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TECHNOLOGY OF LOW-TEMPERATURE PRODUCTION OF PLYWOOD BONDED WITH MODIFIED PHENOL-FORMALDEHYDE RESIN

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ABSTRACT

Technology of low-temperature veneer gluing in the manufacture of phenol-formaldehyde (PF) plywood has been investigated. The research on modification of PF resins by various chemical compounds (resorcinol, melamine, urea, para-formaldehyde, hydrogen peroxide, dichromate ammonium, potassium and sodium) has been done. Such modification gives a possibility to make plywood at reduced pressing temperature of 100 °C in comparison with the usual temperatures of 120-130 °C. The low-temperature pressing results in a significant energy saving process in comparison with high-temperature pressing, without any worsening of mechanical properties of plywood.

KEY WORDS: gluing of plywood, veneer, phenol-formaldehyde resin, combined hardener, low pressing temperature

INTRODUCTION

Composite materials eliminate anisotropy of solid wood and their production enables economically and profitable used secondary wood raw materials. For these purposes, PF adhesives are used in large scale, which creates strong bounds resistible against water and humidity, against weather conditions and biological attack, they are resistant to solvents and ageing.

Effort for lowering of energy consumption, for improving of environment and better exploitation of raw materials is realized by systematic research of new technologies also at production and application of PF adhesives. Intense endeavour to reduce energetic cost of production of glued pressed composite materials leads to find ways, how these costs reduce. There is necessary to apply new technologies, which save energy during the wood processing, increase labour productivity and reduce final price of production. High consumption of energies is also during the pressing process, which depends on the type of the press, heating system and time of pressing, where technologic reserves of heat saving exist in shortening of the pressing time.

The quality of veneer gluing in plywood manufacture is influenced by various factors, concerning both wood and glue, and directly is influenced by technological parameters of pressing – temperature, pressure and time.

In general, 120-130 °C is a typical press temperature for plywood panels bonded with phenolformaldehyde adhesive. The increased temperature accelerates polycondensation reaction (Kulikov 1976) when adhesive is applied on the surface of veneer in either liquid or foil form. However, pressing temperature above 130-135 °C is leading to reduction of cohesive glue line strength (Moskvitin 1974, Krotov and Shilka 1982) and resulting in defective plywood (Chow and Mukai 1972, Chubinskyj 1976a, Chubinskyj 1976b, Okhlopkov 1983).

Another disadvantage of increased pressing temperature, in combination with high moisture content of veneer sheets, is having excessive adhesive penetration into veneer and significantly higher compression coefficient of plywood. An insufficient glue layer leads to the effect of "hungry gluing" and decreases the bonding strength (Mikhajlov 1963, Kulikov 1976).

Several researchers (Chow and Mukai 1972, Chubinskyj 1976b, Voroshilov 1980) concluded the fact, that the pressure of gasvapour mixture in glue line is higher with increasing of pressing temperature. This phenomenon is causing development of bubbles within the glue line (Kulikov 1976, Anisov et al., 1980). In particular, the amount of such bubbles in plywood can increase up to 10 % at the press temperatures of 118-120 °C and reduces at the temperature of 110-115 °C what minimise defects of plywood (Shevando 1985). According to another previous work, it was found that vapours and gas conductivity of hardwood is higher than of softwood (Anisov et al. 1980). Therefore, birch and other hardwood veneers could be pressed at higher temperatures.

Application of pressing temperatures for plywood below 100 °C is not recommended due to its adverse effect on the glue line curing time (Shnabel and Andreeva 1985). However, some authors have revealed that using a lower temperature had no influence if phenolic and resorcinol adhesives combined with different hardeners including combined hardener of dichromate sodium, urea and water (Behunkov 1979, Chubinskyj and Kazakievich 1992, Kazakievich 1992, Orlov et al. 2004, Zalipajev 2004).

The possibility to produce plywood using different PF adhesive compositions with improved reactivity at lowered pressing temperature of 100 °C was stated by (Orlov et al. 2004).

The reaction rate of resorcinols with formaldehyde is considerably higher compared with phenol. Reactivity of different resorcinols at polycondensation was determined by (Christjanson, Köösel 2001).

The influence of oxidizing agents, mainly hydrogen peroxide, was tested in adhesive mixtures for particleboard production (Lecka et al. 1999a, Lecka et al. 1999b 2000). Oxidizing agents activate the lignin structure of wood and chemical bound is created between wood and PF resin, what increases strength properties of glued joints.

Glue composition with active filler (dispersed silica powder), which enabled to press coniferous veneer at temperature of 105-110 °C, has been developed. It enables decreasing of the compression coefficient of plywood by 3 % (Chubinskyj and Kazakievich 1992, Kazakievich 1992). Another filler, graphite, is frequently used as an electroconductive filler, due to its moderate cost and good conductivity. Graphite has also a positive influence on the mechanical properties of glued joint (Novák and Krupa 2004).

Pressing plywood at low temperature does not cause adverse effects on plywood properties due to superfluous of vapourgas pressure developed within the glue line (Dunky 2003). Cold pressing can also be considered as alternative method, but it is limited by the specific equipment and low productivity. Plywood pressing at temperature below 100 °C results in significant reduction of productivity of hot press in the case when one-component resin is used.

Therefore, an increase of reactivity of PF resins by addition of hardeners and active fillers is one of the effective methods of plywood quality improvement. It allows gluing veneer at lower temperatures and eliminates defects, which are inherent at high-temperature pressing.

The aim of this study was to evaluate the strength properties of plywood panels produced experimentally using modified PF resin and reduced pressing temperature of 100 °C without any prolongation of pressing time.

MATERIAL AND METHODS

Commercial birch (*Betula pubescens*) and beech (*Fagus sylvatica*) veneer sheets with moisture content of 4-6 % were used for the experiments. Three-layer plywood with dimensions 300 × 300 mm were manufactured from birch, beech veneer and their combination at technological parameters of pressing as follows: pressure of 1,8 MPa, temperature of 100 °C, press time of 6 min, glue spread of 140 $g.m^{-2}$. The birch and beech veneer samples had thicknesses of 1,5 and 1,8 mm, respectively. For comparison, plywood panels were made at temperatures of 120 and 150 °C.

Phenol-formaldehyde resin modified with resorcinol, alkylresorcinol, paraformaldehyde, melamine, urea, hydrogen peroxide, dichromates ammonium, potassium and sodium was used as a binder. The composition of received adhesive mixtures is summarised in the Tab. 1.

Tab. 1: Composition of adhesive mixtures

Adhesive components	Adhesive mixture								
	0	1	2	3	4	5	6	7	8
PF resin	100	100	100	100	100	100	100	100	100
Alkylresorcinol	-	3	3	-	-	-	-	-	-
Resorcinol	-	-	-	3	3	3	2	3	3
Paraformaldehyde	-	7	7	6	6	10	5	5	5
Hydrogen peroxide	-	-	-	-	1	1	1	1	1
Combined hardener:	-	10	15	13	13	10	7	5	7
melamine	-	-	-	-	-	6	-	-	-
urea	-	24	7	6	6	-	3	3	3
dichromate ammonium	-	-	-	6	6	-	-	-	-
dichromate potassium	-	24	7	-	-	6	-	-	-
dichromate sodium	-	-	-	-	-	-	3	3	3
water	-	52	70	18	18	18	3	3	3

Properties of the proposed adhesive mixtures as working life, setting time, pH and dynamic viscosity were determined according the usual methods. Curing time of glue was determined at three temperatures, namely 100 °C, 120 °C and 150 °C. Rotary viscosimeter RHEOTEST type RV2 and pH-meter HANNA HI 221 were employed to determine of dynamic viscosity and pH of the adhesive mixtures, respectively.

Shear strength of plywood samples was determined according to European standard EN 314-1. Before testing, all plywood samples were conditioned at the temperature of 20 °C and relative humidity of 65 % for two weeks.

Basic properties of proposed adhesive compositions are shown in the Tab. 2.

Tab. 2: Basic properties of the adhesive mixtures

Property	**Adhesive mixture**								
	0	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Dynamic viscosity (mPa.s)	659	776	922	1801	2021	1342	1293	732	849
Working life (min)	400	90	84	55	51	65	69	79	76
pH	11,4	11,0	11,1	10,8	10,4	10,9	10,9	10,9	10,9
Curing time (s)									
at 100 °C	202	124	133	107	98	107	118	121	130
at 120 °C	67	32	26	37	30	25	48	49	50
at 150 °C	-	25	26	30	22	22	39	34	34

RESULTS AND DISCUSSION

The chemical process of PF resins curing under activation of various hardeners forms spatial nets of polymer. It was proved that dichromates of ammonium, potassium and sodium support a process of oxidation-reduction reaction and accelerate PF resin curing.

Resorcinol has the capacity to create a large number of chemically active contact points. The increasing of quantity of reactive groups in the system reduces activation energy of the system. In this case, lower heat energy is sufficient for the beginning of the polycondensation process.

The study of curing time of proposed adhesive compositions showed that glue with the combined hardener, which contains dichromate ammonium, is cured faster. The addition of hydrogen peroxide into the composition of adhesive mixture has reduced setting time by 8,4 %, working life by 7,3 %, and increased viscosity by 12,2 % in comparison with a mixture without addition of hydrogen peroxide.

All investigated compositions of glues do not reach the value of working life of pure PF resin, but nevertheless, they can be used for plywood pressing at low temperatures in practice.

The pH values of proposed glue mixtures are practically not changed and they meet the standard interval.

Shear strength properties of tested plywood, glued with adhesive composition with combined hardener are summarised in the Tab. 3. From the table follows, that most of the proposed adhesive mixtures are suitable for pressing of birch, beech and combined plywood, with exception of mixtures No. 1, 3 and 4 at the temperature of 100 °C.

Tab. 3: Shear strength of plywood

Adhesive mixture	Press temperature (°C)	Type of plywood	Basic statistical characteristics		
			Shear strength (MPa)	Standard deviation (MPa)	Coefficient of variation (%)
0	100	birch	-	-	-
	120		0,3	0,12	37,6
	130		1,7	0,67	40,3
	140		1,8	0,67	36,5
	150		2,3	0,34	14,6
1	100	birch	2,4	0,54	22,2
		beech	1,6	0,25	16,1
		birch/beech	0,0	0,00	0,0
2	100	birch	2,5	0,40	16,1
		beech	1,5	0,45	29,4
		birch/beech	1,5	0,33	22,2
3	100	birch	1,8	0,42	22,7
		beech	1,6	0,33	21,1
		birch/beech	0,8	0,68	87,7
4	100	birch	1,8	0,42	22,8
		beech	1,3	0,31	23,5
		birch/beech	1,0	0,39	39,7
5	100	birch	2,1	0,47	22,0
		beech	2,3	0,29	12,7
		birch/beech	1,5	0,21	13,9
6	100	birch	2,4	0,44	18,5
		beech	2,2	0,21	9,6
		birch/beech	1,4	0,28	20,7
7	100	birch	2,2	0,46	21,5
		beech	2,2	0,29	13,4
		birch/beech	1,7	0,35	20,3
8	100	birch	2,7	0,46	17,3
		beech	2,0	0,31	15,6
		birch/beech	1,7	0,35	20,1

Shear strength values of birch plywood pressed at temperature of 100 °C are comparable with shear strength values of plywood pressed at elevated temperatures of 140-150 °C. It enables to reduce expenses of energy during the pressing process and essentially reduce the compression coefficient of plywood, as well.

From measured average values of shear strength of glued joints follow, that all types of prepared adhesive mixtures fulfil requirements required by appropriate standard. In comparison of shear strength values with the reference sample, we can stated, that all prepared mixtures of additives into PF resin enable the plywood production at pressing temperature of 100 °C.

Obtained values of physical and chemical properties of adhesive mixtures and strength properties of prepared plywood confirmed results obtained in research by (Lecka et al. 1999 b), they tested the influence of oxidising agent on kinetics of hardening of commercial PF resin for industrial particleboard production and on physical and mechanical properties of produced boards.

CONLUSIONS

Wide utilisation of phenol-formaldehyde resins in woodworking industry enables the availability of raw materials, relatively easy application and the property, that PF mixtures provide waterproof joints. Their further advantages are their non-flammability, good heat properties and low content of volatile compounds e.g. free phenol and formaldehyde. Disadvantage of PF resins is their slower hardening at low temperatures. Just this last mentioned property was the subject of this work.

The application of such matters as: resorcinol, hydrogen peroxide, paraformaldehyde, melamine, urea, dichromates ammonium, potassium and sodium into the compositions of combined hardeners, provides the most intensive reduction of setting time of PF resins at the temperature of 100 °C. Reactivity of developed adhesive mixtures is 1,5-2,1 times higher than reactivity of the base component of glue – pure PF resin.

The offered technology of low temperature pressing of birch and beech veneer can be recommended for manufacturing of plywood both from hardwood and softwood. Results are possible to use directly in practise at plywood production, because proposed additives are available and fulfils their task, improves physical, chemical, mechanical and technological properties of adhesive mixtures.

All results are protected by several patents.

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