Chemical modification of wood veneer by acetylation and furfurylation to determine strength properties

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Abstract. The article reviews domestic and foreign research on wood modification processes by chemical means, giving its types and basic properties. The published results prove that chemical modification of wood, fully or partially by acetylation and furfurylation, transforms wood species with low strength into new "green" materials with improved qualities and properties increasing water resistance, moisture resistance, thermal resistance, as well as tensile strength. Research to determine the strength properties of wood veneer that has been chemically impregnated with furfurylation and acetylation methods for 24, 48 and 72 hours, followed by drying, has increased the tensile strength along the fibres. However, for the determination of the tensile strength across the fibres, a significant decrease in the tensile strength is observed in relation to the increase in impregnation time.

1 Introduction

Of all the variety of materials, wood is the most sought after. It has a wide range of applications and is used as a building, finishing, and decorative material. Today wood is one of the few renewable and environmentally friendly materials with unique external characteristics, high specific strength and low energy consumption. However, instability with changes in relative humidity and the ability to biodegrade are significant disadvantages of the material. This has been the main reason for the development of new treatment methods, one of which is the chemical modification of wood.

Chemical modification.

Modification is an effective approach to improve the properties of wood, such as dimensional stability, water resistance and durability. Over the past few years, a large number of wood modification techniques have emerged, the most important of which are thermal, chemical modification, surface modification and impregnation. Where thermal and surface treatments are not able to meet the required strength requirements of structures, it is successfully replaced by acetylated wood or wood treated with furfural alcohol. This material belongs to another type of modified wood raw material, chemically modified wood (CMW),

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so-called dried wood, which has been treated with chemical compounds that give it high strength properties and increased resistance to moisture [3].

Through chemical modification of wood, low-strength species can be transformed into new modified wood products with improved properties without any harmful effects on the natural environment or people [8, 24].

In order to obtain high-quality materials during chemical modification, wood species with good absorbency must be used. Only then will chemically treated wood acquire the properties that make it so advantageously different from thermal wood, such as durability and resistance to warping, which is particularly valuable for construction companies [4].

Chemical modification of wood occurs when a reagent reacts chemically with the polymeric components of wood (lignin, hemicellulose, or cellulose), resulting in a stable covalent bond between the reagent and the cell wall polymers [8, 18, 19].

In general, chemical modification of wood can be considered as an active modification as it leads to distinct chemical changes in the macromolecules of the cell wall. Currently, there are several facts about the action of chemical modification of wood: 1) in modified wood the equilibrium moisture content is reduced and, therefore, it is more difficult for fungi to obtain the moisture required for rotting; 2) there is a physical blockage of penetration of rot fungi into the micropores of the cell wall micropores; 3) inhibition of the action of specific enzymes [8, 22, 23].

To date, the best-known processes that involve chemical modification of the wood cell wall, in whole or in part, are acetylation and furfurylation of wood, respectively; today, both processes have been extended to an industrial level.

Chemical modification is an expensive technology used for the treatment of some wood species.

The first recorded experiment on chemical modification of wood by acetylation was carried out in Germany by Fuchs using the chemical agent acetic anhydride with sulphuric acid as a catalyst. Tarkov was actually the first scientist to describe the use of the acetylation process in an attempt to make wood resistant to swelling in water [18, 19]. Since the 1940s, many laboratories around the world have experimented with wood acetylation in different ways and using different wood species and agricultural resources [19, 20].

The advantages of chemically modified wood include the following properties:

— High strength. Chemical treatment of wood significantly changes the strength of the material for the better. This distinguishes chemically modified wood from thermally modified wood, which, on the contrary, reduces the strength of wood [2];
— Moisture resistance. During chemical modification, the amount of water-absorbing components in the wood's composition decreases. Chemically treated wood can bear excellently constant influence of moisture, differences in humidity indoors, heavy rainfall and so on. At the same time, it does not rot [1];
— Form stability. Chemically treated wood does not swell under the influence of moisture, does not dry out, and retains all its parameters during operation [15];
— Resistance to UV radiation. Chemically treated wood protects it from degradation under the influence of sunlight.
— Wood modified with both resins and metals has low friction coefficients.

Acetylating wood.

Acetylation of wood, mainly using acetic anhydride, was originally carried out as a liquid-phase reaction [19, 20]. Initially, acetic anhydride catalysed by zinc chloride or pyridine was used [18]. Most acetylation reactions today are carried out without the use of catalysts [23, 12].

The reaction of acetic anhydride with wood polymers leads to the esterification of available hydroxyl groups in the cell wall [19] with the formation of the by-product acetic acid. The by-product is mostly removed from the final modified material [11]. Like untreated

wood, acetylated wood consists only of carbon, hydrogen and oxygen and contains completely non-toxic components [8].

Today, the acetylation process applied in the liquid phase produces chemically modified wood that has significantly improved physical, mechanical and biological material properties [13], such as:

— The biological strength of the wood, which matches that of strong tropical species. Acetylated wood has significantly improved biological rot resistance [24, 25].
— Acetylated wood reaches a fibre saturation point below 15% at 20% loading; the cell wall thus becomes highly hydrophobic [21-23]. Consequently, swelling and shrinkage properties are reduced by 70-75% compared to untreated wood [24]. The reason for this is that the cell wall is filled with chemically bound acetyl groups that occupy the space inside the cell wall [12-15].
— Acetylated pine wood with a high acetyl concentration (acetyl weight gain >20%) has been shown to offer excellent resistance to drill bit impact, even after 11 years in the field.
— An increase in hardness of 15-30% can be achieved [4].
— Acetylated wood has a significantly lower carbon footprint than steel and concrete [19].

Furfural wood alcohol.

Furfuryl alcohol is a liquid obtained from agricultural waste such as sugarcane and corn cobs. Furfurylation is carried out by impregnating wood with a mixture of furfuryl alcohol and catalysts and then heating it to induce polymerisation. The purpose of furfurylation is to increase biodegradability and dimensional stability by using a non-toxic, proprietary furfuryl alcohol-based polymer.

The polymerisation of furfuryl alcohol in wood is a complex chemical reaction. Even today, the question of whether furfurylation is a separate chemical modification process remains unanswered [25]. Some scientists believe that it involves a chemical modification process because the polymer furfurylalkol reacts with itself and possibly with lignin in cell walls [10, 16, 6, 13]. Thus, furfuryl alcohol complexes are predominantly deposited in wood cavities and cell walls. Polymerisation of furfuryl alcohol in wood is a complex chemical reaction and results in the formation of furfuryl alcohol resins predominantly in wood cavities and cell walls [13].

Another opinion is that furfurylation leads to a permanent "swelling" of the cell wall, which means a permanent increase in cells [36]. One possible explanation is that the furfuryl alcohol polymer inside the cell wall occupies part of the space that is normally filled with water molecules when the wood swells in humid conditions [10]. Various scientists consider wood furfilling as a polymer-filled modification process in which the properties of the furfured material more closely resemble those of the polymer-filled cell wall. [23, 12].

According to the literature [9, 10, 23, 12, 14], the furfilling process results in a modified wood product that has significantly improved material properties and characteristics.

Mechanical properties of wood, with the exception of impact resistance, are improved when wood is treated with furfuryl alcohol polymer. Furfurfured wood is characterised by greater hardness, elasticity and fracture modulus compared to untreated wood; however, it is also more brittle [12].

Recent studies on the ecotoxicology of furfurfured wood leaching have shown no significant eco-toxicity, while no volatile organic compounds or polyaromatic hydrocarbons above normal combustion levels were emitted from burning the wood.

Furfured wood is a 'green' wood product that is ecologically labelled in the Scandinavian market as 'Swan'. Wood furfurring is therefore considered to be an environmentally friendly process [6].

Today, the largest furfuralised wood company is the Norwegian company Kebony AS (formerly Wood Polymer Technologies). The industrial furfurylated wood process consists of the following production steps:

1. Storage and chemical mixing: The treatment solutions are mixed in a separate mixing tank where various chemicals (furfuryl alcohol, initiators/catalysts, buffer agents, surfactants, water) are added. The mixed solution is pumped into one of the buffer tanks.
2. Impregnation: The wood material (i.e. the softwood or hardwood to be treated) is impregnated with the treatment solution under pressure in a vacuum using a full-cell process with a vacuuming stage, a pressing stage and a short post-vacuuming stage.
3. Reaction / curing: In this step the chemicals are polymerised. The curing chamber is heated by steam, with the temperature reached depending on the use of the product. The chamber operates as a closed system during the curing period, except for a venting period at the end. The venting gas is cooled and the condensate is separated from the gas. The condensate is returned to the tank for reuse.
4. Drying: Final drying of the wood material in a dry kiln is necessary to minimise emissions and to obtain the desired final moisture content.
5. Cleaning: Emissions from the process are controlled by scrubbing the vented gases.

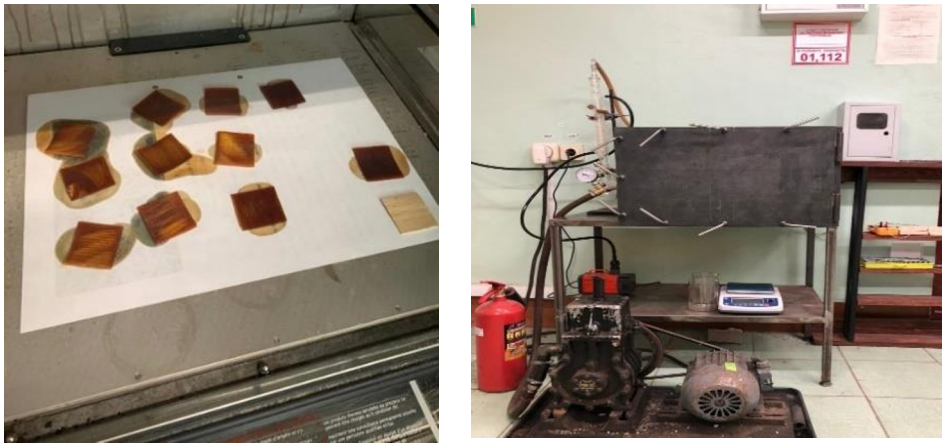
Furfurylation and acetylation modification processes have been extensively studied in an attempt to produce highly efficient and stable wood-based material [13]. As their modification mechanisms differ, these processes have somewhat contradictory effects. For example, furfurylation leads to darkening of wood colour [24]. Although the mechanism responsible for progressive staining has been proposed [26], several studies have been carried out to specifically assess the colour changes of furfurylated wood. Water sorption and mechanical properties of furfurylated or acetylated wood also vary greatly [20, 21]. The effects of modification also differ depending on which wood species are subjected to the process; factors involved include chemical composition, anatomical structure and density [7, 8].

2 Materials and methods

This study used birch veneer samples measuring 30x30x2 mm. The samples were weighed before starting the experiment. The control was the untreated sample.

Chemical modification by acetylation was performed in glacial acetic acid for 24, 48, 72 hours. After each impregnation step the samples were removed and dried for 2 hours at 103 ºC. Then the strength properties were determined.

Furfurylation was carried out by impregnating the veneer samples in 100% furfuryl alcohol. The veneer was pre-impregnated in 3 cycles: Cycle 1 - exposure 24 hours - drying; Cycle 2 - exposure 48 hours - drying; Cycle 3 - impregnation 72 hours - drying. The samples were then weighed again and placed in a microwave vacuum chamber for drying the wood (Fig.1a). The samples were dried in an experimental UHF heating unit developed at the Department of Architecture and Design of Wood Products (Fig. 1b) at 103 ºC, followed by weighing on a laboratory scale depending on the duration of exposure.



a) b)

Fig. 1. The drying phase of the samples: a - view of the samples in the UHF chamber; b - appearance of the UHF drying chamber for wood

In order to determine the mechanical properties of wood chemically treated with furfuryl alcohol and acetic acid, a tensile experiment was carried out on birch veneer along and across the fibres. The change in the tensile strength of the veneer samples as a function of the impregnation cycle for furfuryl treated wood and the impregnation time for acetylated wood was measured with a tensile testing machine.

3 Results and discussion

Wood impregnated with acetic acid and furfural has properties such as strength, bioproofness, hardness, form stability.

Depending on the impregnation method and drying time the tensile strength across the fibre of the wood was observed to change (Fig. 2 a). Compared to the control sample, the furfured veneer shows a decrease in tensile strength across the fibers of wood, its index at the stage of impregnation for 24 hours followed by drying is 1.5 times lower than that of the sample treated by acetylation method. And at 72 hours impregnation and subsequent drying, acetylated samples have a tensile strength 2.5 times greater than those impregnated with furfuryl alcohol. This is explained by the fact that under the influence of high temperatures during drying the plasticity of lignin and spatial size increases, which reduces the intermolecular contact and transverse hemicellulose bonds during tensile strength across the fibers.

However, when determining the tensile strength of veneer along the fibres, a significant increase in tensile strength is observed in both furfured and acetylated wood (Fig. 2b). Deformation of the samples is negligible; only the tissues are stretched. Due to the formation of furan polymer and acetyl groups in the wood cells, the lignin contained in the veneer fills and becomes denser, resulting in a shell-shaped, almost imperceptible tissue tear.

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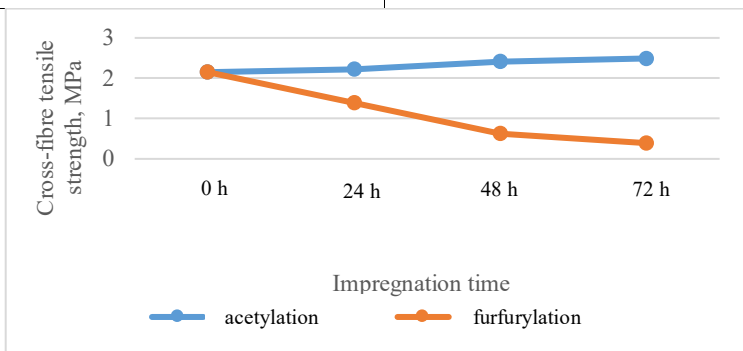

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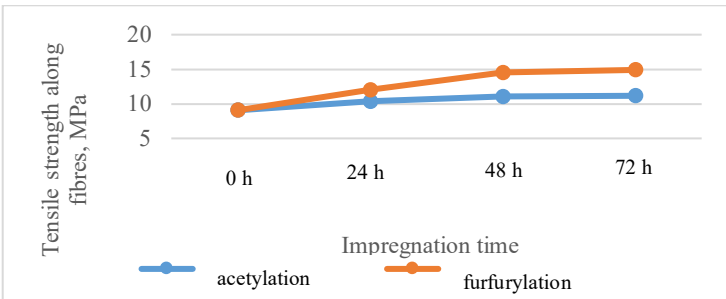

b)

Fig. 2. Tensile strength curves as a function of impregnation time: a) across the wood fibres, b) along the wood fibres

4 Conclusion

In this paper, chemical methods of wood modification (acetylation and furfurylation) have been reviewed. The results show interest among researchers from all over the world and also demonstrate a marked improvement in the mechanical and physical properties of wood through modification.

Thanks to these studies, it has been found that wood impregnated with chemical compositions, through the formation of acetyl groups and furfural polymer, can increase the strength along the fibers, which significantly affects the structure and durability of wood, such as resistance to cracking, chipping and rotting. Due to this, such wood can be used in various types of materials.

However, the strength of the wood fibres is inversely proportional to temperature. Heat has two effects on wood: immediate, which occurs only as long as elevated temperatures are maintained, and permanent, which results from the thermal degradation of wood polymers. In an environment with insufficient humidity, the initial effect of heating the wood is dehydration. This gradually leads to pyrolysis and volatilization of cell wall polymers across the fibres, resulting in loss of tensile strength across the fibres.

In this way, modification technologies provide non-toxic, environmentally friendly materials. Treated wood can offer a durable and environmentally friendly alternative to wood or mixed exterior structures.

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