 h for C3 glue samples up to 0.155 mg/m^2 h for C1 glue samples). The increase in the strength of the

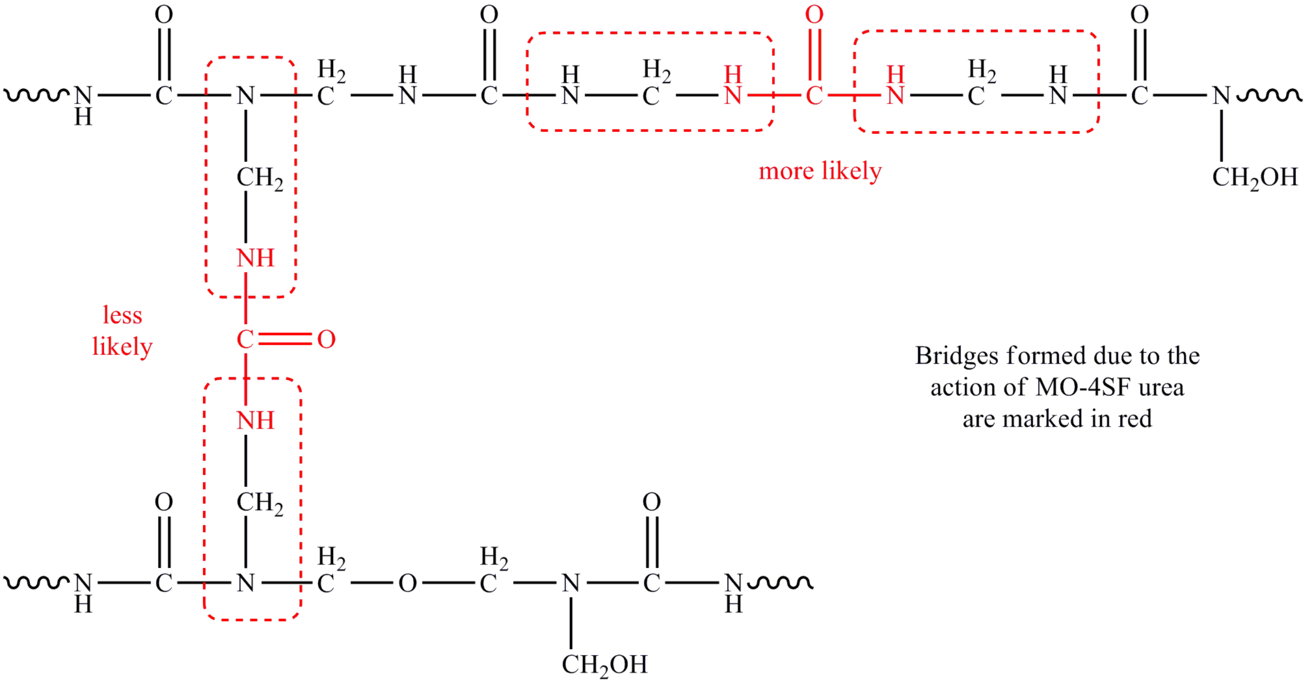


Fig 4 Supposed cured UF resin fragment formed with the participation of MC-4SF urea

Table 6 Plywood properties

Plywood version		Properties				
Pressing time, min	Glue composition	ω, %	σ_1, MPa	σ_2, MPa	σ_3, MPa	E, mg/m^2 h
6	1	6.5	2.87	3.00	3.03	0.155
5	1	4.3	3.32	3.39	3.47	–
4	1	5.4	2.40	3.29	3.16	–
3	1	5.6	2.32	1.72	2.72	0.210
5	2	5.5	2.10	3.07	2.67	–
4	2	5.2	3.36	3.05	2.53	–
6	3	5.5	–	–	2.61	0.280

Designations: σ_1 – glue-line wet shear strength shear along the first glue layer; σ_2 – glue-line wet shear strength when shear along the second glue layer; σ_3 – glue-line wet shear strength when shear along the third glue layer; E – formaldehyde emission (determined by gas analysis method).

finished plywood indicates a high hydrolytic stability of the cured polymer, which confirms the chemical analysis findings. With a pressing duration of 3 min, plywood made of C1 glue has comparable strength to plywood made of C3 glue, but pressed for 6 min. At the same time, the use of MC-4SF reduces the formaldehyde emission by 25% even with a low pressing time (from 0.280 mg/m^2 h for samples from C3 glue to 0.210 mg/m^2 h for samples from C1 glue).

The high efficiency of MC-4SF as a modifier that reduces the toxicity of plywood partially confirms the results of previous experiments and speaks in favor of the scheme presented in Fig. 4. The incorporation of urea into the structure of the curing resin with the formation of new methylene bridges suggests that fewer methylol groups of UF oligomers reacts with each other to form methylene ether bridges and their subsequent transformation into methylene with the emission of formaldehyde. The strength and water resistance of the glue line, which does not deteriorate at the same time, once again confirm that the methylol groups are not just blocked, but a polymer is being formed with the participation of urea MC-4SF.

4 Conclusion

The conclusions of this article are as follows:

1. Modifier-curing agent MC-4SF which are mainly product of interaction citric acid, urea and ammonia combined properties of direct and latent catalysts of UF resin cured. Compared with ammonium sulfate and chloride MC-4SF less efficient when low amount (1–4% for the researched resin mark). However, when increased modifier-curing agent amount to 5–6% the resin cured faster by 10–13% the classic curing agents' usage.
2. When resin cured urea, which is part of the modifier-curing agent, reacts with UF oligomers and built into the structure of forming polymer.
3. Manufacturing tests of MC-4SF showed that replacement to ammonium sulfate to modifier-curing agent allows to significantly reduce the duration of hot pressing nine-layer plywood at 110 °C without increased of formaldehyde emission of final product.

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