

STUDIES ON ADHESION TO THE WOOD OF TWO COMPONENT PVAC ADHESIVES HARDENED WITH ALUMINIUM CHLORIDE*

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Determined was the theoretical maximum adhesion regarding action of surface forces in system beech wood - two component PVAC adhesives, for hardening of which were used diversified amount of catalyst (5 ± 2 w.p. / 100 w.p. of adhesive) in form of 20% solution of AlCl_3 .

On the base of measurements of value of wetting angle of surface of hardened adhesives layers were determined surface free energy, work of adhesion, and surface tension on the interface of phases with dispersion and polar shares.

Key words: PVAC adhesive, hardener, wettability, adhesion

INTRODUCTION

Accordingly to the adsorptive theory of adhesion, the contacting materials are acting on themselves by the surface forces (Boehme and Hora 1996, Hellwig, Sell and Wiest 1968, Liptáková, Kudela and Paprzycki 1991, Paprzycki and Pajdosz 1992). The knowledge on this forces enables therefore determination of the theoretical maximum adhesion between said materials [Liptáková 1980, Zorll 1978].

As the criterion of evaluation of the phenomenon of adhesion is taken work of adhesion (W_a), which accordingly to Dupre' is the difference between total contacting materials (γ_{S1}, γ_{S2}) and surface tension on the limit surface between them (γ_{S1S2}):

$$W_a = \gamma_{S1} + \gamma_{S2} - \gamma_{S1} \gamma_{S2} \quad (1)$$

The maximum adhesion are showing therefore systems, for which $\gamma_{S1S2} \rightarrow 0$. That is so called "principle of minimalization of surface tension on the interface surface of contacting material". Some authors are giving, that this value could not overreach $1-3 \text{ mJ/m}^2$ (Pirmasens 1983, Potente and Krüger 1978). Potente and Krüger (1978) are proposing further criterion stating, that the highest adhesion are showing systems, when:

$$\left(\frac{\gamma_{S1}}{\gamma_{S2}}\right)^d = 1 \quad \text{and} \quad \left(\frac{\gamma_{S1}}{\gamma_{S2}}\right)^p = 1 \quad (2)$$

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$$\left(\frac{\gamma_{s1}}{\gamma_{s2}}\right) = 1 \quad \text{and} \quad \left(\frac{\gamma_{s1}}{\gamma_{s2}}\right)^d = 1 \quad (3)$$

Accordingly to the cited above authors, upon adhesion it is to be concluded above all on the base of relation of polar shares of free surface energy of contacting materials.

As it results from the producers offers as from literature data (Proszek 1996) in form of hardener of two component PVAC adhesives used in the building woodworking industry, commonly is used 20% solution of AlCl_3 . Particular producers of PVAC adhesives are recommending dosage of this hardener in quantity of 5 w.p. in calculation for 100 w.p. of adhesive. Simultaneously they suggest, that the user of adhesives is obliged to precise selection of quantity of hardener on the base of results of application tests. This causes, that in various technical conditions not only users of adhesives, and also certifying - research institutions are establishing the share of hardener in the range from 3 to 7 w.p.

From the literature data (Proszek and Krystofiaik 1997a, b, Proszek Krystofiaik and Winnik 1997) results, that share of hardener on the base of 20% of AlCl_3 in the PVAC adhesives has essential effect upon their properties, in that also upon their strength and resistance of obtained glue-lines.

The aim of this paper was the determination of theoretical maximum adhesion taking into respect action of surface forces in the system wood - PVAC adhesives, for hardening of which were used various amounts of catalyst in form of 20% of AlCl_3 .

EXPERIMENTS

For the tests were used two PVAC adhesives with the trade names Jowacoll 102 30 and 102 40. In the character of catalyst was used hardener marked 195 30 based on 20% solution of AlCl_3 which was dosed in quantities 3, 5 and 7 w.p. in respect to the 100 w.p. of adhesive. Adhesive and hardener was obtained in form of mean laboratory samples from the JOWAT Firm (Lobers u. Frank GmbH) in Detmold. The adhesives were spread on the planned surface of beech samples (*Fagus sylvatica* L.) measuring 200x100x10 mm. The thickness of spread adhesive layers was 210 μm , what corresponds the mean degree of spreading ca. 150 g/m^2 . After 2 h on the samples with set adhesive was placed antiadhesive Mylar polyester foil and adhesives were hardened in the hydraulic press of following parameters: temperature $20 \pm 1^\circ\text{C}$, pressure 0.1 MPa, and the time of pressing 4 h. In such way prepared samples were conditioned ($23 \pm 1^\circ\text{C}$, $50 \pm 5\%$) in the time 168 h.

The surface free energy of hardened adhesives was determined for the smooth surfaces made in the contact with antiadhesive foil. With chromatographic syringe were put on the adhesive layers 10 drops of bidistilled water of volume 2.5 μl . Wetting angles were measured with microscope equipped the goniometric head. After 336 h from spreading of adhesive, were made once more measurements of wetting angles. Results of measurements listed in the table 1 are showing on the sufficient exactness of measurements of wetting angle.

The surface free energy of hardened adhesives layers were calculated accordingly to Neuman et al. (1974) and Liptáková (1980), and dispersion and polar shares of surface free energy accordingly to Kloubek (1974). The values of surface free energy of wood were taken accordingly to Liptáková (1987), for beech $\gamma_S = 67.6 \text{ mJ/m}^2$, $\gamma_{Sd} = 24.7 \text{ mJ/m}^2$, $\gamma_{Sp} = 42.9 \text{ mJ/m}^2$. The said values are different from the prior data contained in papers of

Table 1

Tabela 1

Statistical estimation of the measuring results of contact angle for solidified layers from Jowacoll adhesives with various amount of 195 30 hardener in time of their conditioning

Oszacowanie statystyczne wyników pomiarów kąta zwilżania zestalonych warstw z klejów Jowacoll z różnym udziałem utwardzaczka 195 30 w funkcji czasu ich sezowania

Kind of adhesive Rodzaj kleju	Amount of hardener (% by weight) Ilość utwardzaczka (% m/m)	Time (h) Czas (h)			
		168		336	
		Statistical data ^{x)} Wielkości statystyczne ^{x)}			
		\bar{x} (°)	$\pm\sigma_{n-1}$ (°)	v (%)	\bar{x} (°)
Jowacoll 102 30	3	52.12	1.31	2.93	58.,58
	5	48.00	2.21	4.92	54.34
	7	44.18	2.18	5.18	48.57
Jowacoll 102 40	3	51.24	2.18	4.47	56.04
	5	47.18	1.41	3.57	50.44
	7	43.54	1.53	4.31	47.35

x) \bar{x} - arithmetic mean
 średnia arytmetyczna
 $\pm\sigma_{n-1}$ - standard deviation
 odchylenie standardowe
 v - coefficient of variation
 współczynnik zmienności

Nguyen and Johns (1978), and Wehle (1979). But it can be assumed, that more exactly they are determining the surface free energy of wood, because Liptáková (1987) managed to exclude effect of porous structure of wood and its surface unevenness upon histeresis of wetting.

The work of adhesion for the system wood-adhesive, and surface tension on interface, were calculated in dependence upon relations given in literature (Liptáková 1980, Neumann et al. 1974). Despite to that was calculated ratio of dispersion and polar shares of surface tension on the interface of contacting materials.

RESULTS

The analysis of results of measurements of wetting angles of hardened layers (table 1) shows, that together with the increase of the amount of hardener in adhesives takes place lowering of this angle, what is to be taken as favourable phenomenon in the light of assumptions of adsorptive adhesion theory. In the function of conditioning time took place increase of value of wetting angle, what is the proof, taht in this period takes place further

Table 2

Tabela 2

Influence of the amount of 195 30 hardener in Jowacoll adhesives on surface free energy (γ_s) solidified layers with polar (γ_s^p) and disperse (γ_s^d) shares in time of their conditioning
 Wpływ udziału utwardzaczka 195 30 w klejach Jowacoll na swobodną energię powierzchniową (γ_s) zestalonych warstw wraz z udziałem składowej polarnej (γ_s^p) i dyspersyjnej (γ_s^d) w funkcji czasu sezonowania

Kind of adhesive Rodzaj kleju	Amount of hardener (% by weight) Ilość utwardzaczka (% m/m)	Time (h) Czas (h)					
		168		336			
		Surface free energy (mJ/m ²) Swobodna energia powierzchniowa (mJ/m ²)					
		γ_s	γ_s^p	γ_s^d	γ_s	γ_s^p	γ_s^d
Jowacoll 102 30	3	51.9	21.0	30.9	47.9	16.4	31.5
	5	54.4	24.1	30.3	50.5	19.4	31.1
	7	56.5	26.7	29.8	53.3	23.2	30.1
Jowacoll 102 40	3	52.4	21.6	30.8	49.7	18.4	31.3
	5	54.8	24.6	30.2	52.8	22.1	30.7
	7	56.8	27.2	29.6	54.6	24.4	30.2

Table 3

Tabela 3

Influence of the amount of 195 30 hardener in Jowacoll adhesives on the work of adhesion (Wa) to beech wood with polar (Wa^p) and disperse share (Wa^d) in time of their conditioning
 Wpływ udziału utwardzaczka 195 30 w klejach Jowacoll na pracę adhezji (Wa) kleju do drewna bukowego wraz z udziałem składowej polarnej (Wa^p) i dyspersyjnej (Wa^d) w funkcji czasu sezonowania

Kind of adhesive Rodzaj kleju	Amount of hardener (% by weight) Ilość utwardzaczka (% m/m)	Time (h) Czas (h)					
		168		336			
		Work of adhesion (mJ/m ²) Praca adhezji (mJ/m ²)					
		Wa	Wa^p	Wa^d	Wa	Wa^p	Wa^d
Jowacoll 102 30	3	115.3	60.1	55.2	108.9	53.1	55.8
	5	119.0	64.3	54.7	113.2	57.7	55.5
	7	122.1	67.9	54.2	118.2	63.4	54.8
Jowacoll 102 40	3	116.1	61.1	55.0	111.7	56.1	55.6
	5	119.6	65.0	54.6	116.6	61.5	55.1
	7	122.4	68.3	54.1	119.4	64.7	54.7

Table 4

Tabela 4

Influence of amount of 195 30 hardener in Jowacoll adhesives on the surface tension on the interface in system beech wood - adhesives (γ_{SL}) with polar (γ_{SL}^P) and disperse (γ_{SL}^d) share in time of their conditioning
 Wpływ udziału utwardzacza 195 30 w klejach Jowacoll na napięcie powierzchniowe na granicy faz w układzie drewno bukowe - klej (γ_{SL}) wraz z udziałem składowej polarnej (γ_{SL}^P) i dyspersyjnej (γ_{SL}^d)
 w funkcji czasu sezonowania

Kind of adhesive Rodzaj kleju	Amount of hardener (% by weight) Ilość utwardzacza (% m/m)	Time (h) Czas (h)					
		168		336			
		Surface tension on the interface (mJ/m ²) Napięcie powierzchniowe na granicy faz (mJ/m ²)					
		γ_{SL}	γ_{SL}^P	γ_{SL}^d	γ_{SL}	γ_{SL}^P	γ_{SL}^d
Jowacoll 102 30	3	4.21	3.87	0.34	6.64	6.22	0.42
	5	2.99	2.70	0.28	4.99	4.61	0.38
	7	2.10	1.87	0.23	3.20	2.91	0.29
Jowacoll 102 40	3	3.95	3.61	0.34	5.53	5.14	0.39
	5	2.79	2.52	0.27	3.76	3.43	0.33
	7	2.00	1.79	0.21	2.88	2.60	0.28

Table 5

Tabela 5

Influence of amount of 195 30 hardener in Jowacoll adhesives on the ratio of surface free energy and their shares for beech wood - adhesives

Wpływ udziału utwardzacza 195 30 w klejach Jowacoll na stosunek swobodnej energii powierzchniowej i jej składowych dla układów drewno bukowe - kleje

Kind of adhesive Rodzaj kleju	Amount of hardener, (% by weight) Ilość utwardzacza (% m/m)	Ratio of surface free energy and their shares after 168 h conditioning		
		Stosunek swobodnej energii powierzchniowej i jej składowych po czasie sezonowania 168 h		
		γ_{S1}/γ_{S2}	$\gamma_{S1}^d/\gamma_{S2}^d$	$\gamma_{S1}^P/\gamma_{S2}^P$
Jowacoll 102 30	3	1.30	0.80	2.04
	5	1.24	0.82	1.78
	7	1.19	0.83	1.61
Jowacoll 102 40	3	1.29	0.80	1.99
	5	1.23	0.82	1.74
	7	1.19	0.83	1.58

hardening of adhesives and lowering affinity to the water, and in the same increase of hydrophobic of layers.

In the table 2 are listed values of surface free energy of hardened layers of adhesive. The obtained data are nearly identical for both studied adhesives and are corresponding values given by literature for plastics and lacquer coatings. General analysis of the data in table 2 certifies, that γ_S to some degree is dependent from the share of the amount of hardener in adhesives. And with increase of the amount of hardener in the adhesives took place few percentage increase of value of γ_S of layers.

In the function of conditioning time of the layers is forming indistinct tendency to lowering of this energy at simultaneous increase of value of dispersion component.

Comparing values γ_S of hardened adhesives and wood, it is possible to state, that occurring relations are very favourable from the point of assumptions of adsorptive theory of adhesion, and are indicating upon possibility of mutual action of said materials with the full use of surface forces, what is condition of good interlayers adhesion (Pirmasens 1983, Potente and Krüger 1978, Zorll 1978).

The values of work of adhesion in system wood-adhesive with diversified amount of hardener are presented in the table 3. The obtained values are corresponding with the literature data for the system wood-polymer (Liptáková 1980), indicating the possibilities of close bonds of considered materials.

Among the shares of work of adhesion, resulting from interaction dispersion and polar forces in case of system beech wood - PVAC adhesive, the higher value shows work of adhesion in the range of polar forces. It is understandable, if are taken into respect relatively high value of polar share of the surface energy of beech wood.

In the table 4 are listed results of calculations of surface tension on the interface in the system beech wood - PVAC adhesive. In respect is to be taken the fact, that the obtained values are on the level 3 mJ/m^2 , fulfilling in this way assumptions of mentioned in the introduction of the work principle of minimalization of surface tension on the interface of contacting materials. For both adhesives there is observed close values of dispersion share of surface tension, which is contained for particular systems in the range $0.21 - 0.42 \text{ mJ/m}^2$. For the diversification of value S_L deciding influence has polar share, value of it distinctly decreases together with the increase of amount of hardener in the adhesives.

Analysis of the data from table 5, which were calculated on the base of mentioned in the introduction of paper criterion of Potente and Krüger (1978) certifies, that taken into respect in paper systems wood - adhesive only slightly deviate from theoretical model assumptions presented in formula (3). The value of ratio of the polar shares of both considered materials much more deviates from mentioned assumptions (formula 2), in the light of which is not fulfilled criterion of equivalency of polar shares of surface free energy. Together with the increase of amount of hardener in Jowacoll adhesive took place more favourable relations in the range of quotients of surface free energy and their components for contacting materials.

RECAPITULATION

The system beech wood - two component PVAC adhesives, catalysed with diversified amount of hardener in forms of 20% solution of AlCl_3 , fulfills in conformity to adsorptive theory of adhesion selected criterions established for system with the higher adhesion, namely condition of minimization of surface tension on the interface, and criterion

assuming, that the value of ratio of dispersion components of surface free energy and high value of work of adhesion.

Together with the increase of amount of hardener in two component PVAC adhesives occur favourable relations in the range of theoretical maximization of adhesion between these materials.

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REFERENCES

- Boehme Ch., Hora G. (1996): Water absorption and contact angle measurement of native European, North American and tropical wood species to predict gluing properties. Holzforschung 50 (3): 269-276.
- Hellwig G. E. H., Sell P. J., Wiest H. (1968): Über einen Zusammenhang von grenzflächenenergetischen Größen von Klebstoffen und ihren Verklebungsfähigkeit gegenüber Kunststoffen. Adhäsion 12 (10): 499-505.
- Kloubek J. (1974): Calculation of surface free energy components of ice according to its wettability by water, chlorobenzene and carbon disulfide. J. Colloid Interface Sci. 46 (2): 185-190.
- Liptáková E. (1980): Studium fazového rozhrania dreva s filmotvornými materiálmi. Zborník Vedeckých Prác Drevarskej Fakulty VŠLD Zvolen: 55-67.
- Liptáková E. (1987): Vplyv mechanického spráčovania povrchu na stanovenie povrchovej energie dreva. Medzinárodná Vedecka Konferencia. VŠLD Zvolen: 175-182.
- Liptáková E., Kudela J., Paprzycki O. (1991): The adhesion of polystyrene to wood. Holz als Roh- und Werkstoff 49 (1): 31-37.
- Neumann A. W., Good R. J., Hope C. J., Sejpala M. (1974): An equation-of-state approach to determine surface tension of low energy solids from contact angles. J. Colloid Interface Sci. 49 (2): 291-302.
- Guyen T. Johns W. L. (1978): Polar and dispersion force contributions to the total surface free energy of wood. Wood Sci. Technol. 12 (2): 63-74.
- Paprzycki O., Pajdossz K. (1992): Adhezja żywic mocznikowo- i fenolowoformaldehydowych do drewna wywołana oddziaływaniem sił powierzchniowych. PTPN Poznań. Wydz. Nauk Technicznych. Pr. Komis. Technol. Drewna 13: 87-96.
- Pirmasens M. M. (1983): Die Haftmechanismen von Kunststoff-Klebstoffen als Funktion von Molekül-Struktur und Oberflächenspannung. Adhäsion 25 (11): 11-13.
- Potente H., Krüger R. (1978): Bedeutung polarer und disperser Oberflächenspannungsanteile von Plastomeren und Beschichtungsstoffen für die Haftfestigkeit von Verbundsystemen. Farbe u. Lack 84 (2): 72-75.
- Proszyk S. (1996): Dyspersyjne kleje PVAC i ich stosowanie w przemyśle drzewnym. III Konferencja nt. "Otrzymywanie i zastosowanie wodnych dyspersji i roztworów polimerów. Ustroń-Jaszowiec 19-20.10.1995r. Wydawnictwo OBRKiTW Oświęcim: 57-61.
- Proszyk S., Krystofiaik T. (1997a): Activation energy of the solidification processes and thermal decomposition of PVAC adhesives. Chemické listy 91 (9): 759-761.
- Proszyk S., Krystofiaik T. (1997b): Study on the wettability of solidified PVAC adhesives on the surface of selected wood species. 50. Sjezd Chemickych Spoločnosti. 8-11.09. Zlin: 175-176.
- Proszyk S., Krystofiaik T., Winnik A. (1997): Investigations on the properties of two component PVAC adhesives hardened with aluminium chloride. Folia Forestalia Polonica, ser. B - Drzewnictwo 28: 85-97.
- Wehle H. D. (1979): Zur Bestimmung der Oberflächenspannung von Holz und Oberflächenmaterialien. Holztechnologie 20 (3): 154-158; (4): 219-222.
- Zorll U. (1978): Neue Erkenntnisse über die Bedeutung der Benetzung für die Adhäsion bei Beschichtungs- und Klebstoffen. Adhäsion 20 (10): 320-325.

BADANIE ADHEZJI DO DREWNA DWUSKŁADNIKOWYCH KLEJÓW PVAC UTWARDZANYCH CHLORKIEM GLINU

Streszczenie

Celem pracy było określenie teoretycznej maksymalnej adhezji z uwzględnieniem oddziaływania sił powierzchniowych w układzie drewno bukowe - dwuskładnikowe kleje PVAC. Do badań użyto 2 klejów PVAC o nazwach handlowych Jowacoll 102 30 i 102 40. W charakterze katalizatora zastosowano utwardzacz o oznakowaniu 195 30 bazujący na 20% AlCl_3 , który dozowano w ilościach odpowiednio 3, 5 i 7 cz.m. w stosunku do 100 cz.m. kleju. Kąty zwilżania utwardzonych warstw klejowych mierzone mikroskopem pomiarowym z głowicą goniometryczną. Na podstawie pomiarów kąta zwilżania powierzchni zestalonych klejów określono swobodną energię powierzchniową, pracę adhezji i napięcie powierzchniowe na granicy faz z wyznaczeniem składowych dyspersyjnej i polarnej.

Stwierdzono, że układ drewno bukowe - dwuskładnikowe kleje PVAC katalizowane zróżnicowanymi ilościami utwardzacza w postaci 20% roztworu AlCl_3 spełnia zgodnie z adsorpcyjną teorią adhezji wybrane kryteria ustalone dla systemów o najwyższej adhezji. Ponadto obydwa kontaktujące się materiały wykazują odpowiednio korzystne relacje w zakresie wartości swobodnej energii powierzchniowej oraz dużą wartość pracy adhezji.

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