Gregor Rep, Franc Pohleven

# Wood modification - a promising method for wood preservation

## Modifikacija drva – obećavajuća metoda za zaštitu drva

***Review paper • pregledni rad***
*Received - prispjelo: 25. 04. 2001 • Accepted – prihvaćeno: 22. 05. 2001*
*UDK 630 * 84*

***SUMMARY*** • *Over the last two decades wood modification has been subjected to intensive research. By changing the chemical nature of the polymers in the wood cell wall, many properties such as durability, dimensional stability and UV-stability can be considerably improved. The cell wall structure can be altered with thermal treatments, chemical modification or enzymatic treatments. In some European countries heat-treated wood is already on the market. Some other modification systems, especially acetylation with acetic anhydride, have also been scaled-up and are now in the industrialising phase. Due to improved properties, modified wood is or could be applicable mainly for joinery, urban and garden furniture production, flooring, and decking. This paper describes the need for new methods in wood preservation, and wood modification as a very promising method and possible uses of modified wood.*
***Key words:*** *Wood modification, wood preservation, durability, mechanical properties, timber.*

***SAŽETAK*** • *Tijekom posljednja dva desetljeća provedena su brojna istraživanja na području modifikacije drva. Promjenom kemijske prirode polimera u stijenci drvne stanice, mnoga se svojstva, poput izdržljivosti, stabilnosti dimenzija i UV stabilnosti, mogu znatno poboljšati. Struktura stanične stijenke može se mijenjati toplinskom obradom, kemijskom modifikacijom ili enzimskim postupcima. U nekim europskim zemljama tržište traži drvo obrađeno toplinom. Ostali sustavi modifikacije, posebno acetilacija acetilnim anhidridom, su podjednako uznapredovali i nalaze se sada u fazi industrijske primjene. Zahvaljujući poboljšanim svojstvima, modificirano se drvo primjenjuje, ili se može primijenjivati za stolariju, u proizvodnji namještaja, te u gradnji podova i paluba. Ovaj članak upućuje na nove metode zaštite drva, modifikaciju drva navodi kao obećavajuću metodu primjenjivu u praksi.*
***Ključne riječi:*** *modifikacija drva, zaštita drva, trajnost, mehanička svojstva, građa.*

---

Authors are an assistant and a professor, respectively, at the Wood Department of the Biotechnical Faculty in Ljubljana, Slovenia. The article is a slightly altered version of a paper presented at the conference *Wood in Construction – Tradition and Future* in Zagreb, in April 2001.
Autori su redom asistent i profesor na Oddelku za lesarstvo Biotehniške fakultete u Ljubljani, Slovenija. Rad je u neznatno izmijenjenom obliku predstavljen na konferenciji "Drvo u graditeljstvu – tradicija i budućnost" u Zagrebu, u travnju 2001.

## 1. INTRODUCTION
## 1. UVOD

Wood preservation reduces our demand for replacement wood, thus conserving our forests. The use of biocides enables the elongation of the lifetime of wood products, far beyond that of its natural durability. For example, in temperate climates a normal transmission pole pressure-treated with creosote will have a typical lifespan of 45-60 years, whereas an identical untreated pole will last only 6-12 years (Richardson 1993). In spite of this positive contribution to the improvement of the environment, the chemicals emitted during the use and disposal of treated wood represent the critical issues facing the wood preservation industry today (Barnes and Murphy 1995, Solo-Gabriele and Townsend 2000). Namely, the world consumption of wood preservatives is enormous. Only in North America, for example, 70.000 to 85.000 tons of CCA (inorganic salts containing chromium, copper and arsenic) are expended every year (Preston 2000). In recent decades these topics have come under increased scrutiny and therefore profound environmentally motivated changes occurred in wood preservation. The trend is to decrease the amount of treated wood by choosing proper wood species for a certain purpose, by finding better construction solutions, etc. In most European countries the use of some classical biocides has been forbidden due to their toxicity (e.g. pentachlorophenol, Lindane, wood preservatives containing arsenic).

Tremendous effort has also been invested in developing new, more environment friendly wood preservatives and new methods that could supplement the "classic" wood preservation. The most interesting and promising alternatives are biocontrol (e.g. use of yeast, bacteria and fungi as pest antagonists or the use of growth regulators for protection from insects), use of targeted biocides (less harmful chemicals which prevent only certain types of decay) and wood modification. There are some ongoing projects in the EU connected with these matters, for example Thematic Network for Wood Modification (http://www.woodmodification-network.org/) and COST Action E22 – Environmental Optimisation of Wood Protection (http://www.netmaniacs.com/cost/).

## 2. PRINCIPLES OF WOOD MODIFICATION
## 2. PRINCIPI MODIFIKACIJE DRVA

The wood cell wall consists mainly of cellulose, hemicelluloses and lignin. The chemical structures of these polymers are responsible for most of the physical and chemical properties of wood. Wood modification is designed to enhance many undesirable properties of wood by altering the basic chemistry of the cell wall polymers. Chemical reagents, thermal treatments and enzymes can be used for this purpose. In majority of investigations of wood modification, by far the best results were achieved in the dimensional stabilisation of wood and improvement of wood durability. Also other properties, such as UV-stability, mechanical properties and combustibility were improved in some processes.

## 3. CHEMICAL MODIFICATION
## 3. KEMIJSKA MODIFIKACIJA

Chemical modification can be defined as any reaction between some reactive part of a wood cell wall component and a chemical reagent. Especially in the last two decades numerous reagents have been examined for this purpose. Some reviews of these reagents have already been done (Rowell 1991, Militz *et al.* 1997).

The most reactive sites of wood polymers are hydroxyl groups. These groups are usually involved in reaction with reagents. Furthermore after reacting with hydroxyl groups, cross-linking or polymerisation of reagents occurs in some cases.

A few types of reactions of various reagents with wood components are known. In the next few paragraphs a limited review of the most common reaction types and influences on wood properties is presented.

### *3.1. Esterification*
### *3.1. Esterifikacija*

The most researched reaction is acetylation with acetic anhydride. During acetylation an ester bond is formed between hydroxyl groups and the reagent:

$$\text{wood}-OH + H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3$$

$$\longrightarrow \text{wood}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3 + H_3C-\overset{\overset{\displaystyle O}{\|}}{C}-OH$$

Because most of the hydroxyl groups are blocked after the reaction, the higroscopicity of wood is greatly decreased. Hydroxyl groups are namely responsible for attracting water molecules through hydrogen bonding in natural, non-treated wood. Through this, dimensional stability of the wood is also increased. Besides lower higroscopicity, another possible reason for improved dimensional stability can be the fact that bonded groups of the reagent occupy the space in the cell wall and cause its permanently swollen state. By acetylation the antishrink efficiency, which is normally used for describing the degree of dimensional stabilisation, can reach up to 80 percent (Goldstein *et al.* 1961, Rowell 1991, Militz *et al.*1997).

Durability of wood is also enhanced by these processes. The lower moisture content and the chemical changes (wood is no longer recognised as a nutrient medium by the very specific enzyme systems of degrading fungi) can explain this. Acetylated wood exhibits very good resistance to brown rot, white rot, soft rot fungi and tunnelling bacteria. However, it is not resistant to marine borers and lower fungi, for example blue stain (Beckers *et al.*1994, Brelid *et al.* 2000). Acetylation also changes wood properties by weathering, such as colour change, photodegradation and erosion rate (Placket *et al.*1992, Evans *et al.* 2000). Wood modification can alter some mechanical properties (e.g. strength, hardness) as well. Acetylation slightly improves the mechanical strength of wood (Goldstein *et al.* 1961) and its acoustic characteristics (Chang *et al.* 2000).

During the chemical modification process unwanted by-products often occur. In the case of acetylation with acetic anhydride it is acetic acid, which can cause degradation of the cell wall components because of its acidity. This results in strength loss and an unpleasant odour of the final product. Therefore the characteristics of the product in many cases are dependent on the modification procedure itself.

Modified wood is in some aspects difficult to compare with non-treated wood because of all the above-mentioned transformations triggered by the modification process. Modified wood namely behaves differently during processing (e.g. gluing, finishing) than natural wood. For example, due to improved dimensional stability, the stability and durability of a surface coating can be enhanced. On the other hand, the altered chemical structure can totally change the glueability of wood.

Similar reactions (formation of an ester bond) take place also with some other organic acids and other types of chemical reagents: carboxylic acids (some of them are present in natural oils and fats), acid chlorides, ketenes, epoxides, etc.

### *3.2. Etherification*
### *3.2. Eterifikacija*

In order to form an ether bond with hydroxyl groups of wood alkyl chlorides, epoxides, aldehydes, ketones and some other reagents can be used. The simplest ether that can be formed is methyl ether:

$$\text{wood}-OH + H_3C-Cl \longrightarrow \text{wood}-O-CH_3 + HCl$$

Through reactions with aldehydes and ketones hemiacetals (hemiketals) are formed. These hemiacetals (hemiketals) are usually very unstable and reactive, and they cross-link with another hydroxyl group of wood to give a final acetal (ketal).

In the course of cyanoethylation with acrylonitrile an ether bond is formed as well.

### *3.3. Silylation*
### *3.3 Sililacija*

Some very natural durable wood species contain more silicates than others do. This fact led some scientists to experiment with silicon compounds. Some alkylchlorosilanes for example react very intensively with wood:

$$\text{wood}-OH + Cl-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{Si}}-R_2 \longrightarrow \text{wood}-O-\overset{\displaystyle R_1}{\underset{\displaystyle R_3}{Si}}-R_2 + HCl$$

### *3.4. Formation of a Urethane Bond*
### *3.4. Tvorba uretanskog spoja*

Isocyanates form a urethane bond with hydroxyl groups of wood polymers:

$$\text{wood}-OH + R-N=C=O \longrightarrow \text{wood}-O-\overset{\displaystyle O}{\overset{\|}{C}}-\underset{\displaystyle H}{N}-R$$

This type of reaction also often results in polymerisation or homopolymerisation of the reagent (when di- or polyisocyanates are used).

### *3.5. Modification Processes*
### *3.5. Procesi modifikacije*

Although most of the above-mentioned reagents are rather aggressive chemicals, their toxicity are in many cases low, if compared to biocides. However, from an environmental point of view the main benefit of wood modification as a wood preservation method, is that the chemicals stay permanently bonded in the wood (no leaching) and that the disposal of treated wood does not represent a problem.

Wood properties, which are improved by modification processes, are mainly influenced by reagent type and modification level (weight percent gain). The degree of modification depends mostly on the wood species used (permeability is a crucial factor) and on the reaction conditions (e.g. temperature, catalysts). Inexpensive wood of a fast growing tree species is usually used for chemical modification. Permeability of such wood species is namely high, however, the properties of the initial material are not very important for the quality of the final product. Through studying certain reaction or process an optimum degree of modification and process parameters must be established.

## 4. THERMAL TREATMENTS
## 4. TOPLINSKA OBRADA

The basic idea of thermal treatments is to change the molecular structure of the wood cell wall components by applying heat. During the heating/cooling process, some wood polymers (especially hemicelluloses and lignin) are broken down, and new water insoluble polymers are formed. Heat-treatment usually takes place in an inert gas atmosphere at temperatures between 150 and 260 $C. The presence of oxygen can namely result in severe degradation of the cellulose, which considerably reduces the strength of the timber. One of the biggest challenges of thermal treatments is keeping the strength reduction under control. The main aim in developing certain thermal process is to improve dimensional stability and durability of wood as good as possible, by maintaining mechanical losses at a minimum. Therefore heat-treated wood is mainly applicable for purposes, where heavy burdens are not expected, but dimensional stability and durability of the wood is desired (e.g. window production).

In some European countries and the USA, different thermal treatments have been developed and some of them are already documented in patent specifications. In Europe heat-treated wood is produced in Finland, France, Germany and the Netherlands. Different wood species are used in these processes (the most common are pine, spruce, poplar and birch).

The main difference between the processes is the heating medium. The most often used mediums that enable the elimination of the oxygen in a kiln are nitrogen, steam and different oils. The properties of heat-treated wood are mainly dependent upon the process type, heating parameters (duration, final temperature) and wood species.

Common improvements of wood properties enhanced by these processes are: the reduction of higroscopicity (equilibrium moisture content up to 50 percent), reduction of shrinking and swelling (up to 90 percent), improved durability and limited flammability (Dirol and Guyonnet 1993, Viitanen *et al.* 1994, Tjeerdsma *et al.* 1998, Sailer *et al.* 2000, Tjeerdsma *et al.* 2000). The mechanical properties are worsened in all cases. Wood becomes brittle, especially when high temperatures are used (bending and tension strength can decrease up to 30 percent), it loses some of its mass (up to 15 percent), its colour changes into dark brown (the higher the final temperature, the darker the colour of the wood) and a typical burnt smell occurs, which decreases in intensity after a few days but can remain for several months. The producers can regulate some of these changes with process parameter control. For example, when the final temperature in the process is very high, the product is very durable, but its mechanical properties are poor. On the other hand, low final temperature only slightly improves the product's durability, but mechanical properties are somewhat worsened.

All these alterations of wood properties also demand some adapted processing methods. Because the product is brittle in many cases, sharp blades have to be used to prevent the material from splintering. The sawdust coming from the process is very fine and dry and can cause irritations to the respiratory system. In some cases (depends on the treatment type) certain types of glues and coatings have to be used as well. However, the producers have already found the best solutions for all curiosities of their products.

The problem of external quality control has to be solved in the near future. The producers of heat-treated wood have already developed some methods for internal use, but a quick, non-destructive, universal method is needed. There exists a clear correlation between the mass loss during the process and the beneficial properties of the heat-treated product. A proper solution could be checking of the mass loss and application of some simple analytical methods, such as FTIR (Kotilainen *et al.* 2000).

Recently some studies have been carried out, which study the potential toxicity of the product and by-products. Some toxic, polyaromatic compounds appear to be present in the heat-treated wood, although their proportions seem to be quite low (Kamdem *et al.* 2000). However, the exact research and quantification of this matter should be undertaken before assigning to this type of wood treatment a completely clean health safety label.

## 5. ENZYMATIC TREATMENTS
## 5. ENCIMATSKI POSTUPCI

In some researches boards from laccase treated fibres were made without the use of any glues. Laccase is known to catalyse oxidation of phenolic species in lignin. When heated with lignocellulosic material, it allows bonding to occur.

Lately the possibility of using enzymes for wood modification is being studied.

## 6. APPLICATION OF MODIFIED WOOD
## 6. PRIMJENA MODIFICIRANOG DRVA

Heat-treated wood produced in some European countries is intended to be used mainly in joinery (e.g. windows, doors, flooring, panels in bathrooms and saunas, etc.), garden furniture and playground equipment production, and decking (claddings). Due to improved properties heat-treated wood could be applicable also for housing (e.g. for frameworks, roof trusses), packaging and other products, like toys, music instruments, pencils, etc.

In general, the properties of chemically modified wood are even better. Although it is not yet on the market, it is believed that its possible uses will be wider and more diverse.

## 7. CONCLUDING THOUGHTS
## 7. ZAKLJUČNE MISLI

Wood modification will be an important alternative method in wood preservation in the future. Compared to "classic" wood preservation methods, it has some significant advantages. Besides the durability some other wood properties can be simultaneously improved (dimensional stability is very important). The negative influence on the environment is strongly reduced. However, a lot of work is still left to be done in this field, in order to get modified wood highly accepted on the market.

## 8. REFERENCES
## 8. LITERATURA


1. Barnes, H.M., Murphy, R.J. 1995: Wood Preservation. The Classics and the New Age. For. Prod. J. 45 (9): 16-26.
2. Beckers, E.P.J., Militz, H., Stevens, M. 1994: Resistance of acetylated wood to Basidiomycetes, soft rot and blue stain. The International Research Group on Wood Preservation, Document IRG/WP 94-40021, Stockholm: IRG Secretariat.
3. Brelid, P.L., Simonson, R., Bergman, Ö., Nilsson, T. 2000: Resistance of acetylated wood to biological degradation. Holz Roh-Werkst. 58: 331-337.
4. Chang, S.-T, Chang, H.-T, Huang, Y.-S., Hsu, F.-L. 2000: Effects of Chemical Modification Reagents on Acoustic Properties of Wood. Holzforschung 54 (6): 669-675.
5. Dirol, D., Guyonnet, R. 1993: The improvement of wood durability by retification process. The International Research Group on Wood Preservation, Document IRG/WP 93-40015, Stockholm: IRG Secretariat.
6. Evans, P.D., Wallis, A.F.A., Owen, N.L. 2000: Weathering of chemically modified wood surfaces. Wood Sci. Technol. 34: 151-165.
7. Goldstein, I.S., Jeroski, E.B., Lund, A.E., Nielson, J.F., Weaver, J.W. 1961: Acetylation of wood in lumber thickness. For. Prod. J. 11 (8): 363-370.
8. Kamdem, D.P., Pizzi, A., Triboulot, M.C. 2000: Heat-treated timber: potentially toxic by-products presence and extend of wood cell wall degradation. Holz Roh-Werkst. 58: 253-257.
9. Kotilainen, R.A., Toivanen, T.-J., Alén, R.J. 2000: FTIR Monitoring of Chemical Changes in Softwood During Heating. J. Wood Chem. Tech. 20 (3): 307-320.
10. Militz, H., Beckers, E.P.J., Homan, W.J. 1997: Modification of solid wood: research and practical potential. The International Research Group on Wood Preservation, Document IRG/WP 97-40098, Stockholm: IRG Secretariat.
11. Placket, D.V., Duuningham, E.A., Singh, A.P. 1992: Weathering of chemically modified wood. Accelerated weathering of acetylated radiata pine. Holz Roh-Werkst. 50: 135-140.
12. Preston, A.F. 2000: Wood preservation. Trends of today that will influence the industry tomorrow. For. Prod. J. 50 (9): 12-19.
13. Richardson, B.A. 1993: Wood Preservation. Second edition. London, Glasgow, New York, Tokyo, Melbourne, Madras: E & FN Spon, Chapman & Hall.
14. Rowell R.M. 1991: Chemical Modification of Wood. In: D.N.-S. Hon, N. Shiraishi: Wood and Cellulosic Chemistry. New York: Marcel Dekker, Inc., pp. 703-756.
15. Sailer, M., Rapp, A.O., Leithoff, H. 2000: Improved resistance of Scots pine and spruce by application of an oil-heat treatment. The International Research Group on Wood Preservation, Document IRG/WP

00-40162, Stockholm: IRG Secretariat.

16. Solo-Gabriele, H.M., Townsend, T. 2000: Management Strategies for the Disposal of CCA-Treated Wood. The International Research Group on Wood Preservation, Document IRG/WP 00-50155, Stockholm: IRG Secretariat.
17. Tjeerdsma, B.F., Boonstra, M.J., Militz, H. 1998: Thermal modification of non-durable wood species. 2. Improved wood properties of thermal treated wood. The International Research Group on Wood Preservation, Document IRG/WP 98-40124, Stockholm: IRG Secretariat.
18. Tjeerdsma, B.F., Stevens, M., Militz, H. 2000: Durability aspects of (hydro)thermal treated wood. The International Research Group on Wood Preservation, Document IRG/WP 00-40160, Stockholm: IRG Secretariat.
19. Viitanen, H., Jämsä, S., Paajanen, L., Nurmi, A., Viitaniemi, P. 1994: The effect of heat treatment on the properties of spruce. The International Research Group on Wood Preservation, Document IRG/WP 94-40032, Stockholm: IRG Secretariat.