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Properties of PF resin with an addition of pigmenting agents used in the manufacture of water-resistant plywoods with a light colour glue line

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Abstract: *Properties of PF resin with an addition of pigmenting agents used in the manufacture of water-resistant plywoods with a light colour glue line.* This study presents results of testing for properties of adhesive mixtures used in the manufacture of water-resistant plywoods with a lightened colour of glue line from PF resin. Adhesive mixtures were prepared by the introduction to the PF resiny of titanium dioxide, white mineral fillers mineral, i.e. chalk or barite, as well as an addition of an additive in the form of nanoparticles of synthetic silica in amounts determined on the basis of preliminary and colouristic tests. In this study the following parameters were determined: reactivity of tested adhesive mixtures, their viscosity and pot life, as well as adhesion to wood. On the basis of conducted studies it was also shown that the introduction of these agents to PF resin does not have a significant effect on the reactivity of prepared adhesive mixtures, while significant changes were recorded for viscosity in time; however, this does not limit their suitability for the resination of veneers. Applied colouring agents slightly deteriorate adhesion of glue solutions to wood.

Keywords: plywoods, colour of glue line, titanium dioxide, chalk, barium

INTRODUCTION

Studies conducted by Dukarska et al. (Dukarska and Łęcka 2009, Dukarska et al. 2010, 2011) showed the possibility to manufacture water-resistant plywood resinated with PF resin with a light colouring of glue line. This effect was obtained thanks to the introduction of a white pigment to adhesive resin in the form of titanium dioxide, at present the pigment used most frequently in plastics processing, in the production of chemicals for the construction industry, etc. In view of the high price of TiO_2 and the fact that the application of white mineral fillers together with this pigment makes it possible to reduce the content of TiO_2 in coloured mass, and thus reduce colouring costs, within this study the applicability of a natural calcium carbonate (chalk, $CaCO_3$) and barium sulfate (barite, $BaSO_4$) was also determined. In order to stabilise the *PF resin–pigment* system in the resin solution additionally hydrophilic flame silica was used, serving the role of an additive preventing sedimentation of pigment particle and regulating rheological properties of prepared adhesive mixtures. When selecting these compounds their availability, prices, optical properties, chemical and toxicological immobility, resistance to high temperature and dispersability were taken into consideration. Within the framework of this study, using colorimetric methods, the effect of an addition of these compounds was determined on the lightening of the colour of polycondensed adhesive mixtures as well as water resistance and mechanical properties of manufactured plywoods. It was found that an optimal amount of TiO_2 required for the lightening of colour of the glue line in manufactured plywoods is at least 4.0 parts by weight/100 parts PF resin, while the rate of TiO_2 substitution in the adhesive mass with a chalk filler is 50%, whereas for barite it is 25%. At such established formulations of adhesive mixtures it was possible to manufacture plywoods with properties required for quality grade 3 resination appropriate for plywoods used outdoors, a light colour of the glue line and at the same time lower costs of raw materials. In the course of resination of veneer sheets it was also observed that prepared adhesive mixtures containing titanium dioxide and inorganic fillers exhibited a high degree of

homogeneity, stability in time and markedly better flow properties than the mixture containing a commercial filler.
This study presents results of basic research concerning properties of adhesive mixtures used in the manufacture of water-resistant plywoods with a lighter colour of the glue line from PF resin. Thus the effect of titanium dioxide and its substitutes as well as nanosilica added to PF resin on its reactivity, pot life and adhesion to wood.

MATERIALS AND METHODS

Analyses were conducted applying as a binding agent phenol-formaldehyde resin (PF) used in the production of water-resistant plywood with the following characteristics:

- the content of free formaldehyde 0.17%
- the content of free phenol 0.23%
- the content of dry matter 46.9%
- density 1.218 g/m^3
- pH 9.7
- Ford cup no. 4/20ºC 155 s
- dynamic viscosity 1248 mPas
- gel time at 130ºC 235 s

A detailed characteristic of pigment and fillers was presented in earlier papers (Dukarska and Łęcka 2009, Dukarska et al. 2010, 2011).
Based on the performed preliminary analyses optimal amounts were selected for TiO_2 and fillers contained in adhesive mixtures. The reference mixture comprised a mixture prepared according to the commercial formulation, containing a mimosa filler (UT-10), used in industry in the manufacture of water-resistant plywoods. Thus, in the resination process of birch veneer sheets adhesive mixtures with the following formulations were applied (table 1):

Table 1. Formulations of adhesive mixtures used in the study

Lp.	Amount [parts by weight/100 parts PF resin]				
	UT-10	SiO_2	TiO_2	$CaCO_3$	$BaSO_4$
1	14	-	-	-	-
2	-	1.0	-	-	-
3			4.0	-	-
4			3.0	-	1.0
5			2.0	2.0	-

Due to the fact that colouring of liquid systems consists in the preparation of a concentrate containing all solid components and next dilution of its remaining amount with resin until a final concentration was reached, preparation of adhesive mixtures was performed in stages. In the first stage a small amount of the concentrate was prepared, containing approx. 20% total resin weight and all the other components in accordance with Table 1. Such prepared concentrate was diluted with the remaining amount of PF resin and it was homogenised until a homogeneous consistency was obtained using a high velocity homogenator with fluid rotation regulation.

Such prepared adhesive mixtures were tested in terms of the following properties:

- pot life at a temperature of 20ºC measuring changes in their viscosity immediately after preparation and after 1, 2, 3, 4 and 24 h
- reactivity, determining their:
    - gel times at 130ºC
    - activation energy of the curing process based on DSC analyses according to Kissinger and Ozawa

- changes in the weight of a sample heated under polythermal conditions – thermogravimetric analysis (TG), in open platinum crucibles, in the atmosphere of helium at a flow rate of 2 dm^3/h and heating rate of 3ºC/min within the range of 20 - 200ºC and 5ºC/min within the range of >200 - 650ºC
- adhesion to wood by the wetting method measuring the wetting angle and on this basis determining free surface energy together with its polar and dispersion components, surface tension at the interface and adhesion work of the wood-adhesive system together with its polar and dispersion components.

RESULTS AND DISCUSSION

Table 2 presents results of tests on pot life of adhesive mixtures prepared for resination of veneers, determined on the basis of observations of adhesive mixtures and measurements of changes in their viscosity in time at a temperature of 20ºC. Contained data show that the introduction of nanosilica particles to PF resin at an amount of 1.0 parts by weight/100 parts of PF resin made it possible to obtain viscosity comparable to that of the reference mixture, i.e. mixture containing a commercial filler. In turn, it was found that these mixtures are characterised by a different dynamic of changes in viscosity in time. The reference mixture did not show significant changes in viscosity up to 4 h, while the resin with an addition of SiO_2 was characterised by a gradual increase in viscosity as early as directly after the preparation of the mixture. The greatest increase in viscosity - within the range of 10 -20% - was recorded as early as after 1 h. It results from the thixotropic action of silica on the mixture, which means that after it the end of homogenization, in the course of which it was subjected to shear forces, a gradual increase in viscosity occurred. Still, after a state of equilibrium was reached the adhesive resin with an addition of silica in amounts adopted in this study, i.e. 1.0 parts by weight /100 parts PF resin, even at 24 h after its preparation it exhibited lower viscosity than the reference mixture.

On their basis results of measured changes of viscosity in time depending on TiO_2 substitution with mineral fillers, a 50% share of chalk in the colouring process of PF resin results in an increase in viscosity by approx. 20%. Due to the fact that in adhesive mixtures silica is present, an increase in viscosity was observed to be 15 - 26% as early as after 1 h. Viscosity reached after 24 h is by 60% higher than that of the reference mixture and by 80% in relation to the mixture containing only TiO_2 or SiO_2. In turn, results of viscosity measurements were different in case of the introduction of barite to the adhesive mixture, for which viscosity of the mixture is by 45% higher than that of the mixture containing only TiO_2. It is of significance that despite a higher viscosity recorded after 24 h, these mixtures still proved to be suitable in the resination of veneer sheets.

Results of studies on the effect of titanium dioxide and inorganic fillers on gel time of phenolic resin at a temperature of 130°C and values of activation energy of curing for PF resin and its mixture with an addition of TiO_2, SiO_2 and fillers are presented in Table 3. On their basis it was found that the substitution of a mimosa filler containing considerable amounts of tannin catalysing polycondensation of PF resin with inorganic fillers, chemically inactive in relation to its components, did not have a significant effect on reactivity of prepared adhesive mixtures. Introduction of titanium dioxide and barite to the adhesive resin solution resulted in a slight – max. 10% - elongation of gel time in relation to the mixture containing a commercial filler (UT-10). In turn, substitution of TiO_2 with chalk and barite made it possible to obtain gel times comparable to those of the reference mixture. A shortening of gel time in adhesive mixtures in relation to pure PF resin under the influence of the presence of such chemically inactive fillers may be explained by the fact that their parts initiate overheating of the resin solution in the entire volume of the tested sample and thus

Table 2. Time changes of viscosity in adhesive mixtures mixtures depending on their formulations

Composition of adhesive mixture	Viscosity [mPas]				
	0h	1h	2h	3h	24h
PF + UT-10	2479	2490	2477	2594	3972
PF + SiO_2	2390	2775	2989	3058	3354
PF + SiO_2 + TiO_2	2524	2824	3150	3212	3592
PF + SiO_2 + TiO_2/$CaCO_3$	2960	3676	3912	4200	6432
PF + SiO_2 + TiO_2/$BaSO_4$	3684	3840	3936	4088	4307

Table 3. Gel times and activation energy of adhesive mixtures made from PF resin depending on their composition

Composition of adhesive mixture	Gel time [s]	E_a [kJ/mol]			
		Kissinger		Ozawa	
PF	235	62.74	*1.00**	66.37	*1.00**
PF + UT-10	159	54.53	*0.97*	58.44	*0.98*
PF + SiO_2	165	59.05	*1.00*	62.83	*1.00*
PF + SiO_2 + TiO_2	168	63.19	*0.96*	66.77	*0.97*
PF + SiO_2 + TiO_2/$CaCO_3$	157	55.97	*0.96*	59.80	*0.97*
PF + SiO_2 + TiO_2/$BaSO_4$	159	51.03	*0. 96*	54.89	*0.97*

*-correlation coefficient

result in faster evaporation of water and volatile substances. This confirms the TG analysis presented in Figs. 1 and 2.

Values of activation energy estimated according to Kissinger and Ozawa for adhesive mixtures made from PF resin depending on their composition did not show significant changes in comparison to that of the reference mixture. Activation energy of adhesive mixtures containing TiO_2 and SiO_2 is slightly higher than the value for the reference mixture. In turn, the introduction of mineral fillers to the solution of adhesive mixtures as a substitute of TiO_2 made it possible to reduce the value pf activation energy to the level comparable to that of the mixture containing a commercial filler.

The thermogravimetric analysis of analysed adhesive mixtures made from PF resin containing a pigment and fillers was performed in order to explain the shortening of their gel times at a temperature of 130°C and thus an advantageous effect on the values of activation energy for polycondensation of PF resin. Thermograms of adhesive mixtures containing titanium dioxide, synthetic silica and mineral fillers are presented in Figs. 1 and 2. Conducted thermogravimetric analysis showed that, irrespective of the composition of tested adhesive mixtures, recorded maximum losses of weight ranged from 60 to 63%. In the range ascribed to the curing process of PF resin, i.e. 139 - 151°C changes in weight remained at 30 - 45%. In turn it results from the thermograms that tested adhesive mixtures show a different dynamics of changes in weight in the range of lower temperatures connected with the removal of water, i.e. at 30 - 100°C. Thermograms of PF resin with an addition of TiO_2 and SiO_2 show a 20% weight loss at a temperature by approx. 25ºC lower (at 70ºC) than pure PF resin and with an addition of mimosa filler (at 95°C). Introduction of chalk to the adhesive mixture does not cause significant changes in the TG curve, while in case of barite at over 100ºC a markedly greater loss of weight was recorded in relation to the tested adhesive mixtures.

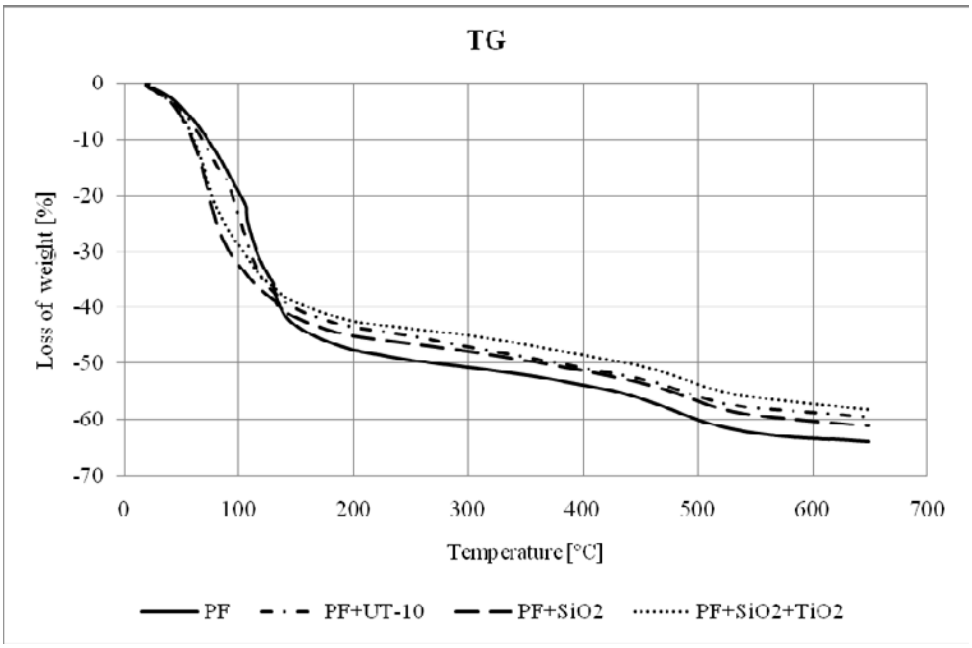

Fig. 1. TG thermograms of adhesive mixtures with an addition of TiO_2 and SiO_2 in relation to PF resin and with no addition of a commercial filler (UT-10)

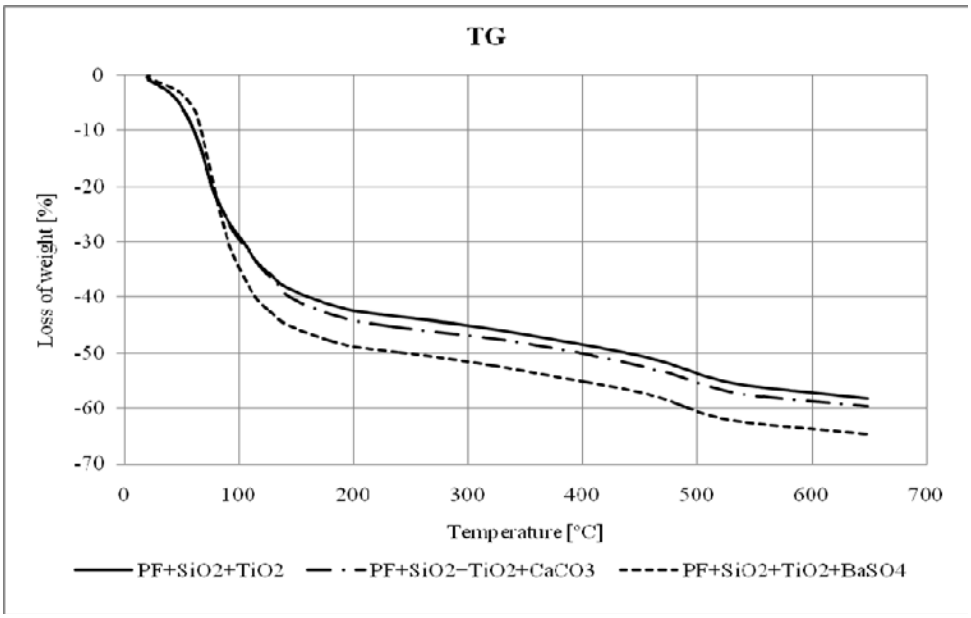

Fig. 2. TG thermograms of adhesive mixtures made from PF resin depending on the type of mineral filler

Table 4 presents values of wetting angle recorded for birch veneer, PF resin and adhesive mixtures prepared with the application of a commercial filler (UT-10) and titanium dioxide and inorganic fillers at assumed amounts. Theoretical values of maximum adhesion work, its polar and dispersion components as well as surface tension at the adhesive-wood interface, and ratios of the dispersion and polar components of free surface energy of contacted materials are presented in Table 5. The *PF resin/veneer* and *PF resin+UT-10/veneer* systems served as reference systems in this section of the study. In view of the applied adhesion criteria the *PF/veneer* system turns out to be most advantageous. Introduction of a tannin filler to PF resin slightly, although perceptibly deteriorates adhesion. Inorganic fillers as well as pigments applied in this study also cause a deterioration of adhesion in relation to the reference system, i.e. *PF resin+UT-10/veneer*. It is also manifested

in an increase in surface tension at the interface and a decrease in adhesion work and a deterioration of the ratio of polar components of surface tension of contacting materials (table 6). The composition of tested adhesive mixtures has a significant effect on these parameters. Relatively slight changes in relation to the reference mixture were recorded in case of the presence of only TiO_2 with SiO_2 in the mixture. In turn, substitution of a part of TiO_2 with such fillers as $CaCO_3$ and $BaSO_4$ markedly deteriorates adhesion. This pertains particularly to $CaCO_3$, for which the rate of substitution of TiO_2 was 50%.

Table 4. Wetting angle of redistilled water for tested surfaces

Material	Arithmetic mean of wetting angle [°]	Standard deviation [°]
Veneer	25.08	4.21
PF	55.32	2.09
PF+UT-10	59.34	3.24
PF+SiO_2	65.20	4.68
PF+SiO_2+TiO_2	65.90	5.14
PF+SiO_2+TiO_2/$CaCO_3$	74.13	5.37
PF+SiO_2+TiO_2/$BaSO_4$	67.90	5.48

Tabela 5.Free surface energy of veneer and tested adhesive mixtures

Material	Free surface energy		
	γ_s	γ_s^d	γ_s^p
	[mJ/m^2]		
Veneer	66.58	25.31	41.27
PF	50.10	31.24	18.86
PF+UT10	47.73	31.53	16.20
PF+SiO_2	43.89	31.63	12.26
PF+SiO_2+TiO_2	39.17	31.07	8.10
PF+SiO_2+TiO_2/$CaCO_3$	42.73	31.56	11.17
PF+SiO_2+TiO_2/$BaSO_4$	46.65	31.60	15.04

Table 6. Parameters determining criteria of adhesion for tested adhesive mixtures to wood

Material	Surface tenstion at interface	Adhesion work			γ_K^d/γ_D^d	γ_K^p/γ_D^p
	γ_{KD}	W_a	W_a^d	W_a^p		
	[mJ/m^2]					
PF	4.64	112.04	56.24	55.80	1.23	0.46
PF+UT-10	6.09	108.21	56.50	51.71	1.25	0.39
PF+SiO_2	8.57	102.31	56.60	45.71	1.25	0.31
PF+SiO_2+TiO_2	8.89	101.58	56.59	44.99	1.25	0.30
PF+SiO_2+TiO_2/$CaCO_3$	13.09	92.66	56.09	36.57	1.23	0.20
PF+SiO_2+TiO_2/$BaSO_4$	9.84	99.46	56.53	42.93	1.25	0.27

CONCLUSIONS

On the basis of conducted analyses it was shown that the introduction, to PF resin solution, of titanium dioxide and its substitutes in the form of chalk and barite as well as nanoparticles of synthetic silica does not cause significant changes in reactivity of prepared adhesive mixtures. Recorded values of gel times and activation energy are comparable or slightly higher than those of the mixture containing a commercial tannin filler. Tested

adhesive mixtures, despite a significant increase in viscosity and considerable dynamics of its changes, particularly under the influence of nanosilica, showed their suitability for the resination at 24 h from the time of their preparation. An addition of titanium dioxide and inorganic fillers applied in this study slightly deteriorates adhesion of adhesive mixtures to wood, although as it results from the conducted tests it does not have a negative effect on resination quality of manufactured experimental plywoods (Dukarska et al. 2010, 2011).

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STRESZCZENIE: *Właściwości żywicy PF z dodatkiem środków pigmentujących stosowanej do wytwarzania sklejek wodoodpornych o jasnym zabarwieniu spoiny klejowej*. W niniejszej pracy przedstawiony wyniki badań właściwości mieszanin klejowych stosowanych do wytwarzania sklejek wodoodpornych o rozjaśnionej barwie spoiny klejowej z żywicy PF. Mieszaniny klejowe zostały sporządzone poprzez wprowadzenie do klejowych żywicy PF ditlenku tytanu, białych wypełniacz mineralnych – kredy bądź barytu oraz środka pomocniczego w postaci nanocząstek syntetycznej krzemionki, w ilościach ustalonych na podstawie badań wstępnych oraz kolorystycznych. W ramach przeprowadzonych badań oznaczono reaktywność badanych mieszanin klejowych, ich lepkość oraz żywotność, a także adhezję do drewna. Na podstawie przeprowadzonych badań wykazano, iż wprowadzenie tych środków do żywicy PF nie wpływa w znaczący sposób na reaktywność przygotowanych mieszanin klejowych, natomiast pod ich następują istotne zmiany lepkości w czasie, co jednak nie ogranicza ich przydatności do procesu klejenia fornirów. Zastosowane środki barwiące pogarszają w nieznacznym stopniu adhezję roztworów klejowych do drewna.

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