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SOME CHARACTERISTICS OF UREA-FORMALDEHYDE POWDER ADHESIVES

Abstract: Urea-formaldehyde (UF) glue resins were the most important type of adhesives in the wood industry last 60 years, especially for the production of wood based panels. More convenient spray dried UF powders went into use last two decades. Small and medium private wood processing plants in Serbia prefer to use such powder adhesives, since they are more convenient for small capacity production. There is no production of UF powder resin in Serbia so, necessary quantities are imported from abroad including producers from Asia. However, their characteristics are variable, dependent on syntheses steps and not well known among users. Objective of this research was to determine conveniences and lacks in application of two imported UF powder resins in comparison to domestic UF emulsion.

Key words: urea-formaldehyde, powder adhesive, characteristics of, application

НЕКЕ КАРАКТЕРИСТИКЕ УРЕА-ФОРМАЛДЕХИДНИХ АДХЕЗИВА У ПРАХУ

Извод: Уреа-формалдехидни (УФ) адхезиви су најважнији адхезиви у дрвној индустрији последљих 60 година, посебно за производњу плоча на бази дрвета. Од пре две декаде ушли су у употребу погоднији уреа-формалдехидни адхезиви у прашкастом стању, произведени распршивањем у вакууму. Мале и средње приватне фабрике за прераду дрвета у Србији радије користе овакве спрашене адхезиве, пошто су погоднији за ниско капацитетну производњу. У Србији се не производе овакви уреа-формалдехидни адхезиви, па се они увозе из иностранства укључујући и азијске произвођаче. Међутим, њихове карактеристике варирају зависно од поступка синтезе и корисници нису добро упознати са

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њима. Циљ овог рада био је одређивање погодности и недостатака примене два увезена прашкаста уреа-формалдехидна адхезива, у поређењу са добро познатом домаћом уреа-формалдехидном емулзијом.

Кључне речи: уреа-формалдехид, прашкасти адхезиви, карактеристике, примена

1. INTRODUCTION

Urea-formaldehyde (UF) glue resins were the most important type of adhesives in the wood industry last 60 years, especially for the production of wood based panels, gluing of furniture elements and veneering (Dunky, 2000). During that period, certain efforts have been undertaken for its improvements like: reduction of gel time and free formaldehyde emission, adhesive bonds fortifying, prolongation of storage life and more convenient transport and application.

At the beginning, water soluble UF adhesives prevailed. Emulsions of UF resin concentrated to 65-69 % of dry matter were prepared within wood industry complexes nearby wood panel factories, or in chemical factories at the distances of few hundred kilometers. Storage life of such emulsions was about 40 days. More convenient, but at the same time, more expensive spray dried UF powders went into use last two decades. Such powders could be redissolved and redispersed in water to different concentrations just before application. Their storage life was prolonged to one year and they could be transported to a longer distances because of absence of water (Dunky, 1997).

Significant changes occurred in Serbia last ten years. The most of the large wood industry combinates do not exist any more and wood based panel production decreased dramatically, together with reduction of high tonnage consumption of domestic UF resin emulsion. On the other side, great number of small and medium capacity private wood processing plants appeared. They prefer more convenient powdered UF resin supplied in small packages with long storage life, which can be prepared in variety of concentrations just before use. Since, there is no production of UF powder resin in Serbia, necessary quantities are imported from abroad including producers from Asia and South America regions.

In this research, standardized laboratory analytical methods were used to determine the conveniences and the lacks in application of two imported UF powder resins in comparison to domestic UF emulsion.

2. EXPERIMENTAL

2.1. Materials

a) The next imported urea-formaldehyde (UF) powder resins were analyzed:

- "UF 2003", appearance-white powder, volatiles at 105°*C* max 3%, bulk density;
- $-500\pm50 \text{ kg} \cdot m^{-3}$, solubility in water completely, storage life in original bags at $20^{\circ}C$ not less than 12 months, country of origin Iran;
- "UF P1001C", appearance white powder, volatiles at $105^{\circ}C$ max 3%, bulk density 700-800 kg·m⁻³, solubility in water completely, storage life in original sealed containers below $25^{\circ}C$ 9-12 months. This UF powder was pre-catalyzed (so called "one-shot" resin) and no catalyst addition was necessary, country of origin Trinidad and Tobago (2004);
- b) The reference domestic resin was:
- ,,UF 600", appearance white water solution, dry matter 67±1%, density 1280-1290 kg·m⁻³, viscosity 100±10 s, storage life one month, country of origin Serbia (PKS Latex) (2002);
- c) Hardener (catalyzer) NH_4Cl ammonium chloride, pro analyze Zorka, Šabac d) filler wheat flour type 400.

2.2. Methods

a) Dissolving of powder resin

Prior to use, powder resin was mixed with distilled water, to convert into solution. This was completed in mechanical low speed stirrer, following producers' directions for use. The homogeneous mix was made by gradual addition of powder into one hall of the total amount of necessary water, at the temperature of $25^{\circ}C$, while the mixer was running. The rest of the water was added later, also under agitation. Once a homogeneous solution has been obtained, other additive and hardener were added to "UF 2003" and to "UF P1001C" (except hardener), while the mixer was running. Dissolving procedure was over after 10 minutes. The powder resins were dissolved completely without clouding or agglomeration within 10 minutes of stirring.

Dilution of liquid UF 600, with distilled water and addition of hardener and additive, was completed in the same low speed mixer.

b) Analytical methods

The analyses of prepared adhesive solutions were conducted according to actual Yugoslav standards: viscosity - JUS.H.K8.022; dry matter and pH value - JUS.H.K8.023; shear strength of adhesive bond - JUS.H.K8.024; gel time - JUS.H.K8.025; density - JUS. H.K8.026.

2.3. Calculation

Aritmetic mean of 3 obtained values from viscosity, pH and dry matter measurements, were calculated.

The accuracies of the viscosity and dry matter measurements were 98% and 99,3% between each two obtained values respectively. The accuracy between two pH measurements was less than 0,1 pH.

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3. RESULTS AND DISCUSSION

Both imported powdered resins were prepared according to producers instructions by dissolving with distilled H_2O having UF: H_2O ratio of 1:0,8 and with catalyst addition to UF 2003 of wt. 2%. UF P1001C already had catalyst incorporated. Catalyst addition to UF 600 was wt. 1% according to Yugoslav standard. Dry matter, viscosity, pH value, gel time and density of prepared adhesives were determined. The results are shown in the table 1. Also, shear strength of glue joint made by those adhesives was determined (table 1).

 Table 1. The characteristics of UF powder adhesives UF P1001C and UF 2003 vs. UF 600 domestic emulsion

Табела 1. Карактеристике увозних прашкастих UF адхезива у односу на домаћу UF 600 емулзију

Nº	Ргорегtу Својство	Unit	Yugoslav	Value Вредност			
		лед. мере	JUS	UF 600	UF P1001C	UF 2003	
1	Dry matter Садржај суве супстанце	%	JUS H.K8.023	67,1	47,7	53,4	
2	Viscosity Вискозитет по Форду F420C	S	JUS H.K8.022	120,0	77,0	109,0	
3	pH value pH вредност	/	JUS H.K8.023	6,2	6,5	6,5	
4	Gel time Време желирања	S	JUS H.K8.025	55,0	59,0	37,0	
5	Density Густина	$g \cdot cm^{-3}$	JUS H.K8.026	1,290	1,190	1,240	
6	Shear strength of glue joint Смицајна чврстоћа лепљене везе	МРа	JUS H.K8.024	2,5	2,7	2,3	

Obtained values of shear strength showed that all three adhesives prepared according to producer instructions fulfilled requirements of Yugoslav standard (min. 2 *MPa*). Delaminating of test samples occurred more than 60% by wood surface. Although, all three adhesives met standard requirements, the best glue joint was obtained with UF P1001C, then with UF 600 and the weakest glue joint was obtained with UF 2003. This is particularly important having in mind differences of dry matter between adhesives.

However, gel time of UF2003 powder adhesive was very short (table 1). Hence, it was interesting to investigate relation of gel time versus pot life of those adhesives, particularly of UF 2003 adhesive, and to enlighten convenience of their application. For this purpose, series of adhesive formulations for veneering and plywood production, with the wheat flour as filler and with different contents of catalyst was prepared (table 2). Beside formulations of UF 600 and UF P1001C adhesives, five different formulations of UF 2003 adhesive were prepared.

	UF 600	UF P1001C	UF 2003	UF 2003	UF 2003	UF 2003	UF 2003		
Component	formulation / рецептура								
компонента	1	1	1	2	3	4	5		
	parts by weight / масени делови								
UF adhesive UF адхезив	30,0	30,0	30,0	30,0	30,0	30,0	30,0		
Wheat flour filler Пшенично брашно као пунилац	8,0	8,0	8,0	8,0	8,0	8,0	8,0		
Catalyst Катализатор (NH ₄ Cl)	0,3	/	0,85	0,30	0,15	0,06	0,03		
Water Вода	20,0	20,0	20,0	20,0	20,0	20,0	20,0		

 Table 2. Formulations of UF 600, UF P1001C and UF 2003 adhesives with filler

 Табела 2. Рецептуре UF 600, UFP1001C и UF2003 адхезива са пуниоцем

The properties of prepared adhesive formulations (shown in table 2), are presented in table 3.

Dry matter and viscosity of prepared formulations were similar (table 3), while content of catalyst and consequently gel time and pot life were different (table 2 and 3). The content of catalyst changes the gel time and to less degree the pot life. This depends of synthesis steps during resin production and of resin buffering (know-how).

Pot life (working time) is the time period from the moment when adhesive is readyto-use (that is with all additives mixed in), to the moment when adhesive cannot be spread and applied to the wood surface, because of its further policondensation and curing i.e. when adhesive is not liquid more (Myers, 1981). Pot life is measured at room temperature of $20^{\circ}C$.

Gel time is the necessary time for adhesive curing at elevated temperature in the hot press (test at $100^{\circ}C$).

Naturally, gel time must be short for the sake of the press capacity, while pot life must be long enough to enable completing of different operations with adhesive before pressing and to enable use of all prepared quantities of adhesive. The longer pot life, the larger quantities of ready-to-use adhesive could be prepared. Gel time of 50-60 seconds (to prevent overcuring) and pot life of min. 2 hours are recommended.

From the table 3 (formulations 1) it might be espied that UF 600 and UF P1001C met this recommendation, while UF 2003 (formulations 2-5) did not meet. Recommended

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values for gel time and pot life of UF 2003 were not achievable by changing of catalyst quantity from 0.1 wt. % even to 2.8 wt. % (dry NH_4Cl/UF dry matter) (table 3 and fig.1). With this adhesive, acceptable gel time assumed too short pot life. On contrary, acceptable pot life assumed too long gel time. This might be consequence of no adequate buffering procedure or syntheses steps during production of this adhesive (Raveendran *et al.*, 1983). Probably, it was the main reason why producer of this resin recommended separate adjusting of pot life by addition of retarder like ammonia or hexamine. Such adjusting was not necessary for UF 600 and UF P1001C adhesive. Impossibility of simultaneous adjusting of gel time and pot life only by catalyst addition, rise difficulties to the user of UF 2003 resin.

Unit Јед. мере	Yugoslav standard JUS	Value / Вредност							
		UF 600	UF P1001C	UF 2003	UF 2003	UF 2003	UF 2003	UF 2003	
		formulation / рецептура							
		1	1	1	2	3	4	5	
%	JUS H.K8.023	56,2	52,2	51,2	51,6	52,0	51,7	52,4	
S	JUS H.K8.022	232,0	223,0	240,0	210,0	225,0	240,0	240,0	
S	JUS H.K8.025	60,0	57,0	45,0	50,0	55,0	80,0	200,0*	
h	JUS H.K8.026	2,0	3,0	0,5	1,0	1,5	2,5	24,0	
	Unit Jeg. Mepe % s s h	Unit Jeд.Yugoslav standard JUSMepeJUS%JUS H.K8.023sJUS H.K8.022sJUS H.K8.025hJUS H.K8.026	Unit Jeg. mepeYugoslay standard JUSUF 600MepeJUS1 $\%$ JUS H.K8.02356,2 s JUS H.K8.022232,0 s JUS H.K8.02560,0hJUS H.K8.0262,0	Unit Jeg. mepe Yugoslay standard JUS UF 600 UF P1001C M M M M JUS $56,2$ $52,2$ M JUS $56,2$ $52,2$ S JUS $232,0$ $223,0$ S JUS $60,0$ $57,0$ h JUS $60,0$ $57,0$	Unit Jeg. mepe Yugoslav standard JUS UF 600 UF P1001C UF 2003 Mepe JUS formultion / M JUS 56,2 52,2 51,2 S JUS H.K8.022 232,0 223,0 240,0 S JUS H.K8.025 60,0 57,0 45,0 h JUS H.K8.026 2,0 3,0 0,5	Unit Jeg. mepe Yugoslav standard JUS UF 600 UF P1001C UF 2003 UF 2003 Mepe JUS formulation / penemr formulation / penemr % JUS H.K8.023 56,2 52,2 51,2 51,6 s JUS H.K8.025 232,0 223,0 240,0 210,0 s JUS H.K8.025 60,0 57,0 45,0 50,0 h JUS H.K8.026 2,0 3,0 0,5 1,0	Unit Jeq. mepeYugoslav standard JUSUF 600 UF UF P1001CUF 2003UF 2003UF 2003MepeJUSI1123 $%$ JUS H.K8.02356,252,251,251,652,0 s JUS H.K8.022232,0223,0240,0210,0225,0 s JUS H.K8.02560,057,045,050,055,0 h JUS H.K8.0262,03,00,51,01,5	Unit Jeg. mepeYugoslav standard JUSUF 600 UF UF P1001CUF 2003UF 2003UF 2003UF 2003MepeUF 600 UF P1001CUF 200320032003MepeUF $1001C$ UF 200320032003MepeIII20032003MepeJUS H.K8.02356,252,251,251,652,0SJUS H.K8.02256,252,251,251,652,051,7SJUS H.K8.025232,0223,0240,0210,0225,0240,0SJUS H.K8.02560,057,045,050,055,080,0hJUS H.K8.0262,03,00,51,01,52,5	

4. CONCLUSION

The longer storage life and wide range of concentration of ready-to-use resin, presents the advantages of UF powder adhesives over UF emulsion adhesives.

UF P1001C one-shot powder adhesive was the most suitable in application, since only addition of water was necessary to form ready-to-use emulsion with appropriate gel time and pot life.

UF 600 emulsion adhesive was somewhat more complex in application, since addition of exact quantity of catalyst was necessary. Gel time and pot life were suitable.



Слика 1. Време желирања и радно време у зависности од додатка катализатора за UF 2003 адхезив

The most complex application showed UF 2003 powder adhesive. Beside the addition of water and exact quantity of catalyst, separate addition of retarders to regulate pot life vs. gel time ratio was necessary. Otherwise, inappropriate gel time reduces capacity of the hot press, while inappropriate pot life reduces necessary time for preparatory operations like adhesive spreading to wood surface, construction setting up, press loading etc. Also, small quantities of ready-to-use emulsion must be prepared. Altogether, this makes application of UF P100C adhesive more complex.

LITERATURE

- Dunky M. (2000): Urea-formaldehyde (UF) glue resins: an Adhesive ever young, The 5th Pacific Rim Bio-Based Composites Symposium, Proceedings, Canberra (205-213)
- Dunky M. (1997): Aminoplastic glue resins: State of the art to meet the challenges of the wood based panels industry, The 3rd international conference on the development of forestry and wood science/technology, Proceedings, Volume I, Beograd (385-392)
- Myers E.G. (1981): *Investigation of urea-formaldehyde polymer cure by infrared*, Journal of Applied Polymer Science Vol. 26 (747-764)
- Raveendran B. *et al.* (1983): *Kinetics and mechanism of urea-formaldehyde reaction*, Polymer Vol. 24 (626-630)
- (2002): Техничко-шехнолошки йодаци, Q4.OS.05.02 PKS Latex, Чачак
- (2004): Technical Data, SR Synthetic Resins and Adhesives International Corp. Trinidad and Tobago

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НЕКЕ КАРАКТЕРИСТИКЕ УРЕА-ФОРМАЛДЕХИДНИХ АДХЕЗИВА У ПРАХУ

Резиме

Прашкасти UF адхезиви су повољнији за примену од UF адхезива у облику емулзије, због дужег века складиштења и могућности подешавања концентрација у ширем опсегу. Потребно је, међутим, обратити пажњу да ли постоји могућност истовременог подешавања времена желирања и радног времена таквог адхезива само са додатком катализатора. Ако то није могуће, доћи ће или до смањења капацитета пресе или до смањења количине везива које се сме припремити у једној шаржи, што подразумева честу припрему малих шаржи. Ово је неповољно за кориснике, јер се морају додавати успоривачи ради посебног подешавања радног времена, што компликује поступак припреме адхезива.