INFLUENCE OF DRYING TEMPERATURE ON PROPERTIES OF WOOD SURFACES

Milan ŠERNEK

Abstract
This article deals with modifications of wood surface properties induced by different drying temperatures. The aim of the study was chemical and physical characterization of a wood surface concerning low and high temperature exposure. Additionally, the correlation between the chemical composition of a wood surface and its wetting capacity was investigated. X-ray photoelectron spectroscopy and contact angle measurements were conducted. Two wood species, yellow poplar (Liriodendron tulipifera) and southern pine (Pinus taeda) were studied. The results showed that the percentage of carbon increased with drying temperature, and consequently, the percentage of oxygen decreased. The samples exposed to high drying temperatures indicated a higher content of extractives on the wood surface. These samples exhibited the highest contact angle and the lowest wettability.

Key words: wood surface, drying, contact angle, XPS, wettability, extractives

VPLIV TEMPERATURE SUŠENJA NA LASTNOSTI LESNIH POVRŠIN

Izvleček

Ključne besede: površina lesa, sušenje, kontaktni kot, rengenska fotoelektronska spektroskopija, omotitev, ekstraktivne snovi
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INTRODUCTION

Drying is an inevitable process in the wood-based composite industry because the high moisture content (MC) of green wood material has to be reduced prior to manufacturing. Otherwise, high water vapor pressure can blow a composite apart during the opening of a hot press. Moreover, shrinkage occurring in wet wood generates internal stresses in the wood-adhesive interface, and the adhesive bond can fail. Thus, a proper MC is one of the preconditions for achieving a strong adhesive bond. In fact, most wood adhesives require a lower MC for adequate adhesive penetration and curing reaction. A low MC, which is close to the equilibrium moisture content (EMC), is desirable because this condition minimizes the dimensional changes of a composite. Accordingly, defects such as warp, bow, twist, and cracks are later negligible (HAYGREEN / BOWYER 1996).

High drying temperatures are necessary in order to obtain a maximum dry output. Temperatures for drying veneers, wood flakes, and wood particles can be very high—up to 400 °C at the beginning, and around 200 °C near the end of the drying process (CHRISTIANSEN 1990). At the beginning of the drying, the temperature of a wood surface is lower than the drying temperature of air because of evaporative cooling. As the MC decreases and falls below the fiber saturation point (FSP), the wood contains only bound water. This water is held more strongly to wood by hydrogen bonding, thus the water diffusion from the bulk to the surface is slower than evaporation of water on the surface. The evaporative cooling effect decreases and the surface temperature starts to climb to temperatures near that of the air in the dryer (CHRISTIANSEN 1990). This is the stage when typical wood surface inactivation occurs (SUCHSLAND / STEVENS 1968).

Surface inactivation is described as a heat-induced change in the wood surface resulting in a loss of bonding ability (TROUGHTON / CHOW 1971). An inactivated wood surface does not bond well with adhesives, because the inactivation process reduces the ability of an adhesive to properly wet, flow, penetrate, and cure (USDA 1999). Thus, the ability to establish intimate contact between molecules of wood and adhesive is diminished. Subsequently, the adhesion attractive forces are weak and rare. Inactivation reflects physical and chemical modifications of the wood surface. Therefore, understanding
surface characteristics is of utmost importance in combating inactivation problems. There are several proposed techniques for quantifying surface inactivation, such as water absorption, contact angle, surface tension, reflectance colorimeter, and X-ray photoelectron spectroscopy (XPS). Of these, the XPS technique is a suitable method for the chemical characterization of a wood surface, while contact angle measurement provides information about the capacity of an adhesive to wet the wood surface.

1.1 X - RAY PHOTOELECTRON SPECTROSCOPY

X-ray photoelectron spectroscopy, also referred to as electron spectroscopy for chemical analysis (ESCA), is a very powerful non-destructive surface analytical technique (REEVE / TAN 1998). The principle of the XPS/ESCA technique is the emission of electrons from atoms by absorption of photons (BRUNE et al. 1997). Electrons are held in the atom by a binding energy, which depends on atomic charge distribution. The binding energy (E_b) of an electron level can be determined by the measurement of the kinetic energy (E_{kin}) of the photoelectron. The binding energy is a characteristic of the atoms, which can be used for identification of elements (REEVE / TAN 1998). For example, carbon bound to itself and/or hydrogen only, has a binding energy of 285 eV (BRIGGS / SEAH 1990). If an element is involved in a chemical bond, then its binding energy will change (YOUNG et al. 1982). This results in a chemical shift, which can be measured and used for the determination of the individual chemical states of atoms.

1.2 WETTABILITY AND CONTACT ANGLE

Wettability is defined as a condition of a surface that determines how fast a liquid will wet and spread on the surface or if it will be repelled and not spread on the surface (USDA 1999). Since the tendency for the liquid to spread increases as contact angle decreases, the determination of contact angles is a useful inverse measure of spreadability or wettability (ZISMAN 1964). The contact angle is an angle formed between the surface of a solid and the line tangent to the droplet radius from the point of contact with the solid.
When in mechanical equilibrium, the relationship among surface tensions and the contact angle ($\theta$) for a liquid drop on a solid surface is expressed by Young's equation (Zisman 1964):

$$\gamma_{SV} - \gamma_{SL} = \gamma_{LV} \cos \theta$$

where ($\gamma$) is interfacial surface tension, $S$ is solid, $L$ is liquid, and $V$ is vapor.

Figure 1: Contact angle and interfacial surface tensions at equilibrium (Zisman 1964)

**HYPOTHESES AND OBJECTIVES**

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It is assumed that during high temperature exposure, an inactivation process modifies the primarily hydrophilic wood surface to a hydrophobic one. This probably originates from either extractive migration to the surface, or from lignin rearrangement on the surface. Both extractives and lignin have hydrophobic characteristics, contrary to the other wood constituents (e.g. hemicelluloses), which have more hydrophilic characteristics. Since the amount and type of extractives vary strongly with wood species, a difference in the severity of surface inactivation between wood species is also expected.

The main objective of this study was to characterize changes in wood surface composition and wettability in regard to different drying temperature exposures. Additionally, the relationship between chemical composition of the wood surface and its wetting capacity was evaluated.
3 MATERIAL AND METHODS
MATERIAL IN METODE

3.1 MATERIAL
MATERIAL

Heartwood samples of yellow poplar (YP) (*Liriodendron tulipifera* L.) and southern pine (SP) (*Pinus taeda* L.) were cut into radial lamellas and then planed to a thickness of 6 mm (Figure 2). Both wood species had green MC above FSP. Wood samples were sorted in to two groups and then each group was exposed to different drying conditions as shown in Table 1. Conventional drying in a convection oven was used to dry samples to a target MC of around 4%. The actual MC was monitored by the weight measurement of the samples during drying. The surface temperature of one lamella was monitored by a thermocouple.

![Planed radial surface](image)

Figure 2: Specimen size (mm) and orientation of wood fibers

*Slika 2: Velikost lesnih vzorcev (mm) in smer lesnih vlaken*

Table 1: Properties of wood samples and drying parameters

*Preglednica 1: Lastnosti lesnih vzorcev in sušilni parametri*

<table>
<thead>
<tr>
<th>Wood Species</th>
<th>Initial MC Končna vlajnost (%)</th>
<th>Final MC Končna vlajnost (%)</th>
<th>Drying Temperature Temperatura sušenja (°C)</th>
<th>Drying Time Cas sušenja (min)</th>
<th>Sample Label Označba vzorca</th>
</tr>
</thead>
<tbody>
<tr>
<td>Yellow poplar (YP) <em>Tulipanovec</em></td>
<td>48,0</td>
<td>3,9 - 4,1</td>
<td>50</td>
<td>300</td>
<td>YP50</td>
</tr>
<tr>
<td>Southern Pine (SP) <em>Južni bor</em></td>
<td>133,6</td>
<td>3,9 - 4,2</td>
<td>50</td>
<td>360</td>
<td>SP200</td>
</tr>
</tbody>
</table>
3.2 XPS MEASUREMENTS

A Model 5400 Perkin-Elmer X-ray photoelectron spectrometer was employed to provide elemental and chemical data of the wood surface composition. The radial surface of early wood was studied. The wood sample with an area of $8 \times 5$ mm and with a thickness of 3 mm was taken from the wood specimen. The sample was fixed on a sample holder by double adhesive tape and then put in the XPS chamber. The sample was exposed to vacuum and cooling. The purpose of the low pressure and the low temperature was to slow the molecular motions of the air, which minimized the influence of air molecules on the results. When a pressure of $6.7 \times 10^{-5}$ Pa was achieved, the X-ray source was activated. X-rays were used from Mg Kα (1253.6 eV) with an incident angle of 45°. A 3 nm$^2$ surface area was observed, and a surface depth of approximately 5 nm was analyzed. In total, eight measurements were obtained (i.e. 2 wood species, 2 drying temperatures, and 2 replications).

1.3 CONTACT ANGLE MEASUREMENT

A sessile drop method was used to measure the contact angle (θ) of a 5 μl distilled water drop, which was applied to the radial wood surface by means of a digital pipette (Figure 1). The image of the liquid drop was captured by a video camera and transferred to a computer screen where the contact angle was measured by digital image analysis software (ImagePro, Media Cybernetics). The image was captured immediately after the water drop was applied. In total, 48 measurements were performed (i.e. 2 wood species, 2 drying temperatures, and 12 replications).
RESULTS AND DISCUSSION
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4.1 CHEMICAL COMPOSITION OF WOOD SURFACES
KEMIČNA SESTAVA LESNIH POVRŠIN

Carbon (C), oxygen (O), and nitrogen (N) elements were detected on the investigated surfaces. The wood surfaces also contained hydrogen (H), but this element cannot be detected by the XPS technique. A typical wide scan XPS spectrum is shown in Figure 4, which represents the intensity of electron emission at the corresponding binding energy. The ratio of the elements, which was calculated by using the atomic sensitivity factor and the curve area under each peak for the detected element (Figure 5), was also determined. This allowed expressing the surface chemical composition by an atomic percentage of the elements, which indicates the relative concentration of an element.
Figure 4: Wide scan XPS spectrum for southern pine surface dried at 200 °C
*Slika 4: Rentgenski fotoelektronski spekter za južni bor sušen pri 200 °C*

Figure 5: De-convolution of XPS spectrum for O1s peak (left) and C1s peak (right)
*Slika 5: Detajlni rentgenski fotoelektronski spekter za kisik (levo) in ogljik (desno)*
The changes in atomic percentage showed that the drying temperature affected the chemical composition of wood surfaces (Table 2). The percentage of carbon increased with drying temperature, and consequently, the percentage of oxygen decreased with drying temperature. The percentage of nitrogen did not change significantly. These trends were obtained for yellow poplar and southern pine samples.

Table 2: Atomic percentages of wood surfaces as determined by XPS

<table>
<thead>
<tr>
<th>Wood Species</th>
<th>Drying Temperature / Temperatura sušenja</th>
<th>50 °C</th>
<th>200 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>C (%)</td>
<td>O (%)</td>
</tr>
<tr>
<td>Yellow poplar (YP)</td>
<td></td>
<td>78,94</td>
<td>20,54</td>
</tr>
<tr>
<td>Tulipanovec</td>
<td></td>
<td>78,32</td>
<td>20,59</td>
</tr>
<tr>
<td>Southern Pine (SP)</td>
<td></td>
<td>78,72</td>
<td>20,59</td>
</tr>
</tbody>
</table>

Besides the atomic percentage, the oxygen to carbon ratio (O/C ratio) and the C1/C2 ratio were calculated. Both ratios are related to the chemical composition of wood constituents, which allows for the identification of the principal components on the wood surface (i.e. polysaccharides, lignin, and extractives). The theoretical value of O/C ratio for cellulose is 0,83; while for lignin and extractives it is much lower at 0,33 and 0,10, respectively (BARRY / KORAN / KALIAGUINE 1990). According to the theory, a high O/C ratio represents a surface containing mostly polysaccharides (BEN et al. 1993). A low O/C ratio reflects a high concentration of extractives and lignin on the wood surface. Figure 6 shows the influence of drying temperature on the O/C ratio of yellow poplar and southern pine. It can be seen that the O/C ratio was the same for YP and SP samples dried at 50 °C. Samples dried at 200 °C exhibited lower O/C ratios, particularly the SP sample, which O/C ratio was 0,14. Since only extractives have an O/C ratio close to this value, one can assume that increasing the drying temperature accelerated the migration of wood extractives to the surface. It is known that the quantity of extractives transported to the surface depends mainly on relative humidity and temperature. Increased temperature accelerated water movement, thus, water-soluble extractives could be transported to the wood surface along with water during the drying operation. On the other hand, water-insoluble extractives might migrate to the wood surface in a vapor phase at high drying temperatures (HSE / KUO 1988). The results also indicated that the wood surface of the SP200 contained a higher amount of extractives than the YP200 sample. This was
expected since, in general, SP contains a higher amount of extractives than YP; 3.5% and 2.4%, respectively (ROWE 1989). Therefore, more extractives could migrate to the surface in case of SP. In addition, the resinous part of SP extractives is mainly comprised of acidic diterpenoids (STANLEY 1969), which have a low O/C ratio (e.g. abietic acid has an O/C ratio of 0.10), which additionally contributed to a low O/C ratio of SP surfaces.

Calculation of the C1/C2 ratio provided additional evidence in support of the O/C interpretation of the wood surface chemistry. The C1 and C2 components represent different chemical bonding states of carbon. The C1 component is related to carbon-carbon or carbon-hydrogen bonds in extractives and lignin. The bond involving C2 can result from all three classes of wood components, but predominantly from the carbohydrates as –CHOH and from lignin as δ-ether and –C-OH bonds. The calculated theoretical C1/C2 ratio for pure cellulose is 0, for lignin close to 1, and for extractives up to 10. This evidence can be used to roughly describe wood surface composition—the higher the C1/C2 ratio, the higher the relative concentration of extractives and possibly lignin on a wood surface (BÖRÅS / GATENHOLM 1999). The results showed that the
C1/C2 ratio increased with drying temperature (Figure 7). The increase in the C1/C2 ratio was mainly due to extractive migration and their concentration at the surface.

![Graph of C1/C2 ratios](image)

*Figure 7: The C1/C2 ratio of wood surfaces*

*Slika 7: Razmerje med Cl in C2 tipom ogljika na lesni površini*

### 4.2 Wettability of Wood Surfaces

OMOČITEV LESNIH POVRŠIN

The lowest contact angle was obtained on wood surfaces that were exposed to a drying temperature of 50 °C and the highest contact angle was obtained on wood surfaces that were exposed to a drying temperature of 200 °C (Figure 8). This relationship was expected since high temperature accelerated extractive migration to the wood surface. This increased the hydrophobic character of the wood surface, which caused a high contact angle. There was no statistically significant difference in the contact angle between wood species, which were dried at 50 °C. On the other hand, the surface of SP, which was dried at 200 °C, exhibited a significantly higher contact angle than YP. The difference was attributed to a higher amount of non-polar extractives in SP (ROWE
Non-polar extractives repeal water, which results in an extremely high contact angle on the surface of the SP200 sample.

The cosine of contact angle (i.e. the index of wettability) is often used as a direct measure of wettability (KAJITA / SKAAR 1992). Wettability of the wood surface increased with the O/C ratio (Figure 9) and it decreased with the C1/C2 ratio (Figure 10). In other words, wood wettability decreased with increased amount of extractives on the surface. When cosθ was plotted against the O/C ratio and the C1/C2 ratio, a linear statistical model explained most of the variability—98 and 79 %, respectively.
Figure 9: Relationship between wettability and O/C ratio
Slika 9: Odvisnost med omočitvijo in razmerjem O/C

Figure 10: Relationship between wettability and C1/C2 ratio
Slika 10: Odvisnost med omočitvijo in razmerjem C1/C2
5 CONCLUSIONS
ZAKLJUČKI

The exposure of the wood to different temperatures affected its surface chemistry. The oxygen to carbon ratio (O/C) decreased, and the C1/C2 ratio increased with the drying temperature. Yellow poplar and southern pine surfaces indicated a higher concentration of extractives for samples exposed to 200 °C than those exposed to 50 °C. The difference was attributed to the temperature-accelerated migration of extractives from the bulk of the wood to the surface. The high temperature modified the wood surface from hydrophilic to hydrophobic, which was more significant for southern pine than for yellow poplar. The highest contact angle or the lowest wettabillity was obtained on southern pine surfaces, which were dried at 200 °C. This was attributed to the higher content of non-polar, hydrophobic extractives at the southern pine surface. Wood wettabillity improved when the O/C ratio increased and the C1/C2 ratio decreased.

6 POVZETEK

Sušenje lesa je nujen proces v industriji lesnih tvoriv, saj mora biti visoka vlažnost lesa znižana na vrednost, ki omogoča učinkovito nadaljnjo obdelavo v industriji lepjenega lesa. Les lahko sušimo pri različnih temperaturah, vendar je hitro in ekonomično sušenje doseženo le pri dovolj visoki temperaturi. Sušenje furnirja lahko v začetni fazi, ko je vlažnost lesa visoka, poteka pri temperaturah do 400 °C. Temperatura lesne površine je sicer bistveno nižja od temperature sušilnega zraka, ker voda na površini lesa izporeva in porablja del energije. Ta hladilni učinek se zmanjšuje z upadanjem vlažnosti lesa; zanemarljiv je na koncu sušenja, ko je vlažnost lesa le nekaj odstotkov. Takrat se lahko zgodi, da temperatura na površini lesa doseže nivo, pri katerem se pojavijo bistvene kemične in fizikalne spremembe na površini lesa. Kadar je lesna površina izpostavljena telo visokim temperaturam, so spremembe na njej tako izrazite, da predstavljajo problem pri omotitvi lesa z leplom in pri kasnejšem utrjevanju le-tega. V takem primeru govorimo o neaktivnosti lesne površine, ki se težko lepi in ne zagotavlja zadostne adhezije; slednja je potrebna za nastanek kvalitetnega lepilnega spoja.
Nastanek neaktivne lesne površine je lahko posledica več pojavov, ki so lahko kemične ali fizikalne narave – npr. migracije ekstraktivnih snovi na površino lesa; zaprtja mikroskopskih por na površini lesa; oksidacije in termične razgradnje lesne površine; onesnaženja lesne površine. Drevesne vrste so različno občutljive na izpostavljenost visokim temperaturam. Neaktivnost lesne površine se pogosto pojavlja pri sušenju iglavcev, ki lahko utrpijo značilne spremembe v lastnostih površine že pri 160 °C. Faktorji, ki vplivajo na ta proces, so vlažnost lesa, čas sušenja, tehnika sušenja, kemična sestava lesa in njegove anatomske lastnosti.


Ugotovili smo, da se odstotek ogljika na površini lesa povečuje z naraščajočo temperaturo sušenja, medtem ko se odstotek kisika zmanjšuje. Ko je bil les sušen pri 50 °C, je bilo razmerje med kisikom in ogljikom (O/C) 0,26 za obe drevesne vrsti. Razmerje se je bistveno znižalo, ko je bil les sušen pri 200 °C, in sicer je bilo 0,21 za tulipanovec in 0,14 za južni bor. Teoretični izsledki kažejo, da ima celuloza O/C razmerje 0,83, lignin okoli 0,33 in ekstraktivne snovi 0,12 ali manj. Potem, ko je lesna površina, ki ima nizko O/C razmerje, bogata predvsem z ekstraktivnimi snovmi. Rezultati so potrdili, da visoka temperatura pospeši migracijo ekstraktivnih snovi na površino lesa. Nizka vrednost O/C razmerja je torej bila predvsem posledica kopičenja ekstraktivnih snovi na površini med sušenjem lesa. To je bilo še posebej značilno za južni bor, ki vsebuje več ekstraktivnih snovi kot tulipanovec.
Podoben zaključek izhaja iz detailne analize ogljika, ki je lahko na različne načine kemijsko povezan z ostalimi elementi. Ogljik je lahko klasificiran kot C1 tip, ki predstavlja ogljikov atom, vezan z drugim ogljikovim atomom ali pa z vodikom. C2 tip ogljika predstavlja ogljikov atom, ki je z enojno vezjo povezan s kisikom. Literatura navaja, da je razmerje C1/C2 zelo visoko za ekstraktivne snovi, kar so potrdili tudi rezultati naše raziskave. Površine tulipanovca, ki so bile sušene pri 50 °C, so imele razmerje C1/C2 enako 2,61. To razmerje se je povečalo na 3,07, ko je bil tulipanovec sušen pri 200 °C. Južni bor je izkazoval izrazitejo spremembo v C1/C2 razmerju; le-to je bilo 3,12 za površine, sušene pri 50 °C, oziroma 5,10 za površine, ki so bile izpostavljene temperaturi 200 °C.

Sprememba v kemični sestavi lesne površine je vplivala na njene omogočitvene lastnosti. Površine lesa, ki so bile izpostavljene sušilni temperaturi 200 °C, so vsebovala visoko koncentracijo ekstraktivnih snovi. Te so pretežno vodooodbojne, zato je bila omogočitev lesne površine slaba. Omočitev se največkrat ugotavlja z merjenjem kontaktnega kota. Velik kontaktni kot predstavlja slabo omogočitev in obratno. Kadar je kontaktni kot enak 0 °C govorimo o popolni omogočitvi površine. Dobra omogočitev je pogoj za nastanek adhezijskih sil pri lepjenju lesa in za povezavo dveh površin v čvrst lepljeni spoji. Kontaktni kot močno varira glede na drevesno vrsto, vendar je v vseh primerih najmanjši na sveže spravljeni površini, kjer je v povprečju znaša 30-60 °C za večino drevesnih vrst. Rezultati vseh raziskav so pokazali podobne vrednosti na površinah, ki so bile sušene pri 50 °C. Kontaktni kot kapljice vode na površini tulipanovca je bil 67,4 °C in na površini južnega bora 64,2 °C. Sušenje pri visoki temperaturi je izrazito vplivalo na spremembo omogočitvene kapacitete lesne površine. Po sušenju pri 200 °C je bil kontaktni kot na površini tulipanovca 79,9 °C, na površini južnega bora pa celo 92,9 °C. Večji kontaktni kot predstavlja slabšo omogočitev; južni bor je torej izkazoval manjšo omogočitev kot tulipanovec, kadar je bil les sušen pri visoki temperaturi. Tak rezultat je bil pričakovani, saj južni bor vsebuje več nepolarnih, vodooodbojnih ekstraktivnih snovi, ki so se pod vplivom naraščajoče temperatur koncentrirale na površini lesa.

Omočitev je bila v močni soodvisnosti s kemično sestavo lesne površine. Ugotovili smo, da je omogočitev v neposredni povezavi z O/C in C1/C2 razmerjem na površini lesa. Omočitev lesne površine se je izboljšala, ko se je razmerje O/C povečalo oziroma azmerje C1/C2 zmanjšalo.
7 REFERENCES

VIRI


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