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ABSTRACT

The curing of urea-formaldehyde resin in the presence of urea used to reduce the formaldehyde content in particleboards was researched. Free urea was added into the adhesive with different amounts of latent curing agent (1 and 3% ammonium sulfate based on dry resin); a urea which is part of the modifiers-curing agents (products of the interaction of citric acid, urea and ammonia) was also studied separately. Based on the results of differential scanning calorimetry, solid-state NMR 13C of the cured resin and tests of model particleboards, it was suggested that the effect of urea is significantly influenced by the pH value of the adhesive before and during curing. At a relatively high pH value (3.50-3.70 after curing at ammonium sulfate content of 1%), urea acts as a classical scavenger, that is, it chemically interacts with formaldehyde to form harmless products. At a reduced pH value (3.00-3.10 after curing at ammonium sulfate content of 3%), urea reacts with resin components (methylolureas and UF oligomers mainly) that is, it participates in the curing of the adhesive.

Keywords: particleboard, urea-formaldehyde resin, curing agents, modifier-curing agent, formaldehyde reduction, pH dependency, differential scanning calorimetry, solid-state NMR, toxicity, wood adhesives.

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ABSTRACT

The curing of urea-formaldehyde resin in the presence of urea used to reduce the formaldehyde content in particleboards was researched. Free urea was added into the adhesive with different amounts of latent curing agent (1 and 3% ammonium sulfate based on dry resin); a urea which is part of the modifiers-curing agents (products of the interaction of citric acid, urea and ammonia) was also studied separately. Based on the results of differential scanning calorimetry, solid-state NMR ^{13}C of the cured resin and tests of model particleboards, it was suggested that the effect of urea is significantly influenced by the pH value of the adhesive before and during curing. At a relatively high pH value (3.50-3.70 after curing at ammonium sulfate content of 1%), urea acts as a classical scavenger, that is, it chemically interacts with formaldehyde to form harmless products. At a reduced pH value (3.00-3.10 after curing at ammonium sulfate content of 3%), urea reacts with resin components (methylolureas and UF oligomers mainly) that is, it participates in the curing of the adhesive. Tests of model samples of particleboards have shown that the mechanism of including urea into the structures of the curing resin is less effective for reducing toxicity than its action as a classical scavenger; at the same time, the formaldehyde content in particleboards with 3% ammonium sulfate and urea is lower in absolute values due to the useful effect of the curing agent. Modifiers-curing agents provide a low pH value of the binder before curing (3.72-4.51 with a content of modifiers-curing agents of 5%), urea in their composition is also involved in curing (according to solid-state NMR data).

Keywords: particleboard, urea-formaldehyde resin, curing agents, modifier-curing agent, formaldehyde reduction, pH dependency, differential scanning calorimetry, solid-state NMR, toxicity, wood adhesives.

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I. INTRODUCTION

Nowadays one of the most popular adhesive for wood boards remains of urea-formaldehyde resins (UF resin) [1, 2]. Its main disadvantage is high toxicity which determined by formaldehyde emission during resin curing. A common way to reduce toxicity is to use formaldehyde scavengers (acceptors) – modifiers that interact with formaldehyde to form harmless products. To date,

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many different scavengers are known [3, 4], but due to the low cost and high availability, urea remains one of the most common modifiers.

Depending on the type of product (particleboard, medium density fiberboard, plywood, etc.), there are many ways to adding urea to the materials composition. The scavenger can be added to the composition or separately from adhesives, in solution or powder form, in one layer (only in core or only in surface layers) or in all volume of wood board, at that its efficiency can be different. It is easier to add urea to the adhesive composition, since it requires a minimum of special equipment and is suitable for both wood boars and plywood. In that case, the action of urea is to interact with resin components, the direction and depth of which define the properties of final product and effectiveness of reducing the release of formaldehyde emission.

It is known that urea reduces the content of free formaldehyde as a result of chemical interaction and the formation of urea methylol derivatives; in particular this principle is used in the synthesis of resin at the third stage in alkaline conditions aiming to capture previously unreached formaldehyde. In addition, urea can interact not only with free formaldehyde, but also with other resin components such as methylolureas and UF oligomers. Hui Wang at al. [5] showed that post-added urea (decrease of F/U molar ratio from 2.0 to 1.2 at pH 8.0–8.5, and further shutter speed at 60 °C for 20 min) may act to urea-formaldehyde oligomers (UF oligomers), that is, it not only neutralizes formaldehyde, but also changes the structure of the main resin components. According to the authors, urea caused the movement of the type II methylol groups from oligomers to modifier with methylolurea forming due to primary amino groups of urea is more reactive than the secondary amino groups of UF oligomers. Vyukov [6] explored the curing of UF resin with urea and 0.3 % of oxalic acid at 20 °C for 10–60; min the author claims that the use of scavenger at reduce of F/U molar ratio from 2.0 to 1.6 and 1.2 leads to distractions of methylene esters bridges of UF oligomers. In first 20 min observed increased of methylolureas amount, but next 40 minutes contents decreased to zero, the methylol group's content stably decreased and free formaldehyde changed slightly. It is assumed that free urea causes of partial destruction of UF oligomers and further curing occurs due to the interaction between methylolureas. In some works it is reported that the curing of UF resin under traditional conditions (after latent curing agent adding and at the heating) it begins with the interaction of urea (unreached during synthesis) with the methylol groups of resin components [7-9].

Thus, it can be assumed that free urea participates to curing on a par with methylolureas and UF oligomers, but its effect on the cured resin is usually negative. The presence of urea leads to reduced of resin reactivity; this is typical both for low molar ratio resins [7, 10] and for resins in which urea is added as a scavenger [11]. As a rule, this leads to a decrease of wood boards properties, primarily water resistance [11-13]. An effective way to preserve the high resin reactivity and satisfactory wood board's properties while maintaining the ability of scavengers to neutralize formaldehyde is the use of urea derivatives. Park et al. [11] showed that the mono-methylolurea is more effective than urea in scavenging of the formaldehyde and in ensuring the adhesive ability of the UF resin. Yang at al. [14] disclosed the possibility of polyurea using for increase of particleboard properties and decreased of formaldehyde emission. Perminova at al. showed the efficiency of glycoluril – product of interaction urea with glyoxal, which reducing the formaldehyde emission of particleboard to 34 % without degradation of strength and water resistant [15].

As derivatives of urea, products of its interaction with organic acids, such as citric acid, can be used. The resulting urea citrate [16] introduced into the resin performs the function of a direct curing catalyst; the addition of ammonia to the formulation makes it possible to give the resulting product the properties of a latent curing agent. The product was named Modifier-Curing agent (MC), because it's able to replace the traditional curing agents (ammonium chloride, sulfate, nitrate etc.) in adhesive compositions and reduce

formaldehyde emissions from wood boards without negative effect on physical and mechanical properties. Action MC as a curing agent showed in article [17], action MC as a modifier required to research.

The aim of this work was to study of free urea and MC urea on the curing of UF resin, structure of UF polymer and properties of particleboard.

II. MATERIALS AND METHODS

2.1 Materials

The UF resin of the KF-MT-15 brand (F/U molar ratio of 1.2/1) was produced by one of the Russian manufacturers. The resin characteristics are given in Table 1.

Table 1: Properties of Commercial UF Resin of the KF-MT-15 Brand

The appellation of the parameter	The value of the parameter
Mass fraction of solid resin, %	65.1
Conditional viscosity according to the viscometer with a nozzle diameter of 4 mm, s	69
Concentration of hydrogen ions, pH	8.3
Curing time with the addition of 1% ammonium chloride at 100 °C, s	43
Free formaldehyde content, %	0.15

Aqueous solutions of ammonium sulfate (Russian State Standards – GOST 9097–82 “Ammonium sulphate. Specifications”) with a concentration of 20% were used as curing agents. The urea’s brand "A", highest grade (GOST 2081–2010 “Carbamide. Specifications”), were used as a formaldehyde scavenger.

We also used modifier-curing agents first series which is a products of interaction of citric acid, urea and ammonia with different molar ratios; MC-1(0.5) – 1/2.5/0.5 espectively, MC-1(1.5) – 1/1.5/1.5 respectively. The properties of the modifier-curing agent are presented in Table 2.

Table 2: Properties of Modifier-Curing Agents

The appellation of the parameter	The value of the parameter	
	MC-1(1.5)	MC-1(0.5)
Appearance	transparent liquid without mechanical impurities	
Mass fraction of the dry residue, %	40	40
Concentration of hydrogen ions, pH	4.2	2.3
Nitrogen content, %	8.2	8.8
The content of amino groups, %	6.3	9.1

2.2 Methods

2.2.1 Curing Time of UF Resin (At 100 ± 1 ˚C)

Compositions (depending of the experiment's objectives, for example resin + water + urea + curing agent) were prepared in such a way that the mass fraction of solid resin in all cases was 55%. 12 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. The mass of adhesive components (curing agent, modifier-curing agent, urea) in all cases, based on solid resin was calculated.

2.2.2 pH-Value of the Cured Adhesive

Compositions (depending of the experiment's objectives, for example resin + water + urea + curing agent) were prepared in such a way that the mass fraction of solid resin in all cases was 57%. 20 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 adhesive were cured at 110 °C for 2 min 26 s (thus, the press-factor of 0.15 min/mm is reproduced for particleboard with a thickness of 16 mm). 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.

The powder were placed in a glass with a capacity of 100 cm^3 and filled with 50 cm^3 of water room temperature. Extraction was carried out for 30 min, after which the pH value were determined.

2.2.3 DSC Measurement

The adhesive samples were prepared in the same way as in clause 2.2.2. DSC measurements were carried out using a Netzsch DSC 204F1 Phoenix. The sample resins were tested by placing about 12.7 mg of each sample into a hermetic pan. Heating rates of 10 °C/min and a temperature range of 30 to 200 °C.

2.2.4 Solid State ^{13}C NMR Spectroscopy

The adhesive samples were prepared, cured and crushed in the same way as in clause 2.2.2. ^{13}C solid-state NMR spectroscopes 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 12.5 kHz; CP/MAS pulse sequence ^{13}C {^1H} was used; relaxation delay – 2 s; contact time – 2 ms; number of pulses – 2048.

2.2.5 Preparation of Model Particleboards and Its Performance

Fourteen one-layer particleboards with dimensions of 200×200×4.0 mm and a target density of 700 kg/m^3 were prepared in the laboratory under a specific pressure of 2.8 MPa, at 110 °C press temperature; the total press time was 2 min 26 s. The solid resin loading was 20% based on dry wood particles; the adhesives composition depended on the objectives of the experiment.

Were tested such properties of particleboard as ultimate bending strength (BS) to GOST 10635–88 "Particle boards. Methods for determining ultimate strength and modulus of elasticity in bending"; water absorption (WA) and thickness swelling (TS) of 24 h to GOST 10634–88 "Wood particle boards. Methods for determination of physical properties"; formaldehyde emission (FE) to WKI method [18].

The aim of manufacturing and testing of the model particleboards was researched the behavior of adhesives under hot pressing temperature of the core layer of particleboards and plywood. For this reason, the thickness of the boards and the pressing temperature has been reduced, and the adhesive content has been increased.

2.2.6 Preparation of Three-Layer Particleboards and Its Performance

Four three-layer particleboards with dimensions of 200×200×16 mm and a target density of 650 kg/m^3 were prepared in the laboratory under a specific pressure of 2.8 MPa, at 220 °C press temperature; the press-factor was 0.15 min/mm of thickness (total press time – 2 min 26 s). The mass fraction of surface layers was 40 %, core layer 60 %. The solid resin loading was 12% based on dry wood particles of surface layers and 10% on particles of core layer; the mass fraction of solid resin in surface layers adhesive was 55 %; in core layer 57 %. The core and surface layers compositions shown to table 3.

Properties of three-layer particleboards which were tested shown in clause 2.2.5; additionally, we determined internal bonding strength (IB) according to GOST 10636–2018 "Wood-shaving and wood-fiber plates. Strength definition method at stretching perpendicularly plate layer".

Table 3: Adhesives Compositions for Core and Surface Layers of Particleboards

Component	Component content, %, regarding to solid resin, for particleboard type							
	1*		2		3		4	
	SL	CL	SL	CL	SL	CL	SL	CL
Ammonium sulfate	1	3	1	3	–	–	–	–
Modifier-curing agent								
• MC-1(0.5)	–	–	–	–	–	–	–	5
• MC-1(1.5)	–	–	–	–	3	5	3	–
Urea	–	–	0.43	2.15	–	–	–	–

** Control samples were made according to composition 1*

III. EXPERIMENTAL

Fig. 1 shows the typically action of ammonium sulfate as a curing agent. Increasing the amount of this catalyst gain of more than 3 % does not lead to decreased of curing time. The addition of 1-5 % urea to the adhesive doesn't leads to a significant change both with an ammonium sulfate content of 1% and with an ammonium sulfate content of 3% (Fig. 2). MC-1(0.5) cures the resin longer than the ammonium sulfate at an amount less than 3 %, but with an increase in the content of this modifier-curing agent curing time decreased by 28-38 %. MC-1(1.5) is inferior to ammonium sulfate even at a high content (with 3-5 % of MC-(1.5) the adhesive cures longer to 10-22 % than with 3 % of ammonium sulfate).

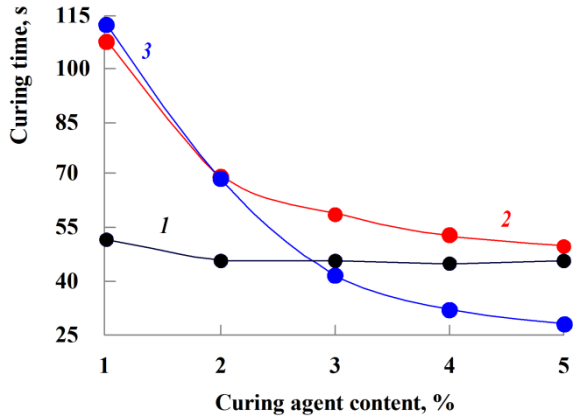

Fig. 1: Curing time of UF adhesive with various curing agents: 1 – adhesive with ammonium sulfate; 2 – adhesive with MC-1(1.5); 3 – adhesive with MC-1(0.5)

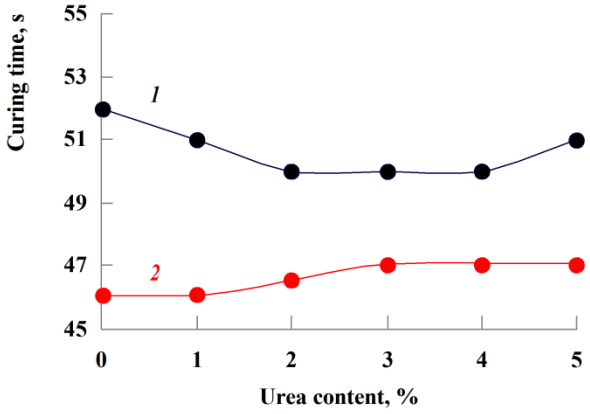

Fig. 2: Curing time of UF adhesive with ammonium sulfate and various urea content: 1 – adhesive with 1 % ammonium sulfate; 2 – adhesive with 3 % ammonium sulfate

Since the increase in the content of ammonium sulfate is over than 3 % doesn't provide a significant effect, in further work the effect of this curing agent was researched only at two levels – 1 and 3 %. The action of modifier curing agents was researched at three levels – 1, 3 and 5 %, as they are influence to adhesive in a wider range of amount. The urea was added only to resin without modifier-curing agents (Table 4); its content was varied in such a way as to correspond to the amount of scavenger introduced with MC-1(0.5) in parallel experiment.

The pH value of the initial and cured adhesive is shown in Table 4. Ammonium sulfate has a slight effect on the resin's pH immediately after addition, but the acidity of the cured adhesive decreases sharply under its action. Similar results

were obtained by Kantieva and Ponomarenko [19] with ammonium chloride. As expected, a larger amount of the curing agent provides a lower pH value during curing, therefore urea in combination with 3 % ammonium sulfate acts in a more acidic environment. Modifier-curing agents, on the contrary, sharply reduce the pH immediately after combining with the resin, so the difference in acidity of the adhesive before and after curing is not so significant. MC-1(0.5) provides the lowest pH value of the cured resin compared to other options; however, the pH value of the cured resin is comparable to the pH of the resin cured of 1 % ammonium sulfate.

Thermal curing behaviors of researched adhesives are shown in Fig. 3 and 4. Almost all of the observed peaks are endothermic, since the meeting was carried out without pressure. Such effects as water evaporation, emission of formaldehyde and reactions water overlap the exothermic effects of resin curing. In area of temperature peaks 67-92 °C endothermic effects may be caused by water evaporation [20, 21], in area 111-112 °C by emission of polycondensation's by-products [22]. Narrow and high peak in high temperatures area may be related with transformation of methylene ether bridges into methylene with formaldehyde's emission.

Table 4: pH Value of Curved UF Resin With Different Adhesive Compositions

Adhesive composition			pH value	
Curing agent type	Curing agent content	Urea content*	Before curing	After curing
Ammonium sulfate	1	0.00	6.72	3.51
		0.43	6.83	3.61
		1.29	6.87	3.72
		2.15	6.91	3.70
	3	0.00	6.61	3.05
		0.43	6.63	3.05
		1.29	6.62	3.02
		2.15	6.59	3.00
MC-1(0.5)	1	0.43	5.18	4.06
	3	1.29	4.04	3.64
	5	2.15	3.72	3.62
MC-1(1.5)	1	0.29	5.56	4.45
	3	0.88	4.69	3.79
	5	1.46	4.51	3.70

** Urea wasn't added when the modifier-curing agents using; in table shown urea which is part of the MC-1(0.5) and MC-1(1.5)*

The adding of urea in adhesive has a significant effect on the DSC curve (not change only curve's form of sample with 3 % ammonium sulfate and 0.43 % urea). For samples with ammonium sulfate (1 %) and urea (Fig. 3, curves 2-4) top of the peaks in area 67-92 and 111-112 °C merge into one big peak in that is, the evaporation of solvent water and the release of reaction water occur simultaneously. With an increase of the scavenger content in the adhesive, the enthalpy of the first endothermic area decreases (Table 4), most likely due to increased exothermic effects [22]. DSC curve of the sample with 3 % ammonium sulfate and 0.43 % urea (Fig. 3, curve 6) not changes compared to the curve of the sample without scavenger. At ammonium sulfate content 3 % and urea amount 1.29 % and 2.15 % in area 84-95 °C appears the exothermic peak (top of the peak 88 °C); at ammonium sulfate content 1 % exothermic peaks not observed. An increase in heat generation may be related to reaction urea with methylol groups of methylolureas and UF oligomers [7-9] or reaction between urea and free formaldehyde [22]. The higher curing agent content contribute to intensification of the exothermic reactions, wherein with the appearance of a peak in the within the temperature range of 84-95 °C suggests that urea

interact mainly with methylol groups, since it's in this area the effects from curing reactions usually observed [6-9, 24, 25].

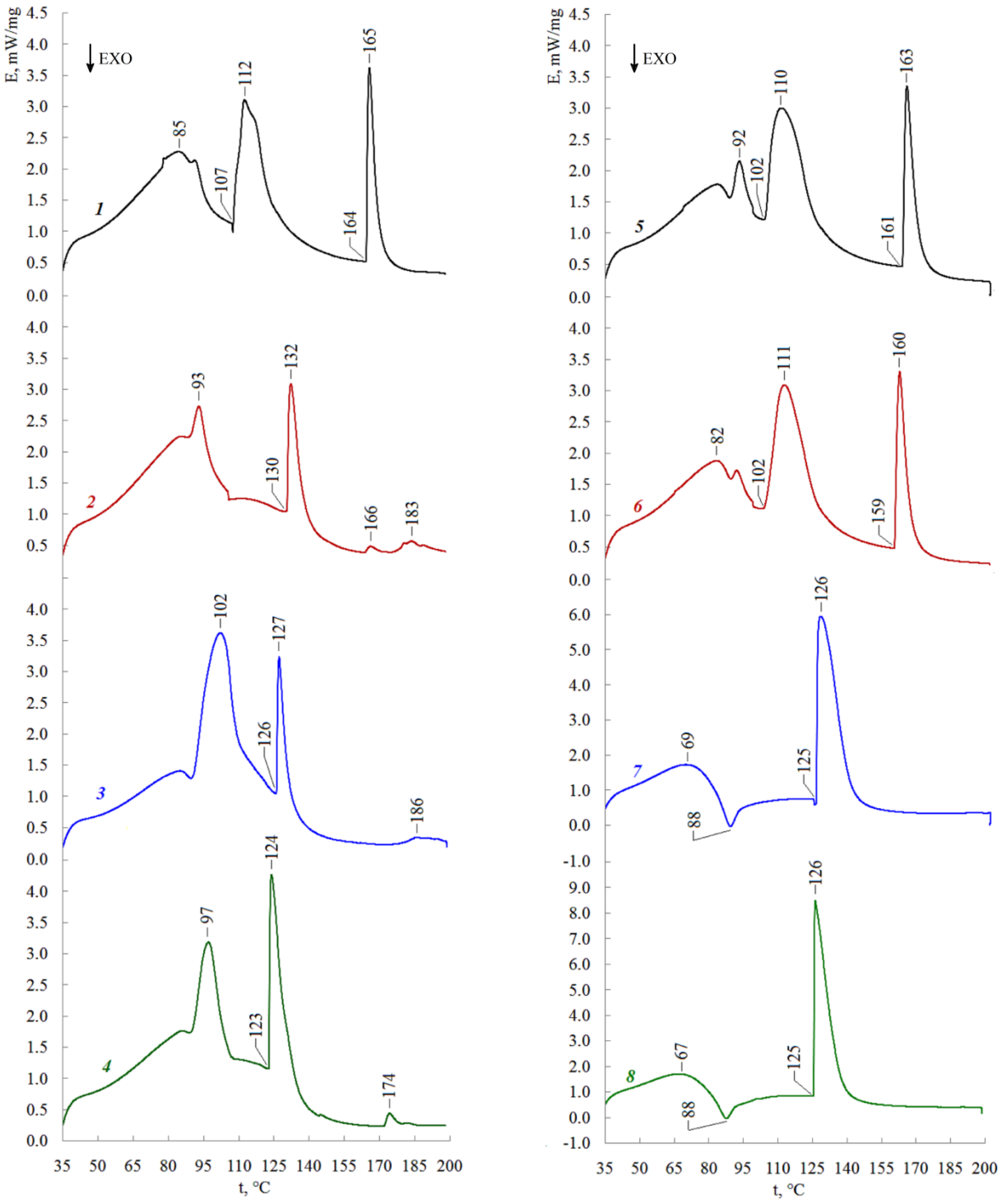

Fig. 3: DSC curves of UF adhesive with different composition: 1 – 1 % ammonium sulfate without urea; 2 – 1 % ammonium sulfate and 0.43 % urea; 3 – 1 % ammonium sulfate and 1.29 % urea; 4 – 1 % ammonium sulfate and 2.15 % urea; 5 – 3 % ammonium sulfate without urea; 6 – 3 % ammonium sulfate and 0.43 % urea; 7 – 3 % ammonium sulfate and 1.29 % urea; 8 – 1 % ammonium sulfate and 2.15 % urea

Thermal curing behavior of resin with MC-1(0.5) and MC-1(1.5) has a more complex dependency (Fig. 4), because at an increasing the content of modifier-curing agents the amount of both curing catalyst and urea in the adhesive is increasing. Deepening of resin curing is accompanied by an increase of the urea's action. The modifier-curing agents at the low content (1%) doesn't provide sufficient intensity of polycondensation; this is evidenced by both long curing time of adhesive (Fig. 1, curves 2, 3) and DSC data (Fig. 4, curves 1, 4); perhaps due to low yield of polycondensation's by-products the endothermic effects of the curing are poorly. The increasing in the content of MC-1(0.5) and MC-1(1.5) leads to curing deepening; weak endothermic effects (Fig. 4, curves 3, 5) can be explained by the intensification of the exothermic reactions. The DSC curve of adhesive with 5% MC-1(0.5) is similar in shape to the curves of samples with 3% ammonium sulfate, 1.29 and 2.15% urea, but there is no exothermic peak in the 88 °C region.

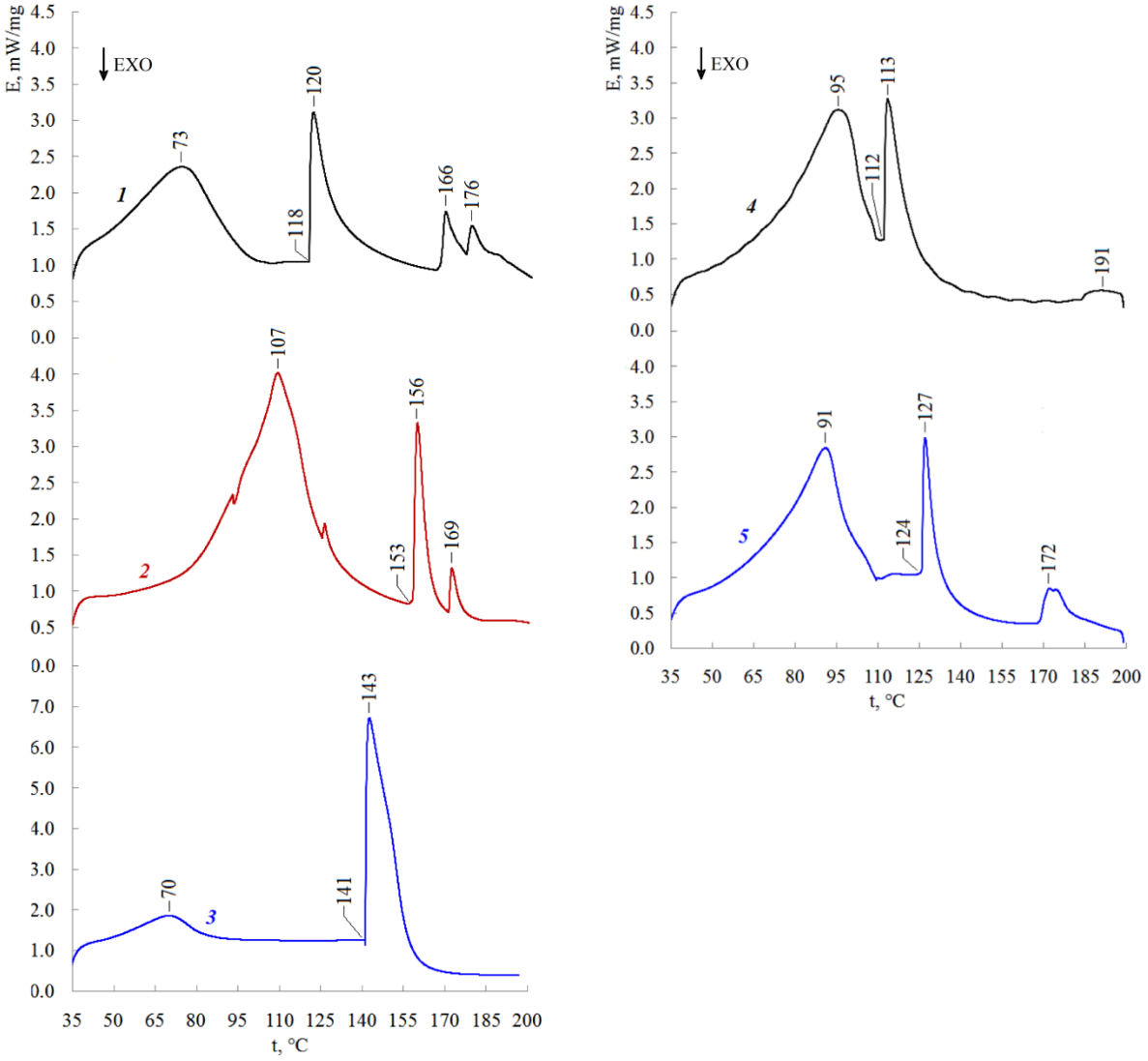

Fig. 4: DSC curves of UF adhesive with modifier-curing agent: 1 – 1 % MC-1(0.5); 2 – 3 % MC-1(0.5); 3 – 5 % MC-1(0.5); 4 – 1 % MC-1(1.5); 5 – 5 % MC-1(0.5)

Solid-state ^{13}C NMR spectra showed significant differences to urea's influence to the UF polymer structural at different ammonium sulfate content (Fig. 5). At catalyst amount 1 % the adding of 1.29 % scavenger leads to decreases the amount of type I methylene bridges, increases amount of methylol groups and methylene ether bridges (Table 5). With a further increase of the urea content (to 2.15 %), there is a sharp increase in the amount of type I methylene bridges (but not

to initial level) and decreases amount of methylene ether bridges. Probably, in combination with 1 % ammonium sulfate urea reacts mainly to free formaldehyde; but at a high content of scavenger (2.15 %), its interaction with resulting methylolureas is possible with the formation of type I methylene bridges.

At the higher curing agent content (3 %) the effects from the ureas action changes; the UF polymer contains a high amount of not only methylol groups and methylene ether bridges, but also type I methylene bridges. Perhaps in this case urea reacts not only with free formaldehyde but also with methylol groups of methylolureas and UF oligomers. Thus scavenger participates in curing along with other resin components, which is consistent with the DSC data.

Table 4: Peak Temperatures of the Studied Adhesives by DSC Measurements

Samples		Peak's area, °C	Top of the peak, °C	ΔH, J/g
1 % ammonium sulfate, at urea content	0.00	35-164	85, 112*	719
	0.43	35-130	93	436
	1.29	35-125	102	439
	2.15	35-122	97	363
3 % ammonium sulfate, at urea content	0.00	36-157	92, 110*	717
	0.43	35-158	82, 111*	690
	1.29	35-85	69	215
	2.15	35-84	67	216
MC-1(0.5) content	1	35-118	73	309
	3	35-153	107	705
	5	35-92	70	262
MC-1(1.5) content	1	35-110	95	389
	5	35-124	91	365

** Two peaks were observed in the considered area*

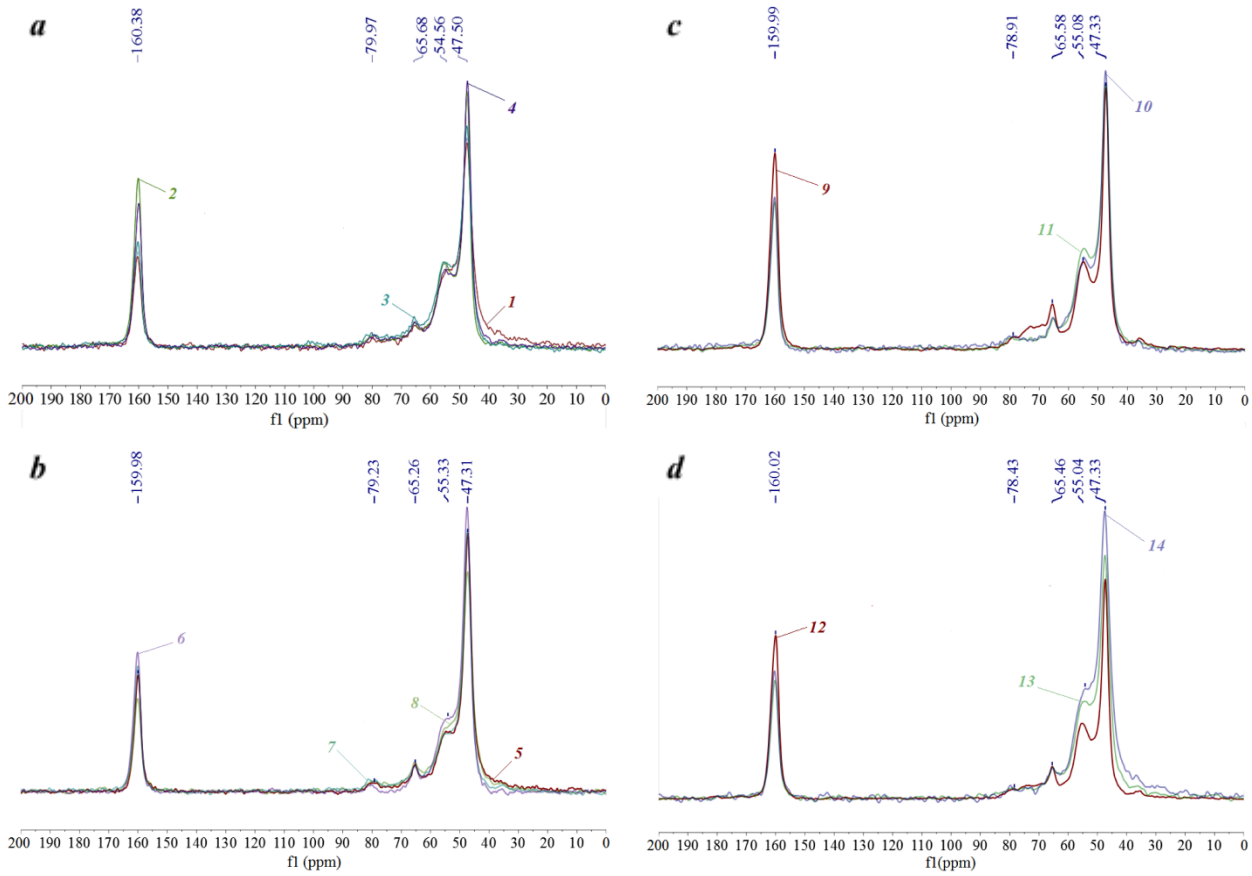

Fig. 5: Solid-state ^{13}C NMR spectra of UF resin cured of (*a*) 1 % ammonium sulfate, (*b*) 3 % ammonium sulfate, (*c*) MC-1(0.5), (*d*) MC-1(1.5): 1, 5 – UF resin without urea; 2, 6 – UF resin with 0.43 % of urea; 3, 7 – UF resin with 1.29 % of urea; 4, 8 – UF resin with 2.18 % of urea; 9, 12 – UF resin with 1 % of modifier-curing agents; 10, 13 – UF resin with 3 % of modifier-curing agents; 11, 14 – UF resin with 5 % of modifier-curing agents

Perhaps at low curing agent content urea act as a classic formaldehyde scavenger, that is react with formaldehyde with harmless products forming. At high curing agent content the activity of urea increased and its starts interacting with other resin components (methyloloureas mainly); in that case urea act as a modifier of UF resin by getting involved to the curing process. The UF polymer is characterized by a relatively low methylene bridge type II amount, thus it has an insufficiently dense cross-linking network, which can cause reduced water resistance of particleboard.

Similar conclusions were made based on the results of works [5, 26]; the authors suggested that as a result of the interaction of urea with methylolureas, linear polymers are formed that are weakly involved in cross-linking reactions. In this case, the structure of the cured resin is largely formed due to physical bonds that are vulnerable to the action of water in the case of amorphous polymers. Vyukov and Vasiliev [27] argue that in case of an excess of acid, free urea is hydrolyzed to form ammonia, which in turn neutralizes formaldehyde. However, due to the destruction of urea and an increase in pH (due to the formation of ammonia), the resin lacks internal resources for curing.

Table 5: Structures and Chemical Shift of UF Resin Cured Using Ammonium Sulfate and Urea

Grope	Chemical Shift (ppm)	Methylenic carbons content, %, at urea mass fraction							
		1 % ammonium sulfate				3 % ammonium sulfate			
		0.00	0.43	1.29	2.15	0.00	0.43	1.29	2.15
–NH–CH_2–NH– *	40–52	62.5	52.9	53.9	59.4	59.3	67.9	69.0	67.6
–NH–CH_2–NH< **	52–61	26.7	32.9	30.5	27.3	26.3	18.7	16.9	18.6
–NH–CH_2OH	62–70	6.4	8.6	7.0	7.2	7.5	9.1	9.0	8.2
>N–CH_2–O–CH_2–N<	72–80	4.4	5.7	8.5	6.1	7.0	4.3	5.2	5.6
Total		100	100	100	100	100	100	100	100

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

The ^{13}C NMR spectroscopy data (Table 6) confirm the deepening of the curing of the UF resin with an increase of the modifier-curing agent's content. With an increase of the MC-1(1.5) content, the amount of methylene bridges type I increased, the amount of methylol groups, methylene ether bridges and methylene bridges type II decreased. Wherein, the urea participates in curing mainly through react with methylolurea and terminal methylol groups of UF oligomers, which leads to increased of methylen bridges type I amount (even compared to adhesive cured with ammonium sulfate without urea).

Table 6: Properties of Model Particleboards Made Using Urea

Grope	Chemical Shift (ppm)	Methylenic Carbons Content, %, at MC Mass Fraction					
		MC-1(0.5)			MC-1(1.5)		
		1	3	5	1	3	5
–NH–CH_2–NH–	40–52	48.4	58.7	57.1	51.6	59.5	64.6
–NH–CH_2–NH<	52–61	29.5	29.3	28.6	30.5	25.7	24.3
–NH–CH_2OH	62–70	11.6	6.7	5.9	9.2	8.1	6.9
>N–CH_2–O–CH_2–N<	72–80	10.5	5.3	8.4	8.8	6.8	4.2
Total		100	100	100	100	100	100

Action of MC-1(0.5) at an amount of 1 and 3% is similar to the effect of MC-1(1.5), however, UF polymers with 5% of various modifier-curing agents are different. The adhesive cured with 5% MC-1(0.5) has more methylol groups, methylene ether bridges and methylene bridges of type II, as well as fewer methylene bridges of type I. Perhaps due to the very fast curing (Fig. 1, curve 3), the urea from the modifier-curing agent doesn't have time to react with the resin components, since the rate of their interaction with each other is higher. This explains the absence of an exothermic peak to the DSC curve of an adhesive with 5% MC-1(0.5) compared to samples cured of 3% ammonium sulfate with 1.29 and 2.15% urea.

According the results of model particleboards tests (Table 7) the increasing of the urea's amount at low ammonium sulfate content leads to toxicity loss and increase of bending strength and water resistance. An increase of the curing agent content leads to a deterioration in the physical and mechanical properties of the boards mainly thickness swelling. Urea's influence to the toxicity of particleboard decreased at the high ammonium sulfate content; when 1 % catalyst used formaldehyde content reduced to 23 % (from 21.9 to 16.8 mg/100 g), when 3 % catalysts used to 9 % (from 16.4 to 14.9 mg/100 g). It is possible that the effectiveness of reducing formaldehyde emissions when free urea is included in the curing process is lower than when it acts as a classic scavenger.

Table 7: Properties of Model Particleboards Made Using Urea

Properties	Urea content, %							
	1 % ammonium sulfate				3 % ammonium sulfate			
	0.00	0.43	1.29	2.15	0.00	0.43	1.29	2.15
Density, kg/m³	723	751	758	786	709	731	703	724
Bending strength, MPa	34.9	38.5	39.4	41.5	30.0	36.9	36.0	36.4
Water absorption, %	72	62	61	62	68	59	51	70
Thickness swelling, %	28	25	25	26	27	26	31	31
Formaldehyde content, mg/100 g	21.9	21.4	18.5	16.8	16.4	15.7	15.4	14.9

It should be noted that increasing of the curing agent amount also has a beneficial effect on reducing toxicity; since ammonium sulfate acts through a reaction with free formaldehyde of UF resin, it can also act as a scavenger. Similarly, Nuno Costa at al [28, 29] explained the positive effect of ammonium sulfate to the formaldehyde emission compared with organic and mineral acids. Vyukov and Vasiliev [27] claim that the curing agent also reacts with methylol groups.

The physic and mechanical properties of particleboards manufactured with MC-1(0.5) and MC-1(1.5) improve with an increase of modifier-curing agents content (Table 8), which confirms the assumption of deepening the curing of the adhesive. In terms of strength and water resistance, they are comparable to boards based on an adhesive with 3% ammonium sulfate and urea (the thickness swelling of boards with modifier-curing agents is even less), but they are significantly inferior in toxicity. The formaldehyde content in particleboards with 5% MC-1(0.5) is 5% lower than in plates with 5% MC-1(1.5), but higher than in plates with 1% ammonium sulfate and 2.15% urea by 20%.

Apparently, the effectiveness of formaldehyde neutralization depends on the pH value provided by the curing agents. Modifier-curing agents cannot provide the same low pH of the cured resin as 3% ammonium sulfate, the effect of their action is comparable to that of 1% ammonium sulfate. At the same time, urea belonging to the modifier-curing-agents is more likely including in the structure of the curing resin rather than acting as a classic scavenger, according to the data of solid-state NMR; perhaps because the pH of the initial binder (before curing) is significantly lower than in the case of ammonium sulfate. The pH value of 4.5-5.0 is sought at the second stage of the synthesis of UF resin of the KF-MT-15 brand, just at the polycondensation stage; that is, under such conditions, it is possible to expect a predominant interaction of urea with methylolureas and UF oligomers. In this case, the thesis of a less effective mechanism for reducing toxicity based on the inclusion of urea in the structure of the curing resin is confirmed. It should also be noted that modifier-curing agents have a complex composition, namely they contain citric acid. The effect of citric acid was not considered separately in this work; however, it can be assumed that its effect on both the action of urea and the structure of the UF polymer may be significant.

Table 8: Properties of Model Particleboards Made Using Modifier-Curing Agents

Properties	Modifier-curing agent content, %					
	MC-1(0.5)			MC-1(1.5)		
	1	3	5	1	3	5
Density, kg/m³	690	755	721	678	713	712
Bending strength, MPa	28.2	34.3	29.6	28.6	30.9	33.5
Water absorption, %	104	69	81	93	79	77
Thickness swelling, %	48	29	28	41	28	24
Formaldehyde content, mg/100 g	33.6	22.1	17.9	33.1	24.4	18.9

The test results of the three-layer particleboards partially confirmed the previously obtained data (Table 9). Samples with urea have the lowest toxicity (30% lower than that of the control – particleboard type 1), but have a high thickness swelling. Samples with modifier-curing agents have physical and mechanical parameters comparable to the control; when using MC-1(0.5) to cure the adhesive of the core layer, it was possible to reduce the formaldehyde content by 9%. Perhaps due to the better heating of the plate, the effectiveness of urea has increased.

Table 9: Three-Layer Particleboards Properties

Properties	Particleboard type			
	1*	2	3	4
Density, kg/m³	629	649	635	655
Bending strength, MPa	22.3	22.1	21.5	25.1
Internal bonding strength, MPa	0.33	0.32	0.36	0.35
Water absorption, %	115	118	110	100
Thickness swelling, %	38	42	36	37
Formaldehyde content, mg/100 g	16.4	11.3	16.3	14.9

** Control samples*

The Table 9 data shown that the combination of modifier-curing agents of the first series makes it possible to obtain three-layer particleboards with satisfactory physical and mechanical properties, as well as to achieve a reduction in the formaldehyde content compared with samples with ammonium sulfate. However, a 9% reduction in toxicity cannot be considered an acceptable result; the effectiveness of the modifier-curing agents needs to be enhanced.

IV. CONCLUSION

The conclusions of this article are as follows:

1. Free urea added to the UF resin-based adhesive acts differently depending on the content of the curing agent. With an ammonium sulfate content of 1% (the pH of the adhesive after curing is 3.50-3.70), urea acts as a classic scavenger, that is, it chemically interacts with formaldehyde to form harmless products. When the content of curing agents is 3% (the pH of the adhesive after curing is 3.00-3.10), urea reacts mainly with the methylol groups of resin components, participating in the curing process. This reduces the sources of free formaldehyde amount.
2. The action of urea through embedding in the structure of the curing resin is less effective for neutralizing formaldehyde than the action as a scavenger. With an amount of ammonium sulfate and urea of 3 and 2.15% respectively, the formaldehyde content in model particleboards decreases by 9.1% compared with plates without a modifier; with an amount of ammonium sulfate and urea of 1 and 2.15% respectively, the formaldehyde content decreases by 23% compared with plates without a modifier. At the same time, the toxicity of plates with high curing agent content is lower in absolute values due to the positive effect of ammonium sulfate.
3. Urea in the composition of modifiers-curing agents, most likely, acts through interaction with the methylol groups of resin components and inclusion in the curing process. Probably due to the low pH value of the binder created before curing (3.72-4.51 with a content of modifiers-curing agents of 5%). Model particleboards made using modifiers-curing agents have relatively high formaldehyde content; by 14-18% less than samples without urea with 1% ammonium sulfate, but by 9-15% more than samples without urea with 3% ammonium sulfate.
4. Tests of three-layer particleboards have shown that, compared with samples without modifiers, samples with urea have comparable strength, reduced toxicity (formaldehyde content is 31% lower) and water resistance (thickness swelling is 10% higher). Samples with modifiers-curing agents have comparable

strength and water resistance, but the toxicity is only 9% lower.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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