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Adhesion Properties between Polyvinyl Acetate Dispersion and Ammonia Modified Oak Wood

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It is known that PVA dispersion exhibits very good adhesion with natural wood. However, still remains unclear what adhesion-related changes occur, when the outside factor, i. e. ammonia, affects bonding or what the stability of bonding strength is, when the moisture content of ammonia modified wood increases. The aim of this work was to assess adhesive properties of ammonia modified oak wood and the bonding strength of PVA adhesive and modified wood, and to evaluate suitability and boundaries of PVA adhesive for bonding ammonia modified wood.

To explore phenomena of adhesive interface of polyvinyl acetate (PVA) dispersion and modified wood ammonia treated oak was bonded using PVA dispersions manufactured by JSC "Achema". Non-water resistant "Lipalas D2" and "Lipalas D3" with enhanced water resistance adhesives comparison allowed examining and comparing gluing performance at variable pH and ammonia content in PVA. In addition bonding strength between PVA adhesive and modified oak wood was evaluated and compared with the adhesive bondline properties for unmodified oak wood. Tests performed in accordance with the standard EN 205:2003 revealed remarkably contrasting effects at dry and wet gluing conditions especially for modified oak. The scanning electron microscope (SEM) enabled image confirmation and explanation changes in the PVA adhesive interfaces after contact with modified and untreated oak wood.

Keywords: PVA dispersion, ammonia modified wood, bonding interface/interphase, bonding strength.

INTRODUCTION

In the academic area modified wood has been researched for more than 50 years, whereas, at the industrial scale a profound interest in modified wood innovations has only recently been significantly enhanced [1]. Wood undergoes modification in order to improve its properties and to alter its color, product's aesthetic appearance, or design. In addition, modification also causes changes in wood physical and mechanical properties. In order to modify wood properties, decay resistance and flammability, while creating new wood composites, wood can be modified using thermochemical, chemical, thermomechanical, chemical-mechanical, as well as radiation-chemical methods [3 – 12]. When modified with ammonia, wood that lacks vivid texture gains a wide spectrum of colors, which creates a possibility to successfully compete with types of wood transported from tropical countries. Furthermore, there is an improvement in wood deformation properties, when it is in a moist state, an increase in density, and acquisition of plastic properties [12]. However, in addition to the mentioned advantages, there are a number of disadvantages as well. Ammonia breaks down cellulose micro fibrils into elementary fibrils, as a result of which cell walls contain water soluble materials. Since there is a considerable increase in the hygroscopisity, ammonia modified wood, when kept in the same environment as natural wood, absorbs larger amount of moisture that negatively affects bonding strength [2]. Therefore, when applying wood bonding technologies, it is necessary to take this property of ammonia modified wood into consideration. There are also differences in the micro-structure of unmodified and ammonia modified wood. Due to the anisotropic structure and highly variable surface roughness of wood, the wood bonding process becomes even more complicated. Moreover, different types of wood have different cellular structures, thus it is very difficult to evaluate and model the interaction between adhesives and wood [13].

Adhesives of specific quality are selected based on bonding materials, their application and properties. In the past urea formaldehyde (UF) resins were quite widely used by the industry of furniture and other wood products for wood bonding purposes. The thorough researches, that were performed to assess the composition of components of the UF resin system, their formation in solutions and hardening, allowed determining that urea and formaldehyde have a reversible reaction and the hardened product hydrolyzes and produces free formaldehyde – a substance that can damage health and cause cancer diseases [14]. As a result of this, a tendency can be observed in Europe to replace formaldehyde resin adhesives with more environment friendly polyvinyl acetate (PVA) dispersion, as such adhesives are multipurpose, inexpensive and show good adhesive properties. A number of investigations concerned with bonding of acetylated composites have been performed [15 – 16]. However, there is quite few studies that deal with bonding properties of ammonia modified wood and types of used adhesives [17 – 20]. PVA

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dispersion is known to have excellent adhesion on natural wood. However, it remains unclear what adhesion-related changes occur, when the outside factor, i. e. ammonia, affects bonding or what the stability of bonding strength is, when ammonia modified wood becomes moist. Hence, the objective of this study was to assess adhesive properties of ammonia modified oak wood and the bonding strength of PVA adhesive and modified wood. The study devoted to clarify boundaries of PVA adhesive suitability for bonding ammonia modified oak wood.

MATERIALS AND METHODOLOGY

Tests were performed using defect-free unmodified and ammonia modified European oak wood (*Quercus Robur L.*). Oak wood underwent modification in a special autoclave by applying the method of double vacuum impregnation. The initial moisture content of unmodified wood specimens was 9.5 % and in the case of ammonia modified oak wood it reached 12.5 %.

Test samples for bond strength evaluation were prepared according to LST EN 205:2003 standard. Oak wood was cut into (150×20×5) mm specimens that were bonded to each other (Fig. 1). In total 150 prepared oak wood samples were used for the experiments. Bonding was carried out by using two types of polyvinyl acetate (PVA) dispersions manufactured by JSC "Achema": dispersion "Lipalas D2" (solid content 60 %, pH 6, dynamic viscosity 4.8 Pa·s), which conforms to adhesive Class D2 according to the LST EN 204 standard, and dispersion "Lipalas D3" (solid content 51 %, pH 3.2, dynamic viscosity 5.3 Pa·s), which corresponds to adhesive Class D3 in accordance with the same standard.

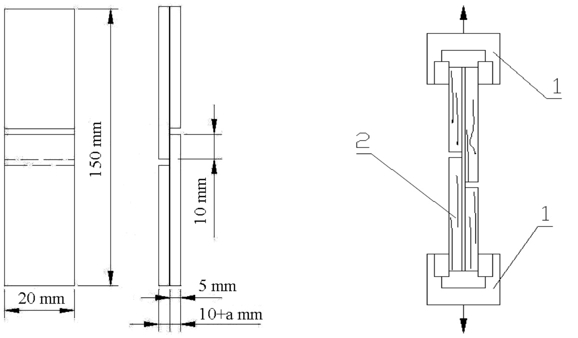


Fig. 1. Specimen dimensions and fixation in the grips: a – thickness of bondline; 1 – grip; 2 – specimen

Prior to the bonding process, wood surfaces were sanded using abrasive paper with grit size F150. Subsequently, specimens were covered with PVA dispersions (consumption (160 ±5) g/m^2) and compressed in a hydraulic press by leaving them for 30 minutes (operating pressure of 0.8 MPa). Samples were bonded at average ambient temperature of 20 °C and relative humidity 63 %. 24 hours later after the bonding was finished, the samples were cut symmetrically, which restricted the testing length up to l_2 = 10 mm (Fig. 1). Then all bonded specimens were conditioned at temperature of (20 ±2) °C and relative humidity of (65 ±5) % for 7 days in order to reduce internal stresses in the bondline and to equally distribute the increased due to adhesive moisture content throughout the whole specimen. After 7 days half of the specimens were tested by splitting them at the bondline until the complete fragmentation of the adhesive joint. The other half of specimens was soaked in distilled water of temperature 20 °C. This allowed determining changes in the strength of the adhesive joint that was exposed to water: by testing specimens bonded with Class D2 dispersion after the 2, 4, 6 and 24-hour soaking duration and those bonded with Class D3 dispersion after the 1, 2, 3 and 4-day soaking duration. The variation coefficient varied within the range of 9.3 % – 19.8 % showing sufficient number of specimens.

Bond strength was tested in a tensile machine P-05 with a feed rate of 50 mm/min. The shear strength *T*, N/mm^2, can be calculated by using the following expression:

$$T = \frac{F_{\max}}{l\,B}\,, \qquad (1)$$

where $F_{\max}$ is the maximum force, N; *B* is the width of tested bonded surface, mm, *l* is the length of tested bonded surface, mm.

The scanning electron microscope (SEM) FEI Quanta 200 FEG was used for the micro scale estimation of the hardened bondline interfaces. After the bonding, specimens conditioned for 14 days and then (2×2×2) mm segments cut out so that the adhesive bondline would remain in the centre for the imaging in the SEM.

For evaluation ammonia content on adhesive Ph various mass rate (1 % to 6 %) of ammonia 25 % water solution applied to the PVA dispersion. This solution possessed an average molar mass 35, density at 20 °C 907 kg/m³, and 11.7 pH. Adhesive dispersion pH tested using pH-meter pH-121.

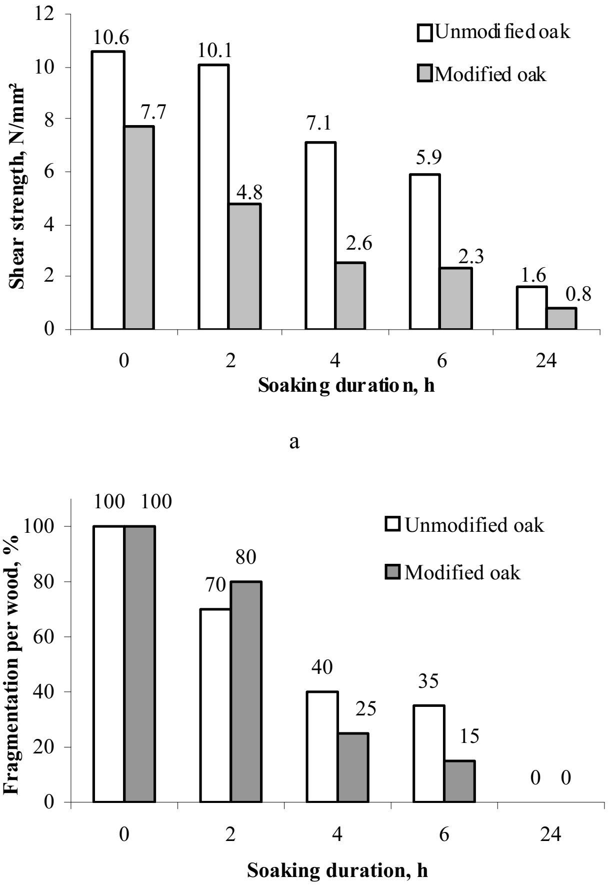
Afterwards the shear strength was evaluated subject to the ammonia amount in the dispersion according to the LST EN 204:2002 standard part 2.

RESULTS AND DISCUSSIONS

The bonding of unmodified wood and ammonia modified oak wood allowed assessing the resistance of the adhesive bondline of water resistant dispersion "Lipalas D2". First, tests were performed on dry bonded specimens. Afterwards, specimens were soaked in water for 2, 4, 6 and 24 hours. The resistance of the adhesive bondline was tested after each soaking period (Fig. 2, a).

Figure 2 shows that as the duration of exposure to water tends to increase, the bonding strength decreases in the case of both unmodified wood and modified oak wood. Fragmentation in relation to wood (Fig. 2, b) also continues to decrease.

It was found that for the dry wood samples the 100 % fragmentation per wood can be observed (both modified and unmodified) (Fig. 2, b). However, the bonding strength of unmodified oak wood is 27.4 % higher than that of ammonia modified wood (Fig. 2, a). After wood soaking in the water for 2 hours, the bonding strength of unmodified and modified oak wood decreases by 4.7 % and 37.7 %, respectively. However, in the case of unmodified oak wood fragmentation at the adhesive bondline was higher by 12.5 % in comparison to modified oak.



a

b

Fig. 2. Water-induced changes on the bond strength of oak wood bonded with PVA dispersion "Lipalas D2": a – dependence between resistance and soaking duration; b – dependence between fragmentation through wood and soaking duration

After the 4-hour immersion in water the percentage of the bond strength of unmodified and modified wood was lower by 33.0 % and 66.2 %, respectively, in comparison to dry wood. In the case of unmodified wood the fragmentation through wood reached 40.0 % and only 5.0 % for the modified wood. When testing the bond strength after the 6-hour soaking the percentage of the bond strength of unmodified and modified wood was lower by 44.3 % and 70.1 %, respectively, in comparison to dry wood. In the case of unmodified wood fragmentation through wood reached 35 %, whereas, in the case of modified wood it increased up to 15 %. 24-hour soaking resulted in reduction of the percentage of the bond strength of unmodified and modified wood respectively by 84.9 % and 89.6 % compared to dry wood. At this stage specimens underwent 100 % lamination at the adhesive bondline. The obtained results elucidate impact of exposure to water and ammonia contribution to the decrease in the bonding strength of modified wood by 1.4 – 2.7 times. Most convincing assumption is that penetrating into wood ammonia does not fully react and starts dissolve in the water during the soaking process what results in pH changes and produces alkaline water. The adhesive film of PVA dispersion is resistant neither to alkalis nor to acids. The film begins to hydrolyze in such environment leading to the loss of bond strength. The nature and dynamics of ammonia effects on the bond strength of tested specimens is best seen by specimen lamination in relation to wood (Fig. 2, b).

Analogous tests performed by bonding specimens with Class D3 PVA dispersion "Lipalas D3" as expected showed enhanced water resistance. Figure 3 shows obtained results. When testing unsoaked specimens, in the case of both unmodified and modified oak specimens there was 100 % fragmentation through the wood. It was determined that the percentage of the bond strength of modified wood was lower by 10.2 % compared to unmodified wood (Fig. 3). When wood is kept in water, the bond strength tends to significantly decrease after 24 hours: by 72.4 % in the case of unmodified wood and by 90.9 % in the case of modified wood. All the joints undergo 100 % fragmentation at the adhesive bondline. By soaking wood for additional 2, 3 and 4 days, the bond strength decreases by 3.7 % – 16.7 % in the case of unmodified wood and by 0.1 % – 14.3 % in the case of modified oak wood.

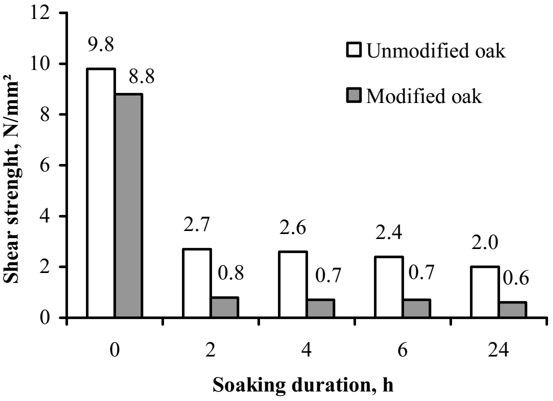
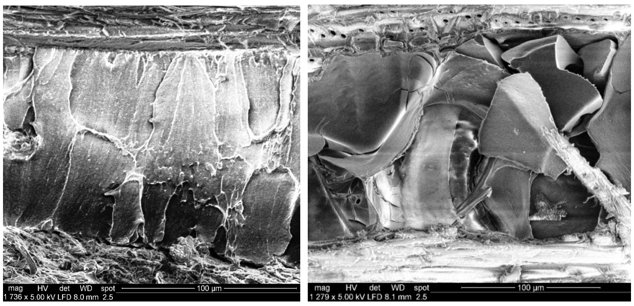


Fig. 3. Water-induced changes on the bond strength of oak wood bonded with PVA dispersion "Lipalas D3"

The test results revealed that when PVA dispersion comes into direct contact with ammonia-modified wood, the bond strength considerably weakens. In all cases dispersion "Lipalas D3" with enhanced moisture resistance showed weaker by more than 3 times bonding strength of modified wood after the exposure to water. When testing dry adhesive joints of both modified and unmodified wood 100 % fragmentation through wood was observed. After keeping specimens in water for 24 hours and bondline splitting testing there was 100 % fragmentation at the adhesive bondline in the case of both modified and untreated wood. The use of PVA dispersion "Lipalas D3" for the bonding of unmodified oak specimens satisfied LST EN 204:2005 standard test sequence No. 3 requirements of at least 2 N/mm^2 bonding strength for Class D3 adhesive. However, ammonia modified oak wood cannot be bonded with this dispersion, when it is necessary to obtain the adhesive joint that conforms to Class D3, since the percentage of the obtained bonding strength is lower by more than 3 times in comparison to the one specified in the standard.

The structure of adhesive bondline was analyzed using SEM. In the case of unmodified wood, the adhesive bondline is unbroken, without any major cracks and shows fine bonding to wood (Fig. 4, a). In the case of ammonia modified wood specimens, the adhesive bondline is more defective: it develops cracks, is heterogeneous and there is no adhesion to wood in some areas (Fig. 4, b).



a b

Fig. 4. SEM image of the adhesive bondline (PVA dispersion "Lipalas D3"): a – unmodified wood; b – modified wood

When PVA penetrates into wood, it binds surfaces as a result of water and air extrusion [21]. When exposed to ammonia, wood becomes darker, which indicates the formation of compounds with an increased number of conjugated double bonds. Such compounds can be produced as a result of the reaction between ammonia and carbonyl functional groups of lignin contained by wood cell walls, and the further condensation of formed amino groups with carbonyl groups (Fig. 5).

It can be assumed that substances of such reactions may have effect on the size of wood pores. A decrease in pores leads to a reduced PVA penetration into wood, which can be observed in SEM images. Another possible reason could be changes in wood pH due to the interaction with NH_3. An increase in pH could have contributed to the coagulation of PVA dispersion resulting in the absence of an even adhesive bondline interface observed on SEM images for bonding modified wood. If wood contains free NH_3 or produced compounds can release it freely, the pH of bonding tends to increase as well. An increase in an alkaline medium intensifies the hydrolysis of PVA bonding which causes the fragmentation of the adhesive bondline.

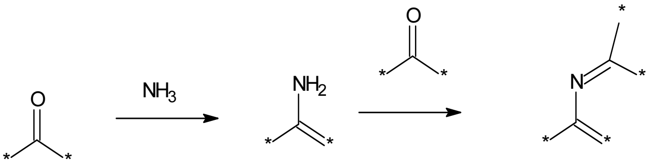


Fig. 5. The formation of compounds with an increased number of conjugated double bonds in ammonia modified wood

Our results are in line with the testing of modified European oak wood bonded with PVA adhesive [18 – 19]. Oak wood specimens were treated with Vacsol Azure by applying the process of double vacuum impregnation [18]. It was found that the bond strength of unmodified oak was 10.043 N/mm^2 (mean value), while in the case of modified oak wood specimens, the bond strength was lower – 6.859 N/mm^2. Another study [19] dealt with the measurement of the shear strength of oak wood specimens impregnated with Imersol-Aqua. Short-term, middle-term and long-term dipping methods were used for impregnation. In addition, the quality of bonded surfaces (sanded, as was at our case, and non-sanded,) was evaluated. The results showed that in the case of non-sanded specimens, wood impregnation reduced the shear strength by about 18 % – 22 % (depending on the impregnation duration), and in the case of sanded specimens, there was a 16 % – 22 % decrease. Sanding or other satisfactory surface roughness formation is bondline interface-interphase performance key-factor.

Research results provided above show that the exposure to ammonia contributes to the destruction of bonding. However, ammonia is one of the constituent parts of PVA dispersion and is introduced during its production. pH value of manufactured PVA dispersion is equal to 2. When ammonia is introduced, an acidic medium is neutralized up to pH = 4 – 6. Special tests were performed for evaluation of 25 % ammonia increase in the dispersion and impact on the pH value and shear strength (Fig. 6). Beech wood was used for obtaining adhesive joints (in accordance with the LST EN 205 requirement). Specimens were kept under standard air conditions for 7 days and tested by splitting them at the seam. While dealing with the obtained results, as seen, there is a significant decrease in an acidic medium of PVA dispersion in the direction of an alkaline, which affects the adhesive strength of PVA dispersion/beech wood and reduces it up to 9.5 times. One explanation is that when exposed to ammonia, polyvinyl acetate dispersion undergoes coagulation and changes in adhesive properties, which results in the reduced shear strength of the adhesive joint.

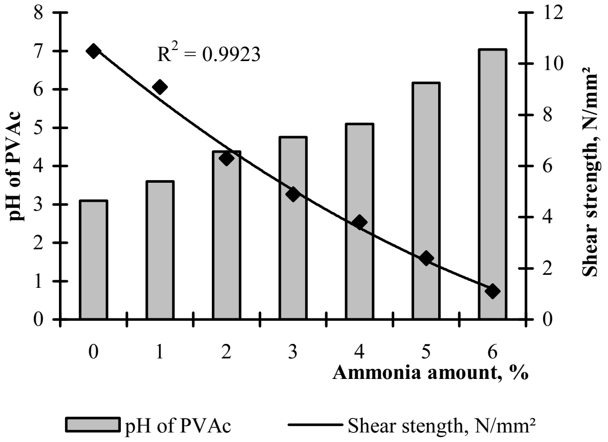


Fig. 6. The dependence of the ammonia amount in the dispersion on the pH value of PVA dispersion “Lipalas D3” and the bond strength

Another assumption is that absorbed by wood ammonia fails fully react and begins to melt in water during the soaking process what changes the concentration of hydrogen ions. The neutral environment of water pH turns into the alkaline one, what causes the hydrolysis of the PVA film and results in weaker bonding strength. In both cases of two types of tested adhesives, wood samples underwent 100 % fragmentation at the adhesive bondline after the 24-hour soaking period indicating weak adhesive bonding.

The testing showed that ammonia has a negative effect on PVA dispersion performance therefore, its application to the bonding of ammonia-modified wood should be avoided.

CONCLUSIONS

1. Bonding strength of dry ammonia modified oak, wood using PVA dispersion Class D2 fall by 30 % compared to dry unmodified oak wood, whereas PVA dispersion Class D3 bondline lose only 10 % of strength. For both adhesive types specimens undergo 100 % fragmentation through wood.
2. Exposure to water stimulates ammonia impacts on adhesive properties. For PVA dispersion Class D2 the bonding strength of modified oak wood reduces 1.4 – 2.7 times depending on the soaking duration; PVA dispersion Class D3 is less resistant to ammonia and strength reduction reach 3.3 – 3.7 times.
3. Moisture-resistant PVA dispersion "Lipalas D3" does not provide the ammonia modified oak wood joints any enhanced moisture resistance showing approximately 1.4 – 2.4 times lower strength compared with in-house PVA dispersion "LipalasD2".
4. PVA dispersions retain ammonia modified wood bondline strength requirements only in a dry environment conditions and in humid conditions bonding strength tends to decrease significantly. Hence, in order to enhance water resistance, it is necessary to modify these dispersions or to search for alternative adhesives.

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