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EFFECT OF DIFFERENT HARDENERS FOR UREA-FORMALDEHYDE RESIN ON PROPERTIES OF BIRCH PLYWOOD

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ABSTRACT

The effects of various types of hardeners (aluminium sulphate, ammonium persulphate, ferrum chloride and combined hardener) on formaldehyde emission, shear strength and characteristics of urea-formaldehyde (UF) adhesives for the manufacture of plywood were investigated. Formaldehyde emission was determined using gas analysis method. The experimental results showed that addition of aluminium sulphate or ammonium persulphate to UF resin effectively reduced the formaldehyde emission of birch plywood down to 10‒36 % without diminishing its shear strength.

Key words: formaldehyde emission, birch plywood, urea-formaldehyde resin, hardener, curing time, viscosity, pH, shear strength.

INTRODUCTION

Woodworking industry should focus particularly on higher value-added products, which could be achieved by the complex utilization of wood raw materials. This effort would improve the contributions of the forestry and timber industries to regional development. In addition, wood-processing should strive to increase its competitiveness by implementing new technologies, or concentrating production on a larger scale. There is also a need for optimal solutions that reflect the principles of sustainable development (HAJDÚCHOVÁ *et al.* 2016, SEDLIAČIKOVÁ *et al.* 2016).

Urea-formaldehyde (UF) resin is widely used for the production of particleboard, medium density fibreboard and plywood as well as a laminating adhesive to bond furniture overlays to panels. The main advantages of UF resin are: low cost, curing at a low temperature, water solubility and lack of colour of the cured resin. On the other hand, the main disadvantage of UF resin is the release of formaldehyde. The formaldehyde was re-classified as a carcinogenic agent in 2005 by the International Agency for Research on Cancer (IARC) (IARC 2006). In addition, the chemical action of formaldehyde can cause disorders of the nervous and immune systems of humans.

The formaldehyde emission of plywood panels depends on its manufacturing process (wood species, type of resin, pressing conditions, etc.) and on its service practice (air humidity and temperature, etc.). Ammonium chloride (NH_4Cl) is most commonly applied as a hardener of UF resin. It is an affordable and relatively inexpensive reagent, but it makes an adhesive layer more fragile. Moreover, gaseous ammonia, which is a toxic substance, and, in small amounts irritates the upper respiratory tract, eyes and mucous membranes of the nose, affects the human central nervous system at high concentrations adversely, is emitted in the process ammonium chloride manufacture. Since formaldehyde can cause cancer in humans and ammonium chloride consist of a toxic substance, the formaldehyde emission level as well as toxicity of a hardener has become a concern issues.

Methods for the reduction of formaldehyde emission levels in wood-based composites have been intensively discussed over the past years. Discussions include: (i) the modification of UF formulations with low molar ratios of urea and formaldehyde (MARUTZKY *et al.* 1979) or the mixing of UF resin with other resins (H'NG 2011, QUEA *et al.* 2007); (ii) additions of copolymerizing substances such as lignosulfonates (ROFFAEL and DIX 1991); (iii) addition of formaldehyde scavenger to the UF resin (COSTA *et al.* 2013, JOHNSSON *et al.* 2014, LORENZ *et al.* 1999, MIGNEAULT *et al.* 2011) or post-treatments of boards using wax emulsions with incorporated urea as a scavenger, ammonia gas and salts or surface treatments with paints, lacquers, veneers, and papers (HEMATABADI and BEHROOZ 2012, ROFFAEL 1982, ROFFAEL 2011); (iv) changing the pressing parameters (time or temperature) (PETINARAKIS and KAVVOURAS 2006) and (v) alternative gluing systems (AMAZIO *et al.* 2011, ERNST 1985, WANG *et al.* 2007).

Further methods refer to the heat treatment of veneer sheets at a temperature range of 150 °C to 170 °C (MURATA *et al.* 2013). The use of inorganic components for the reduction of formaldehyde has been shown by several authors. MATSUO *et al.* (2008) used silylated graphite oxides to remove gas-phase formaldehyde. FUNK *et al.* (2015) demonstrated that loading urea on diatomaceous earth significantly (by 45%) reduced formaldehyde emission of laboratory-made particleboards. KMEC *et al.* (2010) have used zeolite as a filler for UF resin in plywood, also with the goal of reducing formaldehyde releases. A scavenger effect of inorganic additives was also shown by KIM (2009).

The aim of this study is to produce low-toxic birch plywood using UF resin modified by various types of non-toxic hardeners.

MATERIALS AND METHODS

Rotary cut veneer sheets of birch wood (*Betula pubescens* Ehrh.) with dimensions of 300 × 300 mm and a thickness of 1.5 mm and moisture content of 4-6% without visible defects were prepared for the experiments. Commercial UF resin was used in this research. Aluminium sulphate ($Al_2(SO_4)_3$), ammonium persulphate ($(NH_4)_2S_2O_8$), ferrum (III) chloride ($FeCl_3$), combined hardener - mixture of ferrum (III) chloride and urea ($CO(NH_2)_2$) (ratio 1:4) were chosen as hardeners (modifying agents) for UF resin; ammonium chloride (NH_4Cl) was used for the comparison. The hardeners were added to the resin in the form of aqueous solutions.

The adhesives compositions (Table 1) were proposed and the effect of the modifying agents on their properties was investigated. The amount of added modifying agents was of 0.5, 1.0, and 1.5 weight parts per 100 weight parts of UF resin. Viscosity, hydrogen ions concentration (pH), solid content, curing time and free formaldehyde content of adhesive compositions as well as the shear strength of plywood panels were evaluated.

Solid content of the prepared adhesive mixtures was determined by weight method. Curing time of adhesive mixtures was determined at a temperature of 100 °C. Viscosity was measured by Ford cup (4 mm, 20 °C) and hydrogen ion concentration of the prepared adhesives was determined on pH-meter. The content of free formaldehyde was determined by applying the titrimetric method using 785 DMP Titrino Metrohm.

Tab. 1 Adhesive compositions.

Number of adhesive composition	UF resin	Adhesive modifiers, weight parts				
		Ammonium chloride	Aluminium sulphate	Ammonium persulphate	Ferrum (III) chloride	Combined hardener
1	100	0.5	-	-	-	-
2	100	1.0	-	-	-	-
3	100	1.5	-	-	-	-
4	100	-	0.5	-	-	-
5	100	-	1.0	-	-	-
6	100	-	1.5	-	-	-
7	100	-	-	0.5	-	-
8	100	-	-	1.0	-	-
9	100	-	-	1.5	-	-
10	100	-	-	-	0.10	-
11	100	-	-	-	0.15	-
12	100	-	-	-	0.20	-
13	100	-	-	-	-	0.5
14	100	-	-	-	-	1.0
15	100	-	-	-	-	1.5

Five-layer plywood panels with format 300 × 300 mm were made in the electrically heated hydraulic laboratory press. The specific pressing pressure of 1.5 MPa and temperature of 120 °C were used, and the time of pressing was determined for 8 min. The glue spread was 120 g/m^2 based on wet mass. UF adhesive mixture was applied onto one side of every uneven ply. The plies were assembled perpendicularly to each other (veneer sheets were laid up tight/loose) to form plywood of five plies. Glue was applied on the veneer surface with a hand roller spreader. A laboratory testing machine was used for the evaluation of the quality of gluing and the shear strength of plywood was determined according to EN 314-1 after pre-treatment for the intended use in interior conditions. Testing samples were immersed for 24 h in water at 20 ± 3 °C. Ten samples were used for each variant shear strength mechanical testing. During the experiment, all plywood samples were conditioned before testing for two weeks at 20 ± 2 °C and 65 ± 5% relative humidity. A gas analysis method was applied to determine formaldehyde release from the plywood panels according to EN 717-2.

RESULTS AND DISCUSSION

Properties of adhesives

The effects of hardeners on the properties of adhesive compositions are presented in Table 2. The type and content of hardeners in adhesive compositions have different effects on the properties of adhesives (DUNKY 1995, LUFTMAN 2005). A distinguishing feature of the obtained adhesive compositions is that curing time is reduced, viscosity is increased, and solid content is slightly raised with increasing the amount of any investigated hardeners. For example, the reduction of curing time resp. growth of viscosity is 28.2%/11.6% for ammonium chloride, 57.1%/27.1% for aluminium sulphate, 15.4%/5.6% for ammonium persulphate, 64.7%/22.4% for ferrum (III) chloride and 82.8%/20.8% for a combined hardener are observed. As can be seen the highest changes of curing time are observed in a combined hardener following (from higher to lower) ferrum (III) chloride, aluminium sulphate, ammonium chloride and ammonium persulphate. Moreover, the changes in curing time were more pronounced than changes in viscosity (ROFFAEL 2011).

The hydrogen ion concentration of the prepared adhesives is slightly reduced with increasing amount of any investigated hardeners. The lowest values of pH = 2.7–2.8 were recorded for adhesives with aluminium sulphate. This is because aluminium sulphate, unlike other test hardeners, forms a more acidic environment during mixing with the resin (MATSUO *et al*. 2008).

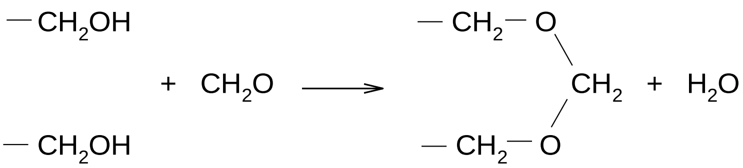
Tab. 2 Characteristics of adhesive compositions.

Number of adhesive composition	Viscosity [s]	Curing time [s]	Solid content [%]	pH	Content of free formaldehyde [%]
1	88.0 (1.2)*	23.4 (1.1)	56.4 (2.9)	3.7	0.10
2	92.4 (0.5)	22.8 (0.8)	58.7 (1.5)	3.3	-**
3	98.2 (1.3)	16.8 (1.5)	59.3 (1.4)	3.2	-**
4	84.6 (1.8)	43.4 (1.1)	58.8 (1.6)	2.8	0.08
5	101.4 (5.0)	23.8 (3.0)	60.2 (2.1)	2.7	-**
6	107.5 (2.2)	18.6 (1.1)	61.2 (2.0)	2.8	-**
7	94.3 (1.0)	26.0 (0.7)	58.4 (1.5)	6.0	0.04
8	94.8 (2.2)	23.8 (0.8)	59.4 (2.2)	5.3	0.03
9	99.6 (0.5)	22.0 (1.6)	60.3 (3.2)	4.6	0.03
10	81.4 (2.1)	65.8 (4.5)	60.0 (1.8)	5.6	0.15
11	91.8 (1.9)	36.2 (3.4)	61.2 (3.6)	5.2	0.14
12	99.6 (3.8)	23.2 (1.3)	61.8 (1.6)	5.1	0.13
13	81.4 (2.1)	74.6 (3.2)	60.0 (2.4)	4.5	0.12
14	94.0 (0.7)	25.6 (1.5)	61.6 (2.8)	4.2	0.11
15	98.3 (6.1)	12.8 (2.2)	61.7 (2.7)	4.0	0.11

* Values in parenthesis are standard deviations.
** The free formaldehyde content in adhesive was less than 0.01% of titrimetric determination error.
The free formaldehyde content in UF resin was 0.13%.

The content of formaldehyde in developed adhesives is much smaller than in UF resin, and in some cases it is not determined by titrimetric at all (QUEA *et al*. 2007). The application of aluminium sulphate and ammonium persulphate allows the reduction in the content of free formaldehyde in adhesive compositions by 20% and 60% respectively in comparison with ammonium chloride. The application of ferrum (III) chloride and combined hardener, on the contrary, increases the level of free formaldehyde most likely due to the partial destruction of UF resin and dominating the process that occurs with free methanol emission. In this case the free formaldehyde content in adhesive compositions is much higher than in the UF resin and adhesives containing ammonium chloride.

Aluminium sulphate hydrolyses actively with the release of free sulphuric acid, which accelerates the polycondensation of the resin. The gradual change in acidity that is responsible for the hardening of the resin ensures the formation of its properties (PETINARAKISM and KAVVOURAS 2006). The application of aluminium sulphate as the hardener increases the depth of hardening of urea-formaldehyde oligomers. Al^{3+} ion forms both covalent bonds with methylene groups and coordinating bonds with oxygen and nitrogen atoms. Quite low values of pH = 2.7–2.8 in the case of using aluminium sulphate deepen urea-formaldehyde oligomers hardening due to the formation of acetal linkage and additional formaldehyde binding:



The mechanism of UF resin hardening in the presence of ammonium persulphate can be represented as follows. In the first stage, the amount of methylene groups reduces due to the emission of free formaldehyde and water during the hydrolysis of the salt:

$$R-NH-CH_2OH \longrightarrow R-NH_2 + CH_2O$$

$$R-NH-CH_2OH \longrightarrow R-N{=}CH_2 + H_2O$$

At the same time the methanol is oxidized by ammonium persulphate to methane acid and persulphate is decomposed into free radical groups. In the second stage of the process, two reactions occur simultaneously: polycondensation, which results in methylene ether linkages and polymerization of azomethylene groups –N=CH_2, formed in the first stage due to free radicals:

$$R-N{=}CH_2 + \acute{R}_1 \longrightarrow R_1-\underset{\displaystyle R}{\underset{|}{N}}-CH_2-\underset{\displaystyle R}{\underset{|}{N}}-CH_2-\underset{\displaystyle R}{\underset{|}{\acute{N}}}- \;.......$$

The deficiency of methylene groups in the second stage of the process results in a significant additional methanol accession and as a result the toxicity of adhesive is decreased (ROFFAEL 1982).

Properties of plywood

The average values of shear strength of plywood panels manufactured using UF resin modified by various hardeners are provided in Table 3.

As can be seen the shear strength values of plywood panels on all investigated hardeners exceed the standard strength rate according to EN 314-2 (more than twice) and shear strength value of adhesive composition using ammonium chloride. The highest shear strength value (3.5 MPa) was obtained for aluminium sulphate added in amounts of 1.0% into the adhesive composition.

Tab. 3 The average shear strength values of birch plywood panels.

Hardener	Content of hardener [%]	Shear strength [MPa]	Shear strength [MPa] according to EN 314-2
	0.5	2.05 (0.33)*	
Ammonium chloride	1.0	2.06 (0.35)	
	1.5	2.10 (0.47)	
	0.5	2.28 (0.08)	
Aluminium sulphate	1.0	3.47 (0.63)	
	1.5	2.94 (0.56)	
	0.5	2.33 (0.26)	
Ammonium persulphate	1.0	2.78 (0.41)	≥ 1.0
	1.5	3.13 (0.50)	
	0.1	2.56 (0.42)	
Ferrum (III) chloride	0.15	2.61 (0.70)	
	0.2	2.47 (0.53)	
	0.5	2.82 (0.39)	
Combined hardener	1.0	3.00 (0.18)	
	1.5	2.84 (0.65)	

*Values in parenthesis are standard deviations.

Toxicity of plywood panels based on the adhesive compositions using ferrum (III) chloride and a combined hardener was not determined, given the high values of free formaldehyde content in these adhesives. Aluminium sulphate and ammonium persulphate, in comparison with ammonium chloride, substantially reduce formaldehyde emission from plywood panels (Fig.1). Moreover, the influence of aluminium sulphate on the formaldehyde emission is more pronounced than the influence of ammonium persulphate. The formaldehyde release stated by the standard of gas analysis method should be lower than 3.5 $mg/h.m^2$.

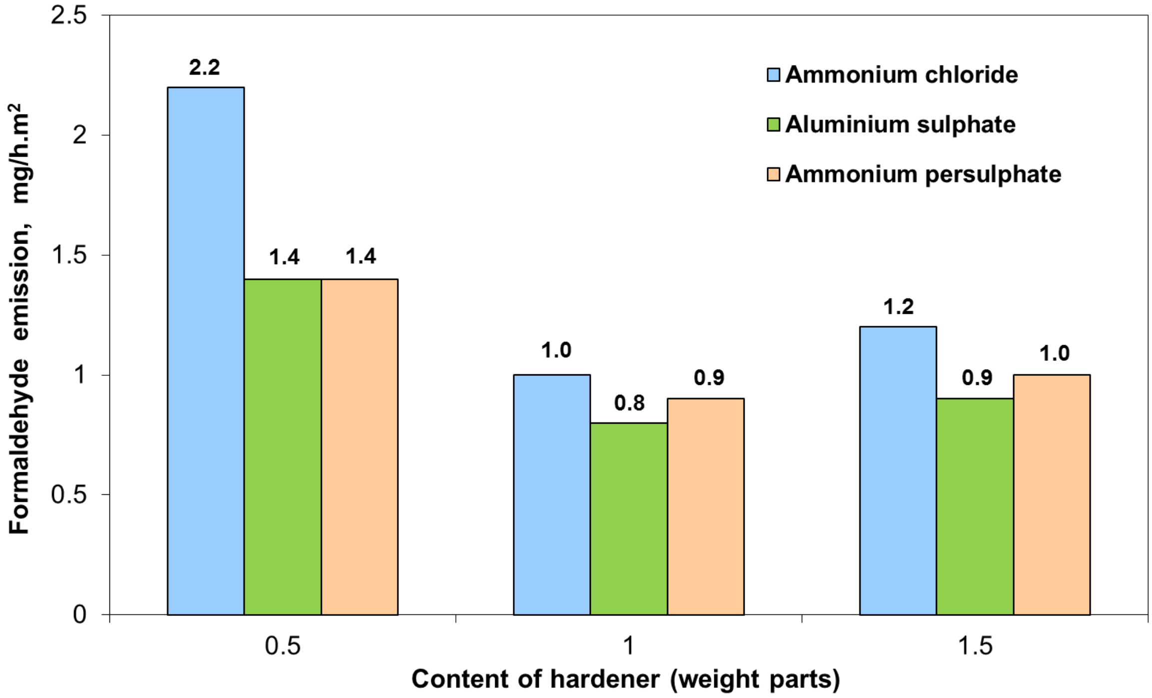


Fig. 1 Formaldehyde emission of birch plywood panels.

CONCLUSIONS

In this study, the effect of various hardeners on the viscosity, curing time, solid content, pH and formaldehyde content of UF resin for plywood manufacture, as well as on the formaldehyde emission and shear strength of plywood made using different adhesive compositions was demonstrated. The results showed that using such hardeners as aluminium sulphate and ammonium persulphate could improve the shear strength of plywood panels and greatly reduce (in 10–36%) their formaldehyde emission in comparison with using ammonium chloride. Obviously, this can be explained by the fact that aluminium sulphate and ammonium persulphate allows the reduction in the content of free formaldehyde in adhesives to 20.0% and 60.0% respectively compared with ammonium chloride. On the contrary, the use of ferrum (III) chloride and a combined hardener could result in the increasing of free formaldehyde content in adhesive compositions.

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