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Strength of Adhesive Joints of Thermally Modified Ash Wood Glued With Polyvinyl Acetate – Based Adhesives

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Adhesives for gluing thermally modified wood were analyzed. The methods for conducting experimental studies to determine the strength of adhesive joints of thermally modified ash wood and unmodified pine wood, using polyvinyl acetate (PVAc)-based adhesives of durability class D4 were described. According to the results of experimental studies based on the proposed methodology, it was established that the strength of adhesive joints of thermally modified ash wood and unmodified pine wood stretched along the fibers after the first stage of testing is 6.21 MPa, after the second stage 4.56 MPa, and after the third stage 3.90 MPa. The average strength of the adhesive joints of the control specimens is 7.12 MPa. According to the obtained research results, the nature of destruction of the adhesive joints of thermally modified ash wood and unmodified pine wood was determined depending on the test stage. The greatest destruction occurred on the adhesive line, and the least on the pine wood. It was assumed theoretically that during the thermal modification of ash wood, hemicellulose decomposes and acetic acid is released, leading to the formation of furfural, which impairs wood surface wetting and affects the adhesive strength of PVA-based adhesive joints.

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Introduction

Wood is one of the main construction materials, which has several advantages, starting from natural recovery, to environmental friendliness and ending with wide use [Vintoniv et al. 2007]. However, some shortcomings limit its use under service conditions, especially those with variable temperature and humidity loads. For optimal use (especially of low-value and low-grade species), wood is modified. There are several methods of wood modification, one of which is thermal modification [Bekhta et al. 2005; Callum 2006]. The use of thermally modified wood will increase the resistance of such wood to varying humidity and temperature service conditions [Kshyvetsk

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and Tyvunka 2018; Thermomodification of wood: domestic experience 2019; Tjeerdsma et al. 1998].

At present, there is a problem with gluing thermally modified wood because during the modification process the action of high temperatures changes the physical and mechanical properties of wood, including its adhesion to adhesive materials. This is a pressing problem today (it remains unresolved) because during bonding it is difficult to provide the adhesive joint the proper performance parameters.

Scientific studies have been carried out on gluing pieces of thermally modified wood together [Ilkiv et al. 2017; Uzun et al. 2016; Can et al. 2021], but there are no such studies on gluing thermally modified wood to unmodified wood. This problem cannot be solved without thorough scientific research in this area.

To glue thermally modified and unmodified wood together, both thermosetting, namely, phenol-formaldehyde, urea-formaldehyde, polyurethane adhesives, among others, and thermoplastic adhesives, mainly polyvinyl acetate adhesives [Kshyvetskyy et al. 2019; Kshyvetskyy 2007], are used. Thermosetting adhesives set quickly, withstand varying ambient humidity and temperature loads, are relatively inexpensive, and form a cross-linked structure of the adhesive joint, which provides the adhesive joints proper water, moisture, and heat resistance. Nevertheless, they have a fairly high percentage of moisture absorption and are toxic both in the preparation of the glue and during the gluing as well as operation of finished products [Kshyvetskyy 2007]. In addition, such adhesives have poor adhesion properties to thermally modified wood, which does not provide the adhesive joints proper performance either during gluing or in their service [Kaboorani and Riedl 2011]. Modern thermoplastic (polyvinyl acetate) adhesives have good adhesion properties to wood, ensure proper strength of the adhesive joints, are eco-friendly, and promising for gluing wood.

Literature review

Gluing is one of the most common types of wood joining [Voytovych 2010; Kshyvetskyy et al. 2019]; adhesives are used in large amounts to manufacture window and door units, blockboards, furniture panels, floor coverings, facing panel materials, as well as to obtain large-sized parts from solid wood and thermally modified wood, etc. This adhesive bonding of wood structural elements is based on the phenomena of adhesion, that is, the ability of molecules to form various kinds of chemical bonds between the materials that are being glued together.

Thermosetting adhesives that are used for gluing have several disadvantages, which limit their use. Thermoplastic adhesives based on polyvinyl acetate have good adhesion properties to wood and wood-based materials, form a linear or sparsely cross-linked structure of the adhesive joint, which provides them proper moisture and heat resistance, are environmentally friendly, technologically advanced, and are able to provide the adhesive joint of thermally modified wood adequate strength [Zygelboim 1978; Thermal modification of wood: domestic experience 2019; Heat treatment and drying of lumber 2017].

Thermally modified wood is widely used today both indoors and outdoors [Kshyvetskyy et al. 2019]. In the process of thermal modification, the chemical composition of wood and its physical and mechanical properties change, which has a positive effect on the working characteristics of products in varying humidity and temperature conditions. At the same time, improving the service characteristics of wood by thermal modification leads to a decrease in the adhesion properties and bonding performance, etc. [Huber et al. 2011; Chubynsky 1992; Fengel and Wegener 1989; ThermoWood: Handbook – Helsinki 2003; Windeisen et al. 2009; Winandy and Rowell 2005].

Therefore, it is difficult to select adhesives for gluing thermally modified wood that would provide proper adhesion strength under service conditions. There are no special adhesives designed for gluing such wood. The problem arises of how to carry out the process of gluing thermally modified wood parts together and how to glue together thermally modified wood and unmodified wood and obtain proper adhesion strength under service conditions.

Since the problem with adhesives for gluing thermally modified wood has not been solved to date, new adhesive compositions are being searched for, existing adhesives are being modified, and the influence of the mode parameters (gluing temperature, glue spread, compacting pressure, etc) on the gluing process is being investigated. Nonetheless, the studies have not led to the desired results yet since the physical and mechanical processes in such thermally modified wood have changed this wood so much that this results in impairing the adhesion strength performance.

Gluing thermally modified wood to unmodified wood could be a promising trend for joinery, mainly in the manufacture of windows, but at present, there is a problem with their durability, especially in their use when exposed to conditions of the outdoors. Modern paint and varnish materials do not provide proper service conditions for windows because of the prolonged negative effects of external factors. This problem can be solved by using a window structure that combines thermally modified wood and unmodified wood.

To solve these problems, we decided to conduct a series of experimental studies to investigate the adhesion strength and durability of a bonded structure made of thermally modified ash wood and unmodified pine wood glued together with thermoplastic polyvinyl acetate (PVAc) adhesives of durability class D4 [Datskiv and Kshyvetskyy 2021].

Aims and objectives of the study

This work aims to study, using the accelerated method, the strength of thermoplastic adhesive joints between thermally modified ash wood and unmodified pine.

To achieve this aim, it is necessary to perform the following tasks:
1. To select and describe the methodology for conducting accelerated experimental studies on the strength of adhesive joints of thermally modified ash wood and unmodified pine wood.
2. To conduct accelerated experimental studies according to the methodology.
3. To analyze the obtained results of the experimental studies.
4. To analyze the nature of destruction of the **adhesive joints of thermally modified ash wood and unmodified pine wood** for further theoretical and experimental research.

Materials and methods

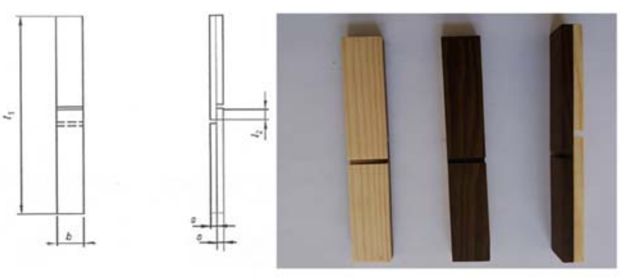
Materials and equipment used in the experiment

The experimental studies to determine the strength of adhesive joints of thermally modified ash wood and unmodified pine wood were carried out according to the proposed methods of specimen preparation and testing. The latter included testing samples at room temperature, soaking them in water, and boiling them. To form an adhesive joint, a thermoplastic adhesive based on RAKOLL ECO 4 polyvinyl acetate durability class D4, was used. The technical characteristics of the adhesive are as follows: acidity pH-3.5, consumption 150-180 g/m^2, pressing pressure 0.1-0.5 N/mm^2.

Preparation of the specimens included the following stages: pine wood preparation, ash wood preparation, thermal modification of the ash wood, adhesive preparation, gluing, specimen preparation, experimental studies, and processing of the results of the investigation.

The formation of adhesive joints was carried out in production conditions using the existing production equipment of the enterprise “Long Life Wood”. The thermal modification of ash wood was carried out in an autoclave at the temperature of 195 °C for 12 hours. The samples were conditioned after the thermal modification (18 hours).

The dimensions of the specimens (lamellas) were 600 × 130 × 5 mm, and 17 pieces were produced. Part of the lamellas were used for research in natural conditions, which will last 2 years. The results of these studies will be presented in a following article. The lamellas were calibrated to a thickness of 5±0.1 mm before gluing. The moisture content of lamellas made of pine wood was 12±1.5% and that of thermally modified ash wood was 6±0.5%. The adhesive was applied manually with a brush before gluing. The glue spread was 160 g/m^2. Before application, the adhesive was stirred well until a homogeneous mass was obtained. After that, the viscosity was measured using a VZ-4 viscometer and adjusted to the requirements of the operating parameters of gluing (70 seconds). After applying the adhesive, a package was formed and pressed using a pneumatic clamp. The pressing temperature was +20 °C and the pressing time was 30 minutes. Technological conditioning after gluing lasted 7 days. The next stage was the preparation of specimens of the appropriate shape and size according to the methodology. The dimensions of the experimental specimens were 150x20x10 mm (Fig. 1).



a) b)

Fig. 1.Specimens for calculating strength of adhesive joint between thermally modified ash wood and unmodified pine wood,
a) diagram specimens; b) photograph of experimental specimens

Methodology for studying strength of adhesive joints

The prepared samples were subjected to accelerated laboratory studies of the effects of humidity and temperature. Following the research methodology, the studies were carried out sequentially in three stages; for this purpose 100 specimens were prepared. This number was determined by the conditions of the experimental studies. All the specimens were divided into four groups, namely, control specimens that were not subjected to any loads, the specimens that were investigated under standard conditions, the specimens that were additionally subjected to soaking, and those subjected to boiling.

In the first stage, the specimens were kept for 7 days under standard conditions at a temperature of 20±5 °C and ambient humidity of 65±5%. In the second stage, the specimens after 7 days of being keptunder standard conditions were subjected to soaking in water for 4 days at a temperature of 20±5 °C. In the third stage, after 7 days of being kept under standard conditions, the specimens were subjected to six hours of boiling and two hours of soaking in water at a temperature of 20±5 °C. After the accelerated experimental studies, the specimens were subjected to a destructive tensile test at a constant load (50 mm/s) using an R-05 tensile testing machine.

The obtained results of the experimental studies were subjected to mathematical and statistical processing, dependence diagrams were constructed and analyzed. Based on the graphic dependences, analysis of the obtained results was carried out, namely, the influence of humidity and temperature on the strength of adhesive joints of thermally modified ash wood and unmodified pine wood that were glued together with thermoplastic polyvinyl acetate adhesives. The study results are presented below.

Results and discussion

Results of studies on strength indicators of adhesive joints

Fig. 2 displays a graphical interpretation of the changes in the strength of adhesive joints of thermally modified ash wood and unmodified pine wood after the first stage of testing and their comparison with the control specimens.

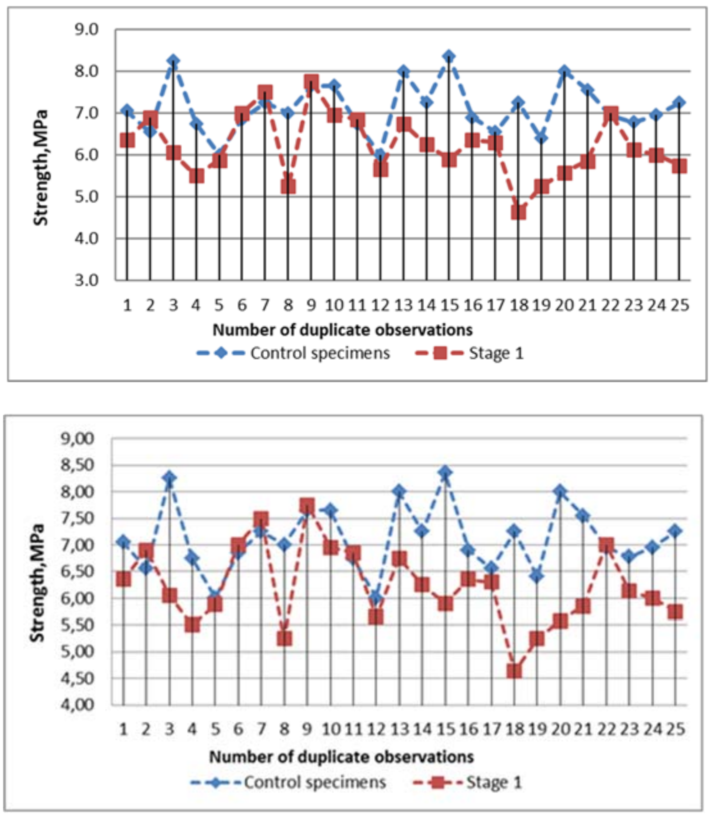


Fig. 2. Strength of control specimens and specimens after first stage of testing

As can be seen from Fig. 2, the strength of the adhesive joint of thermally modified ash wood and unmodified pine wood for the control specimens ranges from 6.00 MPa to 8.35 MPa. The average strength value is 7.12 MPa. The strength of the adhesive joints after the first stage of testing ranges from 4.63 MPa to 7.75 MPa. The average strength value is 6.21 MPa. In percentage terms, the strength after the first stage of testing decreased by 13%.

According to the obtained study results, the number of control specimens that were destroyed along the adhesive joint was 64%, for unmodified pine wood 16%, and for thermally modified ash wood 20%. As can be seen, the specimens in most cases were destroyed along the adhesive joint. This indicates the difficulty of gluing thermally modified wood to unmodified wood. Regarding the destruction after the first stage, the number of specimens that were destroyed along the adhesive joint is 52%, for thermally modified wood 28%, and for unmodified wood 20%.

According to standard data, the strength of unmodified pine wood when shearing parallel to the grain at a moisture content of 12% is approximately 7.5 MPa. According to our studies, the strength of thermally modified ash wood is 8 MPa, which means that it decreases on average by 15% of the initial strength of ash wood, which is around 13 MPa. Based on the information above, it can be concluded that the strength of such an adhesive joint should be in the range of 7.5 MPa to 8 MPa. This behavior of the adhesive joint is explained by the fact that after thermal modification, the structure of wood changes somewhat, namely, the density of wood decreases on average by 12-14%. This leads to a decrease in the adhesion strength of the adhesive to wood, which is confirmed by the percentage ratio of the type of destruction of the experimental specimens.

Fig. 3 presents the results of the experimental studies on the strength of adhesive joints of thermally modified ash wood and unmodified pine wood after the second stage of the experimental studies and their comparison with the control results.

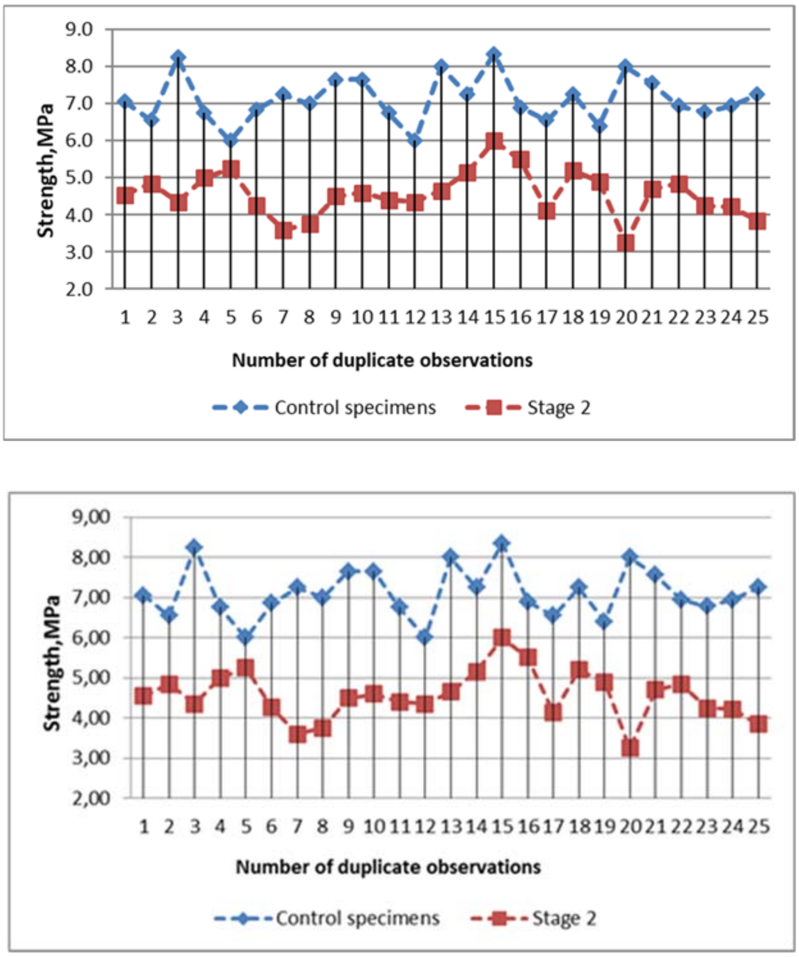


Fig. 3. Strength of control specimens and specimens after second stage of testing

Fig. 3 shows that the strength of the adhesive joint between thermally modified ash wood and unmodified pine wood glued with thermoplastic polyvinyl acetate adhesives ranges from 3.25 MPa to 6.00 MPa. The average strength value is 4.56 MPa. If we compare the results of the experimental studies on strength with the results of the strength of the control specimens, it can be concluded that the adhesive joint strength of the specimens of thermally modified ash wood and unmodified pine wood glued with thermoplastic polyvinyl acetate adhesives decreased by 36% as compared with the initial one. According to the obtained study results, the number of specimens that were destroyed along the adhesive joint was 80%, for unmodified pine wood 4%, and for thermally modified ash wood 16%.

Such a change in the strength of the adhesive joint can be explained by the effect of water during soaking of the specimens for 4 days. Pine wood is more hydrophilic compared to thermally modified ash wood. In addition, the adhesion properties of adhesive materials concerning thermally modified wood deteriorate due to the low density and smooth surface that is formed after modification at the temperature of 195 °C. At this modification temperature, hemicellulose in ash wood is degraded by deacetylation and the release of acetic acid, which leads to the formation of furfural that forms a film on the surface of the thermally modified ash wood. The formation of such a film reduces the surface tension of the wood, thereby deteriorating the adhesion properties.

Fig. 4 displays the results of the experimental studies on the strength of adhesive joints of thermally modified ash wood and unmodified pine wood after the third stage of the experimental studies and their comparison with the control results.

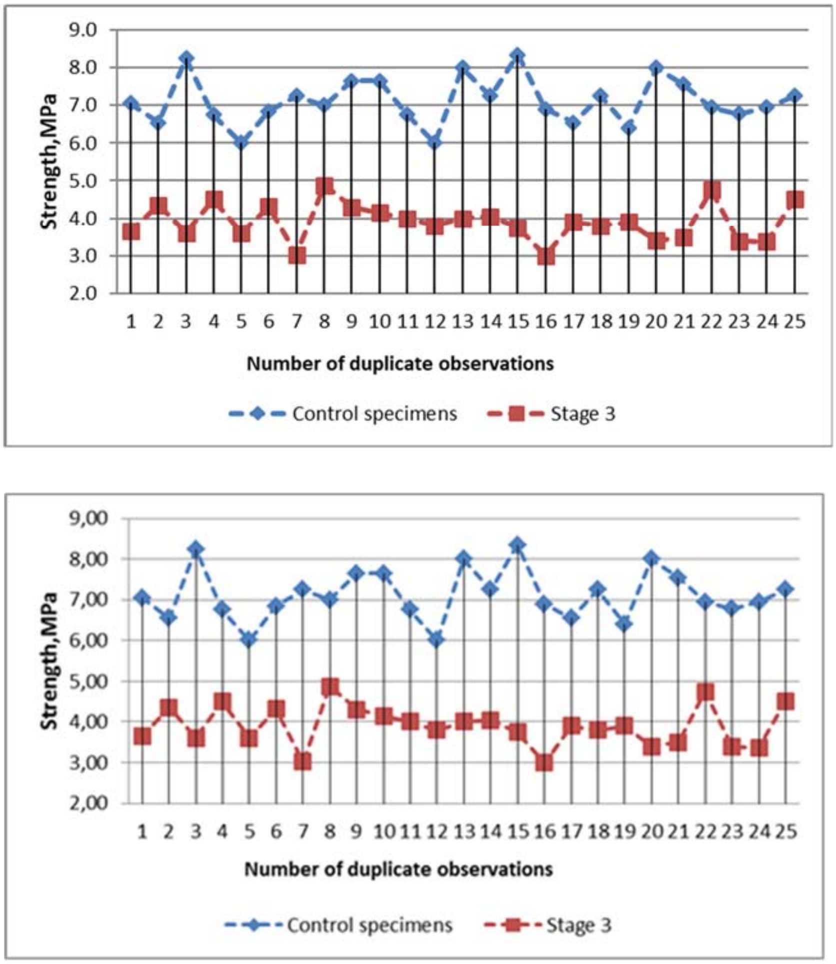


Fig. 4. Strength of control specimens and samples after third stage of testing

As can be observed from Fig. 4, the minimum strength of the adhesive joint is 3.00 MPa, the maximum strength is 4.88 MPa, and the average strength is 3.90 MPa. If we compare these study results with those of the control specimens, we can see that the strength after the third stage of testing decreased by 45%. If these results are compared with the first and second stages of the studies, the strength decreased by 37% and 15%, respectively. Thus, the strength after the third stage of the experimental studies decreases on average by 15%. The number of specimens that were destroyed along the adhesive joint was 92%, for unmodified pine wood 4%, and for thermally modified ash wood 4%.

This indicates that the adhesive joint between thermally modified ash wood and unmodified pine wood glued together with thermoplastic polyvinyl acetate adhesives can withstand moisture loads with a varying water temperature range from 20 to 100 °C. Hence, exposure to elevated temperatures does not significantly reduce the strength of the adhesive joint.

Fig. 5 shows the strength of adhesive joints between thermally modified ash wood and unmodified pine wood for the control specimens and the strength after three stages of testing.

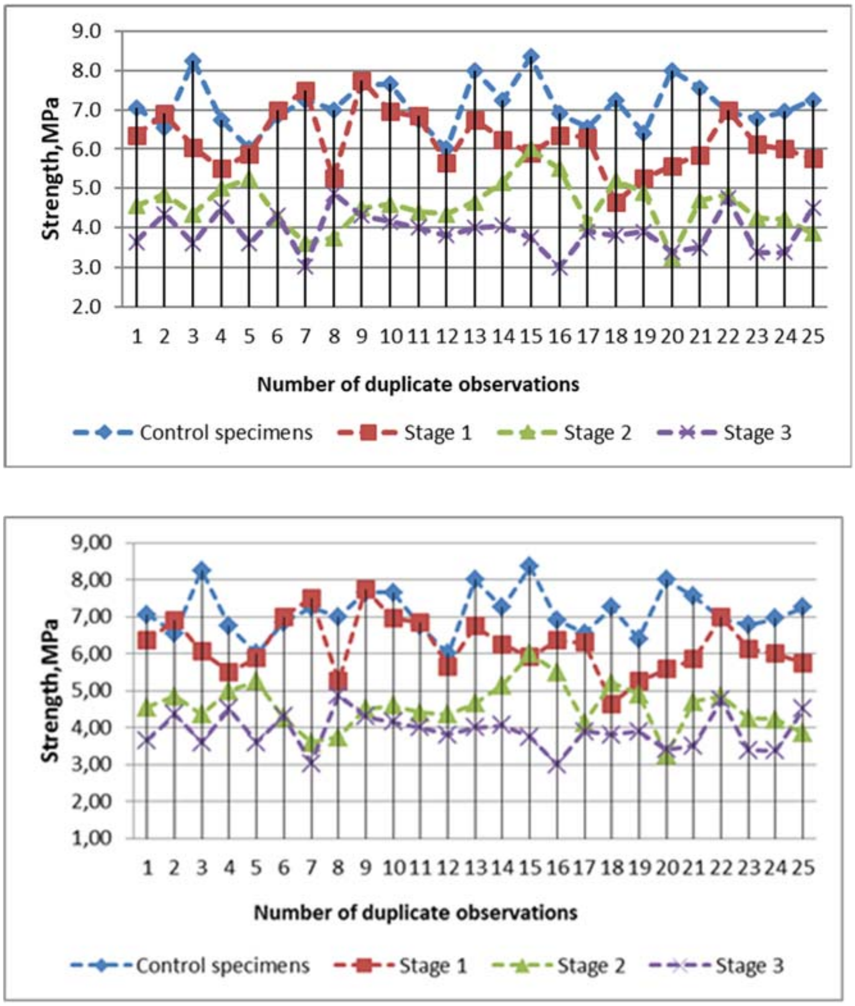


Fig. 5. Strength of adhesive joints between thermally modified ash wood and unmodified pine wood for control specimens and strength after three stages of testing

As can be seen from Fig. 5, the strength of adhesive joints of thermally modified ash wood and unmodified pine wood after the first, second, and third stages varies according to the same dependencies, but with different intensities of strength change, which ranges from 3 MPa to 8.35 MPa. This is consistent with the ultimate strength of thermally modified ash wood after cyclic temperature and moisture testing.

The obtained results on the strength of adhesive joints of thermally modified ash wood and unmodified pine wood glued with thermoplastic adhesives of durability class D4 will be useful to predict the strength of window structures made of the above materials. In addition, the results will be compared with the change in the strength of the adhesive joints according to the long-term method, which is being carried out over two years in natural conditions.

Discussion of results

In thermally modified ash wood at the treatment temperature of 195 °C and duration of 12 hours, irreversible physical and chemical processes occur that change the properties of the wood. Such changes mainly take place at the molecular level. As is known, ash wood contains 40% cellulose, 25% hemicellulose, 26%

lignin, and extractive substances of various kinds. During thermal modification, the wood structure changes. This was discovered during the gluing process as the adhesion properties of thermally modified wood deteriorate. Such wood is not easily wetted with an adhesive and the adhesive does not spread freely on the wood surface because the wetting index during the thermal modification of wood at the temperature of 130 °C decreases sharply [Can et al. 2021].

This behavior can be explained by the fact that first of all decomposition of hemicellulose in the wood occurs with the formation of monosaccharides and oligosaccharides, which are dehydrated to form furfural (pentose) and hydroxymethylfurfural (hexose). The chemical formulas for the possible decomposition of hemicellulose are presented in Fig. 6 [Bächle et al. 2010; Callum 2006].

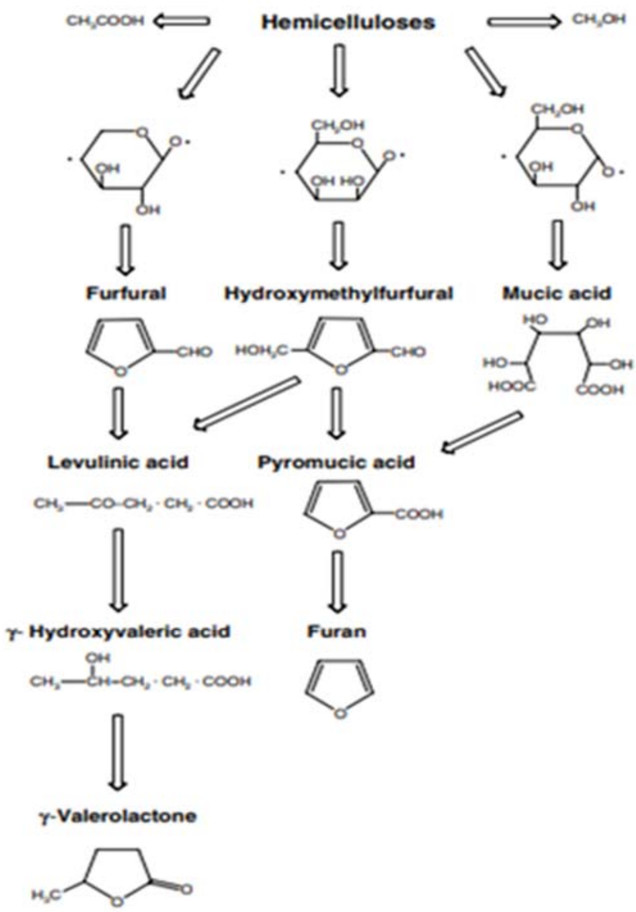


Fig. 6. Chemical processes of hemicellulose decomposition

This behavior of hemicellulose leads to a decrease in the volume weight of the wood. When the modification temperature reaches 130 °C, acetic acid is released, which, with increasing temperature, acts as a catalyst for the decomposition of hemicellulose into soluble sugars, namely, mannose, galactose, xylose, and arabinose. Such processes affect the adhesive and cohesive properties of thermally modified ash wood.

We assume that the strength of the adhesive joint of pine wood can be described by mechanical, diffusion, and chemical theories. According to mechanical theory, the strength of such an adhesive joint is formed by filling pores and surface irregularities with adhesive, thereby forming a strong adhesive joint. According to diffusion theory, the strength of the adhesive joint develops due to the diffusion of adhesive molecules into the wood. According to chemical theory, there is an interaction between the molecules of the adhesive and wood.

Regarding thermally modified ash wood, it is difficult to predict which of the theories will work better since during thermal modification its structure and surface change dramatically. Research on the surface of thermally modified ash wood is being conducted.

Conclusions

Summing up, the following conclusions can be drawn:

1. To glue thermally modified ash wood and unmodified pine wood, polyvinyl acetate adhesives of durability class D4 were proposed, which, according to our research, provide such adhesive joints performance characteristics.

2. The method of accelerated experimental studies on the strength of thermally modified ash wood and unmodified pine wood under the influence of temperature and humidity was proposed. According to the methodology, experimental specimens were prepared.

3. It was found that the strength of adhesive joints of thermally modified ash wood and unmodified pine wood after three stages of testing in accelerated experimental studies decreased by 50%, namely after the first stage of testing by 13% relative to the strength of the control specimens, after the second stage by 36%, and after the third stage by 45%.

4. The nature of the destruction of adhesive joints of thermally modified ash wood and unmodified pine wood was established, namely, for the adhesive line 74.7%, for unmodified wood 9.3%, and for modified wood 16%.

5. It was found that the adhesive joints of thermally modified ash wood and unmodified pine wood glued together with polyvinyl acetate adhesives having durability class D4 provide the products performance characteristics.

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