

Modification of Wood Surfaces by UV Laser Induced Photografting

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ABSTRACT

A system for surface modification of poplar wood by *in-situ* photo-polymerization of monoterpenes (α -pinene and myrcene) using a UV eximer laser to provide the incident radiation was developed. The wood surfaces were characterized by ATR-FTIR spectroscopy, and x-ray photoelectron spectroscopy (XPS). FTIR results indicate that wood modified with monoterpenes had an increased number of carbon-hydrogen bonds on the surface. XPS results showed that the surface of the modified samples had a higher carbon to oxygen ratio than control specimens. These chemical changes indicate the formation of a hydrocarbon layer on the wood surface.

INTRODUCTION

Wood is a low cost, environmentally friendly, option for utilization in a number of composite materials. These composite products are, however, not without problems and shortcomings. Wood is naturally a hydrophilic material, meaning that it is polar, and has a natural affinity for water. Many resin matrices used in composite production (wood plastic composites) are hydrophobic by nature. These non-polar resins are hydrophobic and incompatible with hydrophilic materials such as wood (Lai *et al.* 2003). Therefore, bonding problems can exist (Caulfield *et al.* 2005). This poor interfacial bonding can lead to performance issues due to poor stress transfer between the wood fiber and the polymer matrix (Dominkovics *et al.* 2007). Poor stress transfer between composite components can lead to strength problems and problems with dimensional stability (Lai *et al.* 2003).

Many methods for chemical modifying the wood surface have been developed (Hill *et al.* 1998, Wolkenhauer *et al.* 2007, Denes and Young 1999). However, these methods are often costly and time-consuming. A novel process using a ultra-violet (UV) laser to photograft polymers onto wood surface may provide the modifications that are desired without the difficulties of other treatments. This process utilizes lignin's ability to absorb UV radiation and form highly reactive free-radicals (Anderson *et al.* 1991). These free radicals can then react with chemicals that have appropriate functional groups, such as the alkene groups in monoterpenes. This reaction can form a new free-radical that will react with another functional group and propagate free-radical polymerization (Ehlich and Mortimer 1970). This aim of this study is to investigate the use of UV lasers to modify wood by grafting reactive compounds on the surface. The modified surface would be characterized by a combination of FTIR and XPS spectroscopies.

MATERIALS AND METHODS

Specimen Preparation

Clear sections (knot and defect free) of hybrid poplar veneers (Potlatch Corp, St Maries, ID) were identified, cut into samples and sanded with 200 grit sandpaper until the surface was smooth and uniform. The veneers were then cut into matched 3 x 5 cm specimens and vacuum dried at 60 °C overnight and then placed in a dessicator prior to treatment.

Surface Chemical Modification

Approximately 10 mg of α -pinene and myrcene (Figure 1) were added directly to the wood surface with a disposable pipette. The specimens were then irradiated with a KrF (248.5 nm) excimer laser. The laser settings were determined by a three factor complete factorial design with 5 duplicates of each treatment. The first factor was time; treatment levels were 0, 30, 60, and 120 s. The second factor was laser power at two levels (50 and 100 mJ). The third factor was reactant and the levels were none, α -pinene, and myrcene. Irradiated specimens were vacuum dried overnight to remove any residual monoterpenes.

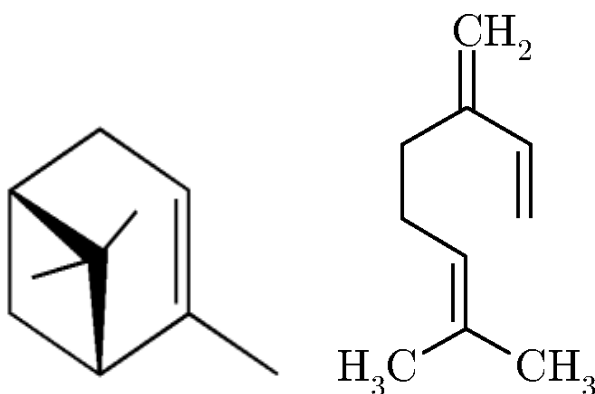


Figure 1: Molecular structure of α -pinene and myrcene.

ATR-FTIR Spectroscopy

Attenuated total reflectance (ATR) Fourier transform infrared (FTIR) spectra were taken for each modified sample using an Avatar 370 FTIR spectrometer (ThermoNicolet) with a single-bounce zinc selenide internal reflection element. All spectra were the average of 64 scans at 4 cm^{-1} resolution. Spectra were analyzed using ThermoNicolet Omnic 7.0 software. All spectra were ATR corrected and then baseline corrected using the polynomial correction function of the Omnic software.

Spectra were quantitatively analyzed for changes in peak areas after modification with varying treatments. The areas of the peaks at 3400, 2800, 1710, 1620, 1505, 1370, and 1000 cm^{-1} were integrated using a common baseline established between the valleys at 3050 and 1515 cm^{-1} . Table 1 correlates infrared absorption bands with wood functional groups present in wood (Tshabalala 2005, Stark and Matuana 2004, Pandey 1999).

Table 1: FTIR spectral bands of interest to the chemical characterization of wood (Tshabalala 2005, Stark and Matuana 2004, Pandey 1999).

Approximate Band Position [cm ⁻¹]	Assignment
3418	O-H stretch vibration (bonded)
2928	C-H stretch vibration
1745	C=O stretch vibration (unconjugated)
1596	Aromatic skeletal and C=O stretch vibration
1507	Aromatic skeletal vibration (C=C)
1465	C-H deformation (asymmetric) and aromatic vibration in lignin
1427	C-H deformation (asymmetric)
1374	C-H deformation (symmetric)
1329	-CH ₂ wagging vibration in cellulose
1270	C-O stretch vibration in lignin, acetyl and carboxylic vibration in xylan
1242	C-O stretch vibration in lignin, acetyl and carboxylic vibration in xylan
1165	C-O-C asymmetric stretch vibration in cellulose and hemicellulose
1128	O-H association band in cellulose and hemicellulose
1083	C-O stretch in cellulose and hemicellulose
1036	C-O stretch
1003	C-O stretch in cellulose and hemicellulose

X-Ray Photo-Electron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed on selected modified and control samples, in duplicate. The XPS was performed on a custom built instrument (Dr. McIlroy, Dept. of Physics) using two monochromators at 1253 and 1487 eV, with a resolution of 50 meV. Charging of the wood samples was suppressed by use of a flood gun. Wide scans were used to determine the carbon to oxygen ratio. The areas of the carbon and oxygen peaks were measured in IGOR Pro v6 software; the carbon peak area was divided by the oxygen peak area to determine the carbon to oxygen ratio.

RESULTS AND DISCUSSION

ATR-FTIR Spectroscopy

Both monoterpenes used in this study, myrcene and α -pinene, contain alkene bonds that provide suitable sites for free radical reactions (Figure 1). These bonds can also perpetuate free-radical propagation leading to polymerization of the terpenoids on the wood surface. If polymerization occurs at the wood surface an increase in C-H stretch bands (2900 and 1370 cm⁻¹) would appear in the FTIR spectra (Figures 2 and 3).

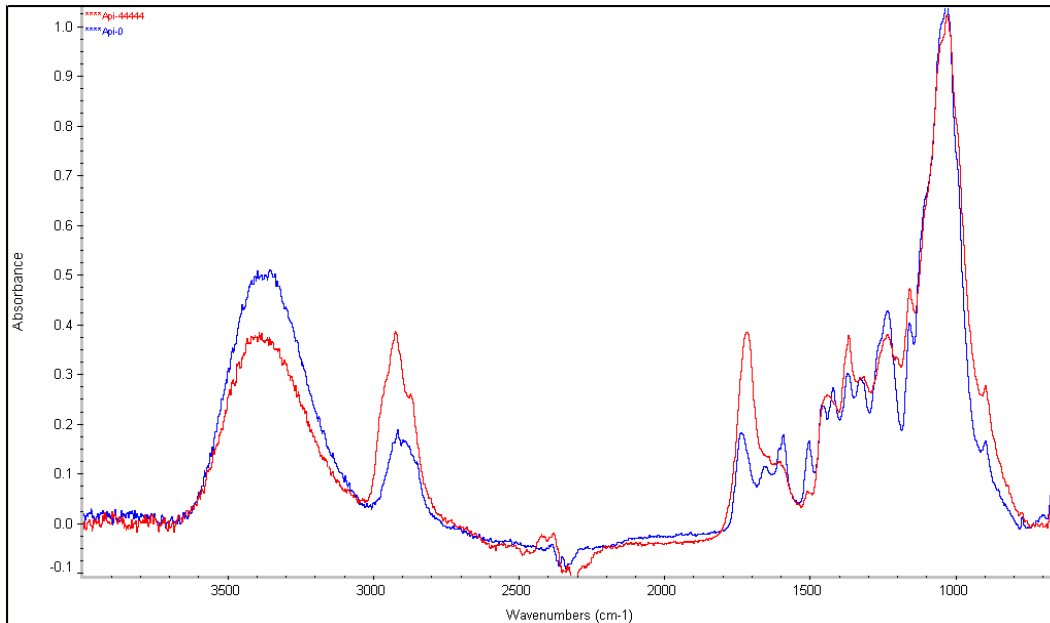


Figure 2: ATR-FTIR spectra of a control poplar sample (blue) and α -pinene modified poplar sample that was irradiated at 100 mJ, 10 Hz, for 120 s (red).

Figures 2 and 3 shows the dramatic increase in the C-H stretch after modification. This indicates a large increase in the hydrocarbon moieties on the wood surface. Also, the carbonyl band at $\sim 1700\text{ cm}^{-1}$ increases greatly. This increase is likely due to oxidation of carbohydrates to ketones, aldehydes, and carboxylic acids (Stark and Matuana 2004). The lignin band at 1505 cm^{-1} (Pandy 1999) is greatly reduced. This decrease shows the propensity of UV light to break the aromatic bonds in lignin, which produces free-radicals (Stark and Matuana 2004).

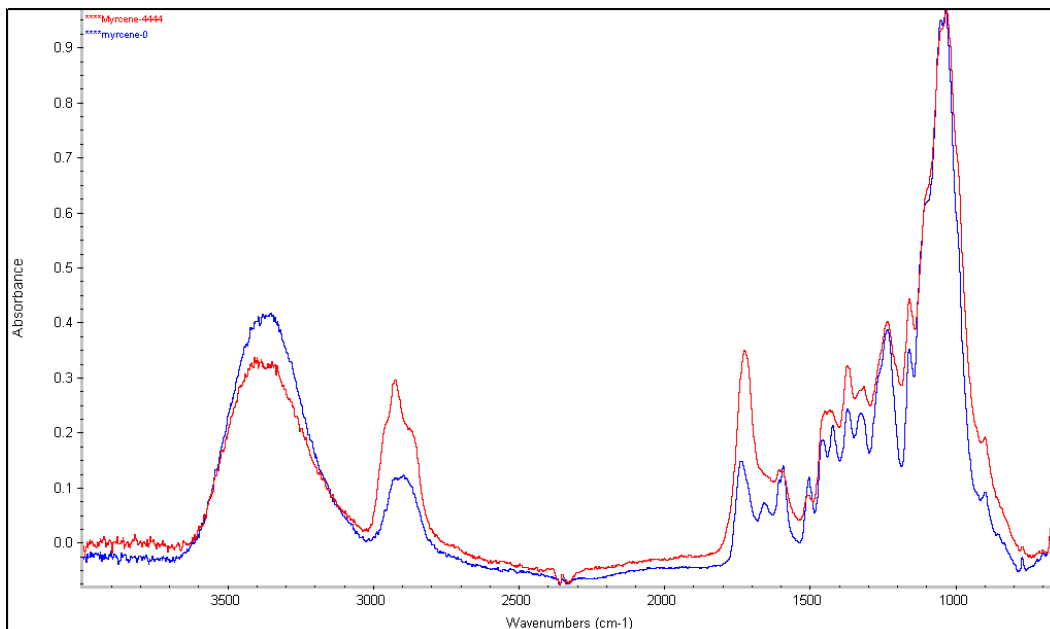


Figure 3: FTIR spectra of control poplar sample (blue) and a myrcene modified poplar sample that was irradiated at 100 mJ, 10Hz, for 120s (red).

X-Ray Photo-Electron Spectroscopy

Wide-scan XPS analysis was performed on control and modified samples in order to calculate the carbon to oxygen ratio on the wood surface. XPS results are of particular interest because it is a true surface technique; the chemical composition of only the top 1-20 nm is analyzed (McDonald *et al.* 1999). This allows a very thin polymer coating to be detected without interference from the bulk properties of the material.

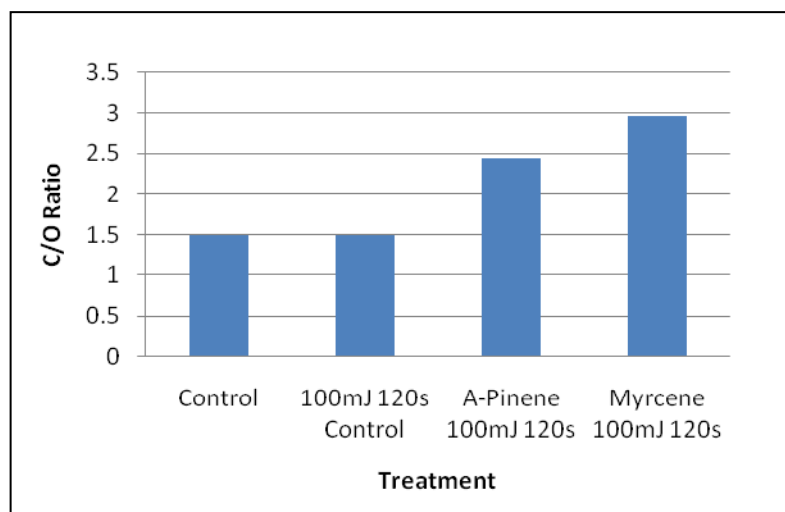


Figure 4: Carbon:oxygen ratios from XPS widescans.

According to Mjorberg (1981) the carbon/oxygen ratio for cellulose is 1.20 and the carbon/oxygen ratio for lignin is 2.77. The poplar control and irradiated poplar control samples both have carbon/oxygen ratios slightly higher than that of pure cellulose. This is expected, considering that hybrid poplar is a low lignin, low extractive wood. The carbon/oxygen ratios of the monoterpene modified poplar samples, 2.45 and 2.95, are much higher than could be expected without the addition of a carbon rich moiety to the wood surface (Figure 4). This strongly supports the hypothesis that a hydrocarbon rich layer is created on the wood surface.

CONCLUSIONS

Wood surfaces can be successfully chemically modified by UV laser irradiation in the presence of monoterpenes. The modified veneers are suspected to contain an aliphatic carbon-rich polymeric layer on the wood surface. This novel surface modification procedure shows promise to modify wood surfaces and other natural fibres for use in composite materials with non-polar resins.

ACKNOWLEDGEMENTS

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