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Usage of Ecologically Perspective Adhesives for Wood Bonding

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Abstract **- Hot melts based on high density polyethylene, polyurethane textile fibre waste and unmodified and modified sulphate lignin adhesives for wood veneer bonding are used. For intensification of interfacial interaction and improving water resistance modifier 4.4 ^{1} diphenylmethane diisocyanate is utilized. Shear strength and water resistance investigations show possibility of usage presented adhesives for wood veneer bonding and different plywood production.**

Key words: **lignin, polyurethane, polyethylene, adhesives, birch wood veneer, plywood, shear strength, water resistance**

I. INTRODUCTION

Plywoods are one of the most important laminated wood composite materials. At present for production of different kinds of plywoods mainly relies on phenol, urea, melamine formaldehyde resins and their modification products. Formaldehyde is a human carcinogenic and petrochemicals are not renewable [1]. During last decades glues based on thermoplastic hot-melts like polyolefines, polyvinyl alcohol, polyurethanes etc. have become very popular. They are more environmentally friendly than formaldehyde containing resins [2, 3], but these glues, hot-melts are not entire biodegradable. Now environmental protection requirements are very strong therefore currently investigated adhesives used for wood bonding are derived from microbial extra cellular polysaccharides, starch, soy protein, and lignin, tannins which are generally non-toxic, absolutely biodegradable and produced from renewable resources [3, 4]. These materials are able to use also as additives for phenol-formaldehyde, urea-formaldehyde, polyurethanes and other thermosetting glues what considerably diminish toxicity of glues, but physic-mechanical properties, for example shear strength maintain on the same level. Often for strengthening of adhesive layers glue are modified with extenders like wood flour etc. [5]. At the same time extenders decrease adhesive toxicity. Authors [6] for wood bonding use glues from mixtures of diphenylmetane diisocyanates with gluten, tannin or maize starch up to 20 %. Modified emulsifiable diisocyanate gives plywood with better strength and wood failure than glue formulations with nonemulsifiable diisocyanate. The aim of our work was to investigate shear strength and water resistance of three layers plywood glued with adhesives based on diphenylmethane diisocyanates and different kinds of lignins. As reference samples single lap joints of birch wood veneer joined with hot melts from high density polyethylene and polyurethane textile fibres waste were used.

II. MATERIALS AND METHODS

In all experiments, a polish birch (Betula verrucosa sort) veneer with thickness of 1,5 mm, made at the „Latvijas Finieris” enterprise, was used as a substrate. The initial moisture content (determined by thermo gravimetric method) in the veneer was 5-6 wt. %. As adhesives were used high density polyethylene (HDPE) of trade mark 276-73 (MFI 0,8 g/10min., P 2,16 kg, T 190^{0}C), polyurethane textile fibre waste (PUW) (MFI 6,4 g/10min, P 2,16 kg, T 230 ^{0}C), company BASF polyisocyanate grade 4.4^{1} diphenylmethane diisocyanates (DIC) with content of isocyanate groups 31,3 % (DIN 53 185), sulphate lignin (LS), and modified sulphate lignin (NLS), presented by Latvia State Wood Chemistry Institute Lignin Laboratory scientists. Adhesive films (0,3-0,4 mm thick) were formed by compression moulding (T 140 and 180 ^{0}C, P 1-2 MPa, t 3 min.) from HDPE and polyurethane textile fibre waste. The gluing of the birch wood veneer/polymer adhesive/birch wood veneer overlap joints were performed in hydraulic press (t 1-10 min. + 3min. preheating) at different temperatures (140, 160, 180, 200 ^{0}C) and pressure 1-8 MPa. The thickness of the adhesive layer after application of contact pressure was 0,1 mm. The geometry of specimens as in [2]. DIC layers were covered on the veneer surface by painter brush, then dried at room temperature 3 min. and overlap joints made as in [2]. Shear strength of single overlap joints was examined and water resistance of plywood’s samples were tested by EW 314-1:2 standards as in [2].

III. RESULTS AND DISCUSSION

Previous investigation [2] showed that for wood veneer bonding very perspective glues are hot melts based on low density polyethylene (LDPE), ethylene vinyl acetate copolymers (EVAC) with different content of vinyl acetate groups, polypropylene (PP) with different fluidity (MFI) and modified with maleated polypropylene (MAPP) PP. These hot melts during solidification and exploitation processes do not educe dangerous products. Made single overlap joints wood veneer/polymer hot-melt/wood veneer adhesive strength (σ) is, for example for LDPE containing samples 4,0-5,0 MPa, for EVAC 3,5–4,5 MPa, but for PP 8–10 MPa, that is more higher than for industrial plywood glued with phenol-formaldehyde (PF) resins (σ=3,66 MPa). These results confirm idea that adhesive strength in laminated wood systems note not only interfacial interaction intensity between wood and adhesive layers, but also own glue cohesive strength. In our case it is modified PP hot melt. It means that in wood containing composites (plywoods) strengthen glue layer is necessary. Adhesive strength after moisture absorption does not decrease, but improve. This phenomenon contradicts the well-known fact that presence of water molecules in composites containing wood leads to a plasticizing effect [8,9] which reduces strength properties and raises the deformability. Wood composites adhesive strength mainly are noted by mechanical adhesion, because wood surface is rather soft and adhesive molecules can penetrate into the surface of wood at the depth of 40-50 mkm [2,10]. Utilization of biodegradable hot melt adhesives like polylactic acid and benzylated lignocellulose fibres for wood veneer bonding [7] showed that single overlap joints shear strength is good (4 -7 MPa), but water resistance is worse than in the case of synthetic thermoplastic hot melt glues [2]. This fact indicates that natural biodegradable hot - melt glues have rather weak hydrolytic stability and presence of water diminishes adhesive layer mechanical properties. Lignins, which are recommended as ecologically perspective adhesives for wood composites [3,9] give not so good results [7]. Shear strength of single overlap joined samples is 2,2-2,8 MPa. Authors [3] also note that pure lignins have not strong adhesive activity against wood therefore use of interfacial interaction activators is necessary. One of the best of them is diphenylmethane diisocyanate [6]. We tried to improve interaction between lignin and wood using 4.4[1] diphenylmethane diisocyanate (DIC). Results of these experiments are presented in Fig.1. Kinetic curves show that optimal technological parameters for wood veneer bonding with DIC and DIC+NLS adhesives are 5-7 min time of contact and temperature 180 ^{0}C. Shear strength of glued veneer is 6,6 MPa for DIC and 7,1 MPa for DIC+NLS. Obviously, usage of DIC interlayer causes considerable increase of lignin adhesive activity in comparison with pure lignin (σ 2,5-2,8 MPa) [7].

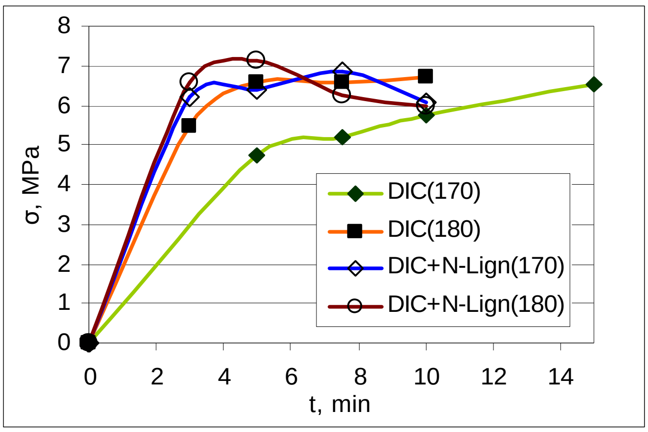

Fig.1. Relationship between shear strength (σ) of single lap joints of laminated systems birch wood veneer/ polymer adhesive/ birch wood veneer and contact time. Adhesives: 4. 4 [1] diphenylmetane diisocyanates (DIC) and DIC + NLS.

Water resistance test results are presented in Table 1. From these results we can see that first and second boiling tests endure samples glued with HDPE, PUW, DIC and DIC+NLS, but do not endure samples with DIC+LS adhesive. Specimens water resistance tests have passed if shear strength of samples maintains more than 1,8 MPa after 4 + 4 h boiling (1st class plywood) and 1,0 MPa (3rd class plywood).after 72 h boiling in water.

TABLE 1

WATER RESISTANCE TEST RESULTS OF OVERLAP JOINED VENEER SAMPLES

Adhesives	Shear strength, MPa		
	Dry	After 4h boiling +16h drying+ 4h boiling	After 72 h boiling
DIC	6,6	4,0	4,3
DIC+NLS	7,1	2,6	1,8
DIC+LS	6,3	1,0	0
HDPE	7,6	2,3	2,1
PUW	5,6	2,2	1,4

Samples bonded only with DIC show the best results (maintained shear strength values are about 4,3 MPa), follows HDPE (2,1-2,3 MPa), PUW (1,4-2,2 MPa), but for DIC+NLS σ=1,9-2,7 MPa. It means that wood veneer/DIC+NLS/wood veneer HDPE and PUW containing systems are able to use for outdoor application, but plywood glued with DIC+LS adhesive only for indoor utilization.

For comparison it was interesting more properly examine wood veneer bonding with high density polyethylene (HDPE) (Fig.2,3) and polyurethane fibre waste (PUW) hot melts (Fig.4) because they have high water resistance (see Table 1) and good physical, mechanical properties relative with lignin [3].

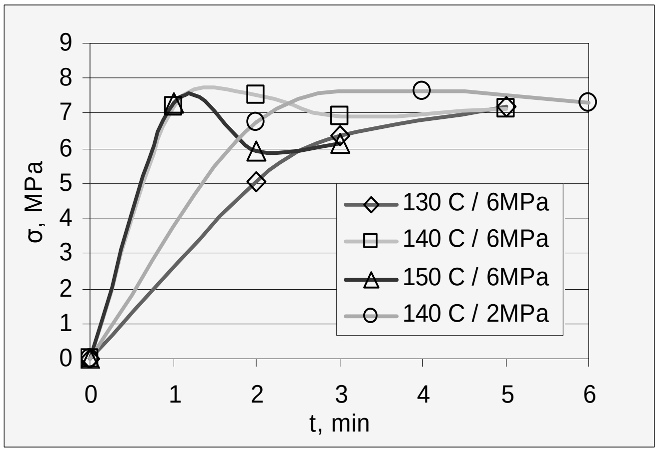

Fig.2. Relationship between shear strength (σ) of single lap joints of laminated systems birch wood veneer/ high density polyethylene/ birch wood veneer and contact time. Contact temperatures 130, 140, 150^0 C and pressure 2 and 6 MPa.

Fig.2,3 show that single lap joints shear strength increases with increase of contact time and temperature (Fig.2) and pressure (Fig.3). Maximum σ values (7,6 MPa) are reached at temperature 140 ^{0}C, time of contact 3-4 min. and pressure 2 MPa which are greater than in cases of DIC and DIC+NLS adhesives. In the same time good water resistance is observed (see Table1). Therefore hot melts based on high density polyethylene are perspective for wood veneer bonding [2].

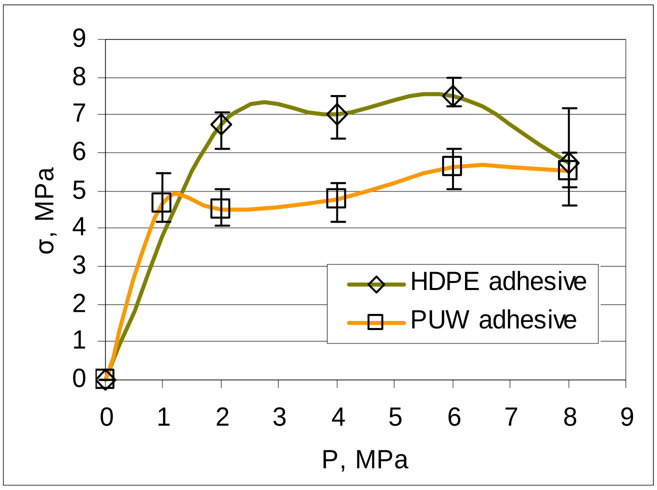

Fig.3. Relationship between shear strength (σ) of single lap joints of laminated systems birch wood veneer/ polymer adhesive/ birch wood veneer and contact pressure. High density polyethylene (HDPE) contact temperature, 140 ^{0}C and time 2 min, polyurethane fibre waste (PUW) temperature 200^0 C, time 3 min.

Recycling and utilization of synthetic polymer waste is actual problem. A lot of waste forms during textile materials manufacturing processes. The main problem to utilise waste is different finishes on the surface of textile fibres or fabrics. Technological parameters influence on shear strength of adhesive joints glued with untreated PUW is presented in (Fig.4).

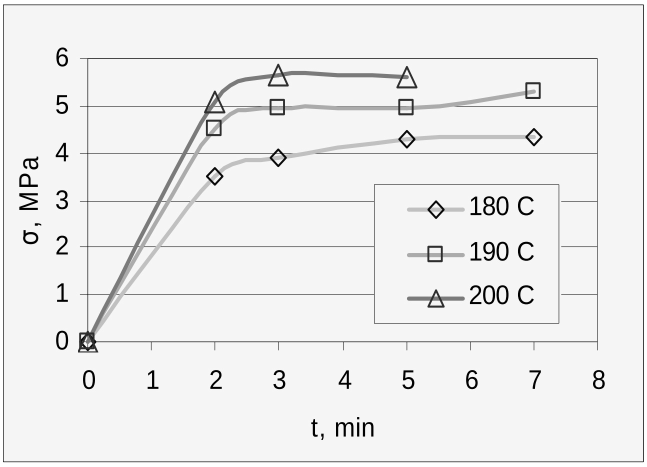

Fig.4. Relationship between shear strength (σ) of single lap joints of laminated systems birch wood veneer/polyurethane fibre waste adhesive / birch wood veneer and contact time. Contact temperatures 180, 190, 200 ^{0}C and pressure 6 MPa.

Kinetic curves show that shear strength of overlap joints increases with increase of contact time and temperature. Maximum of σ are reached at temperature of contact 200 ^{0}C and time of contact 2-3 min. Numerical values of σ depends on temperature and vary from 4,35 MPa up to 5,61 MPa. It is much more than for industrial plywood glued with phenol formaldehyde resins. Textile fibres and fabrics always contain different finishes which could hinder adhesive interaction on surface polyurethane hot melt and wood veneer. Therefore we prepared PU adhesive films from PUW treated with different solvents. Results of these experiments are presented in Fig.5.

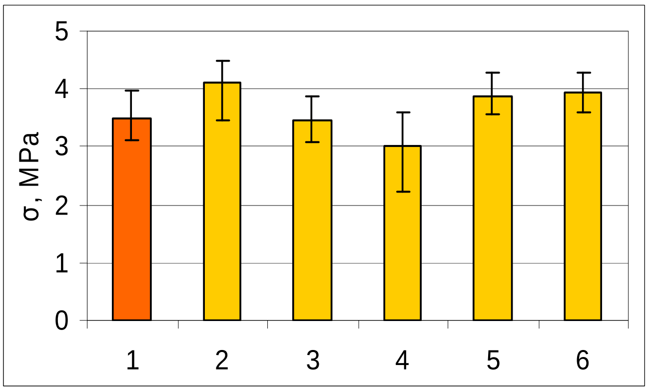

Fig.5. Dependence of shear strength of single lap joints of laminated systems birch wood veneer/polyurethane fibre waste adhesive/birch wood veneer from fibre waste treatment method. Contact temperature 180^0 C, time 2 min. and pressure 6 MPa.
1-adhesive films (AF) processed from crude fibres, 2-AF processed from crude fibre waste and then refined with acetone, 3-AF from fibres washed with water, 4-AF from fibres washed with water and acetone, 5-AF from fibres treated with acetone, 6-AF from fibres washed with boiling water.

Gained shear strength values (Fig. 5) change from 3,5 MPa up to 4,1 MPa (contact temperature 180^{0}C, pressure 6 MPa and time 2min.). The best results show adhesives made from treated films (2) and AF processed from textile fibres waste treated with acetone (5) and boiling water (6). Difference between reached σ values of untreated and treated adhesives is not significant (about 14,1 %), therefore untreated polyurethane textile fibre waste use for wood veneer bonding is possible. This opinion confirms good water resistance of samples (see Table 1). Obviously in this case also the main role for reaching high adhesion strength of samples play mechanical adhesion between hot melt molecules and wood veneer surface [10].

IV. Conclusions

The investigations of shear strength of overlap joints birch wood veneer/polymer adhesive/birch wood veneer joined with hot-melts based on high density polyethylene, polyurethane textile fibres waste and unmodified and modified lignins adhesives show that:

1. All investigated adhesives are possible to use for wood veneer bonding.
2. Use of 4. 4 ^{1} diphenylmethane diisocyanate as interfacial activator promote the increase of shear strength and water resistance of systems.
1. 3. Plywood made from birch wood veneer glued with high density polyethylene, polyurethane textile fibre waste hot - melts, 4.4^1 diphenylmethane diisocyanate and 4.4^1 diphenylmethane diisocyanate + modified lignin are useful for outdoor conditions, but plywood glued with 4.4^1 diphenylmetane diisocyanate + unmodified lignin only for indoor applications.

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Uģis Grīnbergs, Jānis Kajaks, Skaidrīte Reihmane. Ekoloģiski perspektīvu adhezīvu izmantošana koksnes savienošanai
Darbā veikti pētījumi par videi draudzīgāku adhezivu izmantošanas iespējām koksnes līmēšanai līdz šim bieži lietoto termoreaktivo fenola-formaldehīda līmju vietā. Konkrēti, bērza finiera savienošanai izmantoti līmes-kausējumi uz augsta blīvuma polietilēna un poliuretānu šķiedru tekstilapstrādes atlikumu bāzes, kā arī nemodificēta (LS) un modificēta lignīna (NLS) adhezīvi un to maisījumi ar diizocianātu. Adhezīvās mijiedarbības starp finiera loksnēm un iegūtā saplākšņa ūdens izturības palielināšanai izmantots starpfāzu modifikators 4,4[1] difenilmetāna diizocianāts (DIC). Bīdes stiprības un ūdens izturības pētījumu rezultāti, kas iegūti sagraujot finiera pārlaidsavienojumu adhezīvos paraugus, parāda, ka visus izmantotos adhezīvus ir iespējams pielietot finiera salīmēšanai un dažādas kavalitātes saplākšņu ražošanai. DIC izmantošana finiera salīmēšanai dod ievērojamu adhezīvās stiprības un saplākšņa ūdens izturības pieaugumu. Sajaucot DIC ar nemodificētu lignīnu vai modificētu lignīnu un izmantojot tos finiera līmēšanai, novēro atšķirīgus rezultātus. Pētījumos konstatēts, ka pirmo adhezīvu maisījumu sistēmu (DIC+LS) var izmantot saplākšņos, kas paredzēti tikai iekšdarbiem, jo tiem nav pietiekami laba ūdens izturība, bet otrie adhezīvu maisījumi (DIC+ NLS) piedod saplākšņiem lielisku ūdens izturību, kas ļauj tos izmantot arī āra apstākļos.

Угис Гринбергс, Янис Каякс, Скаидрите Рейхмане. Использование экологически перспективных адгезивов для соединения древесины
В работе сделана попытка применить природе более дружных адгезивов-клеев для склеивания древесины вместо применяемой в настоящее время в промыщленности произвдства фанер. Для соединения березового шпона применены клеи расплавы на основе полиэтилена высокой плотности, полиуретановых волокнистых отходов текстильного производства и адгезивы немодифицированных и модифицированных лигнинов. Для интенсификации межфазного взаимодействия использован модификатор 4.4[1] дифенилметан диизоцианат (ДИЦ). Исследования прочности на сдвиг и водостойкости нахлесточных образцов фанер показали возможность применения всех представленных адгезивов для склеивания березового шпона и получения различных промышленных фанер. Адгезивы из чистого и модифицированного лигнина не дают ощутимый прирост сдиговой прочности и водостойкости склеенной фанеры. Напротив, использование ДИЦ в качестве клея-адгезива позволяет значительно повысить адгезионную прочность фанер и улудшить их водостойкость. Применение в качестве клея смеси ДИЦ + немодифицырованный лигнин (ЛС) и ДИЦ + модифицированный лигнин (НЛС) соотвественно дают не однозначные результаты. Первые смеси адгезивов позволяют получать фанеру для использования только внутри помещений а склеивая листы древесины второй смесью клеев получается водостойкая фанера используемая также для наружных работ.