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ADHESION OF MELAMINE-UREA-FORMALDEHYDE ADHESIVES TO WOOD AS AN INTERACTION OF SURFACE FORCES

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Determination of the wetting angle on the surface of solidified MUF adhesive layer. Wetting angle for drops of redistilled water measured with the use of microscope with goniomertic head. On the base of adsorption theory of adhesion was determined energetic characteristics of surface solidified MUF adhesives. Quality of gluing in beech plywood was evaluated on base of requirements of EN 314-2 standard after tests acc. p.5.1.1 and 5.1.3 of EN-314-1.

Key words: MUF adhesive, beech wood, glue layer, wetting angle, surface force, plywood

INTRODUCTION

In Institute of Wood Technology in Poznań are carried out research works on synthesis of modified MUF resins provided for production of wood based products (e.g. Siwek and Warzecha 1978, Siwek et al. 1980, Warzecha and Siwek 1982, Szemiotowicz 1989, Jóźwiak 1989, 1991, 1995). In this article are presented results of investigations on the knowledge of the phenomenon of adhesion of MUF glues to wood on the base of adsorption adhesion theory.

The adsorption theory of adhesion assumes, that the contacting materials are acting on themselves by molecular surface forces, with physical and chemical character. The basic criterium of evaluation of the character of interactions occurring on the boundary of phases is work of adhesion. It is defined as the value of surface tension on the unit of area of adhesion contact, being the difference between the sum of materials surface tension [γ_{s1},γ_{s2}] and surface tension on the boundary of phases [γ_{s1s2}].

From the theoretical point of view for proper adhesion this value has to be in the range of 1-3 mJ/m^2, what is taken as the principle of minimization energy of the surface tension on the boundary of phases (Potente and Krüger 1978).

For determination of work of adhesion and free surface energy and inter-phase tension of solid material are used phenomena of wetting in system liquid-solid (Paprzycki 1991, Comyn 1992, Liptáková and Kúdela 1994).

The scope of this work has been determination of energetic characteristics of surfaces of solidified MUF adhesive on the base of adsorption theory. In studies were taken into respect effect of kind of substrate, composition of glue mixtures, and pressing temperature upon surface properties of solidified glue layers. Besides that was evaluated quality of gluing in beech plywood.

MATERIALS AND METHODS

For the experiment was used modified MUF resin, condensed in the laboratory scale at molar ratio of F:M:U as 3.9:1.0:1.0, which is used for production of water resistant plywood, characterized among others with dry mass content - 61%, dynamic viscosity - 850 mPa·s and gelation time in 100°C - 94 s. From the MUF resin were prepared glue mixtures with addition NH_4Cl in quantity 0.8% of dry mass of resin, and urea in range 10÷30% of dry mass of resin. Glue mixtures were spread in quantity of 180 g/m^2 on the surfaces of beech wood and 5-layers beech plywood having moisture content 8±1%. After 24 hrs of initial solidifying in temperature 20±1°C, created on slots glue layers were hardened at following parameters:

– pressure 1.0 MPa
– temperature / time 80°C / 8 min, 120°C / 3 min, 140°C / 1.5 min.

In aim to avoid sticking of hardened glue layers to the heating plates, pressing was made with the use of polyester antiadhesion foil named „Mylar". Obtained samples were conditioned (temp. 20±1°C and RH 65 ±5%) during 72 hrs. On the glue layers were put with the aid of microsyringe drops of redistilled water having volume 3.0 µl. Then, was measured wetting angle with the use of microscope with goniometric head. For each variant was made minimum 10 measurements. Despite to that was calculated in the range of wetting angles 0÷90° with steps every 1°, theoretical values of free surface energy accordingly to the method proposed by Neumann et al. (1974) with correction of Liptáková (1980) after transformation of following dependence:

$$\cos\Theta = \frac{(0.0015\gamma_S - 2)\sqrt{\gamma_S\gamma_L} + \gamma_L}{\gamma_L(0.0015\sqrt{\gamma_S\gamma_L} - 1)} \tag{1}$$

where: Θ – wetting angle
γ_S – free surface energy
γ_L – surface tension of liquid wetting .

The dispersion and polar shares of surface free energy was calculated accordingly to Kloubek (1974) from following formulas:

$$\sqrt{\gamma_S^p} = \sqrt{\gamma_L^p}\,\frac{1+\cos\Theta}{2} \pm \sqrt{\gamma_L^d}\sqrt{\frac{\gamma_S}{\gamma_L} - \left(\frac{1+\cos\Theta}{2}\right)^2} \tag{2}$$

$$\sqrt{\gamma_S^d} = \sqrt{\gamma_L^d}\,\frac{1+\cos\Theta}{2} \pm \sqrt{\gamma_L^p}\sqrt{\frac{\gamma_S}{\gamma_L} - \left(\frac{1+\cos\Theta}{2}\right)^2} \qquad (3)$$

where: γ_s^d – dispersion share, γ_s^p – polar share , the rest denominations as in formula (1).

There were also determined criteria of interaction of surface forces in system wood solidified resin accordingly to the assumptions given by Potente and Krüger (1978). For calculation were adopted values of free surface energy for beech wood: $\gamma_s = 67.5$ mJ/m^2, $\gamma_s^d = 24.6$ mJ/m^2, $\gamma_s^p = 42.9$ mJ/m^2 (Liptáková 1980).

Besides that was tested effect of pressing temperature upon quality of gluing of 3 –layer plywood made from beech veneers 2.5 mm thick and having moisture content 5±1 %. gluing has been conducted at following parameters:

- glue spread 180±5g/m^2
- assemble time 40±5 min
- prepressing pressure 1.0 MPa
- prepressing time 30 min
- pressing pressure 1.8 MPa
- pressing time 10 min
- pressing temperature (80, 100, 120, 140)°C.

Quality of gluing was evaluated on the base of requirements of EN 314-2 standard after tests acc. to p.5.1.1 and 5.1.3 of EN-314-1 standard.

RESULTS

The result of wettability tests of solidified glue surface are illustrated on Fig.l-3. While on Fig.4 is presented calculated on the base of theoretical considerations dependence of surface free energy, its polar and dispersion shares and interaction of surface forces in the system beech wood - glue layers in respect to the wetting angle taking into respect of minimization energy.

On the base of analysis of the presented results and dependencies of studies it can be stated, that from the point of view of criteria assumptions characterizing high adhesion of studied systems accordingly to adsorption theory, most favorable adhesive properties in system wood - MUF glue mixture, are showing variants hardened in temperature 80°C with addition of urea in quantities properly 20 and 30% of dry mass of resin (Θ - angle 58°20' and 58°40' – beech wood and 49°10' - plywood). That results probably from the great affinity of wetting liquid to the surface of solidified glue, what as its to be assumed caused by interaction of water with hydrophilic hydroxyl groups, and hygroscopic influence effect of unreacted urea. Such state is characteristic for unhardened resins, therefore shown dependence could be used as approximate measure of evaluation of degree of resin hardening. In case of plywood additional effect could have roughness of veneer used for its production.

As it can be observed for other tested variants, the magnitude of wetting angle is contained in the range 67°20' to 75°40'. Therefore it can be stated, that interactions of

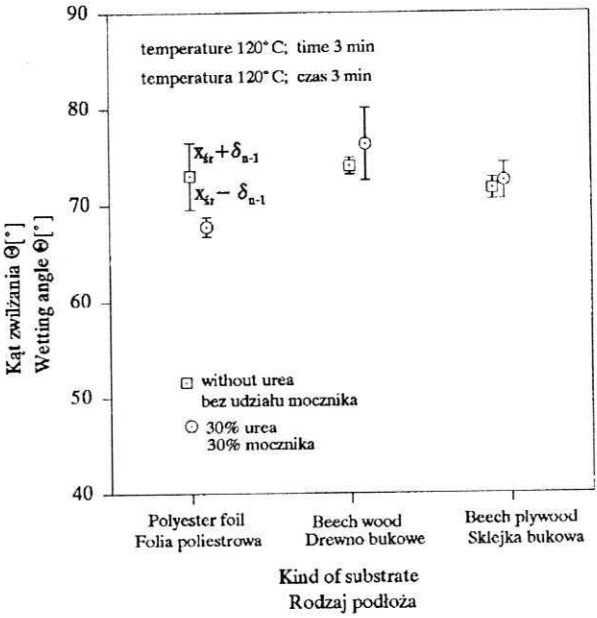

Fig. 1. Influence of kind of substrate on the wetting angle of distillated water on solidified glue layers
Rys. 1. Wpływ rodzaju podłoża na kąt zwilżania wodą destylowaną zestalonych warstw klejowych

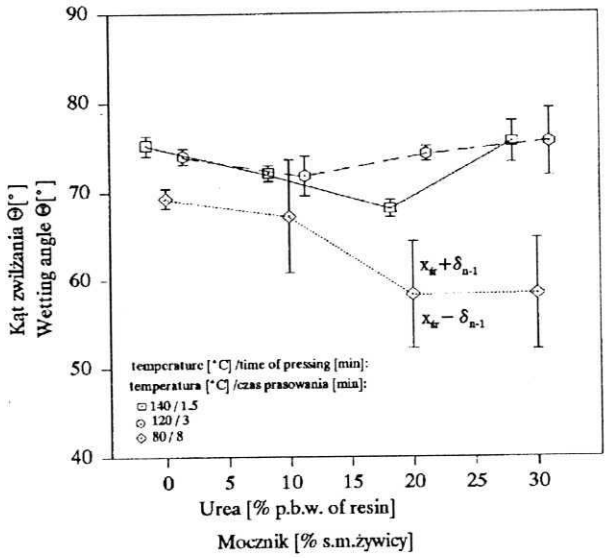

Fig. 2. Influence of pressing parameters and amount of urea in glue mixtures on the course of wetting angle on solidified glue layers
Rys. 2. Wpływ parametrów prasowania i udziału mocznika w masach klejowych na kąt zwilżania zestalonych warstw klejowych

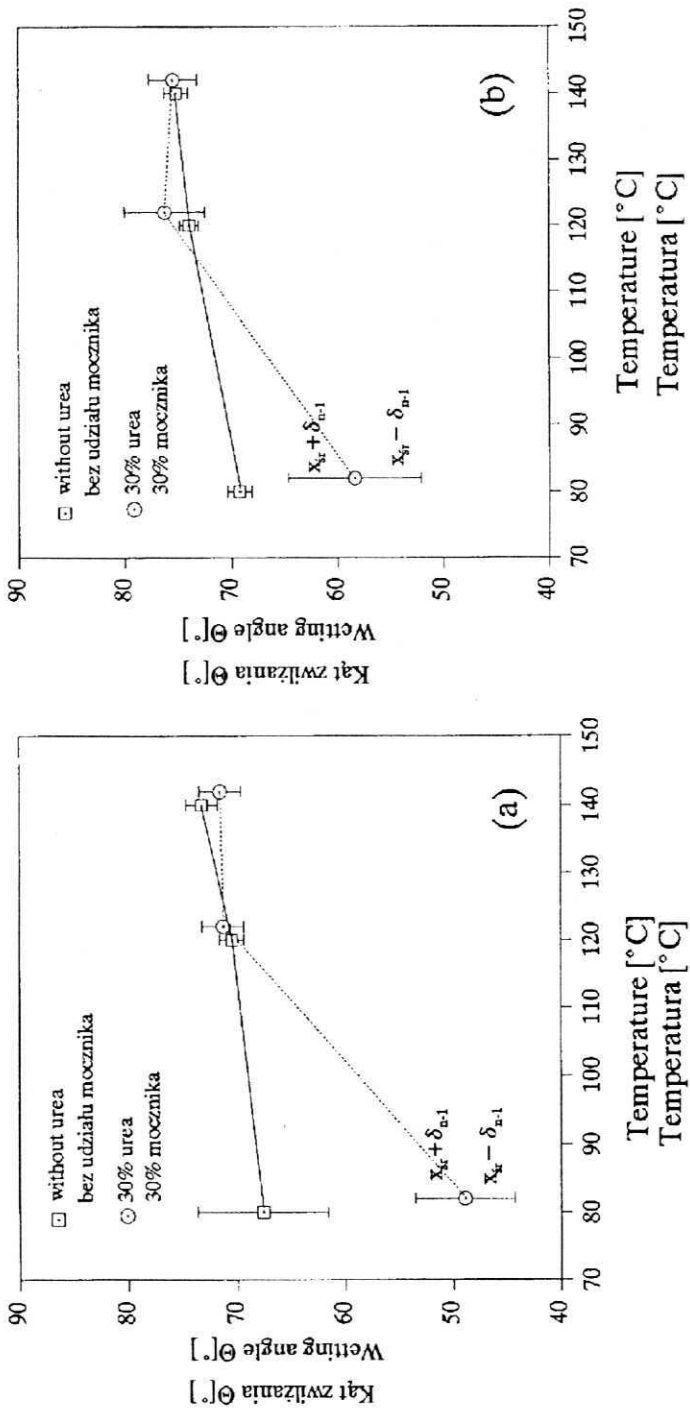

Fig. 3. Effect of pressing temperature of glue layers on the various substrates on the course of wetting angle: a) beech plywood, b) beech wood

Rys. 3. Wpływ temperatury prasowania warstw klejowych na różnych podłożach na kształtowanie się kąta zwilżania: a) sklejka bukowa, b) drewno bukowe

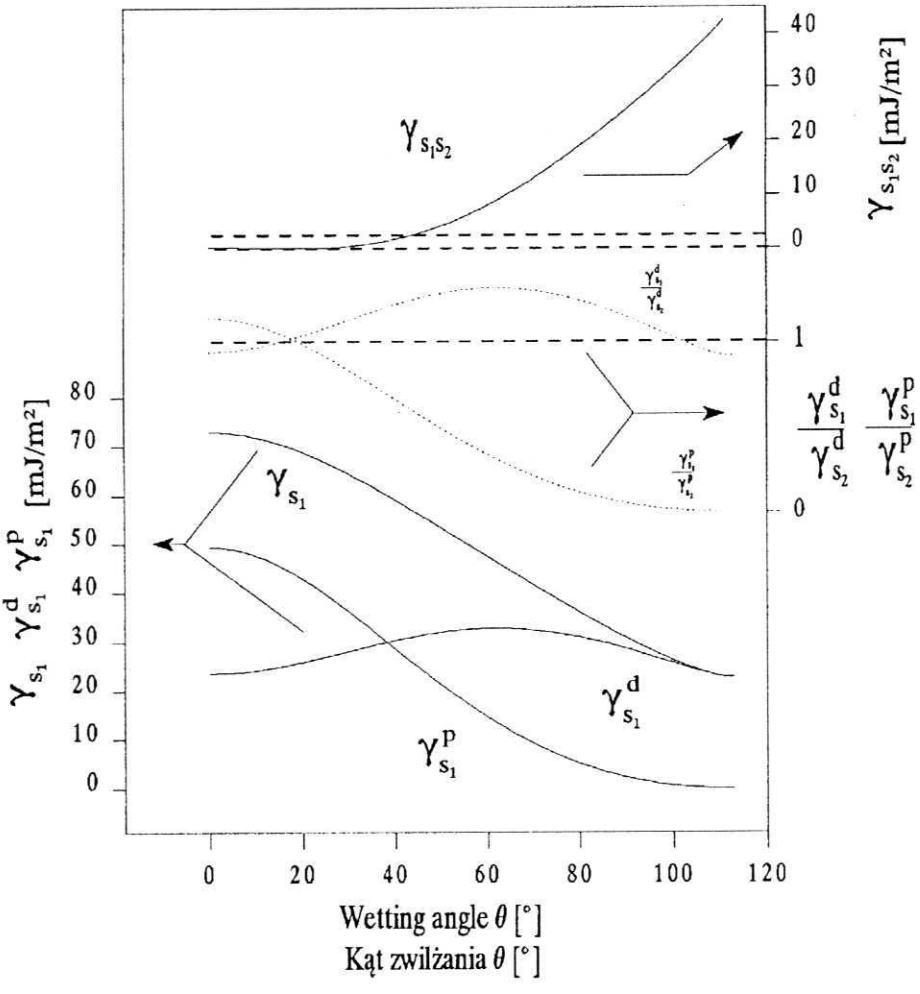

Fig. 4. Changes of free surface energy (γ_s) and its dispersion (γ_s^d) and polar (γ_s^p) shares and influences of surface forces in system beech wood - glue layer in function of wetting angle (on figure one took account criterions of maximum adhesion acc. Potente and Krüger 1978)

Rys. 4. Zmiany swobodnej energii powierzchniowej (γ_s) i jej składowej dyspersyjnej (γ_s^d) oraz polarnej (γ_s^p) i oddziaływania sił powierzchniowych w układzie drewno bukowe-warstwa klejowa w funkcji kąta zwilżania (na rysunku uwzględniono kryterium maksymalnej adhezji wg Potente i Krügera 1978)

surface forces in the system glue layer - substrate of which on index is magnitude of wetting angle in the system wetting liquid - solidified glue layer for remaining variants have close character, independent upon the composition of glue mixtures and hardening parameters.

Table 1
Tabela 1

Shearing strength of glue line of 3-layers beech plywood produced with the use adhesive mixtures of MUF resin with different share of urea and various pressing temperature after water resistance tests acc. to p.5.1.1. and 5.1.3 of EN 314-1 standard
Wytrzymałość spoin na ścinanie w 3-warstwowych sklejkach bukowych wytworzonych przy użyciu mas klejowych z żywicy MUF ze zróżnicowanym udziałem mocznika przy różnej temperaturze prasowania określona po testach wodoodporności wg p.5.1.1. i 5.1.3. normy EN 314-1

Strength after tests acc. to EN 314-1 Wytrzymałość po testach wg EN 314-1			Pressing temperature [°C]: Temperatura prasowania [°C] :															
			80				100				120				140			
Kind of test Rodzaj testu	Statistical parameters Parametry statystyczne	Unit of measure Jednostka miary	Share of urea [% dry mass of resin] Udział mocznika [% s.m.ż.]															
			0	10	20	30	0	10	20	30	0	10	20	30	0	10	20	30
p.5.1.1. (IF-20)	x_{max}	MPa	3.10	3.82	3.12	2.75	2.70	3.57	3.30	2.91	3.76	3.09	3.57	3.58	3.15	3.50	3.65	3.41
	$\bar{x}$		**2.65**	**2.99**	**2.64**	**1.91**	**2.48**	**2.74**	**2.60**	**2.28**	**2.86**	**2.54**	**2.94**	**2.80**	**2.39**	**2.88**	**3.01**	**2.68**
	x_{min}		1.98	2.30	2.30	1.09	2.10	1.95	2.06	1.63	1.79	2.00	2.40	2.00	1.87	2.27	2.54	2.08
	δ_{n-1}		0.36	0.57	0.22	0.45	0.26	0.49	0.41	0.41	0.56	0.33	0.42	0.63	0.40	0.38	0.33	0.46
	υ	%	13	19	8	23	10	18	16	18	19	13	14	23	17	13	11	17
	WF		**86**	**88**	**72**	**39**	**95**	**81**	**86**	**65**	**90**	**91**	**85**	**77**	**83**	**98**	**88**	**71**
p.5.1.3. (AW-100)	x_{max}	MPa	1.95	2.27	2.40	0	1.73	2.27	2.53	1.76	2.11	2.50	2.24	1.89	2.11	2.14	2.08	2.10
	$\bar{x}$		**1.66**	**1.98**	**1.58**	**0**	**1.59**	**1.87**	**1.78**	**0.93**	**1.55**	**1.87**	**1.61**	**1.28**	**1.79**	**1.73**	**1.62**	**1.57**
	x_{min}		1.34	1.41	1.22	0	1.50	1.50	1.25	0.35	1.28	1.31	1.25	0.90	1.34	1.38	1.34	1.25
	δ_{n-1}		0.21	0.34	0.36	-	0.09	0.33	0.48	0.38	0.25	0.32	0.32	0.28	0.28	0.30	0.23	0.32
	υ	%	13	17	23	-	5	18	27	40	16	17	20	22	15	17	14	20
	WF		**40**	**50**	**10**	**0**	**55**	**60**	**50**	**1**	**45**	**25**	**40**	**20**	**45**	**20**	**30**	**25**

WF - wood failure, udział ścięcia spoiny klejowej w drewnie

The obtained results of investigations are convergent with works of other authors characterizing surface properties of polycondensations resins UF, PF, RF and ARF (Paprzycki et al. 1992, Paprzycki and Pajdosz 1992, Paprzycki and Proszyk 1993) as well are corresponding with results obtained for melamine-urea-formaldehyde laminates (Paprzycki et al. 1993).

Having in respect criteria of adsorption adhesion theory characterizing systems of maximum adhesion, determined magnitudes describing surface interactions, as it seems are not reflecting in full real relations during gluing process.

Results of studies of gluing quality through determination of strength of glue line and wood failure are given in Table 1. Analysis of the obtained results certifies that only plywoods made from glue mixtures with addition of 30 % share of urea in pressing temperature 80 and 100°C were showing very low quality of gluing or the lack of gluing after the test AW-100. The causes of above could be sought in the unhardening of the glue mixtures , what corresponds with the obtained in the studies surface properties. In remaining variants obtained glue lines were fulfilling quality requirements of waterproof plywood accordingly to EN 314-2 standard.

CONCLUSIONS

1. System beech wood-hardened MUF adhesive is not fulfilling criterion of minimization of surface tension on the boundary phases .
2. There was not found significant effect of hardening temperature 120 and 140°C and kind of substrate upon formation of magnitude of wetting angle of glue layers from MUF resin.
3. Together with the increase of urea share in glue mixtures hardened in temperature of 80°C, took place lowering of the wetting angle.
4. The value of wetting angle of hardened glue layers given information on the state of crosslinking of MUF polycondensate.
5. Plywood made of glue mixtures with the share of 20 and 30 % of urea , and pressing temperatures 80 and 100°C were showing low quality of gluing or the lack of gluing after the AW-100 test.
6. The full waterproof properties of glue lines was obtained for plywood pressed in temperature 120 and 140°C.

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ADHEZJA KLEJÓW MELAMINOWO-MOCZNIKOWO-FORMALDEHYDOWYCH DO DREWNA WYWOŁANA ODDZIAŁYWANIEM SIŁ POWIERZCHNIOWYCH

Streszczenie

Na podstawie założeń teoretycznych adsorbcyjnej teorii adhezji określono energetyczną charakterystykę powierzchni utwardzonej klejowej żywicy MUF poprzez poznanie oddziaływań występujących na granicy faz drewno bukowe-utwardzony polikondensat. W wyniku przeprowadzonych badań m.in. stwierdzono, że układ drewno bukowe-zestalona żywica MUF nie spełnia kryterium minimalizacji napięcia powierzchniowego na płaszczyźnie granicznej faz, które obowiązuje dla połączeń o najwyższej adhezji.

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