Effects of drying temperature and artificial UV irradiation on the pH of veneer surfaces, water absorption, thickness swelling, as well as shear strength of plywood manufactured from untreated and treated veneer sheets were evaluated. Rotary cut veneer sheets from beech (*Fagus orientalis Lipsky*) log were selected. The veneer sheets were dried at either 100°C or 180°C after peeling. Then the surfaces were exposed to artificial UV irradiation in an UV chamber for 1, 2, and 3 days representing a natural sun irradiation of 2, 4, and 6 months, respectively. Tests by UV microspectrophotometry showed that after high temperature drying and UV irradiation treatment, lignin condensation occurs. Also with increasing drying temperature and UV irradiation duration phenolic extractives are mainly concentrated in parenchyma cells and vessel lumens. HPLC analysis of the treated tissue showed distinct signals of catechin and 2,6-dimethoxybenzoquinon, which are two chromophoric compounds in discolored red hearted beech wood. Increasing drying temperature up to 180°C improved water absorption, thickness swelling, and shear strength of plywood samples. Especially, when veneers were exposed to UV irradiation (6 months), increased water absorption and thickness swelling and decreased the shear strength of plywood samples were observed.

Keywords: Water absorption; Thickness swelling; Drying temperature; UV irradiation; UV microspectrophotometry; Shear strength

Contact information: a: Department of Wood and Paper Science and Technology, Faculty of Natural Resources, University of Tehran, Iran; b: Institute for Wood Technology and Wood Biology, Federal Research Institute of Rural Areas, Forestry and Fisheries (vTI), Hamburg, Germany; c: Department of Chemistry, Payame Noor University, Iran; * Corresponding author: Loyajamalirad@yahoo.com

INTRODUCTION

When wood material is heat-treated, the chemical, physical, and mechanical properties change, and its structure is re-formed. Heat treatment is a well-known approach to improve properties of timber, such as biological durability, dimensional stability, and strength by modification of the main components of wood (cellulose, hemicelluloses, and lignin), (Sandermann and Augustin 1963a, 1963b, 1964; Kollmann and Fengel 1965; Fengel and Wegener 1989; Tjeerdsm et al. 1998). Heat-treated wood can be utilized for various purposes, such as garden, furniture, floorings, fences, claddings, and noise barriers. The adhesive bonding of heat treated wood significantly expands the range of applications of wood. When wood is used for decorative end-uses, the appearance of wood is very important and the color stabilization of natural wood is
required. Drying process can cause discoloration, and such color changes often occur when temperatures are higher in industrial kiln drying. These color changes imply alteration of wood components, which impose adverse effect on wood properties, such as strength. When wood is heated to temperatures of 160 to 260 °C, hemicelluloses start to degrade first, since they have the lowest molecular weight and branched structure among the wood polymers (Tumen et al. 2010). Simultaneously, cellulose starts to degrade due to formation of formic acid and acetic acid, and the crystallinity of wood increases temporarily at around 160 to 200 °C. Researchers have not found any changes in lignin up to 155 °C. Heating at 175 °C initiates lignin condensation, which is increased at temperatures up to 240 °C (Fengel and Wegener 1989).

It has been known for a long time that wood exposed to solar radiation is subject to surface degradation; primarily color changes and mechanical breakdown (Derbyshire et al. 1981). The main factor that causes the greatest changes in the surface properties of wood during outdoor exposure is sun light. Wood is capable of absorbing all wavelengths of electromagnetic radiation to initiate photochemical reactions, which may ultimately lead to wood discoloration and photodegradation (Hon 1981). Apart from reduction in methoxyl content and an increase in carboxyl content of the wood (Leary 1967, 1968), photodegradation also results in increase in cellulose and decrease in lignin concentration on wood surface (Wang and Lin 1991; Evans et al. 1992; Hon 1994, 2001; George et al. 2005), which ultimately leads to reduction of some physical, chemical and biological properties of natural wood.

Scientific literature on adhesion behavior and the mechanical and technological properties of red-heart beech wood is scarce. The application of red-heart beech wood in products of massive volume such as glulam and in the furniture and flooring industries is desirable. The objective of this paper is to provide scientific data on physical and mechanical properties of plywood manufactured from red-heart beech veneer affected by high drying temperature and artificial UV irradiation. The distribution of aromatic phenolic compounds in cell wall layers and vessel lumens is visualized by cellular UV microspectrophotometry (UMSP). Changes in extractive components are determined applying HPLC method. The pH of veneer surfaces, water absorption, thickness swelling, and shear strength of plywood manufactured from treated layers are also measured.

**EXPERIMENTAL**

**Materials**

**Veneer preparation**

A red-heart-containing log, 57 cm in diameter, was steamed for 48 h before veneer production. Then rotary cuts of red-hearted veneer sheets with dimensions of 50 cm × 50 cm × 2 mm were randomly cut from the main veneer sheet. Veneer sheets were dried at 100 °C (normal drying temperature) and 180 °C (high drying temperature).

**Artificial UV light irradiating the veneer**

Dried red-heart-containing veneer sheets were exposed to artificial UV light irradiation in UV chamber for 1, 2, and 3 days (equal to 2, 4 and 6 months in ambient sun
light) (Mayer and Koch 2007). The untreated red heart veneer samples were used as control.

**Methods**

*UMSP method*

Using cellular UV microspectrophotometry (UMSP), with a defined wavelength of $\lambda_{280}$ nm, the distribution of lignin and aromatic phenolic extractives in red heart beech wood tissue, before and after drying and UV light irradiating, were visualized providing two- or three-dimensional image profiles with a local spatial resolution of 0.25 µm$^2$ (Koch and Kleist 2001).

*HPLC method*

For the chemical detection of accessory compounds, wood shaving from red heart beech wood tissue, before and after drying and UV light irradiating, were prepared. The shavings were ground in a rotating knife mill using a 3 mm screen. The extraction was performed using an accelerated solvent extraction (ASE 200, Dionex) with acetone/water (9:1) and methanol/water (3:1). For qualitative separation by reversed-phase HPLC, the acetone and methanol extracts were evaporated to dryness, dissolved in acetonitrile (mobile phase of the HPLC system) and directly injected to the system. The analyses were carried out with a Kontron system using a J. T. Baker Octyl 5µm column (4.6 × 250mm). The mobile phase consisted of A (1 mmol H$_3$PO$_4$ aqueous solution) and B (CH$_3$CN) using the following step-by-step gradient: 0 to 10% of B (10min), then 10% B (15min) with a flow rate of 1.0mol/min. Phenolic compounds were selected with a photo-diode array detector (Kontron 540), monitoring the range of 200 to 340 nm. The chromatograms were evaluated using the software Kroma system 2000, comparing the retention times and UV visible spectra.

*PH measurement*

The pH of veneer surfaces were measured before and after treatments. Veneer sheets with dimensions of 2 cm × 2 cm were prepared. A 50 µL drop of distillated water was placed on the veneer surface at the point where the pH was intended to be measured. Then the electrode of the pH meter was located on the wetted veneer surface. After 2 minutes, the pH was recorded.

*Physical and mechanical measurement*

In order to investigate the influence of drying temperature and UV light irradiation on physical and mechanical properties of red-heart beech wood veneers, plywood (3-ply) was produced from treated veneers using urea-formaldehyde (UF) resin. Liquid UF resin had solid content of 66 percent. For each glue line 120 g/m$^2$ resin were used. The glue contained wheat flour as filler (30 percent of dry weight of resin) and NH$_4$Cl as catalyst (2 percent of dry weight of resin). Then water absorption, thickness swelling and shear strength of plywood samples were measured according to relevant standard test methods (EN 314-2). Plywood manufactured from untreated veneer sheets using UF resin was used as control sample.
RESULTS AND DISCUSSION

UV Spectroscopic Characterization of Aromatic Phenolic Compounds in Red Heart Beech Wood Tissue

Two-and three-dimensional UV image profiles of the veneer surfaces showing the detection of phenolic extractives are given in Figs. 1 to 6. The distribution of lignin within the individual cell wall layers in red-heart beech wood tissue is shown. The color pixels indicate different intensities of UV absorbance at the respective $\lambda_{280}$ nm wavelength. Figure 1 reveals the typical absorbance values of lignified cell walls of fibers in untreated red heart beech wood veneer. The thick S2 layers of the fibers are characterized by relatively uniform UV absorbance at 278 nm in the range of 0.15 to 0.20. The compound middle lamella (CML) and cell corners (CC) of the individual fibres can be distinguished on account of significantly higher UV absorbance in the range of 0.35 (CML) and 0.5 (CC). These results validate early and more recent findings of Koch and Kleist (2001), Koch et al. (2006), Fergus and Goring (1970), Koch and Grünwald (2004), and Lybeer and Koch (2005). These authors demonstrated the applicability of this technique for the topochemical detection of lignin within individual cell wall layers of several hardwoods, e.g. beech, birch, sapeli; as well as softwoods, e.g. spruce, podo; and monocotyledons (bamboo).

With increasing drying temperature up to 180 ºC, the presence of extractives can be easily visualised by spherical conglomerations of high absorbance values ($\text{abs}_{278\text{nm}}$ 0.75 to 1.00 > overflow) in the cell lumen of fibers and ray parenchyma cells compared with the surrounding tissue (Fig. 2). Furthermore, the fiber S2 layers of the heat treated tissue reveal significant increase of the UV absorbance values ($\text{abs}_{278\text{nm}}$ 0.25) as compared to the untreated tissue (comp. Fig. 2, 4, and 5). The increase in lignin absorbance is clearly detectable by the brown color (changing from blue to brown) of the evaluated absorbance intensities. Fengel and Wegener (1989) expressed that heating at 175°C imparted lignin condensation with increasing effect at temperatures up to 240°C. Also Brosse et al. (2010) and Funaoka et al. (1991), declared that the thermal treatment of wood affects lignin polymer through depolymerisation, mainly due to cleavage of β-aryl-ether linkages and recondensation reactions. These recondensation reactions change the guaiacyl units through formation of 5,5'-biphenolic and diarylmethane structures. DPM structures formed in lignin greatly influence the color or the properties of lignin, such as the reactivity and solubility. According to Funaoka et al. (1991), the modification of lignin during heating of wood begins above 120 ºC and mainly involves diphenylmethane condensation. Tumen et al. (2010) reported increased lignin values at higher treatment temperatures and duration. During heat treatment, the degradation of the hydroxyl groups on cellulose chain and hemicelluloses. The broken fragments from cellulose and hemicelluloses bonded to lignin, causing an apparent increase in the lignin ratio in the wood. Since lignin is a hydrophobic substance, it helps to decrease the water absorption and thickness swelling of plywood samples. After UV irradiation, distinct topochemical changes of the UV absorbance within the individual chemical compounds and cell types are observed. Figure 3 represents the deposition of highly condensed phenolic compounds ($\text{abs}_{278\text{nm}}$ 0.75 to 1.00 > overflow) in the ray parenchyma cells of UV-irradiated of red-hearted beech wood veneers (simulation of 6 months UV
irradiation). Among the chemical compounds of woods (cellulose, hemicelluloses, and lignin), lignin is the most important structure in wood photo degradation. Absorption of light by lignin leads to the formation of free radical species (phenoxyl radicals) (Lin and Kringstad 1970; Hon 1981; Hon and Feist 1981; Evans et al. 2002; Petric et al. 2004). These free radicals react with oxygen to produce carbonyl and carboxyl chromophoric groups (Hon 1991; Hon and Feist 1992), which are responsible for wood color changes (Dirkx et al. 1987; Ayadi et al. 2003). Generally, an increase in carbonyl groups and decrease in lignin have been observed with light irradiation (Mitsui et al. 2004).

Fig. 1. UV microscopic profiles of untreated red heart beech wood tissue. The colour-pixels represent different UV absorbance values of the individual cell wall layers (blue color = S2 of fiber, red color = Compound middle lamella CML) measured at $\lambda_{278\text{nm}}$ with geometrical resolution of 0.25µm x µm.

Fig. 2. UV microscopic profiles of treated beech wood (drying temperature of 180°C) illustrating the deposition of phenolic extractives in the cell lumen of fiber and lignin condensation in cell wall layers. The colour-pixels represent different UV absorbance values of the cell wall layers and phenolic extractives measured at $\lambda_{2787\text{nm}}$. 

Fig. 3. UV microscopic profiles of treated beech wood (drying temperature 100°C and aging 6 months) illustrating the deposition of phenolic extractives in the lumen of parenchyma cells. The colour-pixels represent different UV absorbance values of the cell wall layers and phenolic extractives measured at $\lambda_{2787\text{nm}}$.

Fig. 4. UV microscopic profile of treated beech wood (drying temperature 180°C and aging 6 months) illustrating the deposition of phenolic extractives in the cell lumen of vessel. The colour-pixels represent different UV absorbance values of the cell wall layers and phenolic extractives measured at $\lambda_{2787\text{nm}}$.

High Performance Liquid Chromatography (HPLC) Analysis
According to HPLC chromatograms, the separation of the acetone-water and methanol-water extractives of the untreated red heart beech wood tissues show very low concentrations of aromatic phenolic compounds, e.g., coniferylalcohol and signapylalcohol, which are the precursors of the lignin biosynthesis (Fig. 6).
Fig 5. UV microscopic profiles of treated beech wood (drying temperature 180°C and aging 6 months) illustrating the deposition of phenolic extractives in the lumen of parenchyma cells. The colour-pixels represent different UV absorbance values of the cell wall layers and phenolic extractives measured at $\lambda_{2787}$nm.

The chromatograms of the methanol-water extracts of the treated red heart beech tissue (Figs. 7 and 8) represent distinct signals of catechin and 2,6 dimethoxybenzoquinon (retention time of 12 and 16 min). These compounds are regarded as major precursors of chromophoric compounds in discolored beech wood. According to Koch et al. (2003), the separation of the acetone and methanol extracts of discolored beech wood (Fagus sylvatica) shows the presence of different low molecular phenolics such as catechin and 2,6-dimethoxy-benzoquinon, which are transformed into high condensation compounds during thermal treatment and UV irradiation.

Fig. 6. HPLC chromatogram of methanol-water extractives in untreated red-heart of beech wood
Fig. 7. HPLC chromatogram of methanol-water extractives in treated red heart of beech wood (drying temperature 180°C)

Fig. 8. HPLC chromatogram of methanol-water extractives in treated red-heart of beech wood (drying temperature 180°C and aging 6 months)

**pH Value**

The measurements of the pH values of untreated and treated veneers demonstrated that increasing the drying temperature up to 180°C decreases the pH value of veneer surfaces. Tumen et al. (2010) reported that when wood is heated to temperature of 160 to 250°C, hemicelluloses start to degrade first, due to their low molecular weight among the wood polymers. Fengel and Wegener (1984) attributed the lower degradation temperature of hemicelluloses also to their branched structure. The degradation of the
hemicelluloses results in a reduced proportion of hydroxyl groups and the formation of furfural, formic acid, and acetic acid. This results in lower pH (Boonstra et al. 2007; Freeman 1959; Aydin 2004), which is influential in the curing of the adhesives. A low pH of the wood surface could accelerate the chemical reactions of acid catalyzed urea-formaldehyde resin and higher shear strength. Exposure to UV irradiation up to 6 months increases the pH value of veneer surfaces.

### Table 1. pH Value of Red-hearted Beech Veneers

<table>
<thead>
<tr>
<th>UV irradiation period</th>
<th>100 ºC</th>
<th>180 ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>4.90</td>
<td>4.23</td>
</tr>
<tr>
<td>2</td>
<td>4.91</td>
<td>4.25</td>
</tr>
<tr>
<td>4</td>
<td>4.93</td>
<td>4.29</td>
</tr>
<tr>
<td>6</td>
<td>4.94</td>
<td>4.45</td>
</tr>
</tbody>
</table>

### Physical and Mechanical Properties

**Water absorption and thickness swelling**

Figures 9 and 10 reveal that with increasing drying temperature up to 180 ºC, there was a reduction in the water absorption and thickness swelling of plywood samples after 2 and 24 hours immersion in water. As the temperature is increased during heat treatment, changes in the structure of wood which are primarily attributed to the degradation of hemicelluloses, are observed (Militz 2002). The degradation of hemicelluloses results in fewer hydroxyl groups (-OH), but also the formation of O-acetyl groups. With the subsequent cross-linking between the wood fibers substances, wood becomes more hydrophobic (Tumen 2010) and improves the dimensional stability. Simultaneously, cellulose starts to degrade due to formation of formic acid and acetic acid, and the lignin ratio increases due to the binding to lignin of cleaved substances from hemicelluloses and cellulose (Raimo et al. 1996; Gailliot 1998).

The hydrophobic nature of lignin helps the reduction of water absorption and thickness swelling of plywood samples. Furthermore, the compression of wood while heating (170 ºC) causes lignin to flow (initiating the re-arrangement of the cementing material between the cellulose fibers) and relieving the internal stresses. This greatly reduces the tendency of wood to swell when wet and increases the strength (Jones and Callum 2007).

After being exposed to UV irradiation up to 6 months, the water absorption and thickness swelling of plywood samples after 2 and 24 hours immersion in water increases due to higher deposition of phenolic extractives in parenchyma cells and vessel lumens (Fig. 9 and 10). These materials migrate to the veneer surface and cause surface inactivity and lower bonding quality and shear strength, leading to increased water absorption and thickness swelling of plywood samples.
Fig. 9. Water absorption of plywood samples after 2 and 24 hours immersion in water

Fig. 10. Thickness swelling of plywood samples after 2 and 24 hours immersion in water
Shear strength

The shear strength of plywood samples improves at higher drying temperature 180°C (Fig. 11). The improved dimensional stability of heat treated wood improves the bonding performance, because the stresses acting on the adhesive bond due to shrinking or swelling are reduced. On the other hand, heat treated wood is less hygroscopic (Boonstra et al. 2007; Paul et al. 2007), which can alter the distribution of adhesive on the wood surface and its penetration into porous wood structure. Heat treatment results in lower pH (Boonstra et al. 2007; Freeman 1959; Aydin 2004), which can affect the curing of adhesives. A low pH of the wood surface can accelerate the chemical reactions of acid catalyzed urea-formaldehyde resin and increase the shear strength. Theander et al. (1993) showed marked sugar accumulation at the surface, which correlated quite well with a corresponding nitrogen accumulation. They noted that samples with high nitrogen and sugar contents also exhibit yellow surface color, which is probably formed during the drying process by the well-known Maillard reaction. The results showed that drying temperature (180°C) and degradation of hemicelluloses induce the production of sugar monomers, which have an important impact in bond quality and increasing shear strength.

Fengel and Wegener (1989) reported that above 160°C, lignin becomes softer. The lowest softening temperature (165 to 180°C) was determined for milled wood lignin from beech wood (Fengel et al., 1981). When lignin is softened it flows into the micro pores of the wood and makes the wood tissue more homogenous. This greatly reduces the tendency of wood to swell when wet, lowering the internal stresses and providing higher strength. The furfural produced during the degradation of hemicelluloses acts as a cross-linking agent for UF resin, leading to improvement of the bonding quality between layers (Tumen et al. 2010). The shear strength of plywood samples decreased after UV irradiation as expected (Fig.11). According to the UMSP results, at higher UV irradiation duration increased phenolic deposits in parenchyma cells and vessel lumens predicated...
and these extractives decrease the activity of the surface, which leads to a decrease in the bonding quality between layers and a decrease the shear strength of plywood samples. In short exposure times only lignin was affected by UV irradiation, which results in more intensive discoloration. But upon prolonged UV irradiation, carbonyl groups of lignin absorb light and by hydrogen abstraction from the cellulose, cellulose-derived radical is formed and is subsequently converted into carbonyl groups. Thereby, further degradation reactions are facilitated, resulting in both depolymerisation and colour formation. With this phenomenon, the degradation of wood carbohydrates, mainly cellulose, occur, resulting in strength reduction. This can be seen especially by experiments at 6 months UV irradiation.

CONCLUSIONS

1. Higher drying temperature (180°C) initiates degradation of hemicelluloses and formation of acetic acid and formic acid leading to lower pH of veneer surfaces, which can affect the curing of acid catalyzed UF resin and results in improving the shear strength and dimensional stability (water absorption and thickness swelling) of plywood samples.
2. Increasing the UV irradiation period (especially 6 months) causes degradation of lignin and especially cellulose, which decreases the shear strength and increases the water absorption and thickness swelling of plywood samples.
3. The results of UMSP and HPLC methods showed evidence of lignin condensation after drying at a sufficiently high temperature (180°C) as well as initiation of lignin degradation and formation of chromophoric groups after being exposed to UV irradiation. This phenomenon can affect the veneer surface activation.

REFERENCES CITED


