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THE INFLUENCE OF UF MOLAR RATIO ON SELECTED PARTICLEBOARD PROPERTIES

This paper presents the preliminary research results of a project whose main objective is to quantify the impact of formulations and technological parameters on formaldehyde content in and emission from particleboards produced using urea-formaldehyde resin with a low molar ratio of F/U. The formaldehyde content reduction is possible by using a resin with a molar ratio of F/U of 1.065 hardened with 3% solution of urea and ammonium nitrate or a resin with a molar ratio of F/U of 0.96 to which 3% urea was added. For these variants, reductions by 22% and 21% respectively of formaldehyde content in particleboards were obtained, while at the same time, strength properties that meet the requirements of the EN-312: 2011 standard for P2 particleboards were maintained.

Keywords: particleboard, UF, molar ratio, urea

Introduction

In recent decades the content of formaldehyde in and its emission from wood--based panels has been the subject of intensive research [Hse 1974; Kanter 2008; Harmoan 2008] focusing mainly on developing methods for testing the content and emission of formaldehyde, understanding the factors affecting formaldehyde emission from panels [Nemil, Ozturk 2006], and how to reduce the release of this component during production, as well as the use of the boards [Schäfer, Roffael 2000]. In 2004, the International Agency for Research on Cancer (IARC) identi-

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fied formaldehyde as carcinogen which contributed to stricter requirements for minimal permissible emission of this component from wood-based panels [Marutzky 2004; Ruffing et al. 2011]. The consequence was a new perspective on the problem of formaldehyde presence in wood-based panels.

In Europe over 90% of wood-based panels are produced with amino resins, which are the main source of formaldehyde emission in the production process as well as from the finished product [Warcok 2007]. Through extensive research and the involvement of resins and boards producers, over the decades formaldehyde emission from wood-based panels has been reduced by 80 – 90% in relation to the values characterizing panels produced in the 1970s [H'ng et al. 2011]. New resins based on renewable raw materials such as soy, lignin, and tannin, have thus far not found broad application in the industry due to their high price [Properzi et al. 2008]. Therefore, several projects have been conducted with the aim of reducing formaldehyde content in wood-based panels, for example by the modification of amino resins or altering the technological parameters [Tsapuk 1992; Abdullah, Park 2010; Özalp 2010]. One of the most popular and cheapest methods of formaldehyde emission reduction is the lowering of the molar ratio of urea to formaldehyde (F/U) [Deppe, Ernst 2000; Park et al. 2005; Frąckowiak 2006; Quea et al. 2007]. Frequently, in order to meet the requirements of E1 class, resins with a molar ratio of 1.10:1.00 in the case of particleboard, and 1.00:0.85 for MDFs and HDFs are used [Warcok 2007]. Not so long ago reaching this level of molar ratio seemed impossible. After an extensive review of literature, Myers [1984] suggested that using resin with a 1.2 molar ratio of F/U decreases the strength properties of board below the permissible values and deteriorates adhesive joint resistance to water. The above-mentioned problems have already been overcome by more reactive hardeners, UF resin modification with melamine [Hse et al. 2008] or phenol, or through increasing the share of resin in the board. Changes in particleboard manufacturing (the use of particles with proper geometry and low moisture, the precise removal of dust from particles, the use of precision dispensing systems etc.) together with the optimization of adhesive technology [Rusak, Warcok 1997] currently allow the use of resins with molar ratio of F/U below 1.0.

This paper presents the preliminary research results of a project whose main objective is to quantify the impact of formulations and technological parameters on formaldehyde content in and emission from particleboards produced using urea-formaldehyde resin with a low F/U molar ratio.

In order to further reduce the content of formaldehyde in particleboard urea, formaldehyde as the most commonly used sorbent affecting the processes of gelation and resin curing [Jóźwiak 2005], was added to low molar ratios of F/U resin (1.065 – 0.84). The study aims to determine how much formaldehyde content can be reduced in particleboards using a resin with low molar ratio and with the addition of urea, while at the same time maintaining the other properties at the appropriate level.

Materials and methods

Wood

Chips from pine wood obtained from sawmill waste were used as raw material. The wood material was reduced to the desired size with a Pallmann's chipper. For particleboard production, the particles passing through a sieve with a mesh 8.0 mm in diameter and remaining on a sieve with a mesh 2.0mm in diameter were used. The formaldehyde content (EN 120: 1994) in chips with a moisture content of 0.4% was 0.3 mg/100g of oven dry board (o.d.b.). To produce particleboard, particles with a moisture content of 2% ± 0.2% were used.

Chemicals

In order to produce particleboards, three types of urea-formaldehyde resins with different molar ratios of U/F, i.e. 1.065, 0.96, and 0.84, were used. The resin properties are presented in table 1.

In the experiment, two types of hardeners were used: ammonium nitrate (NH_4NO_3; concentration 30%) and urea ammonium nitrate solution (the share of urea in the dry weight of adhesive was 2.3%, the share of ammonium nitrate in relation to the dry weight of adhesive was 3%). Depending on the research variant, urea was added to the resin to the amounts of 2, 3, and 5%.

Table 1. Resin properties
Tabela 1. Właściwości żywic

Properties *Właściwości*	F/U molar ratio *Stosunek molowy F/U*		
	1.065	0.96	0.84
Concentration [%] *Stężenie [%]*	66.0	67.3	68.5
Free formaldehyde content [%] *Zawartość wolnego formaldehydu*	<0.2	<0.2	<0.2
Gel time at 100 ° C with 2% addition of ammonium nitrate [s] *Czas żelowania przy 100 °C z 2% dodatkiem azotanu amonu [s]*	80	79	79
Gel time at 100 ° C with 3% addition of urea and ammonium nitrate solution [s] *Czas żelowania przy 100 °C z 3% dodatkiem roztworu saletrzano-mocznikowego [s]*	67	65	79

The parameters of particleboard production

Twelve one-layer particleboards with dimensions of 500 × 700 × 16 mm and a target density of 660 kg/m^3 were produced. The particleboards were manufactured according the following parameters: pressing pressure – 20.5 MPa, pressing temperature – 210 °C, resination – 9%, pressing time – 5 [s/mm], hardener amount – 2-3% of ammonium nitrate or urea and ammonium nitrate solution, paraffin amount – 0.4% (concentration 65%). The chemicals were dosed in relation to the dry weight of resin, and paraffin to the dry weight of wood.

The panels produced were tested for bending strength (EN 310), internal bond strength perpendicular to the plane of the board (EN 319), and formaldehyde content (EN 120).

The research variants are given in table 2.

Table 2. The research variants and results
Tabela 2. Warianty oraz wyniki badań

F/U molar ratio *Stosunek molowy F/U*	Hardener type and amount *Typ i rodzaj utwardzacza*	Urea addition [%] *Dodatek mocznika [%]*	Formaldehyde content after calculations into humidity value of 6.5% (mg/100g o. d. b.) *Zawartość formaldehydu po przeliczeniu na wilgotność 6,5% (mg/100g o. d. b.)*	Internal bond [N/mm^2] *Wytrzymałość na rozciąganie [N/mm^2]*	Bending strength [N/mm^2] *Wytrzymałość na zginanie [N/mm^2]*	Modulus of elasticity [N/mm^2] *Moduł sprężystości [N/mm^2]*
1.065	ammonium nitrate 2% *azotan amonu 2%*	-	5.9	0.54 (0.028)	15.3 (0.49)	3003 (117.1)
1.065	ammonium nitrate 3% *azotan amonu 3%*	-	4.1	0.62 (0.022)	9.8 (0.98)	2323 (56,8)
1.065	urea and ammonium nitrate solution 2% *roztwór saletrzano-mocznikowy 2%*	-	5.2	0.60 (0.037)	13.5 (1.21)	3500 (189.3)
1.065	urea and ammonium nitrate solution 3% *roztwór saletrzano-mocznikowy 3%*	-	3.2	0.39 (0.060)	15.1 (0.70)	3038 (174.0)
0.960	ammonium nitrate 2% *azotan amonu 2%*	-	3.9	0.47 (0.026)	13.7 (1.36)	2593 (260.6)

Table 2. Continued
Tabela 2. Ciąg dalszy

0.960	urea and ammonium nitrate solution 2% *roztwór saletrzano-mocznikowy 2%*	-	2.8	0.33 (0.030)	12.3 (0.60)	2766 (205.0)
0.840	ammonium nitrate 2% *azotan amonu 2%*	-	2.3	0.28 (0.022)	11.0 (0.81)	2354 (195.1)
0.840	urea and ammonium nitrate solution 2% *roztwór saletrzano-mocznikowy 2%*	-	1.7	-	-	-
1.065 1.051*	ammonium nitrate 2% *azotan amonu 2%*	1.0	5.3	0.53 (0.028)	13.9 (0.67)	2341 (132.4)
1.065 1.025*	ammonium nitrate 2% *azotan amonu 2%*	3.0	4.4	0.51 (0.040)	15.7 (0.97)	2980 (129.0)
1.065 1.000*	ammonium nitrate 2% *azotan amonu 2%*	5.0	3.5	0.44 (0.030)	16.0 (0.86)	3040 (186.0)
0.960 0.948*	ammonium nitrate 2% *azotan amonu 2%*	1.0	3.9	0.45 (0.021)	14.2 (1.08)	2501 (83.1)
0.960 0.925*	ammonium nitrate 2% *azotan amonu 2%*	3.0	3.1	0.42 (0.040)	14.4 (0.98)	2790 (119.0)
0.960 0.902*	ammonium nitrate 2% *azotan amonu 2%*	5.0	2.7	0.35 (0.030)	12.0 (0.80)	2800 (127.0)

*Real molar ratio of F/U after the addition of urea to the resin
**Faktyczny stosunek molowy F/U po dodaniu mocznika do żywicy*

( ) Standard deviation
( ) Odchylenie standardowe

Results and discussion

In the analyzed molar ratio range, i.e. 1.065-0.84, the formaldehyde content varied from 5.9 to 1.7 mg/100 g o.d.b., respectively. The value of the coefficient of determination for the tested correlation was 0.989. This study confirmed the known correlation between the molar ratio of F/U of the resin used and the formaldehyde content in boards (fig. 1). Based on the data shown in the following figures, it was calculated that reducing the formaldehyde content in boards produced according to the established technological parameters to a level close to that characteristic of natural wood, i.e. below 1 mg/100 g o.d.b., would require a reduction in the resin molar ratio to 0.76.

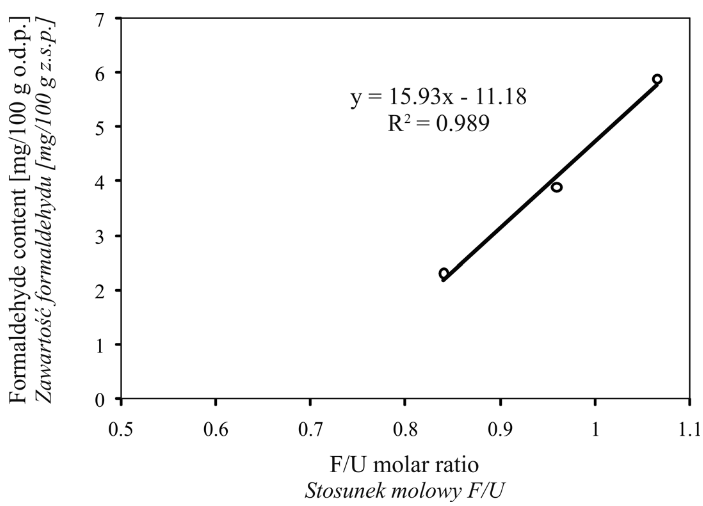

Fig. 1. The correlation between the molar ratio F/U of the resin and the content of formaldehyde in the boards
Rys. 1. Zależność miedzy stosunkiem molowym F/U stosowanej żywicy i zawartością formaldehydu w płytach

As expected, the molar ratio of the resin also had a relevant influence on the resistance of the boards revealed in the internal bond strength, bending strength, and modulus of elasticity (fig. 2, 3).

The coefficients of determination for the correlation between molar ratio of the resin and resistance of the boards were close to 1, similar to the case of formaldehyde.

The strength of the boards in the above-mentioned range was only in accordance with the requirements of the EN-312: 2011 standard when resins with molar ratios of 1.065 and 0.96 were used.

The boards with the resin of a molar ratio of 0.84 met the requirements only in the case of modulus of elasticity at static bending.

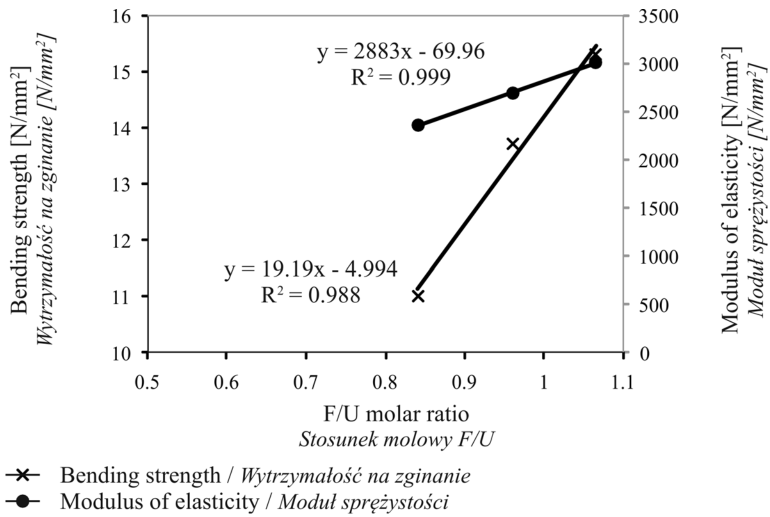

Fig. 2. The correlation between the molar ratio F/U of the resin and the bending strength and modulus of elasticity
Rys. 2. Zależność miedzy stosunkiem molowym F/U stosowanej żywicy i wytrzymałością na zginanie oraz modułem sprężystości przy zginaniu statycznym płyt

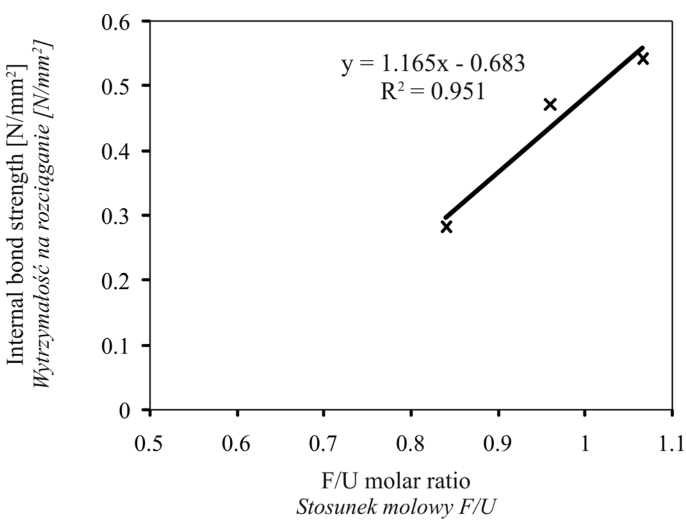

Fig. 3. The correlation between the molar ratio F/U of the resin and the internal bond strength of the boards
Rys. 3. Zależność miedzy stosunkiem molowym F/U stosowanej żywicy i wytrzymałością na rozciąganie płyt

Based on the regression equations it was calculated that the panels produced according to the established parameters would have an internal bond strength and a static bending strength consistent with the currently applicable European standards when using a resin with a molar ratio of not less than 0.89.

In the light of these results and calculations, no further tests on the resin of molar ratio of 0.84 were performed. Instead the research focused on the modification of other resins.

In order to further reduce formaldehyde, urea or urea ammonium nitrate solution, which is also a resin hardener, were added to the resins with molar ratios of 1.065 and 0.96. The results of urea addition to the resins to the amounts of 1, 3, and 5% are shown in Fig. 4 and 5. The application of resins with a low F/U molar ratio modified by the addition of urea caused the deterioration of the internal bond strength of the tested panels and, as expected, a reduction in the formaldehyde content in the particleboards (fig. 6).

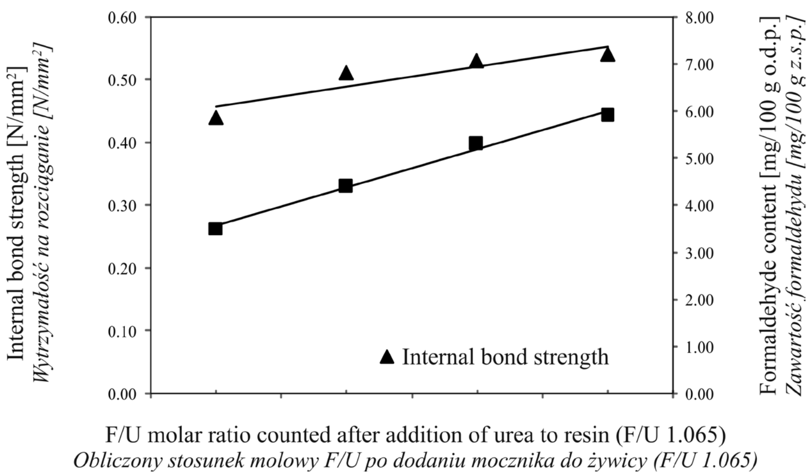

Fig. 4. The effect of urea addition to the resin with the F/U molar ratio of 1.065 on the internal bond strength of the boards and the formaldehyde content
Rys. 4. Wpływ dodatku mocznika do żywicy F/U 1,065 na wytrzymałość na rozciąganie płyt oraz zawartość formaldehydu

A 5% addition of urea to the resin of F/U molar ratios of 1.065 and 0.960 contributed to a reduction in the formaldehyde content by 34% and 31%. The study proved that less than 5% of urea can be added to the resin with a F/U molar ratio of 0.960, because it is probable that an urea addition of 5% or more would result in a tensile strength reduction below the limit values which are standard for this type of panels.

Not without significance was the way the urea was dosed to the UF resin. The study proved that the use of urea and ammonium nitrate solution at 3% in relation to the dry weight of the resin has a similar effect on the reduction of formaldehyde in the particleboard as the addition of 5% of urea in the case of the resin cured with ammonium nitrate (table 2).

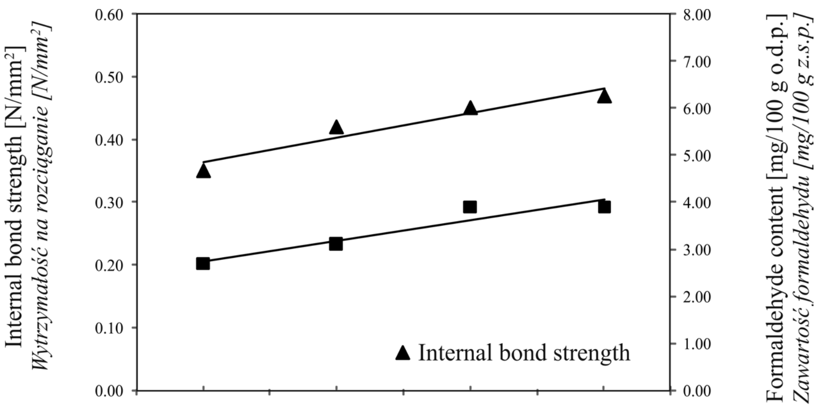

Fig. 5. The effect of urea addition to the resin with the F/U molar ratio of 0.960 on the internal bond strength of the boards and the formaldehyde content
Rys. 5. Wpływ dodatku mocznika do żywicy F/U 0,960 na wytrzymałością na rozciąganie płyt oraz zawartość formaldehydu

A change of hardener from ammonium nitrate to urea and ammonium nitrate solution resulted in a reduction by approximately 22% of the formaldehyde content in the particleboard made from the resin with a F/U molar ratio of 1.065.

Conclusions

These studies present two answers to the question of to what extent formaldehyde can be reduced using unmodified urea-formaldehyde resin with a low molar ratio and the addition of urea, while at the same time maintaining the other properties of the particleboard at the appropriate level. The first solution relates to the resin with a molar ratio of F/U of 1.065 hardened with a 3% solution of urea and ammonium nitrate, and the second to the resin with a molar ratio of F/U of 0.96 to which 3% urea was added. For these variants, reductions in formaldehyde content in the particleboard by 22% and 21% were obtained, while at the same time maintaining the strength properties that meet the requirements of the EN-312:2011 standard for P2 particleboards. An addition of urea to the panels with the resin hardened with ammonium nitrate reduces the tensile strength to a lesser extent than in the case of urea ammonium nitrate solution.

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List of standards

PN EN 310:1994 Płyty drewnopochodne. Oznaczanie modułu sprężystości przy zginaniu i wytrzymałości na zginanie.

PN EN 319:1999 Płyty wiórowe i płyty pilśniowe. Oznaczanie wytrzymałości na rozciąganie w kierunku prostopadłym do płaszczyzn płyty.

PN EN 120:1994 Tworzywa drzewne. Oznaczanie zawartości formaldehydu. Metoda ekstrakcyjna, zwana metodą perforatora.

PN-EN 312:2011 Płyty wiórowe -- Wymagania techniczne.

WPŁYW STOSUNKU MOLOWEGO ŻYWICY UF NA WYBRANE WŁAŚCIWOŚCI PŁYT WIÓROWYCH

Streszczenie

Przedstawiono wyniki badań pierwszego etapu projektu, którego głównym założeniem jest próba kwantyfikacji wpływu receptur i parametrów technologicznych na zawartość i emisję formaldehydu z płyt wiórowych wytwarzanych z zastosowaniem żywicy mocznikowo-formaldehydowej o niskim stosunku molowym F/U. Spośród przeprowadzonych badań wybrano dwa optymalne warianty. Pierwszy dotyczy żywicy o stosunku molowym F/U 1,065 utwardzanej roztworem saletrzano-mocznikowym w ilości 3%, drugi żywicy o stosunku molowym F/U 0,96 utwardzanej azotanem amonu dodanego w ilości 2% w stosunku do suchej masy kleju, do której dodano 3% mocznika. W obydwu wariantach uzyskano obniżenie zawartości formaldehydu w płycie odpowiednio o 22% oraz 21% przy jednoczesnym zachowaniu właściwości wytrzymałościowych spełniających wymagania normy EN-312: 2011 dla płyt wiórowych klasy P2.

Słowa kluczowe: płyta wiórowa, UF, stosunek molowy, mocznik