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INVESTIGATION OF FREE FORMALDEHYDE QUANTITY IN PRODUCTION OF PLYWOOD WITH MODIFIED UREA – FORMALDEHYDE RESIN

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ABSTRACT

This study examined free formaldehyde emission in production of plywood with modified urea-formaldehyde resin (UF). Formaldehyde scavengers- urea and ammonium bicarbonate - were added to the UF resin and its toxicity was determined according to БДС EN 1243:2011 standard. The toxicity of the resulting plywood was measured according to БДС EN 717-3: 2003. The effects of various types of hardeners also was investigated, and 2 % ammonium sulfate in relation to solid content of the resin showed the best values. The results showed that the addition of formaldehyde scavengers- urea and ammonium bicarbonate - to UF resin effectively reduced formaldehyde emission and it can be controlled within acceptable ranges.

Key words: urea-formaldehyde resin (UF), formaldehyde scavenger, plywood, formaldehyde emission

1. INTRODUCTION

Urea–formaldehyde (UF) resins are the most widely used adhesives in production of plywood. This is due to some advantages: low cost, curing at low temperature, good technological properties, easy preparation of the adhesive mixture, resistance to fungal and insect pests, water solubility and lack of colour of the cured resin (Zhu et al. 2010; Dunky 1998; Huang et al. 2011). On the other hand, one of the main disadvantages of UF resins is the release of formaldehyde during gluing. This process continues long after the completion of polymerization processes in the resin (Tohmura et al. 2000; Yu and Crump 1999; Martínez and Belanche 2000).

Formaldehyde is a toxic gas that causes irritation of the skin, eyes and mucous membranes. In addition, the chemical effect of formaldehyde can lead to contact dermatitis, conjunctivitis, disorders of the nervous system, larynx and bronchus. This major disadvantage considerably limits the range of UF resin uses (Zhang et al. 2013; Bohm et al. 2012; Salem et al. 2011; Roffael 2012).

One of the methods for reducing toxicity of plywood and particle board is processing of finished products with special hardeners (Bekhta et al. 2016).

Formaldehyde scavengers regulate the free formaldehyde content by forming relatively harmless products (Sensogut et al. 2009). These substances can significantly influence the plywood strength properties (Ozalp et al. 2013). On the other hand, some formaldehyde scavengers such as urea and ammonium bicarbonate foam the adhesive solution. As a result, the adhesive is applied more evenly and it significantly reduces the glue consumption per unit area. This factor leads to drop in plywood toxicity (Puttasukkha et al. 2015; Dziurka et al. 2014; Costa et al. 2013).

Therefore, the aims of this work were to:
- investigate the influence of different hardeners and fillers on the cure rate and the UF resin toxicity
- evaluate the influence of formaldehyde scavengers on the UF resin toxicity

- determine the toxicity of experimentally obtained plywood plates

2. MATERIAL AND METHODS

Beech veneer sheets with dimensions of 400 mm×400 mm×1,1mm and moisture content of 8 % without visible defects were used to prepare five-layer plywood panels.

In order to determine the influence of the adhesive mixture on the toxicity of the plates, the following technological regime was selected: glue spread of 140 g/m^2, temperature of 140 °C, pressure of 1,1 MPa and pressing time 1 min/mm.

Commercial UF resin E2 type used for gluing of veneer sheets was supplied by Neochim PLC, Bulgaria.

Ammonium persulfate ($(NH_4)_2S_2O_8$)- 1 and 2 %, ammonium phosphate ($(NH_4)_3PO_4$)- 2 %, ammonium chloride (NH_4Cl)- 2 % and ammonium sulfate ($(NH_4)_2SO_4$)- 2 % in relation to solid content of the resin were chosen as hardeners for preliminary research. The hardeners were added to the resin in form of aqueous solutions. Further studies were performed with 2 % $(NH_4)_2SO_4$ because of its best properties.

Based on this, seven recipes for glue were developed: UF resin with solid content- 67 %; hardener- 2 % and filler- 10 % in relation to solid content of the resin.

The quantity of the used formaldehyde scavengers- ammonium bicarbonate (NH_4HCO_3) and urea (H_2NCONH_2) - ranged from 1 to 3 %.

Wheat flour in amount of 10 % in the glue mixture was used as filler. The effect of filler quantity on the gel time of the resin was measured according to БДС 5266-81 standard.

Formaldehyde content of the UF resin was determined according to БДС EN 1243:2011 and the toxicity of plywood panels was evaluated according to БДС EN 717-3: 2003.

3. RESULTS AND DISCUSSION

Analysis with UF resin was conducted in order to obtain adhesives for production of low toxic plywood. Therefore, different composition and amount of hardeners, fillers and formaldehyde scavengers was applied. In order to evaluate the exact influence of these factors on the plywood, the other technological factors were kept constant for all experiments.

3.1. Effect of different hardeners on the UF resin properties. The results from the investigations were shown in Table 1.

Table 1. *Effect of type and quantity of hardener on the resin curing time at 100° C*

Quantity of hardener based on resin solid content (%)	Type of hardener			
	NH_4Cl	$(NH_4)_2SO_4$	$(NH_4)_3PO_4$	$(NH_4)_2S_2O_8$
	Curing time (s)			
1,0	80	80	85	45
1,5	75	75	78	37
2,0	65	70	75	30
2,5	52	65	70	20
3,0	47	60	62	15

Ammonium persulfate showed the best results as hardener. Besides, the worst indexes in relation to the other hardeners were demonstrated by ammonium phosphate, but its values were close to these of ammonium chloride and ammonium sulfate.

3.2. Effect of hardener on toxicity of UF resin

In order to determine the toxicity of the resin, five samples containing different amounts of hardener were analyzed. UF resin without hardener (Table 2) was used as a control sample

Table 2. *Toxicity of UF resin depending on the type and quantity of the hardener*

Type and quantity of hardener based on resin solid content (%)	Free formaldehyde content (%)
control sample	0,12
1 % $(NH_4)_2S_2O_8$	0,17
2 % $(NH_4)_2S_2O_8$	0,22
2 % $(NH_4)_3PO_4$	0,18
2 % NH_4Cl	0,19
2 % $(NH_4)_2SO_4$	0,16

The lowest toxicity was found in the sample containing 2 % ammonium sulfate, while the highest was recorded for the sample with 2 % ammonium persulfate.

The results indicated that the quantity of hardener had significant impact on toxicity of cured resin. An increase in the amount of hardener led to an increase in free formaldehyde amount. The next experiments were carried out with ammonium sulfate.

3.3. Effect of filler on gel time of UF resin.

The data obtained from investigation of the influence of active filler wheat flour with different percentage composition in relation to solid content of the resin, are given in Table 3.

Table 3*. Gel time of the resin depending on the quantity of filler*

Quantity of filler (%)	Gel time (s)
0	75
10	80
20	83
30	85
40	90

The best results were observed by using 10 % active filler. The addition of fillers to the UF adhesives results in variations in the cure rate because of drop in the adhesive mixture concentration. On the other hand, however, active fillers improve the elasticity of the adhesive-bonded joint.

3.4. Effect of formaldehyde scavengers on the properties of the UF resin.

Two kinds of formaldehyde scavengers- urea and ammonium bicarbonate - in different quantities, were added to the UF resin. The obtained values for gel time depending on type of formaldehyde scavenger are summarized in Table 4.

Table 4. *Effect of formaldehyde scavengers on the gel time of UF resin*

Formaldehyde scavenger (%)	Gel time (s)
1 % H_2NCONH_2	85
2 % H_2NCONH_2	85
3 % H_2NCONH_2	87
1 % NH_4HCO_3	115
2 % NH_4HCO_3	143
3 % NH_4HCO_3	180

As one can see from the table, better results were established by using urea as formaldehyde scavenger into the resin composition. Free formaldehyde content depending on different amounts of urea and ammonium bicarbonate, is shown in table 5.

Table 5. *Toxicity of UF resin depending on the type and quantity of formaldehyde scavenger*

Type and quantity of formaldehyde scavenger	Quantity of hardener $(NH_4)_2SO_4$ (%)	Free formaldehyde content (mg/100 g binder)
1 % H_2NCONH_2	2	150
2 % H_2NCONH_2	2	98
3 % H_2NCONH_2	2	90
1 % NH_4HCO_3	2	158
2 % NH_4HCO_3	2	154
3 % NH_4HCO_3	2	150

An increasing quantity of formaldehyde scavenger causes reduction of free formaldehyde content in the resin. This is the most noticeable at urea. The increase of its quantity initially leads to significant decrease in toxicity, but the addition of urea at the levels above 3 % is not as much effective. This is due to the depletion of free formaldehyde content because of its reaction with urea. The effect of ammonium bicarbonate is significantly weaker.

3.5. Effect of formaldehyde scavengers on toxicity of plywood.

Studies of free formaldehyde content in experimentally produced plywood using urea and ammonium bicarbonate as a supplement to UF resin are given in Table 6.

Table 6. *Toxicity of plywood depending on the type and quantity of formaldehyde scavenger*

Type of formaldehyde scavenger	Quantity of formaldehyde scavenger (%)	Free formaldehyde content (%)
control sample	-	0,54
NH_4HCO_3	1	0,42
NH_4HCO_3	2	0,32
NH_4HCO_3	3	0,25
H_2NCONH_2	1	0,52
H_2NCONH_2	2	0,49
H_2NCONH_2	3	0,42

According to data listed in Table 6, both substances significantly affected the toxicity of the plywood. A considerable reduction in free formaldehyde content was observed by using 3% ammonium bicarbonate.

4. CONCLUSIONS

Based on the results obtained, it has been found that the addition of urea or ammonium bicarbonate to the adhesive mixtures results in decrease in the amount of free formaldehyde.

On the other hand, the addition of formaldehyde scavengers can be conducted without any particular disturbances in the technological process.

In regard to plywood production technology, the type and amount of hardener contribute to variation in curing rate of the resin. The best results were observed by using ammonium persulfate at concentration of 3 %.

The results of the studies performed showed that the lowest value of toxicity (0.16%) was measured for resin containing 2% ammonium sulfate. Besides, the highest value (0.22%) was obtained for resin containing 2% ammonium persulfate. The longest durability of the resin (180 s) was established by addition of 3 % ammonium bicarbonate, while the lowest value (85-87 s) was obtained by addition of 1-3% urea. Moreover, the amount of filler into the resin substantially affected the durability and open time of adhesives, as well as their toxicity.

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