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THE EFFECT OF MODIFICATION OF PHENOLIC RESIN WITH ALKYLRESORCINOLS AND H_2O_2 ON PROPERTIES OF PLYWOOD

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Abstract. The study analysed the effect of modification of phenolic resin with alkylresorcinols and H_2O_2 on properties of softwood and hardwood plywood resinated with such modified PF resins. Conducted tests showed that the application of PF resin modified with alkylresorcinols makes it possible to manufacture plywood with improved properties, especially bond quality, than those of the control plywood pressed under identical conditions. In turn, the introduction of H_2O_2 both to pure PF resin and resin modified with alkylresorcinols improves properties of plywood as a result of enhanced reactivity and increased chemical adhesion of resin to wood. Moreover, applied PF resin modification methods make it possible to manufacture plywood with very good properties at pressing time reduced by 25%.

Key words: PF resin, alkylresorcinols, hydrogen peroxide, plywood

INTRODUCTION

Literature on the subject of increasing the reactivity of PF resins presents numerous possibilities of enhancing its reactivity both during manufacture and through modification of the final product using substances accelerating curing. Numerous attempts have been made to synthesize PF resin, using in part or in 100% a substrate other than phenol, with the best properties shown by resins, in which it was completely replaced by resorcinol. Sellers et al. [1988] proved that due to its high reactivity, ability to penetrate wood and possibility of complete curing at a relatively low temperature resorcin-formaldehyde (RF) resins may be used in the manufacture of absolutely water resistant, formaldehyde-free boards. However, despite high stability of adhesive-bonded joints pure resorcin adhesives have not been applied in the production of wood-based materials type V 100, due to their high price. In order to reduce production costs phenol-resorcin-formaldehyde (PRF) resins are produced, which exhibit quality similar to that of pure PF resins and may be used to resinate hardwood, yielding products with very

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good properties [Hse 1980]. In turn, tests conducted by the authors showed that the application of phenolic resin modified with alkylresorcinols makes it possible to manufacture particleboards with good properties at pressing time reduced by 30% or at pressing temperature lowered by 20°C [Dziurka et al. 2006].

However, a method preferred by many researchers and wood-based material producers is the modification of ready-to-use resins with an addition of substances accelerating curing or reducing the temperature of this process. This direction for the enhancement of PF resin reactivity seems especially promising due to the large number of compounds, both organic and inorganic, triggering this phenomenon. In case of inorganic compounds the role of oxidizing compounds, especially hydrogen peroxide, has been stressed for a long time now [Czarnecki and Łęcka 2001]. It results from the analyses conducted by those authors that the application of H_2O_2 as a modifier of PF resin makes it possible to manufacture particleboards with very good physical and mechanical properties as well as facilitates a reduction of pressing temperature or shortening of pressing time by approx. 30% [Czarnecki and Łęcka 2003].

Promising results concerning improvement of properties of particleboards and the observed possible improvement of efficiency of the manufacture process when applying PF resin modified with alkylresorcinols and H_2O_2 showed the advisability of investigations comprising this study on the applicability of such modified resin in the manufacture of exterior plywood.

Thus the aim of this study was to investigate the effect of PF resin modified with alkylresorcinols and an addition of hydrogen peroxide to the resin on properties of exterior plywood manufactured with this resin.

MATERIAL AND METHODS

The analysis was conducted on resol phenol-formaldehyde resin produced as a result of condensation of phenol and the alkylresorcinol fraction with formaldehyde in the presence of NaOH (aRPF). The alkylresorcinol fraction with brand name Honeyol (Estonia) was added at 0.6% in relation to the total weight of the solution. Reference resin was unmodified PF resin with a mole phenol:formaldehyde ratio of 1:2.4.

Properties of resins used in the analyses are presented in Table 1.

Hydrogen peroxide (H_2O_2) was applied as a modifier of phenolic resin, added at 1 and 3% in relation to resin dry weight and UT-10 was used as a curing agent of the adhesive mixture.

Three-layer plywood was manufactured from beech and pine veneers of 1.4 × 1.7 × 1.4 mm thickness, using the following pressing conditions:

– temperature – 135°C,
– pressure – 1.6 $N \cdot mm^{-2}$ for beech plywood and 1.4 $N \cdot mm^{-2}$ for pine plywood,
– time – 240 and 180 s,
– amount of adhesive mixture applied onto veneers – 160 $g \cdot m^{-2}$.

In the manufacture of plywood at pressing time shortened to 180 s resin modified with H_2O_2 was used only in the amount of 3%. Analyses of properties of manufactured plywood were conducted following the respective standards:

– bending strength and modulus of elasticity according to PN-EN 310

Table 1. Properties of resins used in the analyses
Tabela 1. Właściwości żywic stosowanych w badaniach

Property Właściwość	Unit Jednostka	Measurement results for resin properties Wyniki pomiarów właściwości żywic	
		aRPF	PF
Density Gęstość	$g \cdot cm^{-3}$	1.209	1.213
Dymanic viscosity Lepkość dynamiczna	mPa·s	498	594
No. 4 Ford Cup viscosity Lepkość umowna	s	33	46
pH	–	11.55	11.53
Gel time Czas żelowania	s	208	216
Solids content Zawartość części nielotnych	%	45.6	44.76
Free phenol content Zawartość wolnego fenolu	%	0.0	0.0
Free formaldehyde content Zawartość wolnego formaldehydu	%	0.32	1.8
Alkali content Zawartość alkalii	%	7.16	7.21
Miscibility with water Mieszalność z wodą	–	1:∞	1:∞

– bond quality according to PN-EN 314-1, with samples pretreated according to points 5.1.1 (24 h soaking in cold water, tested wet) and 5.1.3 (4 hours boiling water + 16 hours 70°C drying + 4 hours boiling water, tested wet), following the recommendation of the standard 314-2.

RESULTS AND DISCUSSION

Results of investigations concerning the effect of the modification of PF resin with alkylresorcinols in the process of its synthesis on properties of manufactured plywood are presented in Figures 1-2 and Tables 2-3. It results from given data that this method of PF resin modification makes it possible to manufacture plywood with better properties than the control plywood pressed under identical conditions, resinated with pure PF resin. Especially striking parameters include an increase in bond quality in the shear test, of as much as 62 and 78%, respectively, for pine and beech plywood, irrespective of the type of accelerated ageing test (Fig. 1 and 2). Such a considerable increase in bond quality indicates an advantageous effect of applied modification on cross-linking of PF resin, which determines the stability of formed adhesive-bonded joint. However, it needs to be assumed that these reactions take place mainly within resin, to a lesser

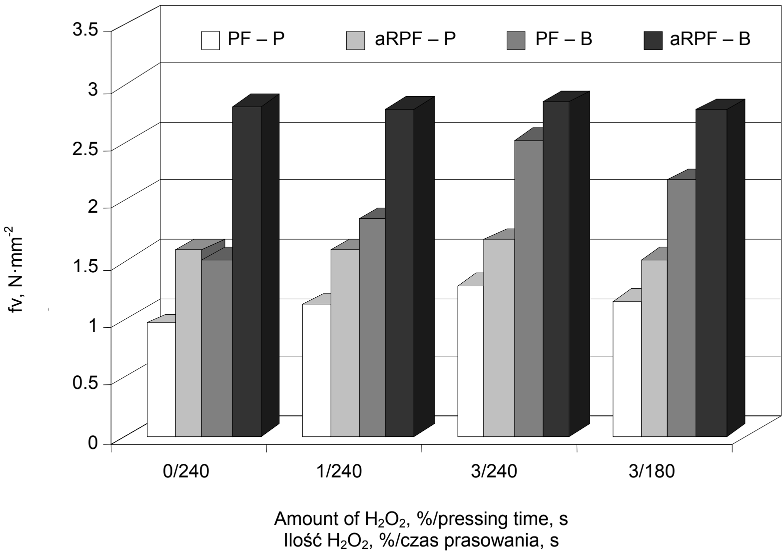

Fig. 1. Shear strength of plywood manufactured with modified PF resin after soaking in cold water: P – pine, B – beech
Rys. 1. Jakość sklejenia określana w próbie ścinania po moczeniu w zimnej wodzie: P – sosna, B – buk

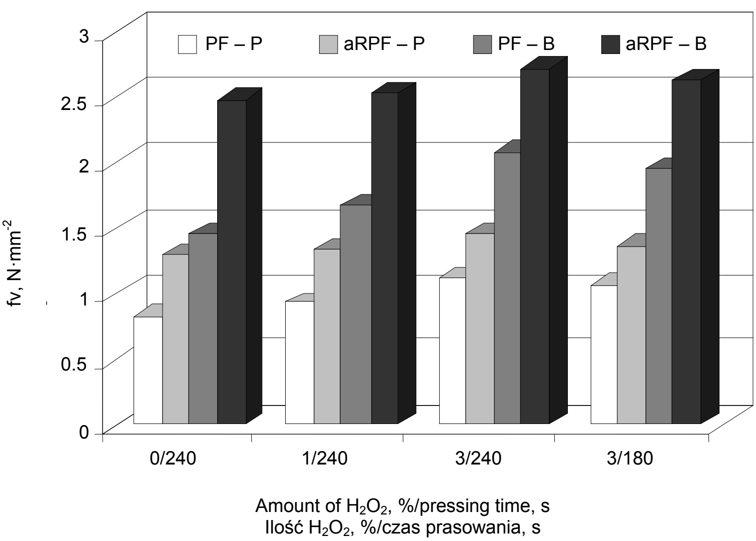

Fig. 2. Shear strength of plywood manufactured with modified PF resin after boiling test: P – pine, B – beech
Rys. 2. Jakość sklejenia określana w próbie ścinania po próbie gotowania: P – sosna, B – buk

Table 2. Properties of beech plywood depending on the type of applied resin, amount of H_2O_2 and pressing time
Tabela 2. Właściwości sklejek bukowych w zależności od rodzaju zastosowanej żywicy, ilości H_2O_2 oraz czasu prasowania

Type of resin Rodzaj żywicy	Amount of H_2O_2 Ilość H_2O_2 %	Pressing time Czas prasowania s	Bending strength Wytrzymałość na zginanie $N \cdot mm^{-2}$		Modulus of elasticity Moduł sprężystości $N \cdot mm^{-2}$	
			‖	⊥	‖	⊥
PF	0	240	122	33.4	12 030	1 450
			12[*]	*2.2*	*1 430*	*140*
	1	240	124	33.7	12 820	1 600
			14	*3.1*	*950*	*120*
	3	240	139	40.8	13 280	1 680
			16	*5.0*	*1 300*	*170*
	3	180	135	38.0	12 020	1 670
			14	*3.2*	*1 060*	*190*
aRPF	0	240	132	34.8	12 420	1 690
			16	*3.3*	*980*	*140*
	1	240	150	35.9	13 520	1 760
			16	*4.1*	*1 130*	*140*
	3	240	159	40.9	13 840	1 770
			12	*4.2*	*1 550*	*200*
	3	180	158	39.7	13 150	1 600
			11	*5.1*	*1 170*	*190*

[*]Standard deviation.
[*]Odchylenie standardowe.

extent at the resin-wood interface, as it is shown by testing results of bending strength. An increase in the value of this property recorded irrespective of the type of plywood and testing methods was on average only by 6% (Tables 2 and 3). The trend was similar for testing results of the modulus of elasticity of manufactured plywood. These results were consistent with earlier findings of these authors, which showed that the application of such modified PF resin in the manufacture of particleboards results in an increase in their tensile strength by as much as 60%, at an only 13% increase in bending strength [Dziurka et al. 2006].

In turn, studies on the modification of both types of resin with hydrogen peroxide showed that its application, especially as a modifier of pure PF resin, significantly affects bond quality of manufactured plywood. Thus, as shear strength after the boiling test for the maximum addition of H_2O_2 to resin modified with alkylresorcinols on average increases by 11%, in case of pure PF resin this increase was 35 and 42%, respectively,

Table 3. Properties of pine plywood depending on the type of applied resin, amount of H_2O_2 and pressing time
Tabela 3. Właściwości sklejek sosnowych w zależności od rodzaju zastosowanej żywicy, ilości H_2O_2 oraz czasu prasowania

Type of resin Rodzaj żywicy	Amount of H_2O_2 Ilość H_2O_2 %	Pressing time Czas prasowania s	Bending strength Wytrzymałość na zginanie N·mm^{-2} ‖	 ⊥	Modulus of elasticity Moduł sprężystości N·mm^{-2} ‖	 ⊥
PF	0	240	102	25.5	11 080	1 180
			*9**	*2.7*	*840*	*100*
	1	240	107	26.7	11 500	1 350
			9	*2.8*	*1 280*	*90*
	3	240	111	27.8	11 380	1 210
			9	*3.1*	*1 110*	*90*
	3	180	105	25.8	10 200	1 130
			6	*3.3*	*1 030*	*110*
aRPF	0	240	106	27.1	12 020	1 320
			8	*3.5*	*1 320*	*130*
	1	240	115	28.4	12 500	1 230
			6	*3.2*	*970*	*120*
	3	240	118	29.8	12 410	1 330
			8	*3.1*	*820*	*140*
	3	180	112	27.8	12 360	1 180
			10	*2.4*	*1 220*	*130*

*Standard deviation.
*Odchylenie standardowe.

for pine and beech plywood (Fig. 2). However, it needs to be stressed that already the modification in the synthesis process of PF resin with alkylresorcinols results in a considerable, from 0.47 to 1.22 N·mm^{-2}, increase in strength of manufactured plywood after tests accelerating ageing in relation to plywood resinated with pure resin, and thus an addition of hydrogen peroxide only slightly affects it further improvement. Moreover, an advantageous effect of the applied modifier was observed on the fluctuations in bending strength of plywood. For maximum amounts of H_2O_2 (3%) introduced to both types of resin, irrespective of the testing method, its average increase is by 10 and 18% for pine and beech plywood, respectively (Tables 2 and 3). Thus it may be assumed that H_2O_2 on the one hand accelerates polycondensation processes of PF resin, both in the pure form and that modified with alkylresorcinols, while on the other hand it promotes its copolymerization with functional groups of cellulose or lignin in wood. As a consequence this leads to increased chemical adhesion of resin to veneers and thanks to bigger rigidity of the formed bond an increase in bending strength is recorded. Such an interpretation is supported by the results of studies by Czarnecki and Łęcka [2001, 2003]. Those authors showed that the presence of H_2O_2 causes an acceleration of PF resin cross-linking and an increase in its reactivity towards cellulose, probably thanks to the formation of carboxyl units in the resin, followed by the formation of ester bonds in the resin-cellulose system.

These assumptions are also confirmed by the results of testing properties of plywood manufactured at pressing time shortened by 25%. These analyses showed that bending strength of beech plywood manufacture under such conditions, irrespective of the testing direction, was higher than strength of the respective control plywood on average by 12 and 17%, respectively, for pure resin modified with H_2O_2 and aRPF (Table 3). A similar trend was also found for pine plywood (Table 2). Moreover, it was shown that an addition of hydrogen peroxide to pure PF resin makes it possible to manufacture plywood at pressing time reduced by 1 min, which strength determined in the shear test after accelerated ageing test for pine plywood was on average by 26%, and for beech plywood by 38% higher than strength of the reference plywood pressed for 4 min (Fig. 1 and 2). In turn, strength of plywood resinated with H_2O_2 – modified aRPF resin generally was at the level of strength for the control plywood resinated with aRPF resin unmodified with H_2O_2. However, it needs to be stressed that strength of plywood manufactured with this resin is on average by 30% higher than strength of plywood resinated with pure PF resin modified with H_2O_2. Such fluctuations in testing results for plywood manufactured at a shortened pressing time results probably from the fact that H_2O_2 to such an extent increases reactivity of resin that it facilitates an appropriate course of its cross-linking, resulting in the manufacture of plywood with good properties, even at pressing time shortened by 25%.

CONCLUSIONS

1. The application of PF resin modified with alkylresorcinols makes it possible to manufacture plywood with better properties, especially bond quality, than plywood resinated with pure PF resin.
2. In turn, the introduction of H_2O_2 both to pure PF resin and that modified with alkylresorcinols, improves properties of plywood, as a consequence of increased reactivity of resin and its enhanced chemical adhesion to wood.
3. With the applied PF resin modification methods it is possible to manufacture plywood with very good properties at pressing time shortened by 25%.

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WPŁYW MODYFIKACJI ŻYWICY FENOLOWEJ ALKILOREZORCYNAMI ORAZ H_2O_2 NA WŁAŚCIWOŚCI SKLEJEK

Streszczenie. W pracy zbadano wpływ modyfikacji żywicy fenolowej alkilorezorcynami oraz H_2O_2 na właściwości sklejek iglastych oraz liściastych zaklejanych zmodyfikowanymi żywicami PF. Przeprowadzone badania wykazały, iż zastosowanie modyfikowanej alkilorezorcynami żywicy PF umożliwia wytworzenie sklejek o lepszych właściwościach, zwłaszcza jakości sklejenia, niż sklejka kontrolna prasowana w tych samych warunkach. Natomiast wprowadzenie H_2O_2 zarówno do czystej żywicy PF, jak i modyfikowanej alkilorezorcynami polepsza właściwości sklejek wskutek podwyższenia reaktywności i zwiększenia adhezji chemicznej żywicy do drewna. Zastosowane sposoby modyfikacji żywicy PF umożliwiają ponadto wytworzenie sklejek o bardzo dobrych właściwościach w czasie prasowania skróconym o 25%.

Słowa kluczowe: żywica PF, alkilorezorcyny, H_2O_2, sklejka

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