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INVESTIGATIONS ON THE PROPERTIES OF TWO COMPONENT PVAC ADHESIVES HARDENED WITH ALUMINIUM CHLORIDE

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Determined the influence of the amount of hardener based on 20% solution of $AlCl_3$ on the properties of two component PVAC adhesives applied in woodworking industry. The conventional viscosity, rheological characteristics, pH value and open assembly time were determined in liquid state of adhesives. The solid content and relative hardness was studied for solidified adhesive layers. Strength and water resistance according to durability classes D3 and D4 of PN EN 204 standard was tested for glue lines.

Key words: PVAC adhesive, hardener, property, glue line, strength, durability

INTRODUCTION

Two components systems catalysed with various hardeners have a very important position among PVAC adhesives applied in woodworking industry. These adhesives may present specific properties both as to application features as well as functional features of glue lines. Possibilities offered by those adhesives include, among others, glue lines which have a very high level of thermostability, and water resistance, thus meeting the requirements set out by D4 durability class according to PN EN 204. Glue lines made of these adhesives may also show an increased static load resistance and greater resistance to varnishing solvents (Boehme 1993, 1995a; Głogowski 1996, Homanner 1993, Proszyk 1996, Proszyk, Bernaczyk and Krystofiak 1995).

The above mentioned features allow multidirectional use of these adhesives in woodworking industry. Lewis' acids in the form of $AlCl_3$, or less frequently $Cr(NO_3)_3$ solutions are the most commonly used as PVAC adhesive hardeners, and over the last few years cross-linking agents, which contain isocyanate groups are being introduced (Sedliačik, Ružinska and Sedliačik 1993). It is a well known fact that the type of hardener used may have an influence on the properties of adhesives, especially on the glue lines (Boehme 1995b, Gos 1990). The experience gathered hitherto with application two component PVAC adhesives indicates that the highest level of water resistance may be achieved when isocyanate hardeners, or successively $Cr(NO_3)_3$ based hardeners are used (Gos 1996). However, glue lines obtained from PVAC adhesives catalysed with $Cr(NO_3)_3$ have a dark colour and contain Cr^{+3}, which causes many users to resign from those hardeners.

According to both market offers of the producers and the literature data, 20% $AlCl_3$ solution is commonly used as a hardener for PVAC adhesives. Individual producers of PVAC adhesives suggest, that the hardener should be dosed in the amount of 5 parts by weight in proportion to 100 parts by weight of adhesives. At the same time, producers claim that the user is obliged to make a precise choice of the amount of hardener based on the results of application tests. This is the reason why not only the users, but also research and certification centers set the hardener fraction within the range of 3 to 7 parts by weight.

A separate, but closely connected issue is the problem of unintentional technological errors, which may occur in the procedure of dosing the hardener to the adhesive due to, e. g. inaccurate measuring devices or the negligence of the workers performing those tasks. It should also be observed that the relatively high price of the hardener compared with the price of adhesive may also be an incentive to minimize its partition. These short considerations lead to the conclusion that in manufacturing practice there may be circumstances under which particular users of binary PVAC adhesive users dose the hardener in various amounts.

The analysis of comprehensive literature data (Gos and Jaworski 1995, Gos and Kuciński 1995, Homanner 1991, Proszyk, Biniek and Krystofiak 1997) devoted to various problems from the field of the area of modification and use of PVAC adhesives leads to the conclusion that until present time results of studies devoted to the subject matter of the influence of the amount of hardener based on $AlCl_3$ on selected properties of PVAC adhesives has not been published. In order to bridge this gap an experimental study was undertaken, aiming at cognition of the influence of the above mentioned hardener on the properties of PVAC adhesives in liquid state, as well as in the form of solidified layers and glue lines.

EXPERIMENTS

Two PVAC adhesives were chosen for the study. Their trade names were Jowacoll 102 30 and 102 40. Hardener based on 20% solution of $AlCl_3$ with trade name 195 30 was used as a catalyst, which was dosed respectively in the amounts of 3, 5 and 7 parts by weight for each 100 parts by weight of adhesive. The adhesives, and hardener were obtained from JOWAT Lobers u. Frank GmbH firm in Detmold.

Research on properties of the adhesives in liquid state

Conventional viscosity of the adhesives was determined with a Ford cup equipped with a 10 mm nozzle according to BN-78/6357-05 standard. Viscosity measurements were started 15 min. after the adhesive had been prepared, and then viscosity was measured over an 8 h period of time (with 1 h intervals). The final measurement was taken after 24 hrs.

Rheological properties of the adhesive were measured with a Höppler rheoviscometer according to the PN-86/C-89408 standard.

Chemical reagent (pH) of the adhesives was measured with a pH-meter type N-512 (Mera-Elwro), equipped with a set of electrodes: calomel-glass, and measurements were taken at the temperature of 20 ± 0.5 C.

Open assembly time for the adhesives was determined according to the general provisions set out in the BN-78/6357-05 standard; these studies were conducted in an air-conditioned laboratory (23 ± 1^0C, 50 ± 5%).

Research on properties of the adhesives in the form of solidified layers

These studies were aimed at determining of the solid content, and relative hardness of solidified adhesive layers.

The solid content in adhesives containing hardener was measured as follows. The adhesive was applied in thin films to glass plates in the amount of 1 g (with 0.001 g precision). Subsequently the samples were placed in a dryer with induced circulation and dried in the temperature of 120^0C for 2.5 h and after a subsequent, 20 min. cooling in a desiccator over P_2O_5 , reweighed and then calculations were made.

Hardness studies were conducted according to PN-79/C-81530 standard with the use of Persoz pendulum. Glass constant for the pendulum which was utilized in the studies was 420 s.

The adhesives were applied with an applicator to glass plates of overall dimensions 100x100x3mm. The thickness of layers was respectively 90, 150 and 210 μm. After 72 h of solidifying the layers in an air-conditioned laboratory hardness measurements were taken. Measurements were repeated after 168 and 336 h after the layers were applied.

Research on the properties of glue lines

The shearing strength of the glue lines was determined to the PN EN 205 standard. The adhesives were applied in the amount of 150 g/m^2 to beech wood (*Fagus sylvatica* L.) of overall dimensions 330x50x5 mm, which had been planed before the adhesive was applied. After the lapse of open assembly time (table 2) the sets were placed in hydraulic press. The pressing was conducted at unit pressure 0.8 MPa, and temperature of 23±2^0C at a relative humidity 50±5% in 40 min. After the lapse of that period of time the sets were conditioned for 7 days according to PN EN 204 standard, and then samples were prepared.

Samples were tested in conditions set out by D 3 and D 4 durability classes according to PN EN 204 standard. After the lapse of the assumed conditions for particular tests shearing strength of the glue lines were tested. Strength was determined in a test machine produced by Zwick, model 1445 with PC Software 27005 at the speed load 50 mm/min.

RESULTS

Evaluation of properties of the adhesives in liquid state

On the fig. 1. is illustrated the dependence depicting the influence of the amount of 195 30 hardener on the conventional viscosity of Jowacoll adhesives as a time function. An overall analysis of data in fig. 1 proves that along with the increasing amount of the hardener the viscosity of particular adhesives is subject to inconsiderable decrease. It must be emphasized that differentiation of the portion of hardener within the range of 3 - 7 parts by weight does not affect the usability of adhesives.

Fig. 2. illustrates the apparent viscosity as a function of stresses. An analysis of the obtained dependencies leads to the general conclusion that the portion of hardener does not affect the rheological properties of Jowacoll adhesives. The adhesives which were subject to evaluation represent the category of nonnewtonian liquid thinned by shearing.

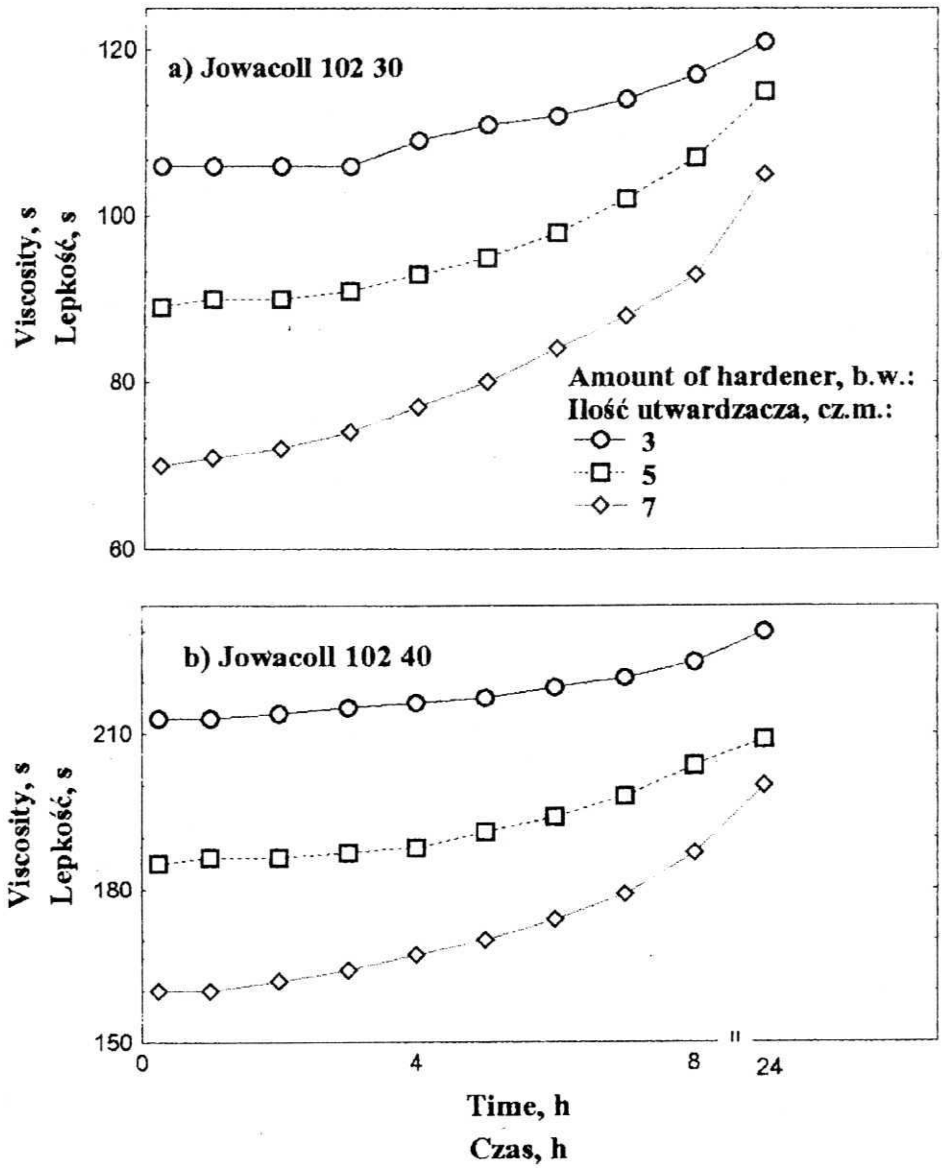

Fig. 1. Influence of amount of 195 30 hardener on the course of conventional viscosity of Jowacoll adhesives in time function

Rys. 1. Wpływ ilości utwardzacza 195 30 na kształtowanie się lepkości umownej klejów Jowacoll w czasie

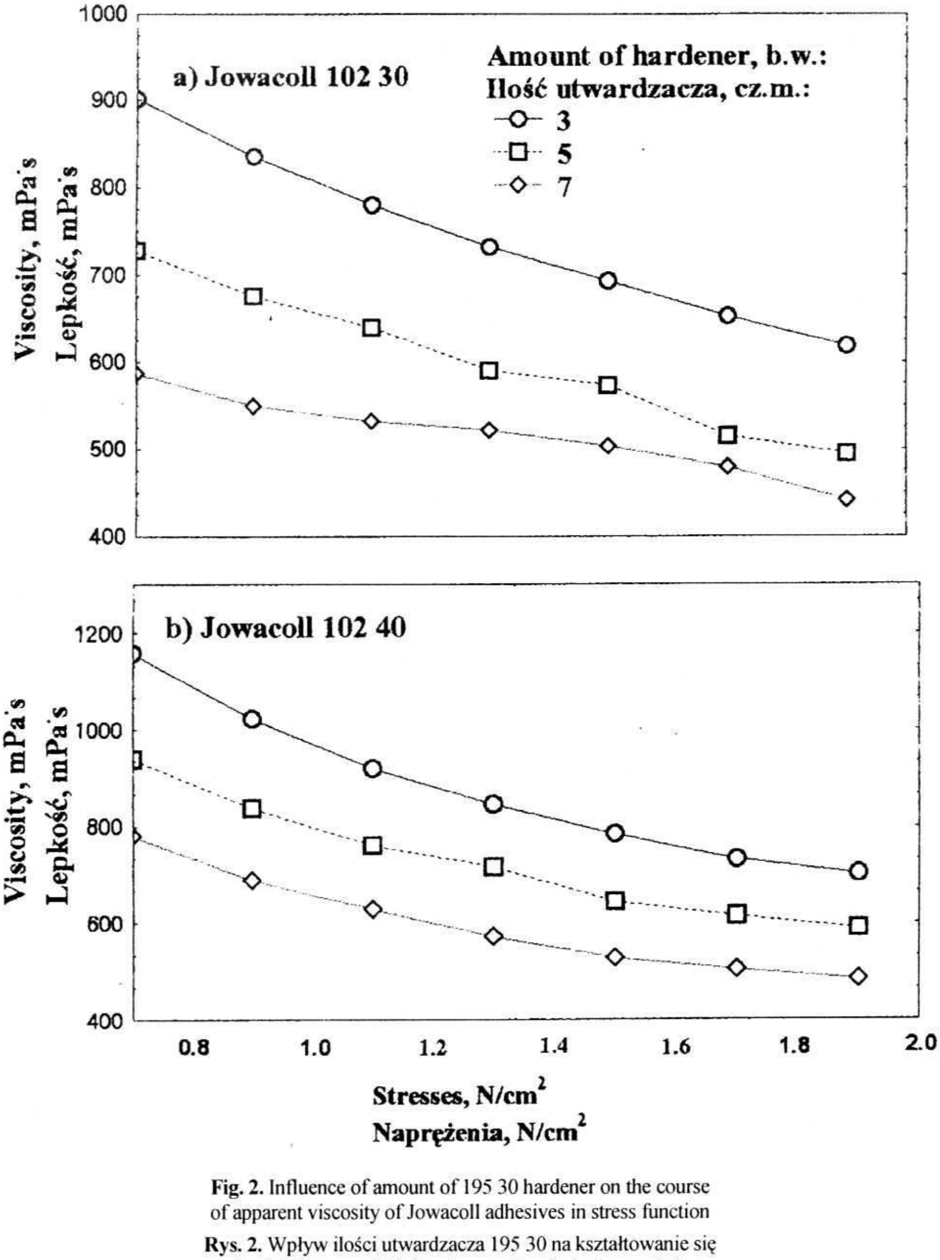

Fig. 2. Influence of amount of 195 30 hardener on the course of apparent viscosity of Jowacoll adhesives in stress function

Rys. 2. Wpływ ilości utwardzacza 195 30 na kształtowanie się lepkości pozornej klejów Jowacoll w funkcji naprężeń

It means that their relative viscosity decreases along with the increase of shear stress. It should be mentioned that in a study by Proszyk, Krystofiak and Tucholska (1995) dedicated to research on the rheological properties of PVAC adhesives conducted with a rheoviscometer with coaxial cylinders it was proved that these adhesives may be numbered among rheostable liquids by concluding that, among others, the experimental data describing the relations as to apparent viscosity as a function of shear stress approximates the Ellis model.

In the table 1 are presented the results of pH value measurements as a function of the amount of hardener in adhesives. Analysis of the data in table 1 leads to the conclusion that an increase of the amount of hardener in the adhesives causes an inconsiderable decrease of the pH values of the adhesives, which, as it was proved in the research on the conventional viscosity, does not affect the time of usability.

Table 1

Tabela 1

Influence of amount of 195 30 hardener on pH value of Jowacoll adhesives

Wpływ udziału utwardzacza 195 30 na odczyn chemiczny klejów Jowacoll

Kind of Jowacoll adhesive Rodzaj kleju Jowacoll	Amount of hardener (% by weight) Ilość utwardzacza (% m/m)			
	-	3	5	7
	pH value Odczyn, pH			
102 30	3.0	2.7	2.5	2.3
102 40	4.9	3.8	3.6	3.4

Table 2 presents the results of open assembly time measurements for adhesives with various amounts of the hardener. Analysis of the data contained in this table indicates that along with increasing amount of the hardener in the adhesives the open time tends to get shorter, which fact may be explained with the decreasing viscosity of the adhesives and the increasing base penetration ability.

Table 2

Tabela 2

Influence of amount of 195 30 hardener on open assembly time of Jowacoll adhesives

Wpływ udziału utwardzacza 195 30 na czas otwarty klejów Jowacoll

Kind of Jowacoll adhesive Rodzaj kleju Jowacoll	Amount of hardener (% by weight) Ilość utwardzacza (% m/m)		
	3	5	7
	Open assembly time (min) Czas otwarty (min)		
102 30	8	5	4
102 40	6	4	3

Evaluation of properties of the adhesives in the form of solidified layers

The studies on the solid content gave interesting results (table 3). Obtained results prove that in the conditions in which the determination was conducted cross-linking of the bonding agent contained in the adhesive took place. Therefore it may be suggested that monomer volatile part of the bonding agent is incorporated into the polymer structure in the hardener environment.

Table 3

Tabela 3

Influence of amount of 195 30 hardener on the solid content in Jowacoll adhesives

Wpływ udziału utwardzacza 195 30 na zawartość substancji stałych w klejach Jowacoll

Kind of Jowacoll adhesive Rodzaj kleju Jowacoll	Amount of hardener (% by weight) Ilość utwardzacza (% m/m)			
	-	3	5	7
	Solid content (%) Zawartość substancji stałych (%)			
102 30	49.27	54.82	52.84	50.00
102 40	49.85	55.32	53.18	50.70

Fig. 3-5 illustrates the results of relative hardness studies of the solidified adhesive layers. An overall evaluation of the results indicates that an increase of the portion of the hardener in Jowacoll adhesives causes inconsiderable downward trends within layer hardness after 72 and 168 h of conditioning. It was not before the lapse of 366 h when an increase in the hardness was observed, which proves that the simultaneous processes of coalescence and hardening of two component adhesives on glass surfaces are prolonged. Together with an increase of the thickness of adhesive layers slight tendencies towards a decrease in the hardness of the layers were observed, which fact can be caused by the influence of the glass surface on the hardness data. At the same time the lower the thickness of the layer applied, the greater the influence of the base on the hardness results. In the context of the aforementioned supposition it may be assumed that cohesion forces in solidified layer are close to one another regardless of the amount of hardener in the adhesives and the thickness of the solidified layers.

Evaluation of the strength and water resistance of the glue lines

In order to conduct a comparative study of the influence of the amount of the hardener in the adhesives on the strength and durability of the glue lines appropriate diagrams were made based on the acquired data (fig. 6 and 7), which present the average results along with PN EN 204 standard. The analysis of this data leads to the conclusion that together with an increase of the portion of the hardener in the adhesives an increase strength and durability is observed. Hardener portion of 5 and 7 parts by weight for 100 parts by weight

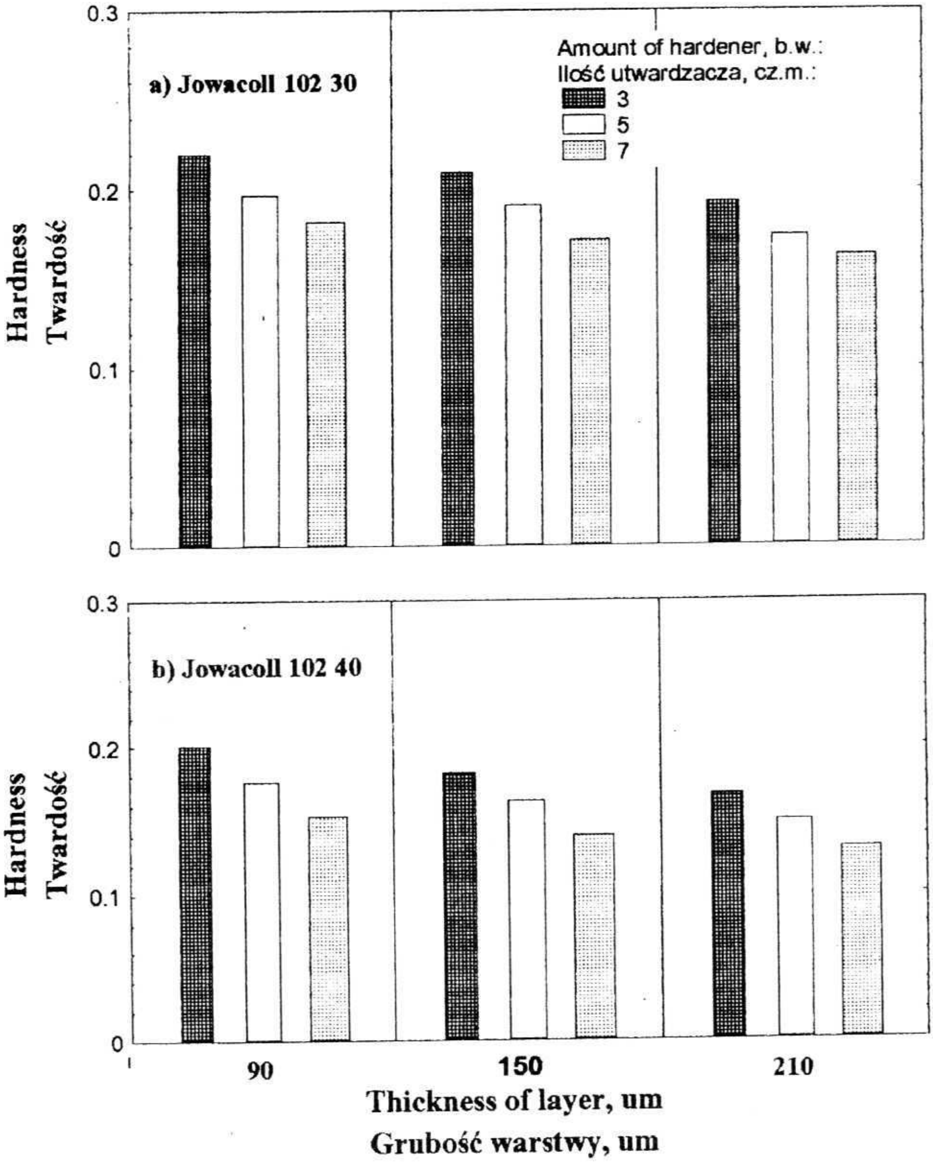

Fig. 3. Influence of amount of 195 30 hardener in Jowacoll adhesive on the relative hardness of solidified layers in thickness function after 72 h of their conditioning

Rys. 3. Wpływ ilości utwardzacza 195 30 w klejach Jowacoll na twardość względną zestalonych warstw w funkcji grubości nałożonej warstwy po 72 h klimatyzowania

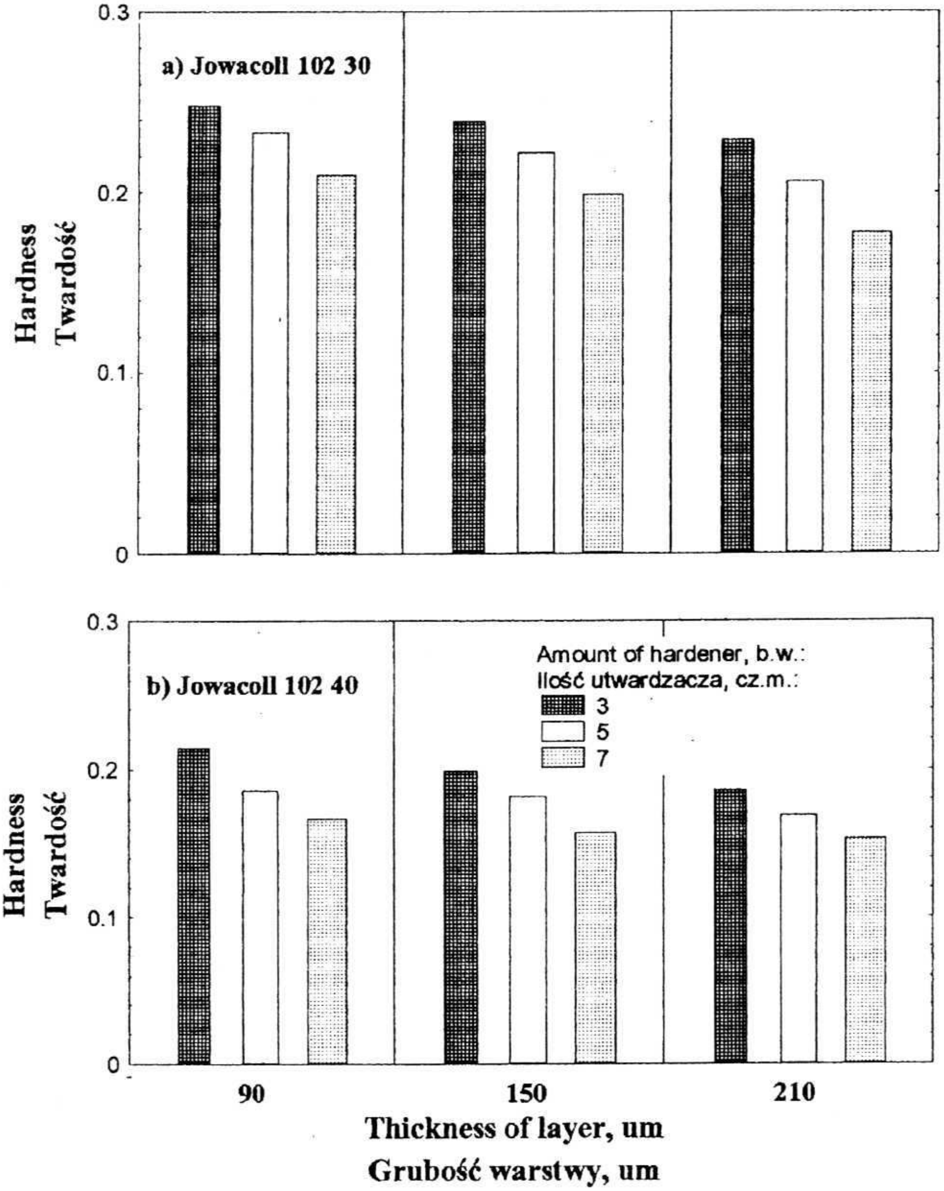

Fig. 4. Influence of amount of 195 30 hardener in Jowacoll adhesive on the relative hardness of solidified layers in thickness function after 168 h of their conditioning

Rys. 4. Wpływ ilości utwardzacza 195 30 w klejach Jowacoll na twardość względną zestalonych warstw w funkcji grubości nałożonej warstwy po 168h klimatyzowania

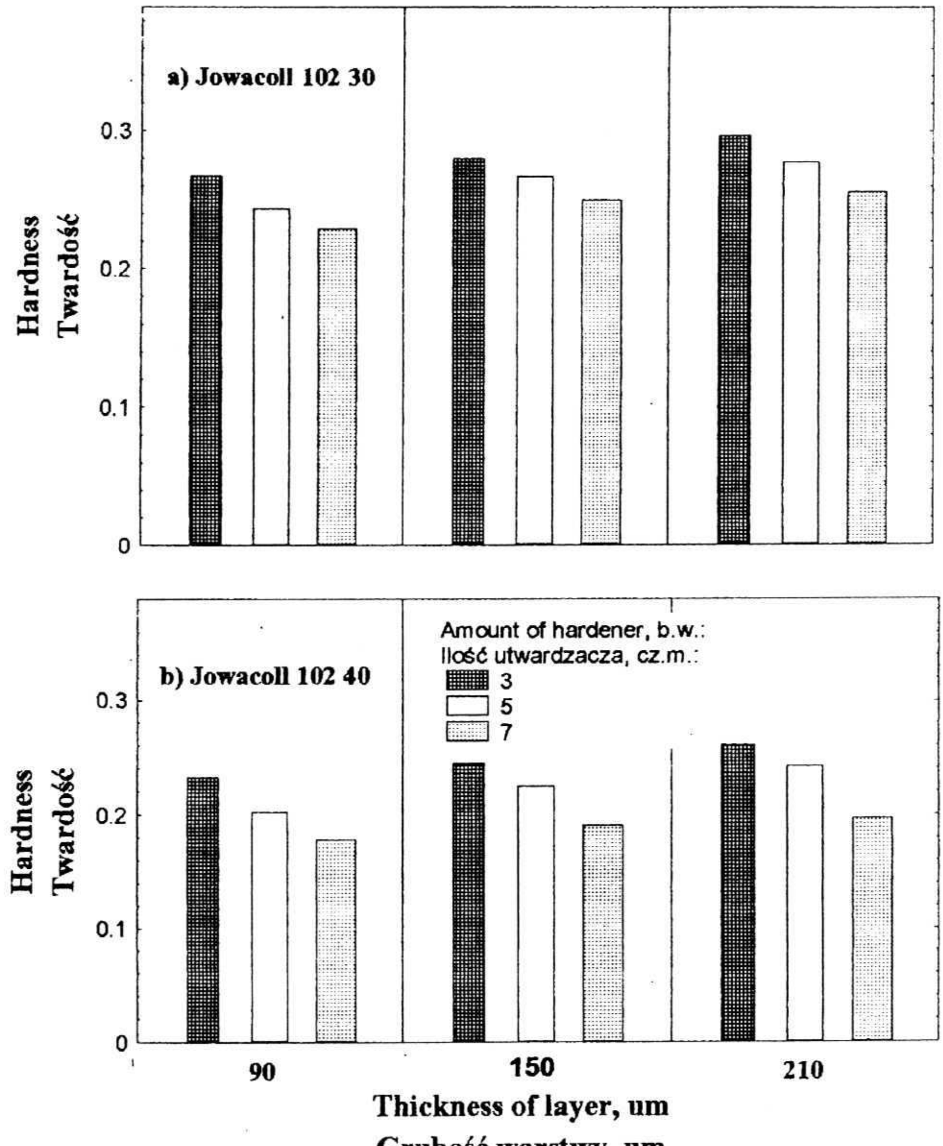

Fig. 5. Influence of amount of 195 30 hardener in Jowacoll adhesive on the relative hardness of solidified layers in thickness function after 336 h of their conditioning

Rys. 5. Wpływ ilości utwardzacza 195 30 w klejach Jowacoll na twardość względną zestalonych warstw w funkcji grubości nałożonej warstwy po 336h klimatyzowania

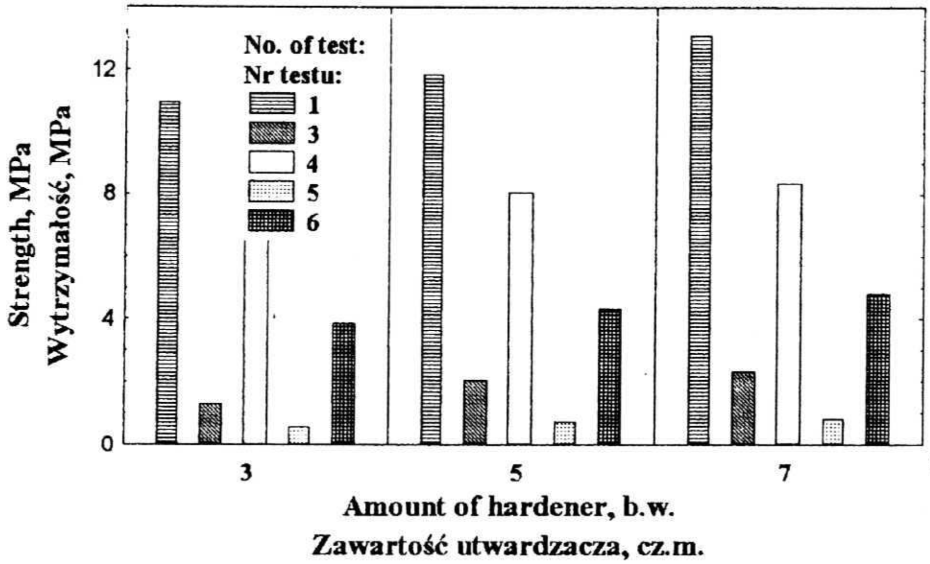

Fig. 6. Influence of amount of 195 30 hardener on shearing strength of glue lines from Jowacoll 102 30 adhesive after selected durability tests accordingly to PN EN 204 standard

Rys. 6. Wpływ ilości utwardzacza 195 30 na wytrzymałość spoin z kleju Jowacoll 102 30 po wybranych testach odpornościowych według normy PN EN 204

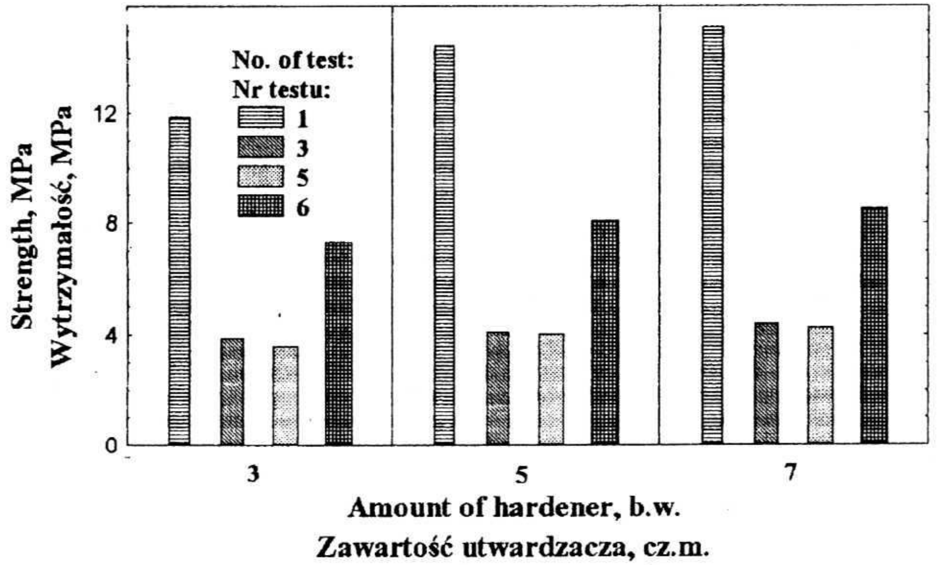

Fig. 7. Influence of amount of 195 30 hardener on shearing strength of glue lines from Jowacoll 102 40 adhesive after selected durability tests accordingly to PN EN 204 standard

Rys. 7. Wpływ ilości utwardzacza 195 30 na wytrzymałość spoin z kleju Jowacoll 102 40 po wybranych testach odpornościowych według normy PN EN 204 of adhesive guarantees that glue lines compliant with D3 durability class for Jowacoll 102 30 and D4 for Jowacoll 102 40 are acquired. At 3 parts by weight portion of the hardener the glue lines did not meet the specified durability classes.

CONCLUSIONS

1. A differentiation of 20% $AlCl_3$ based hardener within the range between 3-7 parts by weight in Jowacoll 102 30 and 102 40 adhesives affects the following properties of those adhesives in the liquid state:

- it insignificantly differentiates the pH value and conventional viscosity of the adhesives without affecting the usability time of the particular adhesives and their rheological properties,

- it differentiates the open assembly time of adhesives, which gets shorter along with an increase in the amount of hardener in the adhesives.

2. Along with the increasing amount of the hardener in Jowacoll adhesives the relative hardness of the solidified layers is reduced respectively after 72 and 168 h of their conditioning and an increase of the relative hardness after 336 h.

3. An increase of the amount of the hardener in the adhesives caused an increase strength and durability of glue lines. At a hardener portion of 5 and 7 parts by weight for 100 parts by weight of adhesive, glue lines represented D3 durability class in the case of Jowacoll 102 30 and D 4 in Jowacoll 102 40 adhesive. A hardener portion of 3 parts by weight did permit obtaining the specified durability classes of the glue lines according to PN EN 204 standard.

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REFERENCES

Boehme Ch. (1993): Belastungsprüfungen an Montageklebungen mit Buche und Meranti unter definierten Klimaeinwirkungen. Holz Zbl. 119 (100): 1553-1554.

Boehme Ch. (1995a): Load test of adhesive assembly bonding under defined climatic conditions with beech and meranti. Holzforschung 49 (2): 158-162.

Boehme Ch. (1995b): Vorbehandlung von Holz-schleifen oder finieren. Adhäsion 39 (5): 36-39.

Głogowski M. (1996): Kleje i klejenie drewna w produkcji okien. Materiały Budowlane 22 (4): 31-34.

Gos B. (1990): Untersuchungen zur Erhöhung der Wasserresistenz von Klebschichten aus Polyvinylacetat-Klebstoffen. Holztechnologie 30 (2): 77-79.

Gos B. (1996): Wybrane kleje polioctanowinylowe do klejenia drewna warstwowego z tarcicy. Sympozjum Naukowe pt. Drewno i materiały drewnopochodne w konstrukcjach budowlanych. Referaty. Szczecin-Międzyzdroje: 89-95.

Gos B., Jaworski Z. (1995): Wpływ sposobu nanoszenia wybranych klejów polioctanowinylowych na wytrzymałość spoin klejowych. Przemysł Drzewny 46 (2): 23-24.

Gos B., Kuciński S. (1995): Modyfikacja kleju polioctanowinylowego (Wikol). Przemysł Drzewny 46 (1): 25-27.

Homanner A. (1991): Einfluss der Verleimungsart bei der Herstellung der Prüfkorper für die Untersuchung von PVAC-Leimen. Adhäsion 35 (9): 36-39.

Homanner A. (1993): Effect of join assembly and preparation of the wood test pices on test results obtained with PVAC adhesives. Kunstharz Nachrichten 28: 30-34.

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., Bernaczyk Z., Krystofiak T. (1995): Kleje i technologie klejenia w meblarstwie. Cz. II. Kleje montażowe. Materiały Seminarium nt. Jakości w meblarstwie oraz stanu badań i normalizacji. NOT SITLID w Poznaniu: 97-104.
Proszyk S., Biniek P., Krystofiak T. (1997): Badania wytrzymałości spoin z dwuskładnikowych klejów PVAC przy wybranych szybkościach obciążeń. Przemysł Drzewny 48 (1): 9-12.
Proszyk S., Krystofiak T., Tucholska B. (1995): Wpływ temperatury na właściwości reologiczne wybranych klejów PVAC. PTPN. Wydz. Nauk Techn. Prace Komisji Technol. Drewna. Poznań 14: 57-64.
Sedliačik M., Ružinska E., Sedliačik J. (1993): Študium interakcie dreva a katalyzovanych PVAC disperzii. Zbornik referátov. XI. Sympozium. Pokroky vo výrobe a použiti lepidiel v drevopriemysle. Zvolen: 1-12.

BADANIA WŁAŚCIWOŚCI DWUSKŁADNIKOWYCH KLEJÓW PVAC UTWARDZANYCH CHLORKIEM GLINU

Streszczenie

Celem pracy było poznanie wpływu ilości utwardzacza w postaci 20% roztworu $AlCl_3$ na właściwości klejów PVAC w stanie ciekłym, w postaci zestalonych warstw i spoin klejowych.

Do badań użyto 2 klejów PVAC o nazwach handlowych Jowacoll 102 30 i 102 40, do których dodawano utwardzacz w ilościach odpowiednio 3, 5 i 7 cz.m. w stosunku do 100 cz.m. kleju. W stanie ciekłym określono kształtowanie się lepkości umownej klejów, badano właściwości reologiczne, odczyn chemiczny i czas otwarty. Dla zestalonych warstw określono zawartość substancji stałych oraz twardość względną, zaś dla spoin badano wytrzymałość i wodoodporność według PN EN 204.

Na podstawie wyników przeprowadzonych badań stwierdzono, m.in., że zwiększanie ilości utwardzacza w klejach Jowacoll powodowało wzrost wytrzymałości i wodoodporności uzyskiwanych spoin. Przy zawartości utwardzacza w ilości 5 i 7 cz.m. na 100 cz.m. kleju, spoiny wykazywały klasę odporności D 3 w przypadku kleju Jowacoll 102 30 i D 4 dla kleju Jowacoll 102 40. Zawartość utwardzacza w ilości 3 cz.m. nie pozwalała na uzyskanie wyszczególnionych klas odporności spoin według kryteriów PN EN 204.

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