Impact of Aliphatic Isocyanates to PVA Dispersion Gluing Properties

Darius MINELGA¹*, Kristina UKVALBERGIENĖ¹, Valdas NORVYDAS¹, Gintaras BUIKA², Mindaugas DUBININKAS²

¹ Department of Wood Technology, Kaunas University of Technology, Studentų St. 56, LT-514241 Kaunas, Lithuania ² Department of Organic Chemistry, Kaunas University of Technology, Radvilenų pl. 19, LT-50254 Kaunas, Lithuania

Received 11 September 2009; accepted 04 July 2010

Poly(vinyl acetate) is used as adhesive for natural wood bonding. Modifying PVA dispersion it is possible to improve its bonding characteristics. The paper presents studies of polyvinyl acetate dispersion modified with water dispersible crosslinkers RHODOCOAT WAT, XWAT-3, XWAT-4, based on aliphatic isocyanates. In this research used isocyanates have positive property to emulgate in water; therefore it is very easy to add them into various polymers prepared on water basis. These polymers increase heat resistance and resistance to humidity while applying other adhesives. For the studies beech wood pieces of 12 % moisture content and 300 mm length, 150 mm width and 5 mm thickness respectively were chosen. Plastered with modified PVA dispersion samples were compressed in the hydraulic press " Π -472B", keeping them for 30 minutes and compressing with 0.8 MPa operating pressure. Three temperatures – 20, 60, 125 °C – were used for gluing. The glued pieces were cut into samples of b = 20 mm width and $l_1 = 150$ mm length and tested in an universal tensile machine "P-0.5". It was found that PVA modification with aliphatic isocyanates improves resistance to water of glued joints and are perspective for further research.

Keywords: PVA dispersion, aliphatic isocyanates, modification, wood bonding.

INTRODUCTION

Polyvinyl acetate (PVA) is clear, colourless thermoplastic polymer. Its molecular weight varies from 20 000 to 100 000. Polymer of lower weight melts easily and becomes brittle in cold. Products with higher molecular weight melt at temperatures from 50 $^{\circ}$ C to 100 $^{\circ}$ C.

According to its physical nature, polyvinyl acetate dispersion is $0.05 \ \mu\text{m} - 3 \ \mu\text{m}$ particles of polyvinyl acetate polymer suspended in water [1]. It is a common practice in industry to modify polyvinyl acetate dispersions with plasticizers – compounds that change mechanical properties of polymer by reducing temperature of polymer vitrification. These polymers form slicks at lower temperatures [2]. When dispersion dries, globules merge, creating a homogeneous elastic slick.

PVA dispersion generally is used for natural wood bonding, as well as leather, fabric and paper. It is even used for products such as armoured doors, when steel sheet is pasted with natural wood [3]. One of the requirements for glued materials is to absorb humidity with one of the glued surfaces at least.

PVA dispersion has its own advantages and disadvantages. The main disadvantage of glue seam is non-resistance to water, heat and cold. In order to remove these disadvantages, adhesives are modified. Recent literature gives the researches on the dispersion properties improvement. PVA dispersion can be modified with formaldehyde resin, adding 10% - 30% of it. This helps to get a wide range of adhesives with different exploitation properties [3]. Melamine-carbamide-formaldehyde pitches are also used for modification in order to increase resistance to humidity and to reduce creep [4]. Dispersion

is modified with acrylic acid and vinyl acetate copolymer, as well as butyl acrylate copolymer [5, 6]. In order to increase bond, dispersion is modified with tetraethyl orthosilicate, ethyl silicate or organic silicon monomer, acrylate, dibutyl phthalate [7, 8].

One-component isocyanate adhesive systems consist of chains with isocyanate groups on chain ends or on branching sites. These isocyanates groups can react with the moisture content of the surfaces to be bonded and are hardened system forms from theis addition reaction [9].

Other one-component isocyanate adhesive systems are used only in such adhesives systems as UF-Resins, PUR adhesives, PRF and MUF fast-setting, one-component PU adhesives, UF- and MUF-adhesives, EMDI resins [10]. Polyvinyl acetate dispersions modified with typical isocyanates are known as emulsion polymer isocyanate (EPI) [11].

Basic industrial diisocyanates used as croslinkers in glue systems are MDI, TDI, HDI and IPDI. Nevertheless, usage of such chemicals has some disadvantages: negative impact on human health as well fast reaction of isocyanate groups with water which may cause rather poor crosslinking between polymers in water based glue systems. In order to solve mentioned issues self emulsified isocyanate crosslinker WAT was used for modification of polyvinylacetate dispersion. In industry such two-component adhesives can be produced in many ways to give the optimal performance with respect to water resistance, curing speed etc. Nevertheless, no information about usage of WAT aliphatic isocyanates for polyvinylacetate dispersion modification was found.

The aim of this study is to determine how PVA dispersion modified with aliphatic isocyanates changes bond strength and what kind of humidity resistance they provide to the glued compound.

^{*} Corresponding author. Tel.: +370-37-353863; fax: +370-37-353989. E-mail address: *darius.minelga@ktu.lt* (D. Minelga)

MATERIALS AND METHODOLOGY

For the study, beech wood pieces of 12 % moisture content were cut into samples with 300 mm length, 150 mm width and 5 mm thickness respectively.

Prior to gluing wood surfaces are prepared, i. e. they are refurbished with abrasive paper, the grain of which is 150 according to FEPA standard. Then samples are plastered with the analyzed modified dispersion and compressed in the hydraulic press " Π -472B", keeping them for 30 minutes and compressing with 0.8 MPa operating pressure. Three temperatures – 20, 60, 125 °C – were used for gluing. Glued pieces were cut into samples of b = 20 mm width and $l_1 = 150$ mm length (Fig. 1). Symmetric cuts in the samples limit testing length to $l_2 = 10$ mm.

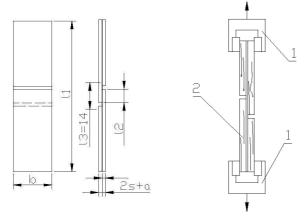


Fig. 1. Sample measurements and fixation in the grips: b - sample width; l1 - sample length; l2 - testing surface length (10 mm); l3 - width of used adhesive area; s - sample thickness, 1 - grip; 2 - sample

On the base of dispersion, PVA DP51/10 and PVA D51 adhesives were made. Various amounts of modifying additives were added to the adhesives. PVA DP51/10 is plasticized dispersion. Dispersion glued adhesive joint is colourless and almost never breaks when the product is being bend. This type adhesives are used as D2 class adhesives for gluing wood [12]. PVA D51 is unplasticized dispersion.

Aliphatic isocyanates WAT, XWAT-3, XWAT-4 were used in the research. They are harmless and rather cheap. Isocyanates differ in their chemical properties: viscosity and amount of isocyanatic groups (Table 1).

Due to rapid reaction to moisture, the use of prior analysed isocyanates in hydrous emulsions was very complicated. In this research used isocyanates have positive property to emulgate in water; therefore it is very easy to add them into various polymers prepared on water basis. These polymers increase heat resistance and resistance to humidity while applying other adhesives [13]. From 0.25 % to 20 % (of dispersion mass) of analyzed isocyanates were added to the dispersions. 7 days after gluing prepared samples were immersed into a bath with distilled water of 20 °C temperature. Samples were kept in the bath 4 days. Then they were tested splitting along the bond line, as required. This helps to find out whether modifying additive gives D3 water-resistance class for dispersion [14].

Table 1. Technical properties of modifying additives

Element	Viscosity (mPas)	NCO groups (%)	Solids content (approx., %)
WAT	4.000	19.0	100
XWAT-3	1.150	21.5	100
XWAT-4	4.000	18.6	100

Modified adhesive joint strength was tested in universal tensile machine "P-0.5". The sample was fixed in two grips and was pulled to collapse at 50 mm/min speed (Fig. 1).

RESULTS AND DISCUSSIONS

A research was carried out in order to determine dependence of bond strength on the amount and type of modifying additive. For this aim, DP51/10 dispersion was modified with 0.25, 0.5, 0.75, 1 % WAT, XWAT-3 and XWAT-4 additives respectively. Samples were glued with testing dispersion at 20 °C temperature. In order to determine wood bond strength, samples were processed under 3 sequence of standard EN 204 and tested by splitting adhesive line to collapse [15].

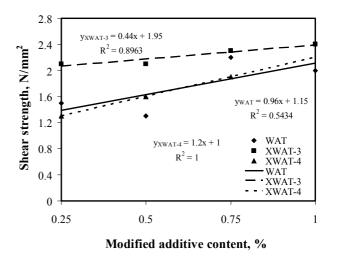


Fig. 2. Dependence of the bond strength of samples glued at 20 °C with PVA DP51/10 dispersion on the type of modifying additive: ◆ - DP51/10 + WAT; ■ - DP51/10 + XWAT-3; ▲ - DP51/10 + XWAT-4

According to the standard requirements for D3 adhesive class, bond strength should be not less than 2 N/mm². During this test without modifying additives required strength is unobtainable neither dispersion DP51/10 nor D51 due to lamination of bond joints. In order to achieve required strength, it was enough to add 0.25 % of the mass of dispersion modifying additive XWAT-3 and 0.75 % WAT and XWAT-4 additives into DP51/10 dispersion (Fig. 2). When D51 dispersion was modified in the same conditions, bond strength was 50 % lower than required by standard EN 204 (Fig. 3).

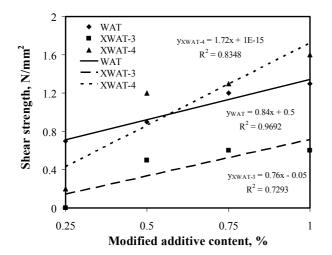
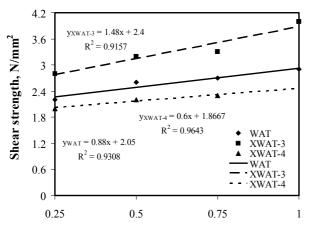


Fig. 3. Dependence of the bond strength of samples glued at 20 °C with PVA D51 dispersion on the type of modifying additive: ◆ - D51 + WAT; ■ - D51 + XWAT-3; ▲ - D51 + XWAT-4

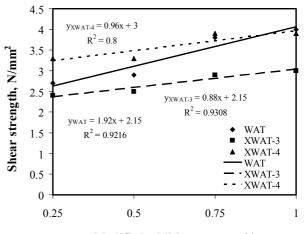


Modified additive content, %

Fig. 4. Dependence of the bond strength of samples glued at 60 °C with PVA DP51/10 dispersion on the type of modifying additive: ◆ - DP51/10 + WAT; ■ - DP51/10 + XWAT-3; ▲ - DP51/10 + XWAT-4

A research was carried out in order to determine dependence of bond strength on gluing temperature. The same modifying additives and content of them were used for gluing samples at 60 °C temperature. The obtained results are presented in Figures 5 and 6. In order to conform the D3 adhesive class in accordance with the standard methodology described in sequence 3, sufficient content of modifying additive was 0.25 % of dispersion mass in all cases. The maximum bond strength gluing at 60 °C temperature was achieved modifying dispersion DP51/10 with additive XWAT-3 and dispersion D51 – with additive XWAT-4.

Bond strength increased when the content of modifying additives was increased. While analyzing obtained results, it was noted that gluing temperature increases bond strength: bond strength increased 1.6 times on the average for samples glued with dispersion DP 51/10 (with any content and type of modifying additive) and for samples glued with dispersion D51 – 3.5 times on the average.



Modified additive content, %

Fig. 5. Dependence of the bond strength of samples glued at 60 °C with PVA D51 dispersion on the type of modifying additive: ◆ - D51+WAT; ■ - D51+XWAT-3; ▲ - D51+XWAT-4

Manufacturer of modifying additives indicates that the increase of gluing temperature even up to 180 °C positively affects bond strength. Indicated temperature can negatively affect external surface of glued wood, i. e. it is potential of wood coal or change in colour. Consequently, tests at 125 °C gluing temperature (often used in wood processing industry) were carried out (Figs. 6, 7). DP51/10 and D51 dispersions were modified with 1 % of dispersion content WAT additive.

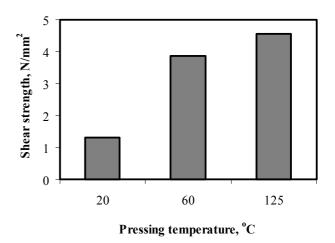


Fig. 6. Dependence of the bond strength of samples glued with DP51/10 + 1 % WAT dispersion on press temperature

When modifying dispersion DP51/10 with 1 % WAT additive (Fig. 6), it was determined that bond strength of 2 N/mm², required by the standard, was achieved or even exceeded at all used gluing temperatures -20 °C, 60 °C, 125 °C.

At 125 C gluing temperature, bond strength was 1.5 times higher than required by the standard. After modifying dispersion D51 (Fig. 7) with the same content of additive and pressing temperatures, it was estimated that at $20 \,^{\circ}$ C gluing temperature bond strength was $35 \,^{\circ}$ smaller than required by the standard. However, when temperature was

increased to 60 °C and 125 °C, bond strength exceeded required 2 N/mm² limit, 1.9 and 2.3 times respectively.

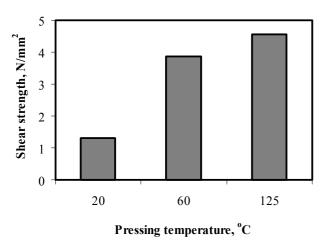


Fig. 7. Dependence of the bond strength of samples glued with PVA D51 + 1 % WAT dispersion on press temperature

This research showed that modifying additives are very perspective in the technology of wood gluing and it is significant to continue the research.

CONCLUSIONS

- It was estimated that PVA dispersions can be used both for hot gluing and cold gluing. However, adequate content of additive WAT, XWAT-3, XWAT-4 respectively, determined during research, should be added for each distinct gluing case.
- 2. It was determined that glued samples' bond strength for PVA dispersions modified with additives depends on chosen gluing temperature: bond strength increases when gluing temperature is increased.
- It was estimated that plasticized dispersion (DP51/10) showed best results after adding modifying additive XWAT-3, while unplasticized dispersion (D51) – after adding additive XWAT-4.

REFERENCES

 Kliger, R., Pellicane, P. J. Shear Properties of Components Used in Stressed-Skin Panels *Journal of Materials in Civil Engineering* 8 (2) 1996: pp. 77–82.

- 2. Petrie, Edvard M. Handbook of Adhesives and Sealants. Copyright by The McGraw-Hill Companies, 2007: p. 1048.
- Frihart, K. Z, Charles, R. Handbook of Wood Chemistry and Wood Composites. Wood Adhesion and Adhesives. Boca Raton, Fla.: CRC Press, 2005: pp. 215–278.
- 4. Volan. Coupling Agents and Adhesion Promoters for Composites, Du Pont Technical Information.
- 5. Poly(vinyl acetate) Adhesive. United States Patent 3619346, 1971.
- 6. Wood Glue. United States Patent 5091458, 1992.
- Qiao, L., Coveny, P. K., Easteal, A. J. Modifications of Poly(vinyl alcohol) for Use in Poly(vinyl acetate) Emulsion Wood Adhesives *Pigment & Resin Technology* 31 (2) 2002: pp. 88–95.
- Erbil, Y. H. Vinyl Acetate Emulsion Polymerization and Copolymerization with Acrylic Monomers. CRC Press, 2000: 336 p.
- Pizzi, A., Mittal, K. L. Handbook of Adhesive Technology, Second Edition, Marcel Dekker, New York, 2003: pp. 913–916.
- Proceedings of the International Symposium on Wood Based Materials: Wood Composites and Chemistry. Sesion 2 "Adhesives and Glueing". BOKU Vienna, Austria, 2002 September.
- 11. TKH-Technical Information Sheet. EPI Adhesives. Publisher: Technical Committee of Wood Adhesives. Düsseldorf, 2007.
- Šipailaitė-Ramoškienė, V., Fataraitė, E., Mickus, K. V., Mažeika, R. The Adhesion, Mechanical Properties and Water Resistance of Vinyl Acetate Copolymer Based Blends *Materials Science (Medžiagotyra)* 9 (3) 2003: pp. 271–274.
- Bassett, David R. Hydrophobic Coatings from Emulsion Polymers *Journal of Coatings Technology* 73 (912) 2001: pp. 43-55.
- 14. Batrak, V. E., Bobyashov, V. W. Sealing of Building Structures *Polymer Science* D 1 (2) 2008: pp. 12–115.
- 15. Lithuanian Standard LST EN 204:2005 "Classification of Thermoplastic Wood Adhesives for Non-structural Applications.

Presented at the National Conference "Materials Engineering'2009" (Kaunas, Lithuania, November 20, 2009)