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POSSIBILITIES OF LIMITING FORMALDEHYDE CONTENT IN PARTICLEBOARDS TO A LEVEL CHARACTERISTIC OF NATURAL WOOD

The article presents the results of research on the influence of selected technological parameters, changed within a range similar to values presently used in industry, on the properties of three-layer particleboards produced from pine particles obtained from sawmill waste. The particles were glued with amine resins. The panels, produced using urea-formaldehyde resin modified with melamine, were characterised by the lowest content of formaldehyde, i.e. below 2 mg/100 g of ovendry board, after conversion into a value corresponding to the moisture content of the panels equalling 6.5%. The emissions of formaldehyde determined by the chamber and gas analysis methods were much lower than the threshold values recommended in international regulations and used as a basis for the classification of particleboards.

Keywords: particleboards, formaldehyde content and emission, panel strength

Introduction

This article is publication prepared on the basis of research carried out within the framework of project no. NN309 078 338, whose aim was to reduce formaldehyde content in particleboards to a level similar to that characteristic of natural wood. In previous publications the following test results were presented: the influence of the molar ratio of glue resins and the addition of urea on formaldehyde content and emission, the results of tests for formaldehyde content in various raw lignocellulosic materials, i.e. in the wood of species most often used for panel pro-

Iwona FRACKOWIAK, Wood Technology Institute, Poznan, Poland e-mail: i_frackowiak@itd.poznan.pl Franciszek WARCOK, Pfleiderer Silekol Sp. z o.o., Poland e-mail: silekol@silekol.pl Ryszarda BENDOWSKA, Wood Technology Institute, Poznan, Poland e-mail: r_bendowska@itd.poznan.pl Andrzej IDZIAK, Wood Technology Institute, Poznan, Poland e-mail: a idziak@itd.poznan.pl duction, in alternative raw materials, whose suitability for panel production was proved in statutory research carried out in the Institute, and also in post-consumer wood and particles randomly sampled at different particleboard producers plants.

These publications also discussed literature concerning methods to reduce formaldehyde content in wood-based panels. The latest articles on formaldehyde in wood-based materials now frequently concern legislative issues, as well as the costs and economic effects of their implementation. They also discuss the test methods and threshold values for permissible formaldehyde emissions which are the basis for the classification and certification of wood-based panels [Steckel 2009, Fischer 2013]. The United States Environmental Protection Agency suggests that, as regards wood-based materials, the United States on their territory should introduce rigorous standards for formaldehyde emissions, developed by the California Air Resources Board (CARB) [IKEA 2009]. A Congress decision has already been signed by the US President; however, the date for its enactment has not yet been decided. Europe has also been discussing changes in the regulations concerning formaldehyde emissions from wood-based panels. Presently, the Swedish concern IKEA requires that its suppliers provide materials with a formaldehyde content reduced to the level determined by CARB [IKEA 2009]. A critical review of the methods of formaldehyde testing, the factors influencing the results obtained by the various methods, and the difficulties resulting from producers and certification bodies using different methods were addressed, inter alia, at a conference in Hannover [Steckel 2009]. A scientific conference in Gottingen, where factors deciding the emission level and possibilities of its reduction were discussed, was also devoted to the possibilities and results of tightening the requirements within this area [Fischer 2013]. The conference also drew attention to the factors that may cause an excessive concentration of formaldehyde and other volatile compounds, e.g. as much as a hundredfold reduction, compared to the 1960s, in air exchange in rooms in buildings, the use of inappropriate materials, and the lack of protection against the excessive insolation or dampness of materials during construction and service life. The effect, most often negative, of the implementation of known solutions for formaldehyde reduction on the quality and the effectiveness of wood-based panel production was also discussed. The results of the research carried out by Roffael [2011] and Kraft et al. [2012] concerning formaldehyde emissions from particles and wood fibres and the influence of factors connected with the processes of their obtainment in wood-based panel production on these properties, are interesting in terms of the determination of formaldehyde emission threshold values and research aimed at the reduction of the emissions to a level characteristic of natural wood. Warcok [2013] exhaustively discussed the development, properties, structure, advantages and disadvantages of amine resins, methods for the reduction of formaldehyde content in and emissions from panels produced using these resins, as well as the economic aspects of the implementation of new solutions. The review of formaldehyde reduction methods carried out by the author suggests that the most effective method is still a reduction in the resin

F/U molar ratio and the addition of urea to the glue. The author also proved that there is no possibility of substituting another compound for formaldehyde, for there is no raw material base which would facilitate the production of over 4 M tonnes of glue resins per year, i.e. the amount already produced in Europe in 2005.

Materials and methods

Raw wood material

The panels were produced using particles from pine chips obtained from sawmill waste. The particles were cut using a flaker-mill type DD01 (Pallmann set), knife position -0.9 mm. After preliminary drying to a moisture content of $8\pm1\%$, the particles were sorted to the fractions required for particular layers of the panels (using an Allgaier sorter). The fraction composition of the particles for the outer layers and the middle layer of the panels is given in tables 1 and 2.

 Table 1. Fraction composition of particles intended for outer layers, moisture content of particles 8.1%; bulk density 127.91 g/dm³

Dimensions		Mass and	Mean share				
of the square	[g]	[%]	[g]	[%]	[g]	[%]	of fraction
meshes in sieves [mm]]	[I	I	Π	II	[%]
2.00	4.99	1.52	7.96	2.38	4.29	1.25	1.72
1.00	76.74	23.40	81.57	24.42	72.07	23.03	23.61
0.50	218.74	66.69	217.86	65.23	209.01	66.78	66.23
0.25	25.60	7.80	24.81	7.43	26.14	8.35	7.86
< 0.25	1.85	0.56	1.57	0.47	1.74	0.56	0.57

Table 2. Fraction composition of particles intended for the middle layer, moisture content of particles 8.6%; bulk density 103.17 g/dm³

Dimensions		Mass and percentage share of fraction							
of the square	[g]	[%]	[g]	[%]	[g]	[%]	Mean share		
meshes in sieves [mm]]	Ι	I	Ι	Ι	II	of fraction [%]		
8.00	0.09	0.02	0.12	0.03	0.30	0.07	0.04		
4.00	66.87	14.57	67.00	15.30	69.83	16.79	15.55		
2.00	199.85	43.54	194.25	44.35	176.88	42.52	43.47		
1.00	171.80	37.43	162.39	37.08	155.35	37.34	37.28		
0.50	16.21	3.53	10.99	2.51	11.63	2.80	2.95		
0.25	1.41	0.31	0.67	0.15	0.92	0.22	0.23		
< 0.25	1.82	0.40	0.81	0.18	0.97	0.23	0.27		

Table 3 presents the results of the measurement of the geometry of the particles intended for the middle layer of the panels.

Value	Length	Width	Thickness	Slenderness	Flatness	
value		[mm]		Sienderness	Flatiless	
X	15.93	1.97	0.72			
X _{max}	51.31	7.68	1.60	22	2.7	
X _{min}	3.50	0.20	0.13	22	2.7	
σ	7.304	1.222	0.287			

Table 3. Geometry of particles used for the middle layer of panels

Glue resins

The particleboards were produced using urea-formaldehyde resins of various molar ratios (F/U 1.03, 0.96, and 0.85) and urea-formaldehyde resin of molar ratio F/U 0.91–0.93 modified with melamine during the condensation process (three batches). The results of tests of the resins' properties are compared in table 4. The properties of the resins were tested according to the following standards:

PN-C-04504:1992 Chemical analysis. Determination of density of chemical products – liquid and solid in the form of powder.

PN-C-04963:1989 Chemical analysis. Determination of pH of water solutions of chemical products.

PN-C-89352-3:1996 Adhesives for wood. Test methods. Determination of gelation time.

PN-EN ISO 12058-1:2005 Plastics. Determination of viscosity using viscometer with falling ball. Part 1 Hoeppler method.

PN-EN 827:2006 Adhesives. Determination of conventional and constant content of dry substance.

Tests of the mass average molecular mass were performed using a GPC chromatograph by Agilant Technologies; RID detector, eluant DMSO, sample concentration 10–20 mg/l, PSS column – Proteema 100, and calibration was performed using a PMMA.

Determination of the F/U molar ratio was carried out using a CN analyzer by LECO TruSpec CN.

Pagin property		Unit of			Resin	marking		
Resin property		measure	1 2 3 4 5				6	
pН		-	8.7	8.8	8.6	8.6	8.4	8.1
Viscosity		[mPa*s]	380	120	440	420	420	460
Dry substance content	[%]	67	69	66.3	66.8	67	66.8	
Gelation time	[s]	60	78	63	98	97	118	
Molar ratio F/U		-	1.03	0.85	0.96	0.91	0.93	0.91
	50	20.9	20.8	23.2	23.6	21.1	21.6	21.6
	100	5.6	7.6	5.7	6.5	8.3	8.6	8.6
	500	12.4	10.9	8.6	11.2	12.7	13.5	13.5
Mean content of fraction of mean molecular mass ¹	10^3	36.0	37.5	36.4	36.6	34.0	33.5	33.5
of mean morecular mass	10^4	12.2	11.6	12.9	12.2	12.0	10.4	10.4
	10^5	11.6	10.3	11.1	8.2	8.9	7.8	7.8
	10^6	1.5	1.2	2.1	1.0	3.0	4.7	4.7

Table 4. Characteristics of glue resins used

¹ tests carried out using a GPC Chromatograph by Agilant Technologies; RID detector, PSS Column by Proteema 100

Parameters of particleboard production

The following parameters were constant in all the test variants:

- wood raw material: pine particles,
- fraction composition and geometry of particles tables 1–3,
- panel composition: three-layer; share of layers: outer 32%, middle 68%; nominal thickness – 16 mm,
- nominal density 670 kg/m³,
- moisture content of particles after drying $-2 \pm 1\%$,
- gluing degree: ol 11%, ml 9% (ol panel outer layers; ml panel middle layer),
- type of hardener: water solution of ammonium nitrate -45% + urea -35%,
- type and amount of paraffin (emulsion 65%) 0.35% in relation to dry mass of particles,
- pressing parameters: unit pressure -2.5 MPa, pressing temperature -210° C.

Parameters that were changed are given in the section "Results and discussion".

The panel properties were tested in accordance with the following standards:

- moisture content acc. to PN-EN 322:1999,
- bending strength and modulus of elasticity in bending according to PN-EN 310:1994,
- tensile strength perpendicular to the planes according to PN-EN 319:1999,

- formaldehyde content according to PN-EN 120:1994,
- formaldehyde emission by the flask method according to PN-EN 717-3,
- formaldehyde emission by the chamber method according to ASTM D 6007-02,
- formaldehyde emission by the gas analysis method according to PN-EN 717-2.

The density and density profile of the panels was determined using a Gre-Con DA-X apparatus.

Results and discussion

Table 5 presents the results of the research on the properties of the panels pressed for various times and produced using urea-formaldehyde resins (1 and 2) and urea-formaldehyde resin modified with melamine during the condensation process (4). The content of the formaldehyde in the panels containing resins 1 and 2 was the same irrespective of the pressing time, and the differences in the values of formaldehyde emissions from the panels were within a range admissible at testing of one sample. The changes in the formaldehyde content in and emissions from the panels containing the resin modified with melamine were in line with the known trend of the favourable influence of pressing time lengthening on the above-mentioned properties; however, these changes were also insignificant. On the other hand, the effect of the resin used was clear: the panels containing urea-formaldehyde resin modified with melamine were characterised by lower content and lower emissions of formaldehyde irrespective of the pressing time. The pressing time had a significant bearing only on the bending strength of the panels containing urea-formaldehyde resin; whilst a shortening of the pressing time had no significant bearing on the value of the modulus of elasticity and tensile strength perpendicular to the planes of these panels. On the other hand, the influence of the pressing time on the strength of the panels containing urea-formaldehyde resin modified with melamine was quite different. The results of the calculations of the significance of the differences between the discussed results are given in table 6

Table 5. The influence of pressing time on the properties of panels produced using urea-formaldehyde resins of F/U molar ratio 0.85 (2) and 1.03 (1), and urea-formal-dehyde resin modified with melamine during the condensation process (4)

			Molar ratio of F/U resin									
			ol –	0.85, ml –	1.03	0.	.91 ol and 1	nl				
			hardener addition [%]									
Tested	Value	Unit of	С	ol – 2, ml –	5	ol	l – 3, ml –	10				
property	value	measure			urea a	ddition						
				10			10					
				Press	sing time co	peffcient [s/	/mm]					
			$8(x_1)$	6(x ₂)	$4.5(x_3)$	8(x ₁)	6(x ₂)	4.5(x ₃)				
Fz	х	[mg/100g]	2.3	2.3	2.3	1.7	1.6	1.8				
E _b	Х	[mg/kg]	2.5	2.2	2.5	1.6	1.7	2.0				
E _k	Х	[ppm]	0.045	0.043	0.046	-	-	-				
Eg	Х	$[mg/(m^2h)]$	1.4	1.5	1.3	-	-	-				
	Х	[N/mm ²]	11.9	9.3	8.6	13.2	11.9	12.2				
Rg	σ		0.63	0.47	0.42	1.17	0.87	0.90				
	v	%	5.3	5.1	4.9	8.9	7.3	7.4				
	Х	[N/mm ²]	3100	3160	2970	3290	3090	3160				
Е	σ		134	51.5	103	155	181	137				
	v	[%]	4.3	1.6	3.5	4.7	5.9	4.3				
	х	[N/mm ²]	0.44	0.42	0.42	0.41	0.37	0.37				
Rr	σ		0.02	0.02	0.03	0.02	0.02	0.02				
	v	[%]	4.5	4.8	5.8	5.0	5.4	5.4				
d	Х	[kg/m ³]	675	683	677	677	679	682				
d_{\min}/d_x	X	[%]	88.5	86.9	86.9	86.1	87.5	86.0				

x – mean value

 σ – standard deviation

v – variability coefficient

F₂ – formaldehyde content according to PN-EN 120:1994,

 E_{b} – formaldehyde emission determined by the flask method according to 717-3:1999

 E_k – formaldehyde emission determined by the chamber method according to

- ASTM D 6007-02(08) E_g – formaldehyde emission determined by the gas analysis method according to PN-EN 717-2:1999,
- Rg bending strength according to PN-EN 310:1994
- E modulus of elasticity at bending according to PN-EN 310:1994
- Rr tensile strength perpendicular to planes according to PN-EN 319:1999,
- d_x mean density determined by a Grecon DA-X apparatus,
- d_{min}^{2}/d_{x}^{2} relation of minimum density to mean value (based on the programme of the Grecon DA-X apparatus)

Table 6. Calculations of the significance of differences between bending strength, modulus of elasticity and tensile strength perpendicular to planes of panels produced using urea-formaldehyde resins of F/U molar ratio 0.85 (2) and 1.03 (1), and urea-formaldehyde resin modified with melamine during the condensation process F/U - 0.91

Resin	Pearson formula	Droporty		Value	Result	
Kesin	Pearson formula	Property	$\begin{array}{c c} x_1 - x_3 & 3\sqrt{\sigma_1^2/n_1 + \sigma_3^2 n_3} \\ \hline 3.3 & 0.77 \\ \hline 130 & 179.3 \\ \hline 0.02 & 0.047 \end{array}$		Kesult	
			3.3	0.77	significant	
1 and 2	1 and 2 $x_1 - x_3 \ge 3\sqrt{\sigma_1^2/n_1 + \sigma_3^2/n_3^2}$	Е	130	179.3	insignificant	
		Rr	$\begin{array}{c cccc} x_1 - x_3 & 3\sqrt{\sigma_1^2/n_1 + \sigma_3^2 n_3} \\ \hline 3.3 & 0.77 \\ \hline 130 & 179.3 \end{array}$	0.047	insignificant	
		Rg	1.0	1.6	insignificant	
4	$x_1 - x_3 \ge 3\sqrt{\sigma_1^2/n_1 + \sigma_3^2 n_3}$	Е	130	253	insignificant	
		Rr	0.05	0.024	significant	

The results of the testing of the panels produced using resins stored for 8, 14, 36 and 50 days after they were produced are given in table 7. Based on these results, the influence of the resin storage period on the content and emissions of formaldehyde cannot be determined unambiguously. The values of these properties determined after various storage periods are slightly diverse and what is more they do not demonstrate any trend towards change, irrespective of the emission determination method used. Therefore, it can be assumed that the formaldehyde content in and emissions from the panels containing the applied urea-formaldehyde resins was independent of their storage period up to 50 days.

On the other hand, the bending strength of the panels containing resins stored for various periods was clearly diverse; at the same time, changes in this property did not demonstrate any constant trend. The differences between the initial mean value and the values determined after particular storage times were significant (table 8). The influence of the resin storage period was favourable only up to 36 days. The bending strength of the panels containing resin stored for 50 days was 15% lower than the initial value, and 30% lower than the maximum value. The modulus of elasticity demonstrated a similar trend, i.e. its value was the highest in the case of the use of resins after 36 days and the lowest after the longest storage period; however, the differences between the mean values of the same property were significant only in the case of resin storage for 36 days. The panels containing resin stored for 36 days were also characterised by the highest tensile strength perpendicular to the planes; changes in this property were also significant for the storage period of 36 days. After 50 days, the tensile strength decreased almost to the initial level. Changes in the strength of the panels in the examined resin storage period were relatively insignificant; however, they may be of importance in practice, for their values vary within the range required by the effective standard. An explanation for the reasons for the observed phenomena requires a continuation of the research, taking into account an instrumental analysis of resins.

Table 7. Properties of panels produced according to constant parameters using ureaformaldehyde glue resins stored for different periods in the same conditions at a temperature of $20\pm3^{\circ}$ C. The molar ratio of resin for ol – 0.96 (3), for ml – 1.03 (1), hardener addition in ol – 2%, ml – 7%, urea addition ol – 15%

Terret				Storage	e period			
Tested property	Value	Unit of measure	days					
property			8(x ₁)	$14(x_2)$	36(x ₃)	50(x ₄)		
Fz	X	[mg/100g]	2.3	2.0	2.1	1.9		
E _b	x	[mg/kg]	2.0	2.4	2.5	2.3		
E _k	X	[ppm]	0.058	0.054	0.046	0.050		
Eg	X	$[mg/(m^2h)]$	1.0	1.5	1.3	1.2		
	x	[N1/mm2]	10.6	11.8	13.1	9.2		
Rg	σ	$[N/mm^2]$	0.6	0.9	0.4	0.7		
	v	[%]	5.7	7.5	3.1	7.6		
	x	ENT /	2900	2980	3380	2790		
Е	σ	$[N/mm^2]$	125	163	197	54		
	v	[%]	4.3	5.5	6.2	1.9		
	x	ENT /	0.28	0.35	0.36	0.30		
Rr	σ	$[N/mm^2]$	0.031	0.033	0.032	0.030		
	v	[%]	11.1	9.4	8.8	10.0		
d	x	[kg/m ³]	671	672	670	675		
d _{min} /d _x	x	[%]	85.8	84.0	79.3	86.3		

Table 8. Calculation of the significance of differences between the modulus of elasticity and the tensile strength perpendicular to planes of panels produced using urea-formaldehyde resins of F/U molar ratio 0.96 (3 – ol) and 1.03 (1 – ml)

Pearson formula	Dronartz		Result	
Pearson formula	Property	X ₁ -X _n	$3\sqrt{\sigma_1^2/n_1 + \sigma_x^2/n_x}$	Kesun
	Rg _{x1-x2}	1.2	0.96	significant
	Rg _{x1-x3}	2.5	0.43	significant
	Rg _{x1-x4}	1.4	0.75	significant
	Rr _{x1-x2}	0.07	0.043	significant
$x_1 - x_n \ge 3\sqrt{\sigma_1^2/n_1 + \sigma_n^2/n}$	Rr _{x1-x3}	0.08	0.044	significant
	Rr _{x1-x4}	0.02	0.040	insignificant
	E _{x1-x2}	80	218	insignificant
	E _{x1-x3}	400	218	significant
	E _{x1-x4}	110	137	insignificant

The strength of the panels containing the urea-formaldehyde resin modified with melamine stored for different periods was connected with their density (table 9).

The influence of density was especially visible in the period of resin storage up to 36 days. For this period, determination coefficients R^2 calculated for the relations between the panel bending strength, modulus of elasticity and tensile strength equal Rg - 0.98, E - 1.0, and Rr - 1.0, respectively, and after taking into consideration the results obtained using the resin stored for 50 days, the coefficients decrease and equal Rg - 0.86, E - 0.50, and Rr - 0.80, respectively. Hence, one can assume that the weakening of the said relations was due to the changes in the resin resulting from its lengthy storage.

The resin storage period had no influence on the formaldehyde content in the panels; whilst the formaldehyde emissions determined by the flask method decreased as the storage period lengthened, i.e. after 36 days, the emissions decreased by almost 40%. Research on the influence of a storage period lasting from 36 to 50 days on the properties of panels and on the changes in the resin over this period could bring nearer the development of a resin of a structure favourable in terms of both formaldehyde emission and panel strength.

Table 9. Properties of panels produced according to constant parameters using urea-
-formaldehyde glue resin modified with melamine (4) stored for different periods
in the same conditions at a temperature of 20±3°C. The resin F/U molar ratio 0.91,
hardener addition to the outer layer – 10%, to the middle layer – 3%, urea addition
to the middle layer – 10%

				Storage	e period			
Tested property	Value	Unit of measure	days					
			8	14	36	50		
Fz	х	[mg/100g]	1.8	1.6	1.7	1.6		
E _{eb}	х	[mg/kg]	1.8	1.7	1.3	1.1		
	х	[N/mm2]	14.1	11.9	11.9	12.3		
Rg	σ	$[N/mm^2]$	1.27	0.87	0.38	0.59		
	v	[%]	9.2	7.5	3.3	4.6		
	х	[N1/	3530	3090	3030	2920		
Е	σ	$[N/mm^2]$	226.1	181	93.7	86.6		
	v	[%]	6.6	5.6	3.2	3.0		
	х	[N/mm2]	0.41	0.35	0.34	0.35		
Rr	σ	$[N/mm^2]$	0.03	0.03	0.03	0.03		
	V	[%]	7.3	8.6	8.8	8.6		
d	х	[kg/m ³]	714	679	673	696		
d _{min} /d _x	х	[%]	87.5	87.5	86.8	88.4		

Table 10 presents the results of tests of the panels produced using resins 1 (ol) and 3 (ml). Urea was added to the resin used for the outer layers, and the amount of hardener was changed in the middle layer. Although the amount of hardener

was changed only in the middle layer of the panels, it had a favourable influence on both the content and emissions of formaldehyde, and thus a 2% increase in the amount of hardener (from 5% to 7%) resulted in a reduction in formaldehyde content of over 30%, and reductions in formaldehyde emissions of 40%, using the flask method, and of 32%, using the chamber and the gas analysis method.

Table 10. Properties of panels produced using urea-formaldehyde resins with various
amounts of hardener in the middle layer and various amounts of urea in the outer
layer, pressing time coefficient – 6 s/mm

			Molar ratio of F/U resin						
			ol – 0.96 (3), ml – 1.03 (1)						
			hardener addition [%]						
Tested property	Value	Unit of measure	ol – 2, ml – 5	ol – 2, ml – 6	ol – 2, ml – 7				
property				urea addition [%]					
				ol – 10					
			Pressin	g time coefficient –	6 s/mm				
Fz	Х	[mg/100g]	3.4	2.3	2.3				
E _b	X	[mg/kg]	3.5	3.1	2.1				
E _k	Х	[ppm]	0.062	0.055	0.042				
Eg	X	$[mg/(m^2h)]$	1.9	1.6	1.3				
	х	[N1/mm2]	11.6	12.1	11.6				
Rg	σ	[N/mm ²]	0.91	0.16	1.0				
	v	[%]	7.8	1.3	8.6				
	х	[N1/mm2]	2510	2790	2850				
E	σ	[N/mm ²]	99.5	118	121				
	v	[%]	3.9	4.2	4.2				
	х	[N]/mm ²]	0.37	0.39	0.40				
Rr	σ	[N/mm ²]	0.02	0.02	0.03				
	v	[%]	5.4	5.1	7.5				
d	X	[kg/m ³]	668	674	681				
d _{min} /d _x	X	[%]	88.0	87.6	86.6				

However, due to the differences in panel density, it is difficult to unambiguously state that the level of panel strength was connected with the amount of hardener. Nevertheless, it may be said that increasing the amount of hardener did not result in a decrease in the values of the examined properties. Fig. 1 presents the relations between the amount of hardener and the content and emissions of formaldehyde determined by various methods.

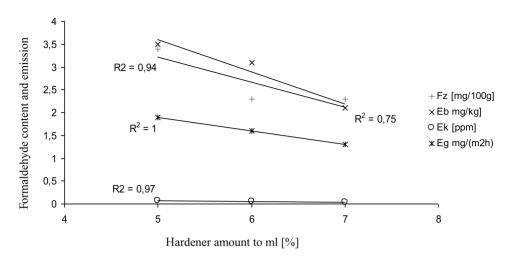


Fig. 1. The influence of the amount of hardener on formaldehyde content and emissions determined by various methods

To identify the diversity of panel properties resulting from the possible variability of different batches of resin of the same type, the influence of the urea amount was tested using a urea-formaldehyde resin modified with melamine during the condensation process (5 and 6). The parameters of the panel production, apart from the amount of urea added to the resin, were constant. Urea was added to the resin intended for the outer layers, and in some variants also to the resin intended for the middle layer. The results of the tests are presented in table 11.

Table 11. The influence of the amount of urea added to urea glue resin modified with
melamine (4, 5, 6) on the properties of particleboards produced using this resin, pres-
sing time coefficient – 7 s/mm

Tested property	Value	Unit of measure	Molar ratio of F/U resin – 0.91								
			hardener addition ol – 3%, ml – 10%								
			resin								
			5	6	4	6	5	6	5	6	
			urea addition [%]								
			0	0	ol – 10	ol – 10	ol – 12	ol – 12	ol – 12, ml – 2	ol - 12, ml - 2	
1	2	3	4	5	6	7	8	9	10	11	
Fz	Х	[mg/100g]	1.7	1.9	1.7	1.9	1.6	1.7	1.5	1.6	
E _b	х	[mg/kg]	1.3	1.5	1.1	1.1	0.9	1.0	1.0	1.1	
E _k	х	[ppm]	0.025	0.30	-	-	-	-	0.022	0.025	
Rg	х	[N/mm ²]	12.8	13.8	13.1	13.1	12.5	13.0	12.4	11.9	
	σ		0.79	0.26	1.08	1.01	1.08	1.30	0.61	1.21	
	v	[%]	6.2	1.9	8.2	7.7	8.6	10.0	4.9	10.2	

1	2	3	4	5	6	7	8	9	10	11
Е	х	[N/mm ²]	3040	2950	2950	2820	3000	2920	3070	2903
	σ		110	42.9	122	124	213	206	166	165
	v	[%]	3.6	1.5	4.1	4.4	7.1	7.0	5.4	5.7
Rr	х	[N/mm ²]	0.41	0.44	0.37	0.43	0.38	0.41	0.38	0.42
	σ		0.02	0.04	0.03	0.03	0.03	0.02	0.02	0.03
	v	[%]	4.9	9.1	2.7	6.9	7.8	4.9	5.3	7.1
d	х	[kg/m ³]	673	690	693	685	688	687	686	698
d_{min}/d_x	х	[%]	86.7	87.9	88.2	88.4	87.1	87.0	87.7	88.1

Table 11. Continued

The content of formaldehyde in the panels produced using tested batches of urea-formaldehyde resin modified with melamine without the addition of urea differed by 0.2 mg/100 g; whilst the emissions determined by the flask and the chamber methods differed by 0.2 mg/kg and 0.005 ppm, respectively. These differences, insignificant as regards the assessment of the panels, remain also when urea is used, irrespective of its amount, therefore it may be assumed that they result from the characteristics of the resins applied. It should be stressed that the formaldehyde content and emissions were very low irrespective of the method applied and that the urea had very little bearing on these values.

An analysis of the impact of the resin batch and the addition of urea on the panel strength is difficult due to the varying density of the panels; however, irrespective of the strength value and the addition of urea, the properties tested fulfilled the requirements described in standard PN-EN 312: February 2011 for type P2.

Conclusions

The tests performed suggest the possibility of limiting the formaldehyde content in particleboards to a level approximate to the maximum value determined at the previous research stage for natural wood, i.e. to approximately 1.4 mg/100 g (pine, sapwood). A formaldehyde content below 2 mg/100 g of ovendry board, after conversion into a value corresponding to the moisture content of the panels equalling 6.5%, was characteristic of the panels produced using the urea-formaldehyde resin modified with melamine. The formaldehyde emissions, determined by the flask and the chambers methods, were within a range of 1.0–1.8 mg/kg and 0.022–0.030 ppm, respectively. Pressing time, within a range of 4.5–8 s/mm, as well as the addition of urea and its amount were deemed insignificant in terms of their influence on the said properties of the panels. The above-mentioned values are much lower than threshold values suggested in pending international regulations used as a basis for the classification of particleboards in terms formaldehyde content and emissions. The strength of the particleboards was in accordance with the requirements of standard PN-EN 312:2011 for type P2.

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List of standards

- ASTM D 6007-02:2008 Determining Formaldehyde Concentration in Air from Wood Products Using a Small Scale Chamber
- PN-C-04504:1992 Analiza chemiczna. Oznaczanie gęstości produktów chemicznych ciekłych i stałych w postaci proszku (Chemical analysis. Determination of density of chemical products – liquid and solid in the form of powder)
- PN-C-04963:1989 Analiza chemiczna. Oznaczanie pH wodnych roztworów produktów chemicznych (Chemical analysis. Determination of pH of water solutions of chemical products)
- PN-C-89352-3:1996 Kleje do drewna. Metody badań. Oznaczanie czasu żelowania (Adhesives for wood. Test methods. Determination of gelation time)
- **PN-EN 120:1994** Tworzywa drzewne Oznaczanie zawartości formaldehydu Metoda ekstrakcyjna, zwana metoda perforatora (Wood based panels – Determination of formaldehyde content. Extraction method called the perforator method)
- **PN-EN 310:1994** Płyty drewnopochodne oznaczanie modułu sprężystości przy zginaniu i wytrzymałości na zginanie (Wood-based panels. Determination of modulus of elasticity in bending and of bending strength)

PN-EN 312:2011 Płyty wiórowe - wymagania techniczne (Particleboards. Specifications)

PN-EN 319:1999 Płyty wiórowe i płyty pilśniowe – Oznaczanie wytrzymałości na rozciąganie w kierunku prostopadłym do płaszczyzn płyty (Particleboards and fibreboards. Determination of tensile strength perpendicular to the plane of the board)

- **PN-EN 322:1999** Płyty drewnopochodne Oznaczanie wilgotności (Wood-based panels. Determination of moisture content)
- **PN-EN 717-2:1999** Płyty drewnopochodne Oznaczanie emisji formaldehydu Emisja formaldehydu metodą analizy gazowej (Wood-based panels. Determination of formaldehyde release. Formaldehyde release by the gas analysis method)
- **PN-EN 717-3:1994** Płyty drewnopochodne. Oznaczanie emisji formaldehydu. Emisja formaldehydu metodą butelkową (Wood-based panel products – Determination of formaldehyde release by the flask method)
- **PN-EN 827:2006** Kleje. Oznaczanie umownej i stałej zawartości suchej substancji (Adhesives. Determination of conventional and constant content of dry substance)
- **PN-EN ISO 12058-1:2005** Tworzywa sztuczne. Oznaczanie lepkości za pomocą lepkościomierza z opadającą kulką. Część 1 Metoda Hoepplera (Plastics. Determination of viscosity using viscometer with falling ball. Part 1 Hoeppler method)

MOŻLIWOŚCI OGRANICZENIA ZAWARTOŚCI FORMALDEHYDU W PŁYTACH WIÓROWYCH DO POZIOMU CHARAKTERYZUJĄCEGO DREWNO NATURALNE

Streszczenie

W artykule przedstawiono wyniki badań wpływu wybranych parametrów technologicznych, zmienianych w przedziale zbliżonym do wartości aktualnie stosowanych w przemyśle, na właściwości trzywarstwowych płyt wiórowych wytwarzanych z wiórów sosnowych pozyskanych z odpadów tartacznych. Do zaklejania wiórów stosowano żywice aminowe. Najmniejszą zawartością formaldehydu, poniżej 2 mg/100g zupełnie suchej płyty, po przeliczeniu na wartość odpowiadającą wilgotności płyt – 6,5%, charakteryzowały się płyty wytworzone z żywicą mocznikowo-formaldehydową modyfikowaną melaminą. Emisja formaldehydu badana metoda komorową i analizy gazowej była znacznie mniejsza od wartości granicznych, obowiązujących i proponowanych w przepisach międzynarodowych, jako podstawa klasyfikacji płyt wiórowych.

Słowa kluczowe: płyty wiórowe, zawartość i emisja formaldehydu, wytrzymałość płyt

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