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VZROKI BARVNIH SPREMEMB MED TERMIČNO IN HIDROTERMIČNO OBDELAVO LESA

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Izvleček

Članek obravnava kemijsko zgradbo termično in hidrotermično obdelanega lesa. Predstavljeni so degradacijski in modifikacijski procesi med hidrotermično obdelavo. Opisane so kemijske spremembe lesa, ki vplivajo na izboljšano dimenzijsko stabilnost, znižano ravnovesno vlažnost in izboljšano biološko odpornost hidrotermično obdelanega lesa. Podrobno so opisane kemijske reakcije, ki povzročijo temno barvo hidrotermično obdelanega lesa. Vzroki barvnih sprememb so pojasnjeni z različnih vidikov, ki vključujejo degradacijske procese hemiceluloz, oksidacijske reakcije in polimerizacijske reakcije lignina. Vmesni degradacijski produkti lignina so predstavljeni kot glavni vir barvnih sprememb hidrotermično obdelanega lesa.

Ključne besede: les, hidrotermična obdelava, barva, kemijske spremembe, vzroki

REASONS FOR COLOUR CHANGES DURING THERMAL AND HYDROTHERMAL TREATMENT OF WOOD

Abstract

The chemical composition of wood in relation to its thermal and hydrothermal treatment is discussed. The degradation and modification processes, which take place during hydrothermal treatment, are presented. The chemical reasons for the increased dimensional stability, reduced moisture content and improved biological durability of hydrothermally treated wood are given. Particular attention is given to the chemical reactions that can cause the darker tonality of hydrothermally treated wood. The literature review of chemical explanations for wood colour changes ranges from the degradation of hemicelluloses through oxidation reactions to lignin polymerization reactions. Intermediate lignin degradation products are considered to be the main source of colour changes in hydrothermally treated wood.

Key words: wood, hydrothermal treatment, colour, chemical changes, reasons

UVOD INTRODUCTION

The use of hydrothermal treatment to modify the properties of wood has become more popular in recent years due to environmental concerns, as this kind of treatment can produce a "new material" without adding harmful chemicals. Hydrothermal treatment drastically changes the properties of wood. Temperatures above 150°C alter the physical and chemical properties of wood permanently (AKGÜL / GÜMÜSKAYA / KORKUT 2007). In spite of reduced mechanical resistance (KUBOJIMA / OKANO / OHTA 2000; JOHANSSON / MORÉN 2006), wood is hydrothermally treated in order to improve its biological durability (BOONSTRA et al. 2007; PAUL / OHLMEYER / LEITHOFF 2007), to reduce the equilibrium moisture content of wood (KOLLMANN / COTE 1968, METSÄ-KORTELAINEN / ANTIKAINEN /

VIITANIEMI 2006), and to improve its dimensional stability (HILLIS 1984; HSU et al. 1988; INOUE et al. 1993; ESTEVES et al. 2007a). At times, hydrothermal treatment is also used to change the aesthetic properties of wood, which allows the use of light-coloured woods that is usually less appealing to the consumer.

The simultaneous effects of heat and moisture generate radical changes in wood structure, resulting in a dynamic colour change. The colour of the wood is modified, acquiring a darker tonality. The higher the temperature and/or the longer the treatment time, the darker is the colour, which can be achieved by the hydrothermal treatment of wood (ESTEVES et al. 2007b). The effect of thermal and hydrothermal treatment on the colour changes of wood has been studied extensively in the past (TJEERDSMA et al. 1998; KOCH / PULS / BAUCH 2003; SUNDQVIST / KARLSSON / WESTERMARK 2006; VARGA / VAN DER ZEE 2007). However, the chemical rea-

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sons for wood colour changes have not yet been fully clarified, although they seem to originate from complex changes and degradation of hemicelluloses, lignin and certain extractive compounds (SUNDQVIST / MORÉN 2002). The aim of this paper is to provide a literature review about the influence of chemical changes induced by thermal/hydrothermal treatment on the colour of wood. Colour is a very important property for the end use of wood products. It is therefore important to know how the process parameters of thermal/hydrothermal treatment can affect the aesthetic properties of wood. Furthermore, knowledge of the chemical reactions that take place during the hydrothermal treatment of wood is essential for the understanding of hydrothermally treated wood and its properties. In addition, such data are valuable for the understanding of the behaviour of densified wood, since wood densification processes utilize hydrothermal treatments.

THE COLOUR OF HYDROTHERMALLY TREATED WOOD

BARVA HIDROTERMIČNO OBDELANEGA LESA

The colour of a solid material can be attributed to the reflection, scattering and absorption of light within the visible range that is caused by certain molecules called chromophores. In wood, light is mainly absorbed by lignin below 500 nm and by phenolic extractives (tannins, flavanoids, stilbenes, quinines) above 500 nm, whereas cellulose and hemicellulose do not absorb light within the visible range (SUNDQVIST 2004).

In the event of hydrothermal treatment, the colour of wood becomes darker. It has been ascertained that noticeable colour changes can be obtained for a small mass loss of 2-4%, but that the effect depended on the length of treatment time and on temperature (ESTEVEZ et al. 2007b; BEKHTA / NIEMZ 2003). In heat treatment with air, the rate of lightness reduction is greater up to a mass loss of 4%, when the heat-treated wood becomes by about 50% darker than the original wood. Darker tonality is often justified by the formation of coloured degradation products from hemicelluloses (SUNDQVIST 2004) and from extractives that seem to participate in the colour formation of hydrothermally treated wood (SUNDQVIST / MORÉN 2002). Colour change has also been related to the formation of oxidization products such as quinines (BEKHTA / NIEMZ 2003).

CHEMICAL CHANGES CAUSING COLOUR CHANGES

KEMIJSKE SPREMEMBE, KI POVZROČAJO BARVNE SPREMEMBE

AVAILABILITY OF WOOD COMPONENTS

DOSTOPNOST LESNIH KOMPONENT

SUNDQVIST (2004) has discussed the availability of components in the wood structure as an important factor in the explanation of chemical changes caused by thermal and/or hydrothermal treatment. The most embedded and least available structural component in wood is cellulose (it is not easily affected by solvents, water, etc.). Hemicelluloses and pectins are bonded to the surface of the cellulose microfibrils and fill in the voids between the microfibrils. The hemicelluloses therefore have a higher availability than the cellulose, and are more easily affected by solvents. The fibres as well as microfibrils, based mainly on the cellulose and hemicelluloses, are impregnated with lignin, and held together by bonds between the lignin units and the hemicellulose units. The lignin is therefore, in general, as available as the hemicelluloses, and is clearly more susceptible to the effects of solvents and water than cellulose. The extractives that are mostly found in horizontal and vertical resin canals are, however, available to solvents and water to a much greater extent than the structural components.

REACTIVITY OF WOOD COMPONENTS

REAKTIVNOST LESNIH KOMPONENT

It is well-known that lignin is the least reactive wood component, but at high temperatures the bonds within the lignin complex will be cleaved, resulting in a higher concentration of phenolic groups (TJEERDSMA / MILITZ 2005; WINDEISEN / STROBEL / WEGENER 2007). The increased reactivity of the lignin allows the occurrence of various condensation reactions of aldehydes and lignin and of the auto-condensation of lignin. At temperatures around 120°C, changes in the lignin structure start to occur, and with further increases in temperature the changes increase (SUNDQVIST 2004). In the presence of oxygen, the degradation of lignin clearly increases in comparison with conditions where no oxygen is present. At temperatures around 180°C, the degradation of lignin is significant. The cleavage of β -ether linkages and the formation of

radicals in lignin have been found for wood samples and the formation of condensation products, and possible cross-links between lignin and polysaccharides have also been reported (SUNDQVIST 2004). Lignin is not changed as much as the hemicelluloses when subject to hydrolytic conditions below 200°C. Mild acidic hydrolysis of lignin is thought to be the result of the breaking of cyclic α -aryl ether bonds, resulting in various lignin fragments such as lignols. Above 200°C, the lignin degradation rate and the concentration of radicals that is formed have been reported to increase strongly (AKGÜL / GÜMÜSKAYA / KORKUT 2007). A high degradation rate has been observed particularly in the case of lignin units containing phenolic groups, which account for approximately 10% of all units. Furthermore, the α - and β -aryl ether bonds linking the lignin units (comprising 50-70% of all bonds) are more easily broken than carbon-carbon bonds (SUNDQVIST / KARLSSON / WESTERMARK 2006).

CHEMICAL CHANGES INDUCED BY HYDROTHERMAL TREATMENT

KEMIJSKE SPREMEMBE MED HIDROTERMIČNO OBDELAVO

The heat treatment of wood modifies the cell wall components. A number of chemical changes to heat treated wood have been reported. SUNDQVIST (2004) reviewed the studies of chemical changes caused by heat and hydrothermal treatment. The relevant temperatures are listed. The first chemical changes begin at temperatures within the 40 - 90°C range; these are predominately caused by certain extractives. At temperatures within the range 90 - 150°C, changes occur in all wood components. In wet conditions, approximately 100°C is considered to be the plasticization temperature of wood, which is related to changes in the lignin structure. Splitting of β -aryl ethers and the formation of lignin condensation products at 100 - 120°C was found for maple, and hemolytic cleavage of phenolic β -aryl ether in wood lignin was found at around 130°C. At temperatures of 150 - 250°C, major changes occur in wood components, both degradations and modifications. The degradation rate of wood is reported to be higher for steaming and in the presence of air during heating than for dry and air-free conditions.

HAKKOU et al. (2005) recorded FTIR spectra on beech samples treated at 160 and 260°C for 8 h. A number of spectral modifications appeared after the heat treatment, even if the general aspect of the spectra remained unchanged. Com-

pared to the aromatic band at 1595 cm^{-1} , heat treatment at 260°C led to a significant decrease of the carbonyl band at 1730 cm^{-1} , indicating degradation of hemicelluloses. The authors also noticed a significant decrease in the 1465 cm^{-1} band characteristics of the lignin C-H vibration, which is the consequence of the thermo-condensation of lignin through aromatic electrophilic substitutions of aromatic nuclei. At 260°C, a doublet occurred at 1315 and 1335 cm^{-1} , which is characteristic of celluloses with a high crystallized cellulose I content. This indicated an increase of crystallinity. Another modification occurred in the evolution of the band at 1385 cm^{-1} , which shifted to 1375 cm^{-1} after treatment at 160°C and to 1370 cm^{-1} after treatment at 260°C. This modification could be attributed to conformational changes in wood glycosidic components. In the ensuing study by HAKKOU et al. (2006), using the same heat treatment, it was established that the generation of extractives begins at 160°C and becomes significant at temperatures higher than 200°C.

YILDIZ, GEZER and YILDIZ (2006) examined the chemical changes in the chemical structure of wood that had been heat treated at four different temperatures, between 130°C and 200°C, for three different durations (2, 6 and 10 h). They established that the cellulose content remains unchanged in the case of all of the studied treatments, whereas the hemicelluloses values exhibited a decrease with increased exposure duration and temperature, and the lignin values increased with increasing treatment temperature and duration.

YILDIZ and GÜMÜSKAYA (2007) studied the effect of heat treatment at 150, 180 and 200°C for 6 and 10 h in the presence of air on the crystalline structure of cellulose, using FTIR spectrometry. The crystallinity of the cellulose was determined by the ratio of peaks areas at 1370 (CH bending) and 670 cm^{-1} (C-OH out-of-plane bending mode). They concluded that the crystallinity of cellulose increased with temperature and duration of heat treatment.

WIKBERG and MAUNU (2004) studied the chemical changes after 44 h of heat treatment at 195°C under steam. They established that thermal modification causes the degradation of hemicelluloses and amorphous cellulose, resulting in an increase in the cellulose crystallinity, and in the cleavage of the β -O-4 linkages, which induces changes in the lignin structure.

PHUONG, SHIDA and SAITO (2007) have suggested that lignin relocation occurs at relatively low temperatures, around 160°C, and that crystallites were formed after 2 h of heat treatment at 160°C in an inert atmosphere. AKGÜL,

GÜMÜSKAYA and KORKUT (2007) have reported that the changes in crystallinity related to the heating temperature and the duration of heat treatment. BHUIYAN, HIRAI and SOBUE (2000), and BHUIYAN and HIRAI (2005), studied the crystalline behaviour of heat-treated wood cellulose, and concluded that the increase in the degree of crystallinity of wood cellulose caused by heat treatment under moist conditions is almost twice that obtained by oven-dry heating. They also reported that the activated steam produced by the high-moisture heat treatment degrades the lignin.

INARI et al. (2007) reported that char formation in wood begins within the range of temperatures between 200 and 240 °C, when heat treatment is carried out under an inert atmosphere. The result suggests that the lignin modification reported in the literature for heat treatment, in the case of mild pyrolysis, is actually the consequence of char formation.

TJEERDSMA and MILITZ (2005) investigated the chemical changes in combined hydrothermally and dry heat-treated wood. They found that the cleavage of the acetyl groups (i.e. the formation of carbonic acids, mainly acetic acid) of the hemicellulose occurs in the first step of heat treatment at temperatures between 165 and 195°C, under moist conditions. In the next step, however, under dry conditions at 180°C, esterification occurred (with an increase in the specific ester carbonyl peak at 1740 cm⁻¹ in the FTIR spectrum), which contributes to the decrease of hydroscopicity. In spite of results obtained, the authors stated that esterification has a minor influence in the decrease of hydroscopicity compared to the influence of cross-linking reactions of the lignin network, which occur during thermal treatment of wood, since the proportion of free hydroxyl groups still available after heat treatment did not change.

BOONSTRA and TJEERDSMA (2006) compared the chemical changes of two-stage heat-treated wood. During the first stage (hydro-thermolysis), depolymerization of hemicelluloses and hydrolysis cleavage of acetic acid from their acetyl groups occurred. During the second stage, the lignin content of the treated wood was increased, due to the depolymerization of carbohydrates. The effect of two-stage heat treatment had a limited effect on cellulose.

DWianto et al. (1999) considered that steaming below 200°C causes permanent fixation of compression deformation due to chain scission of hemicelluloses accompanied by a slight cleavage of lignin.

CHEMICAL REASONS FOR COLOUR CHANGES KEMIJSKI VZROKI ZA BARVNE SPREMEMBE

SUNDQVIST, KARLSSON and WESTERMARK (2006) determined the formic acid and acetic acid concentrations occurring during the hydrothermal treatment of birch wood under nine different sets of conditions. Three different temperatures (160, 180 and 200°C) and three different times (1.0, 2.5 and 4.0 h) were used. It was established that during such hydrothermal treatment considerable amounts of acetic and formic acid can be released into the wood material; high concentrations of acetic and formic acids are related to high treatment temperatures and long treatment times. The paper shows that high concentrations of acids are related to low lightness and low hue. Possible degradation reactions, coupled with the colour in relation to acid formation, are discussed. The reactive compounds can include degradation products from the cleavage of α - and β - ether bonds in the lignin and degradation products from the hemicelluloses. The reddish colour and increased colour saturation that is substantiated as a decrease in hue and an increase in chroma is explained by the formation of secondary condensation products and/or degradation products of the quinone and quinonemethide types. Quinone and quinonemethide are intermediate lignin degradation compounds, which are strongly coloured. In the study it was also reported that a rapid decrease in lightness occurs early in the heat-treatment process, where the largest change can be found between 0- and 1-h treatment, indicating that much of the decrease in lightness occurs already after a short period of time and at fairly low temperatures.

MAYER and KOCH (2007) investigated the colour changes during the hot water treatment of American black cherry (*Prunus serotina*) for 12, 48 and 72 h, at 60 and 70°C. With increasing duration of the heat treatment, the wood colour darkened. An increase in the treatment temperature to 70°C accelerated the colour changes, which were ascribed to structural changes of the phenolic compounds (oxidation and/or polymerization).

KOCH, PULS and BAUCH (2003) showed that changes in the lignin structure, with an influence on wood colour, can be expected during hot water treatment at temperatures higher than 80°C. The paper describes different possible reaction mechanisms, which can explain the difficult chemical identification of the accessory compounds responsible for the discoloration of beech during thermal treatment. Steaming can

initiate cleavage of lignin-polysaccharide complexes by the release of organic acids from the hemicelluloses. On the other hand, it is assumed that some interactions of wood cell wall components lead to the formation of a secondary lignin-carbohydrate linkage which, eventually, causes discolorations. Due to the separation of the hydroxyl groups, conjugated double bonds at C₃ of the lignin molecule might be formed. The steam treatment also mobilizes the water-soluble compounds (soluble carbohydrates and starch) or hydrolysis products, which can initiate discolorations by oxidation and condensation. The changes in the lignin structure can result in strong darkening and reddening of the wood tissue, which may cover the colour variations caused by wood extractives. The lignin reaction causes a uniform, reddish colour of beech during steaming, whereas the irregular discolorations in beech wood are caused by chemical reactions of unevenly distributed phenolic compounds.

TJEERDSMA et al. (1998) explained the chemical reactions that take place during the two-step (first humid, and then dry) thermal modification of wood. In the first, humid step the changes occur mostly to the hemicelluloses, whereas some begin to occur at lignin-free reactive sites on the aromatic ring of some of the lignin units. In the second dry step, changes in the lignin complex mostly occur. The extent of these reactions is very small, but nevertheless they result in an increase in cross-linking within the lignin-carbohydrate-complex (LCC), with consequent improvement in the hygroscopicity and dimensional stability of the wood, which is explained by the fact that the cellulose microfibrils are surrounded by a firm and more inelastic network due to increased cross-linking within the lignin complex. Hemicelluloses are transformed selectively, and react into a hydrophobic network. The darker colour of the thermally modified wood is explained by oxidation products such as quinines.

BURTIN et al. (2000) studied the effects of steaming time (4, 8, 16, 24 h) and temperature (75, 100 and 125°C) on wood colour, and the phenolic compounds involved in wood colour changes during steaming. Hydrojuglone glucoside, gallic and ellagic acid derivatives were regarded as major precursors of artificial wood colouring, providing chromophores through a degradation process.

AYADI et al. (2003) demonstrated that wood photodiscolouration is mainly due to lignin photodegradation, i.e. photochemical reactions occurring in the lignin. The absorption of light by chromophoric groups of lignin leads to the formation of free radicals that react with oxygen to produce chromophoric

groups such as carbonyl and carboxyl groups, which are responsible for the wood colour changes.

CONCLUSIONS SKLEPI

The thermal and/or hydrothermal treatment of wood leads to chemical changes in the treated wood. The extent of these changes depends on the used temperature and duration of the treatment. The wood components undergo degradation and modification processes, which result in increased dimensional stability, reduced moisture content, improved biological durability and darker tonality of the treated wood. Based on the given literature review, it can be concluded that the major source of the darker colour of hydrothermally treated wood consists of the lignin polymerization reactions, which occur during wood treatment. The cleavage of α - and β - ether bonds in lignin produces intermediate lignin degradation compounds as quinone and quinonemethide, which are strongly coloured and cause the darker colour of hydrothermally treated wood. The darker colour could also be the result of oxidation and the condensation of soluble carbohydrates.

POVZETEK

V zadnjih letih je opazen nagel porast termične in hidrotermične obdelave lesa z namenom modificiranja lastnosti lesa. Hidrotermična obdelava nad 150 °C povzroči trajne spremembe fizikalnih in kemijskih lastnosti lesa. Les termično in hidrotermično obdelujemo z namenom, da povečamo njegovo biološko odpornost, znižamo ravnovesno vlažnost in povečamo dimenzijsko stabilnost, a tudi z namenom, da spremenimo njegove estetske lastnosti. Takšna modifikacija pa ima tudi nezaželene učinke, saj se lesu zmanjšajo mehanske lastnosti – zniža se mu trdnost in žilavost.

Vzporedno delovanje toplote in vlažnosti med hidrotermično obdelavo lesa povzroči radikalne spremembe v lesni strukturi, ki se kažejo tudi kot barvne spremembe. Ker je barva lesa pomembna lastnost z vidika končne uporabe lesnega produkta, so potrebne raziskave vpliva parametrov hidrotermične obdelave lesa na njegove estetske lastnosti. Les se začne barvno spreminjati že pri temperaturah hidrotermične obdelave okoli 70 °C, kljub majhni izgubi mase (2 – 4 %). Les potemni sorazmerno z višino uporabljene temperature in s trajanjem hidrotermične obdelave. Višja ko je temperatura in daljši ko je čas hidrotermične obdelave, temnejši je les

po obdelavi. Kljub številnim raziskavam barvnih sprememb med hidrotermično obdelavo lesa še vedno ni popolnoma jasno, kateri so glavni razlogi za te spremembe. Gre namreč za kompleksne kemijske spremembe, saj hidrotermična obdelava lesa povzroči degradacijske reakcije lesnih komponent. Vplivom hidrotermične obdelave lesa so najbolj izpostavljeni lesni ekstraktivi, ki jih večinoma najdemo v smolnih kanalih. Značilna struktura lesa je vzrok, da so strukturne lesne komponente, celuloza, hemiceluloze in lignin, različno izpostavljene vplivom hidrotermične obdelave. Celuloza je najbolj vklopljena strukturna komponenta lesa in zato tudi najmanj izpostavljena vplivom hidrotermične obdelave lesa. Na površino celuloznih mikrofibril so vezane molekule hemiceluloz, ki so zato bolj izpostavljene vplivom hidrotermične obdelave. Vlakna in mikrofibrile so med seboj povezane z ligninom. Zato je lignin na splošno enako dostopen vplivom hidrotermične obdelave kot hemiceluloze, kljub temu da je lignin najmanj reaktivna lesna komponenta. Pri visokih temperaturah se namreč pojavijo spremembe v strukturi lignina, poveča se njegova reaktivnost, kar dovoljuje nastanek kondenzacijskih reakcij aldehydov in lignina.

Prve kemijske spremembe se med hidrotermično obdelavo lesa pokažejo v ekstraktivih pri temperaturah med 40 – 90 °C. Pri temperaturah med 90° C in 150° C pa se kemijske spremembe pokažejo v vseh lesnih komponentah. V primeru termične obdelave v vlažnem stanju les preide v plastično območje pri 100° C, ko nastanejo prve spremembe v strukturi lignina. Pri temperaturah med 150 – 250° C pa se pojavijo bistvene spremembe v vseh lesnih komponentah. Kemijske spremembe oziroma stopnja degradacijskih reakcij je višja pri hidrotermični obdelavi in ob prisotnosti zraka kot pri termični obdelavi v suhih razmerah brez prisotnosti zraka.

Glede na dosedanje raziskave in podatke iz literature so barve spremembe med hidrotermično obdelavo posledica degradacijskih reakcij hemiceluloz, oksidacijskih in polimerizacijskih reakcij lignina ter določenih ekstraktivov. Na barvo hidrotermično obdelanega lesa vplivajo degradacijski produkti, ki nastanejo pri cepitvi α - in β -eterskih vezi lignina ter pri degradaciji hemiceluloz. Rdečkasta barva, ki nastane po obdelavi, je posledica tvorjenja sekundarnih kondenzacijskih produktov in/ali degradacijskih produktov. Na barvne spremembe vplivata predvsem kinon in kinonometil, ki sta močno obarvana. Kinon in kinonometil nastaneta pri degradaciji lignina kot vmesna produkta. Barvne spremembe pa so lahko tudi posledica strukturnih sprememb fenolnih komponent, ki nastanejo zaradi oksidacije ali polimerizacije med hidroter-

mično obdelavo lesa. Na stopnjo barvnih sprememb vplivata predvsem temperatura in trajanje termične oziroma hidrotermične obdelave, čeprav bistvene barvne spremembe nastanejo že na začetku obdelave. Na stopnjo potemnitve pa vpliva tudi uporabljena lesna vrsta. Variabilnost lesa se namreč kaže tudi v kemijski zgradbi lesa. Zato se različne lesne vrste v enakih razmerah hidrotermične obdelave vedejo različno, kar še otežuje razlago kemijskih sprememb med hidrotermično obdelavo lesa.

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