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PROPERTIES OF PARTICLEBOARDS GLUED WITH PHENOL-FORMALDEHYDE RESIN MODIFIED WITH ESTERS
PART A. THE INFLUENCE OF THE KIND OF ALCOHOL THAT FORMS THE ESTER

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Abstract. The paper investigates the influence of the alkyl substituent in the alcohol group of esters of organic acids upon their effectiveness as modifiers of phenolic resin used in the production of particleboards. In the course of the research esters of ethyl, butyl and amyl alcohol were used. The modification of the phenolic resin with the applied esters results in the shortening of gel time and decrease in the activation energy of the resin. It also improves the physical and mechanical properties of particleboards. The improvement of the studied properties of particleboards is observed as the length of carbon chain of alcohol substituent and the amount of the introduced ester grow. Best results were obtained for amyl acetate used as a modifier.

Key words: PF resin, particleboard, ester

INTRODUCTION

Particleboards glued with phenol-formaldehyde resins are characterized by good mechanical properties and high water-resistance. However, the cost of their production is relatively high due to the long pressing time and high temperature required in the curing process. Therefore, researchers aim at improving the technological and economical aspects of the process of manufacturing particleboards glued with PF resins, mainly by means of increasing the reactivity of the resins.

Studies made so far show that the reactivity of phenolic resins of the resol type can be increased through the addition of various agents, such as e.g. esters of organic acids (methyl ester of γ-ketone capronic acid, methyl formate, glyceryl triacetate, phenyl acetate, methyl salicylate, methyl butyrate) [Kobel and Smith 1973, Fidelus 1983, Pizzi

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and Stephanou 1994] and esters of inorganic acids (propylene carbonate, ethyl carbonate) [Fidelus 1983, Stephanou and Pizzi 1993, Tohmura and Higuchi 1995]. The research carried out in this domain proves the addition of some of the esters to the resins makes it possible to decrease the temperature or shorten the time of pressing, or improve the parameters of the boards in the pressing parameters used so far. Another advantage of some of the esters is their relatively low price.

The aim of the present work is to investigate the influence of the alkyl substituent in the alcohol group of esters of carboxylic acids introduced into PF resin upon the reactivity of thus modified resin and the properties of particleboards produced with its use.

MATERIAL AND METHODS

For the study purposes, PF resin applied to the production of particleboards of increased water-resistance was used. The resin is characterized by the following:
– dry mass 45.2%
– density 1.112 g·cm^{-3}
– free phenol content 0.02%
– free formaldehyde content 0.026%
– viscosity by Ford no. 4/20°C 106 s
– gel time at 130°C 146 s
– pH 12.52

The amounts of ethyl acetate, butyl acetate and amyl acetate added to the resin were from 0.01 to 0.15 mole per 100 g of dry resin solids.

The properties of the modified resin were determined by the measurements of gel time at 120-150°C, viscosity and stability at 20°C.

On the basis of the measurements of gel times within the range temperatures 120--150°C the activation energy was calculated by using the Arrhenius equation.

Single-layer particleboards with the dimensions of 600 × 500 × 12 mm and density of 700 kg·m^{-3}were produced from pine particles with use of the modified resin. The boards were pressed in a semi-automatic press manufactured by "Simpelkamp" with the heating panels having the dimension of 1000 × 800 mm. The following pressing parameters were applied:
– resination 8%
– temperature 180^{o}C
– pressure 2.5 MPa
– time 5.0 minutes.

Thus produced boards were subjected to the following tests:
– swelling in thickness after 24 h according to EN 317,
– water resistance (V 100 test) according to EN 1087-1,
– internal bond (IB) according to EN 319,
– modulus of rupture (MOR) according to EN 310,
– modulus of elasticity (MOE) according to EN 310.

DISCUSSION OF RESULTS

Table 1 shows the results of investigations on the gel time at 130°C of the resin modified with esters. The data included in it prove that even a slight amount of the modifier considerably shortens the gel time of the resin and this effect intensifies as the amount of the added ester grows. Adding 0.01 mole of the ester results in shortening the gel time by 21 to 24%, and 0.15 mole of the ester reduces the time by 38 to 41%. Moreover, it has been found out that the kind of ester introduced to the resin does not affect the gel time of the resin at 130°C.

Table 1. Influence of the modification of phenolic resin upon the gel time at 130°C
Tabela 1. Wpływ modyfikacji żywicy fenolowej na czas żelowania w temperaturze 130°C

Amount of additive, mole/100 g d.m.r. Ilość dodatku, mol/100 g s.m.ż.	Kind of ester Rodzaj estru		
	ethyl acetate octan etylu	butyl acetate octan butylu	amyl acetate octan pentylu
	gel time, s czas żelowania, s		
0.000		165	
0.010	130	126	127
0.025	123	124	126
0.050	120	123	123
0.100	102	111	109
0.150	91	97	103

As expected, the addition of esters into the phenolic resin results in a decrease in the dynamic viscosity of the resin (Table 2). Investigations show that the decrease in the viscosity intensifies as the amount of the added modifier grows. The lowest values of viscosity were obtained by the resins modified with ethyl acetate.

Table 3 shows the influence of the kind and amount of esters added to fluid PF resin upon its pot life at 20°C. The data included in it prove that PF resin modified with ethyl acetate is the least stable; the pot life of this solution decreases rapidly as the amount of introduced ester increases. The addition of ethyl acetate in the amount of 0.15 mole/100 g of dry resin solids after four hours makes the viscosity increase six times, and after 12 hours the viscosity reaches 1632% of its initial value.

Resin modified with the addition of butyl acetate and amyl acetate behaves in a similar way. However, due to the growth of the length of carbon chain in the alcohol that forms the ester the increase in the viscosity of the modified resin decelerates significantly. For these modifiers, in the initial eight hours the increase in the viscosity of the resin is slight and the investigated solutions are characterized by such a degree of viscosity that makes it possible to use them in the production of particleboards. This kind of behaviour can be explained by the fact that in the alkaline environment of PF resin, esters undergo the irreversible reaction of alcohol and acid hydrolysis [Tohmura and Higuchi 1995, Higuchi et al. 1994], here, esters made of low-molecular weight alcohol

Table 2. The influence of modifying the phenolic resin with esters of organic acids upon its dynamic viscosity
Tabela 2. Wpływ modyfikacji żywicy fenolowej estrami kwasów organicznych na lepkość dynamiczną

Amount of additive, mole/100 g d.m.r. Ilość dodatku mol/100 g s.m.ż.	Kind of ester Rodzaj estru		
	ethyl acetate octan etylu	butyl acetate octan butylu	amyl acetate octan pentylu
	dynamic viscosity, mPa·s lepkość dynamiczna, mPa·s		
0.000	530		
0.010	530	525	525
0.025	500	515	520
0.050	450	475	490
0.100	415	465	470
0.150	360	425	430

Table 3. Increase in the dynamic viscosity in the relation to initial viscosity of the investigated resins
Tabela 3. Przyrost lepkości dynamicznej w stosunku do lepkości początkowej mieszanin klejowych

Kind of ester Rodzaj modyfikatora	Amount, mole/100 g d.m.r. Ilość mol/100 g s.m.ż.	Measurement times, h Pomiar po upływie czasu, h					
		4	8	12	24	48	72
		increase in dynamic viscosity, % przyrost lepkości dynamicznej, %					
–	0.0	0	0	0	1	1	1
Ethyl acetate Octan etylu	0.01	42	54	65	70	196	331
	0.05	102	229	327	429	982	1258
	0.10	597	1197	1532	–	–	–
Butyl acetate Octan butylu	0.01	3	5	10	20	54	86
	0.05	14	24	37	59	107	188
	0.15	35	62	75	130	1160	–
Amyl acetate Octan pentylu	0.01	1	4	6	13	37	59
	0.05	7	12	19	41	81	160
	0.15	24	47	51	78	199	606

are most prone to this reaction. That is probably why, the most rapid growth of the viscosity in time is observed in case of PF resin modified with ethyl acetate and the smallest increase in case of modification of amyl acetate; in both cases the acid radical remained constant (CH_3COO^-). Therefore, it can be assumed that the reactivity of PF resin at 20°C is directly proportional to the rate of hydrolysis of the added esters.

The influence of the kind and amount of ester upon the gel time in the temperature range from 120°C to 150°C is shown in Table 4. The data included in the table prove that the greatest shortening of the gel time, due to the addition of esters into the resin, is observed in the lower temperature range and the effect intensifies as the amount of the introduced ester grows. However, no evidence was found of the influence of the kind of ester upon the gel times in particular temperatures with the same amounts of modifiers.

Table 4. Influence of modification of PF resin with esters of organic acids upon the gel time in temperatures from 120°C to 150°C
Tabela 4. Wpływ modyfikacji żywicy PF estrami kwasów organicznych na czas żelowania w temperaturze 120-150°C

Kind of ester Rodzaj estru	Amount, mole/100 g d.m.r. Ilość mol/100 g s.m.ż.	Temperature, °C Temperatura, °C			
		120	130	140	150
		gel time, s^{-1} czas żelowania, s^{-1}			
0	0	0.0025	0.0044	0.0071	0.0111
Ethyl acetate Octan etylu	0.025	0.0030	0.0051	0.0074	0.0110
Butyl acetate Octan butylu		0.0030	0.0051	0.0074	0.0110
Amyl acetate Octan pentylu		0.0030	0.0050	0.0072	0.0109
Ethyl acetate Octan etylu	0.050	0.0032	0.0055	0.0081	0.0114
Butyl acetate Octan butylu		0.0032	0.0054	0.0079	0.0111
Amyl acetate Octan pentylu		0.0031	0.0053	0.0078	0.0110
Ethyl acetate Octan etylu	0.100	0.0035	0.0060	0.0086	0.0118
Butyl acetate Octan butylu		0.0034	0.0058	0.0084	0.0116
Amyl acetate Octan pentylu		0.0033	0.0055	0.0081	0.0112
Ethyl acetate Octan etylu	0.150	0.0036	0.0064	0.0100	0.0128
Butyl acetate Octan butylu		0.0036	0.0061	0.0095	0.0128
Amyl acetate Octan pentylu		0.0036	0.0063	0.0097	0.0125

Based on the measurements of the gel times in the temperature range from 120°C to 150°C, the activation energy of the curing process was calculated with use of Arrhenius equation. The results of these studies are shown in Figure 1.

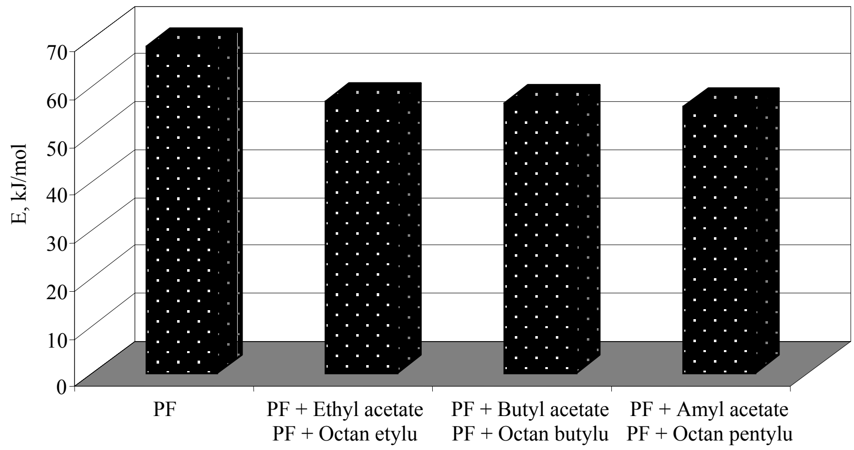

Fig. 1. Influence of the modification of PF resin with esters of organic acids added in amount of 0.1 mole/100 g of dry resin solids upon the activation energy of the curing process
Rys. 1. Wpływ modyfikacji żywicy PF estrami kwasów organicznych dodawanych w ilości 0,1 mol/100 g s.m.ż. na energię aktywacji procesu żelowania

The data illustrated in the figure show that despite considerable differences in the gel times of pure PF resin and resin modified with esters (Table 4), the investigated esters only slightly (by 20%) decreased the activation energy of the curing process.

Table 5 shows the results of studies upon the properties of particleboards produced with use of PF resin modifies with various amounts of esters. The data presented in the table show that the kind and amount of ester added to the resin do not significantly affect swelling in thickness after 24 hours of soaking in water. The obtained results are similar to those obtained for the control board. Only the addition of amyl acetate in the amount of 0.10 mole resulted in slightly greater decrease in swelling by approx. 15%. However, water-resistance of particleboards glued with modified PF resin, measured by internal bond after a boil test, considerably increases in comparison with board glued with non-modified resin (Table 5, Fig. 2), and it is clearly related to the amount of the introduced ester. The highest level of water-resistance is achieved for boards in which the amount of the added ester was 0.1 mole/100 g of dry resin solids. With this amount of ester, in relation to the control board, the value of IB increased by 0.17 MPa, 0.27 MPa and 0.35 MPa for, respectively, ethyl acetate, butyl acetate and amyl acetate (Table 5); for amyl acetate this result means a decrease by as much as 97% (Fig. 2). Further rise in the amount of the added modifier does not lead to the increase in water-resistance. Such a great increase in the internal bond after a boil test is also observed by Zhao et al. [1999]. These authors show that water-resistance of boards glued with PF resin modified with glyceryl triacetate in the amount of 7.5% increases by as much as 0.46 MPa (over 400%) in relation to the control board. Further more, the data included

Table 5. Properties of particleboards depending upon the kind and amount of the ester added to PF resin
Tabela 5. Właściwości płyt wiórowych w zależności od rodzaju i ilości dodanego estru do żywicy PF

Kind of addition Rodzaj dodatku	Amount, mole/100 g d.m.r. Ilość, mol/100 g s.m.ż.	Swelling Spęcznienie 24 h, %	Internal bond Wytrzymałość na rozciąganie prostopadłe do płaszczyzn płyty	Moisture resistance after V-100 Wytrzymałość po próbie gotowania	Bending strength Wytrzymałość na zginanie	Modulus of elasticity at bending Moduł sprężystości
			MPa			
0*	0	29.5	0.91	0.36	16.3	1 840
Ethyl acetate Octan etylu	0.01	31.8	0.91	0.39	18.9	2 510
	0.025	32.2	0.92	0.44	19.0	2 600
	0.05	31.6	0.90	0.49	20.6	2 740
	0.01	30.6	0.88	0.53	18.8	2 490
	0.15	30.8	0.85	0.40	17.0	2 060
Butyl acetate Octan butylu	0.01	28.7	0.97	0.61	19.5	2 510
	0.025	28.0	1.08	0.63	20.6	2 780
	0.05	30.0	1.05	0.63	23.0	3 220
	0.10	29.2	1.04	0.63	20.1	2 710
	0.15	28.3	1.06	0.60	18.1	2 440
Amyl acetate Octan pentylu	0.01	29.1	1.03	0.60	20.0	2 620
	0.025	28.4	1.07	0.66	21.3	2 860
	0.05	27.6	1.14	0.68	23.6	3 220
	0.10	25.4	1.16	0.71	21.9	3 040
	0.15	25.6	1.23	0.62	18.5	2 500

*Control board.
*Płyta kontrolna.

in Table 5 show that along with the growing amount of esters added to the resin, mechanical properties of the boards, such as modulus of rupture, modulus of elasticity at bending and internal bond improve considerably.

The influence of the kind and amount of ester upon modulus of rupture is illustrated in Figure 3. The presented data prove that even slight amount of esters, i.e. 0.01 mole, increases the value of MOR by approx. 20%. However, the highest values were obtained for the amount of 0.05 mole. In this case the average value of MOR was 37% greater. Although further growth in the amount of ester results in a decrease in MOR, the absolute values are still higher than in terms of control board. The greatest value of MOR is observed for boards glued with PF resin modified with amyl acetate added in the amount of 0.05 mole/100 g of dry resin solids; the value was 47% higher than that of the control board.

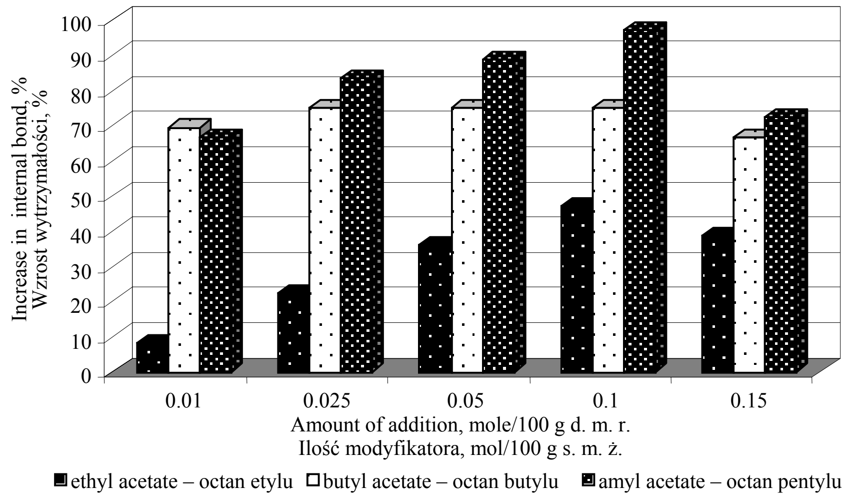

Fig. 2. Percentage increase in water-resistance of particleboards glued with PF resin modified with esters determined by boil test
Rys. 2. Procentowy wzrost wodoodporności określanej próbą gotowania płyt wiórowych zaklejanych żywicą PF modyfikowaną estrami

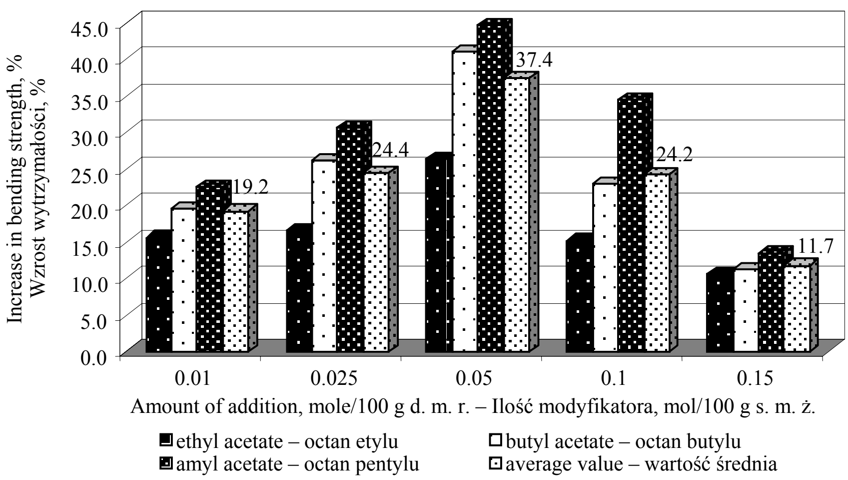

Fig. 3. Percentage increase in modulus of rupture of particleboards glued with PF resin modified with esters
Rys. 3. Procentowy wzrost wytrzymałości na zginanie płyt wiórowych zaklejanych żywicą PF modyfikowaną estrami

The analysis of the obtained values of modulus of elasticity at bending (Table 5) leads to the conclusion that their behaviour is quite similar to that of modulus of rupture. The increase in the ester amount from 0.01 to 0.05 mole results in the growth of MOE value from 2500 MPa to over 3200 MPa. Further increase in the amount of the added modifier decreases the discussed value down to 2400 MPa; yet, the value is still higher than that of the control board. The highest values of MOE are achieved by boards glued with resin with the addition of 0.05 mole of butyl acetate and amyl acetate: their values are higher that those of the control boards by 1380 MPa and they amount to 3220 MPa. Data included in Table 5 show also that the addition of amyl acetate to the resin leads to the greatest increase in modulus of elasticity as, in relation to other esters added in the same amount, amyl acetate increases the elasticity from 4% to 24%.

The data presented in Table 5 show that the addition of esters significantly affects the internal bond. Both butyl acetate and amyl acetate lead to the increase in this property, yet, the increase is proportional to the amount of introduced modifier. However, ethyl acetate behaves in a different way: here, the growing amount of the modifier slightly decreases the value of IB. These results correlate closely with the results of investigations on the reactivity of the modified resins (Tables 1 and 2), which prove that PF resin with the addition of ethyl acetate is characterised by the highest reactivity. Taking into account the presence of wood in the polycondensation process [Troughton 1969] presumably, in case of resin modified with ethyl acetate, the cross-linking process within the resin is accelerated and, therefore, fewer wood-resin bonds are formed, and that results in the observed decrease in the internal bond of particleboards.

CONCLUSIONS

The research results confirm it is possible to improve the properties of particleboards of increased water-resistance produced with use of PF resin modified with esters of organic acids. It has been found out that the quality of produced boards is affected not only by the amount of the ester introduced into the resin, but also by the kind of alkyl substituent in the ester group. Particleboards of the best physical and mechanical properties were obtained by means of adding esters of acetic acid in the amount of 0.05-0.10 mole/100 g of dry resin solids. The increase in the length of alkyl chain in the alcohol group of the ester, while the mole fraction of ester in the resin remains unchanged, resulted in the improvement of properties of the produced boards, especially the water-resistance determined in a boil test. It should be emphasised that the addition of amyl acetate into the resin in the amount of 0.10 mole increases the water-resistance determined by boil test by as much as 97%.

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WŁAŚCIWOŚCI PŁYT WIÓROWYCH ZAKLEJANYCH ŻYWICĄ FENOLOWO-FORMALDEHYDOWĄ MODYFIKOWANĄ ESTRAMI CZĘŚĆ A. WPŁYW RODZAJU ALKOHOLU TWORZĄCEGO ESTER

Streszczenie. Zbadano wpływ podstawnika alkilowego w grupie alkoholowej estru kwasu organicznego na jego skuteczność jako modyfikatora żywicy fenolowej stosowanej do wytwarzania płyt wiórowych. Badaniom poddano estry takich alkoholi, jak etylowy, butylowy i pentylowy. Stwierdzono, iż modyfikacja żywicy fenolowej stosowanymi estrami powoduje skrócenie czasu żelowania żywicy oraz obniżenie energii aktywacji. Wpływa także na polepszenie fizycznych i mechanicznych właściwości płyt wiórowych. Poprawa badanych właściwości płyt wiórowych następuje zarówno w miarę wzrostu długości łańcucha węglowego podstawnika alkoholowego, jak i ilości wprowadzonego do żywicy fenolowej estru, przy czym najlepsze efekty można uzyskać stosując jako modyfikator octan pentylu.

Słowa kluczowe: żywica PF, płyta wiórowa, estry

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