

Laser Activated Bonding of Wood

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It was found that laser modified wood surfaces can be bonded together to create a wood composite without the need of any additive. This bonding method removes the need of applying adhesive, potentially lowers cost, and eliminates off gassing of petroleum resins, creating a wood product with many eco-friendly attributes. This body of work reports on the initial chemical analysis of the laser modified wood surface, its bond strength, and the optimization of factors that control the strength of the bond.

Surface chemical analysis on laser modified wood was conducted using photo acoustic Fourier Transform infrared spectroscopy (PA-FTIR) and X-Ray photoelectron spectroscopy (XPS). Light microscopy and scanning electron microscopy were utilized for surface topology analysis. Differential scanning calorimetry (DSC) quantified the thermal properties of the modified wood surface. Screening of multiple factors that would contribute to surface modification and adhesion was performed utilizing mechanical testing. Optimization of significant factors that affect bond strength was determined statistically utilizing a design of experiment approach.

Chemical analysis of the laser modified surface revealed changes in the carbonyl and aromatic regions indicating modification of the hemicellulose and lignin components, intensifying with increasing laser modification. The C1/C2 ratios found via XPS revealed that one or more of the following is occurring: more extractives have moved to the surface, condensation reactions among lignin units, and the loss of methoxy and breakage of aryl ether linkages occurred. Microscopy images showed color changes to a darker caramel color with a smoothing of surface topology, suggesting the occurrence of the softening and/or melting of wood polymers. DSC verified chemical and/or physical changes in the wood with the modified material now having a glass transition temperature between 130-150°C. DOE found that laser parameters (power and focus) as well as hot press parameters (temperature and pressure) were significant in optimizing the bond.

The impact of the study is the first documentation of the ability to laser modifies wood surfaces and subsequently bond them together. The ability of the wood polymers at the surface to undergo flow at elevated temperature is implicated in the adhesion mechanism of the laser modified wood.

Dedicated to

My Friends and Family

The folks who made me who I am, and got me where I am

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Glossy of Terms and Symbols

XPS	x-ray photoelectron spectroscopy
DSC	differential scanning calorimetry
T _g	glass transition
PA-FTIR	photo acoustic fourier transform infrared spectroscopy
LM	light microscopy
SEM	scanning electron microscopy

Chapter 1: Introduction

The current wood composites industry depends on petroleum-derived chemicals for wood bonding. In recent years the use of these products has been in question in terms of health and environmental issues, creating a need for building materials that are more "green"[1]. The consumer demand for greener building practices has led to regulatory demands that push the wood composites industry to reduce their impact on the environment[1]. If the wood composites industry could remove the hazardous adhesive chemicals, which are classified as carcinogens at worst or nauseating at best, then the industry could reduce its environmental impact [2].

Several possible solutions that remove or minimize the need of petroleum based adhesives are being studied or already on the market. Soy protein based adhesives are an alternative technology that has had success in the market, but still requires some petroleum based components to work as an adhesive. Successful research indicates that by applying oscillatory friction between two wood components leads to a bond that requires no adhesive, known as wood-to-wood welding. At this point in time, this method has not reached the market and only works for small applications, typically involving dowels or small surface areas.

This thesis demonstrates that using laser technology, a bond can be created without the need of an external adhesive, having credence to become a disruptive technology in a mature wood composites industry. The method entails laser modifying two wood surfaces and then bonding them with a hotpress at some time later. The wood serves in a dual role, acting both as the adherend and adhesive. The goal of the work was to understand the new modified surface, factors that affect it, and mechanical strength of laser activated wood bonding. In Chapter 3, initial experiments were undertaken to better understand the chemistry and morphology of the laser modified surface including chemical analysis via X-Ray photoelectron spectroscopy (XPS) and photo acoustic Fourier Transform infrared spectroscopy. Surface topology changes were analyzed via light microscopy and scanning electron microscopy. After determining the effect of the laser light on the wood surface, research was undertaken as described in chapter 3, to understand the parameters, including both laser-related and composite fabrication variables that would affect the bond strength. A design of experiment study was carried out in order to statically identify the factors playing a role in laser bond strength, as well as identifying interactions between factors. Lastly, a benchmark comparison was made to an industrial

adhesive for wood composites already on the market. In addition, to the DOE experiments, Appendix A contains a host of variables explored in relation to understanding this new process of laser bonding of wood. The results of the chapters are reported in the conclusion, which indicate laser-modification of wood holds great promise for the creation of new wood composite materials.

1. Pizzi, A., *Recent developments in eco-efficient bio-based adhesives for wood bonding: opportunities and issues*. Journal of Adhesion Science Technology, 2006. **20**(8): p. 829-846.
2. Rowell, R., *Handbook of wood chemistry and wood composites*. 2005.

Chapter 2: Literature Review

2.1 Introduction

In order to modify the surface of lignocellulosic material with a laser for wood bonding, one must understand lasers, woody polymers and their response to heat and light, and the current state of wood adhesion[1, 2]. With Lasers, specifically understanding how a laser works, how laser light is fundamentally different from other types of light, and current laser applications and abilities give an insight to optimal operation during laser ablation. Understanding what woody polymers constitute wood, how they interact with laser light and heat, give a solid base knowledge for which to optimize surface modification. Understanding the current state of wood adhesives creates a need for an adhesive free wood bonding process, as well as generates a base line for which to compare bond properties.

Laser modification of wood can be separated into 2 categories: modification via heating (thermal energy) or modification via light (interactions between photons and wood polymers)[3, 4]. It is suggested that the modification is primarily due to heating, with perhaps a small amount of degradation due to wood/light interaction [5]. Modification via light is hypothesized to be a more direct and more efficient process where photons directly interact with individual chemical bonds. These interactions cause either melting or softening. Modification via heat requires the photon energy to be transferred into heat energy, most likely a less efficient process. The heat energy is then transferred to the bonds, in essence vibrating the bonds until breakage occurs. The following sections describe the response of wood to thermal energy, laser technologies, and laser light interaction with wood, applications of lasers in the wood industry, variables related to laser applications, and wood adhesives and composites.

2.2 Woody polymer response to heat

The interaction between heat and wood is useful information as laser modification imparts heat to wood samples. During the past decade heat treated wood has come to market in Europe and is now making headway in the United States [6]. Untreated wood is susceptible to degradation from heat, light, weathering and moisture, as well as biological attack[2]. Heat

treatment addressed these issues. Understanding how woody polymers, specifically cellulose, lignin, and hemicellulose as well as extractives change due to heat application gives a good insight to effects associated with wood heating during laser irradiation.

Effects of thermal energy exposure on wood

Wood heat treatment for property improvement, including equilibrium moisture, dimensional stability, durability, and mechanical properties has become a successful product in Europe over the past decade [6, 7]. Wood modification by heat treatment is a subset of wood modification, defined as a process that creates a new wood material with improved properties that does not pose increased environmental hazards at the end of its life cycle [6].

Although heat treatment of wood has been investigated since the 1920s, it is thought that due to the availability of high quality wood, heat treated wood has been unsuccessful in the market until recently [6]. There are multiple companies creating heat treated wood with the purpose of heating the wood in a controlled manner to enhance performance properties. Thermowood, seen in Figure 2.1 below, the most successful company in heat treatment, producing about 90% of Europe's heat treated wood, heat treatment process includes multiple heating steps [8]. All of these processes are the same in terms of processing temperatures, but vary in terms of processing conditions such as shielding gas, humidity, and sometimes additional chemical usage [9]. First the wood is heated in a humid atmosphere at 150°C or higher for 2-10 h, without pressure, then heated to 185-230°C for 2-3h [10]. This heat treatment causes significant changes in wood including chemical transformations, anatomical changes, decrease in equilibrium moisture, improved dimensional stability, improved durability, a decrease in mechanical properties, and a change in color [6].



Figure 2.1: Product photo of heat treated Thermowood[11]. Used with permission of Thermowood Inc.

Out of the three primary polymers in wood, hemicellulose is the most affected compound by heat treatment. Degradation of hemicelluloses occurs by impacting the labile bonds; deacetylation releases acetic acid, that then depolymerizes polysaccharides, which leads to the formation of aldehydes [12, 13]. During the process dehydration with a decrease of hydroxyl groups also occurs. Cellulose's crystallinity is a primary factor in being more resistant to degradation during heat treatment (relative to the hemicelluloses), with the only significant change being an increase in crystallinity with heat treatment [14, 15] at the temperatures used in the heat treatment of wood. Higher temperatures lead to the formation of another degradation products like levoglucosan. Lignin typically undergoes polycondensation reactions, resulting increased crosslinking as labile ether linkages are broken and new bonds are formed [13]. The decrease in equilibrium moisture is due to the reduction in hydroxyl groups (switching from hydrophilic to hydrophobic), increased cellulose crystallinity, and lignin crosslinking [16]. The chemical changes undergone in the wood have created a material that is unrecognizable by fungal enzymatic systems. A combination of decreased moisture uptake and increased resistance to fungal attack make the heat treated wood less susceptible to weathering, increasing the life of the wood, specifically in outdoor applications, such as decking.

Fast heating rates

The world's largest biomass is wood, and therefore pyrolysis of wood is a large area of research and in the industry for the conversion into fuels[17, 18]. Many variables come into play for pyrolysis, including heating rates, temperature and wood properties[18, 19]. Pyrolysis

of wood via lasers have been evaluated, as higher heating rates minimize unwanted products and possibly increase the efficiency of the process [19, 20]. Products from laser pyrolysis of cellulose include levoglucosan, active cellulose and cellulose with a lower DP[20]. Usually biomass heating at high heating rates generates “bio-oil” and gas products such as hydrogen, carbon dioxide, and carbon monoxide. Depolymerization and breakage of the monomeric units into these products occurs at temperatures between 500 to 1000°C [18].

2.3 Laser technology

Lasers

Laser is an acronym for Light Amplified by Stimulated of Radiation [21]. Although there are 6 main laser categories, and 4 classes of lasers, they all work on a similar principle [21]. In this study a carbon dioxide laser was utilized therefore how this specific type of a laser works will be described in this section.

History

The concept of a laser was first developed by Albert Einstein, when in 1921 he established the term stimulated emission [22]. The concept explained how energy could be generated in a coherent, monochromatic, narrow beam of light. Einstein’s theory was coupled with Dirac, an English physicist’s, who hypothesized that under certain conditions atoms could radiate in phase to create a highly coherent radiation that could be maintained indefinitely. These ideas eventually came to fruition in 1960 when the first functional laser was demonstrated by Theodore Maiman at Hughes Research Laboratories [22]. Since then, laser technology has grown, with a growing array of laser types, increases in efficiency, and numerous applications ranging from LASIK eye correction to metal welding.

Although there are many different categories of lasers, they all work on the same principle. Typically electrical energy is converted to photons, via pumping and population inversion [21]. These photons are then gathered in a resonator until they achieve a certain amount of energy, where upon exiting a laser beam is formed [21]. Most types of lasers fit into these categories: solid state lasers, semiconductor lasers, gas lasers, chemical lasers, liquid lasers,

excimer lasers, and free electron lasers [21]. In this study a gas laser was used, specifically a carbon dioxide laser due to its availability.

How a Laser Works

A Carbon Dioxide Laser is based upon infrared transitions between energy levels of carbon dioxide [21]. Figure 2.2 illustrates the basic design of a carbon dioxide laser. First nitrogen gas is excited by introducing an electric discharge through the gas. The nitrogen then transfers energy to the carbon dioxide during a collision [23]. As the carbon dioxide electrons return to lower energy levels, photons are emitted. These photons are released depending on how the energy was stored in the carbon dioxide molecule. Since energy is stored in molecular vibrations as stretching and bending vibrations a variety photons are emitted with wavelengths between 9 and 11 microns [21]. Special modifications to the mirrors create a uniform beam with a wavelength at 10.6 microns. The photons then oscillate between the total reflector and output coupler, creating a laser beam. Once the beam has achieved enough power, it exits the laser tube via the output coupler, which is only partially reflective, then enters a series of optics to focus the beam and direct its path to the work piece. Along with photons generated, molecular vibrations release heat. The heat along with photons striking the sides of the laser tube creates a need for heat dissipation. A combination of utilizing helium, a better thermal conducting gas, and cooling systems, in our case air cooling, allows for heat removal. The process is about 5-20% efficient for typical carbon dioxide lasers [21].

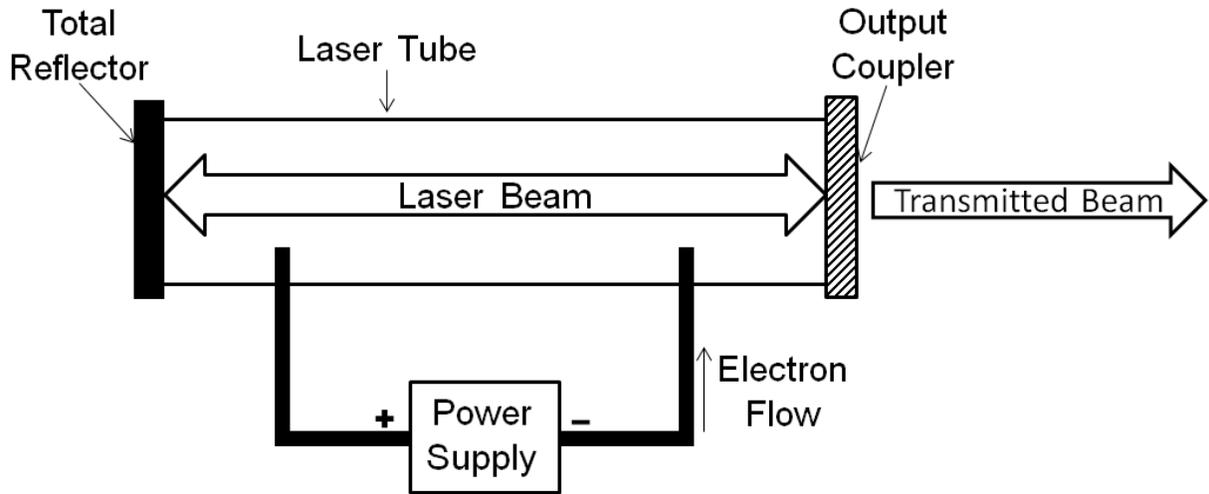


Figure 2.2: Diagram of a Carbon Dioxide Laser

Properties of Laser Beams

Lasers differ from other light in their high degree of directionality, monochromaticity, and phase consistency, which together are all described as a laser's coherence. Visible light has a bandwidth of about 300 nanometers, as it includes the entirety of the visible spectrum from 400nm to 700nm, while laser light often has bandwidths of less than one nanometer [21, 22]. This smaller bandwidth of lasers is defined as the tendency of a laser to be monochromatic. Lasers have a finite bandwidth, otherwise they violate the uncertainty principle[21, 24]. Laser wavelength should be dictated by the application required; as certain materials absorb specific wavelengths of light, a specific wavelength should be chosen based on the substrate being irradiated.

The high degree of directionality is defined as the lasers ability to not diverge. This property is imparted to the beam by the resonating cavity. In Figure 2.2, the mirrors on both ends of the laser cavity combined with the laser cavity is referred to as a resonator. As the photons oscillate between the mirrors their divergence decreases. The divergence is minimized by the mirrors which are slightly concave, in order to organize photons into a laser beam with minimal divergence. Although laser beams have little divergence, it is impossible to none, due to diffraction [21, 24].

A combination of near monochromaticity, a high degree of directionality, and the same phase results in a property known as coherence. This property allows for both the transport of energy over long distances and more importantly for this work; enables the focusing of energy to small points of high intensity [21]. By controlling the amount of energy, wavelength, and application rate, a laser becomes a fitting tool for optimal surface modification.

2.4 Laser light interaction with wood

Heat affected zone

Laser light interaction with wood results in charring, ablation, and melting, depending on a multitude of variables that are related to wood properties and laser parameters. Laser light affects the irradiated area and the resulting laser modification is described in 3 levels, which are cumulatively known as the heat affected zone, or HAZ. This zone can be up to 100 microns thick, depending on wood variables, laser variables, and their interaction. Parameswaran described the first level as a black, smooth laser cut surface that is approximately 25 microns thick [25]. The other two zones do not contain pyrolysis products and/or are not melted, and approach the original chemistry of the wood when moving away from the first zone into the wood.

Wood polymer modification

Chemical and/or physical changes occur in one or more of the primary components in wood, broken primarily into 4 classes: cellulose, lignin, hemicellulose, and sometimes extractives. The modification of these components is dependent on their thermal properties, outlined in Figure 2.3 below.

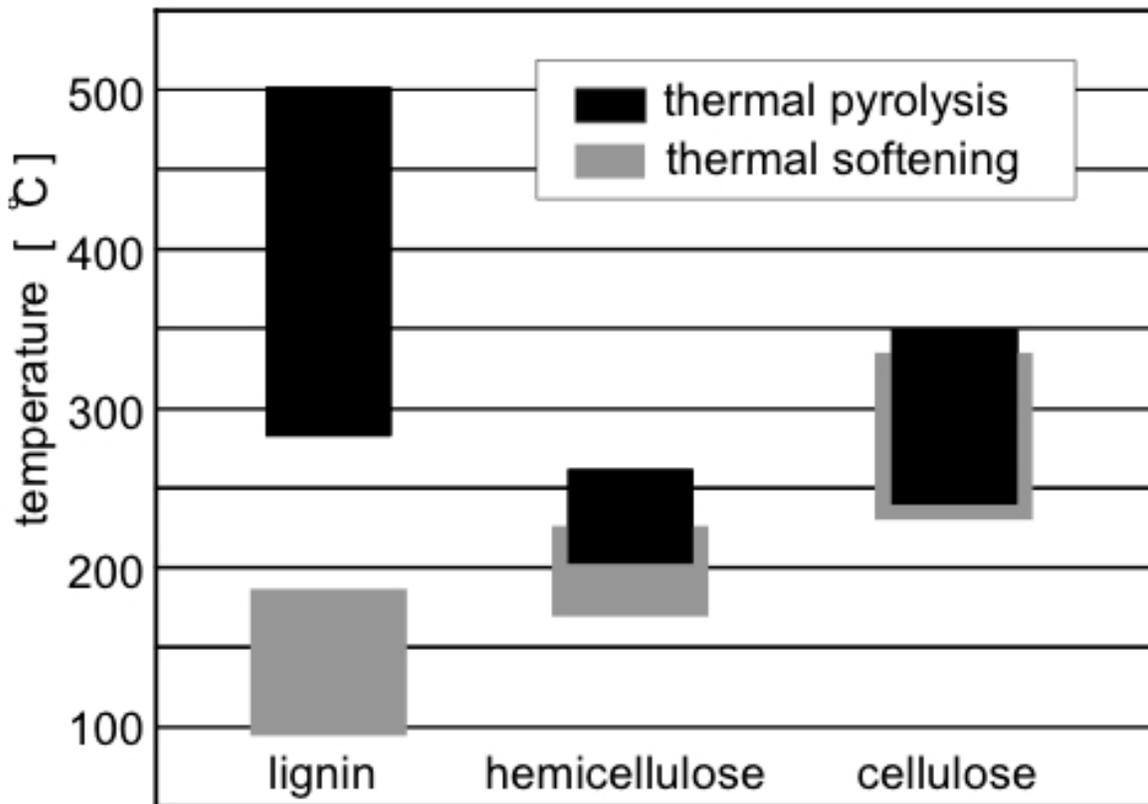


Figure 2.3: Pyrolysis temperature of wood constituents. Used with permission of Rightslink Copyright Clearance Center, Applied Surface Science Journal, 2007. [4]

Figure 2.3 shows the three primary components of wood and their corresponding temperature ranges for softening (glass transition) and degradation during wood pyrolysis.[26] Due to the high quantity of energy transferred, in a short period of time, lasers are able to modify wood differently than other modification methods with slower heat rates. Softening and melting as a result of laser light and wood interaction suggests the process is such that kinetics of softening and melting may surpass the kinetics of thermal degradation.[26]

Past research indicated that the laser modification of wood affects the lignin and hemicellulose components to the greatest extent, while effecting cellulose to a lesser degree [26, 27]. Changes to the wood anatomy as well as thermal properties support this view. As seen in Figure 2.3, lignin has the lowest thermal softening temperature; therefore it would be logical for it to be modified to a greater degree than components with higher softening and pyrolysis temperatures. However, it needs to be noted, the glass transitions of wood polymers in the native

state are not fully resolved because of intimate associations. In addition to thermal softening, it was found that laser modification primarily caused degradation of hemicellulose and lignin [27]. Specifically the hemicellulose underwent deacetylation, while bond cleavage occurred in lignin, specifically the aryl-alkyl ether bonds in lignin were broken. This bond cleavage induced further condensation reactions [27]. Other research indicated that the modification of components was preferential towards reducing the methoxy side groups of lignin [5, 28]. The variation in modification of components is broad described in the limited research on the subject, which is logical due to the large variety of wood and laser variables.

Additional studies have investigated laser modification specific to cellulose. The studies were based on the concept of applying enough energy, induced by a combination of frictional heat and via laser, in order to chemically and/or physically change viscose grade wood pulp, which is noted to have a high α -cellulose content, into clear films. A calculation was made for the amount of energy required to “weaken and unlock” the intermolecular hydrogen bonds in cellulose. It was found that this energy would need to be 20kJ/mol, or 3.3×10^{-20} J per bond, which is equivalent to 1 photon with a wavelength of 6 microns [26]. In practice 50x the amount of photons was used to modify the cellulose fibers to ensure light penetrated the sample [26]. In this experiment however, the investigators suggested their modification of the cellulose to be primarily a physical change, and not chemical as IR spectra indicated little changes due to laser modification with the lack of new peaks from degradation products, (as well as the addition of shear and compressional forces). Although the IR spectra indicated little change, seen in Figure 4, qualitatively it was evident that the material changed from a fibrous opaque structure to a transparent smooth structure, seen in Figure 2.5. With these results the researchers concluded they were able to melt cellulose.

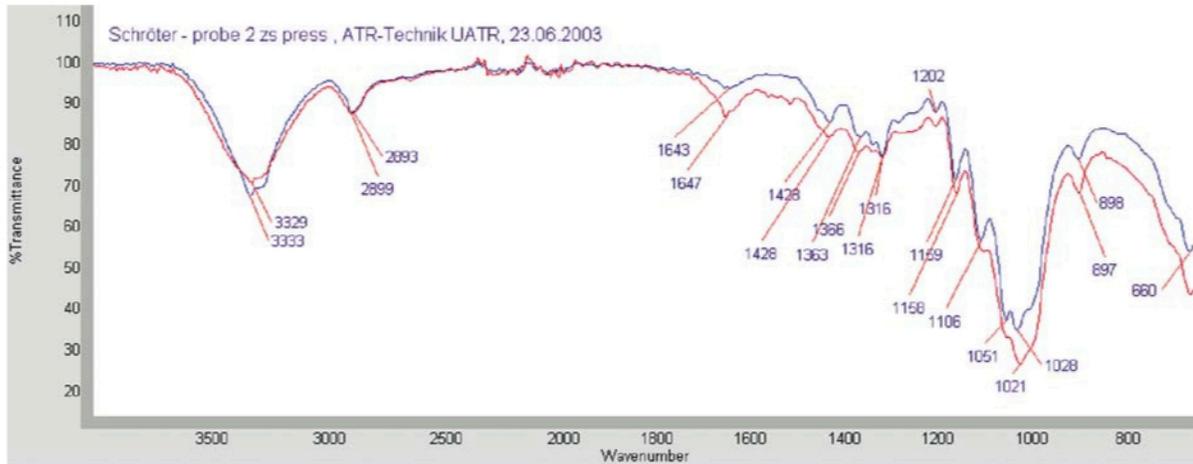


Figure 2.4: IR spectrum comparing unmodified cellulose (red) to laser modified cellulose (black). Used with the permission of Rightslink Copyright Clearance center, Cellulose Journal, 2005. [26]

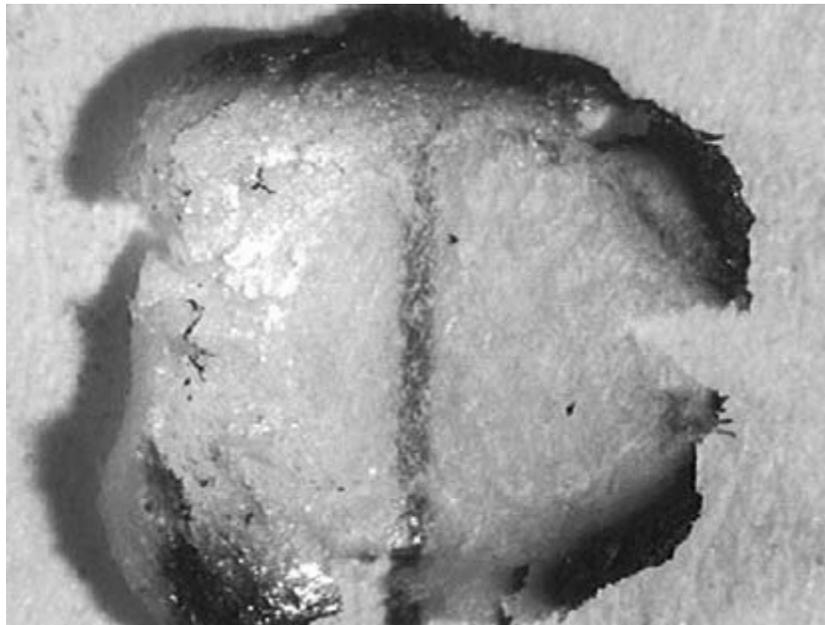


Figure 2.5: Cellulose wool (Buckeye V-60) after high dose laser treatment. The fibrous structure disappeared. Used with the permission of Rightslink Copyright Clearance center, Cellulose Journal, 2005. [26]

One other study examined laser modified lab filter paper with the products analyzed via liquid chromatography. The primary recovered products included glucose with a degree of polymerization (DP) of two (cellobiose), DP of three (cellotriose), and levoglucosan. Unlike the Schroeter's study [26], there was evidence for chain scission, or breaking up of the units,

occurring [29]. It should be noted that Schroeter's study provides little detailed analysis of the FTIR spectra as changes can be noted in Figure 2.4 related to cellulose morphology.

Wood modification by lasers is heavily dependent on the wavelength of the laser[30]. Due to the intrinsic molecular structure of wood, certain wavelengths are absorbed by the wood substrate more optimally than others[4]. Both XeCl lasers and carbon dioxide lasers have wavelengths that fit within areas of high light absorptivity for wood, research showed a twenty-fold increase in ablation going from XeCl to CO₂ laser modification[30]. The research did not indicate the fluence of the lasers but indicated the pulse length, with XeCl at 40ns, and CO₂ at 1.2ms. For a model cellulose substrate, Whatman filter paper, laser modification at 308 nm resulted in photo-oxidative degradation of cellulose. The degradation resulted in the increased content of oxidized groups, either carbonyl or carboxyl, and a severe decrease in the degree of polymerization [31]. Kolar showed that pure cellulose is an extremely poor absorber of UV light greater than 200nm [31]. This fact agrees with Haller who reported that pure cellulose ablation (at 308nm, 20×10^6 W/cm²), causes a change in color and melting of a thin surface layer [4]. Haller indicated that mainly thermal ablation occurs at wavelengths above 300nm with reduced degradation arising from photo-oxidation. However, a reduction in the degree of polymerization (DP) was found during the laser treatment of sulphate pulp at many wavelengths of 308nm, 532nm, and 1064nm with fluences less than 2.5J/cm²) [31]. Hence, wavelength has a direct impact on the mechanism of degradation but it is not clear how much the wavelength impacts the degradation product for cellulose.

Morphological and topological changes of the wood surface

Previous researchers have observed the melting of lignocellulosic materials with laser modification, some suggesting lasers melting only related to a specific component, with other suggesting that all wood components can undergo thermal softening and melting [4, 26, 32]. Figure 2.6 shows the laser modified surface of pine wood after laser ablation via CO₂ laser.

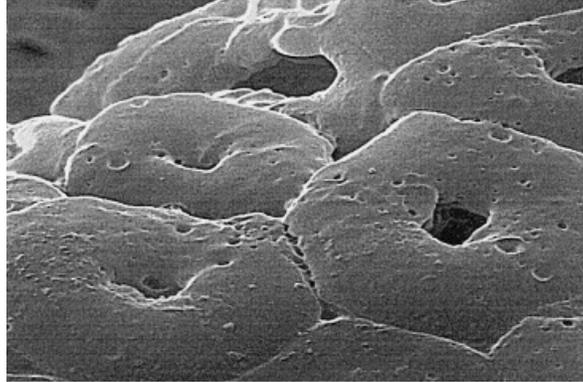


Figure 2.6: SEM showing the melting of the surface during excimer laser ablation of beech (cross cut) Used with the permission of the US Forest Products Laboratory, Forest Products Journal, 1975. [33].

Evident in the Figure is the presence of molten material, with an open slit remaining between the cells where the lignin had been [25]. Unmodified wood exhibits a well-defined cellular structure with no evidence of molten material flow (not pictured).

Some SEM images of initial studies of laser modified lignocellulosic materials indicated a reduction in fibrillar structure, as seen in Figure 2.7. This change in microstructure is coupled with a formation of bubbles is hypothesized to be gaseous pyrolysis products captured by the lignocellulosic material when it was in a liquid like state [25, 32]. The significance of this discovery is the first evidence of cellulose melting along with hint that there may be some direct conversion of cellulose into gaseous degradation products, also known as the ablation process.

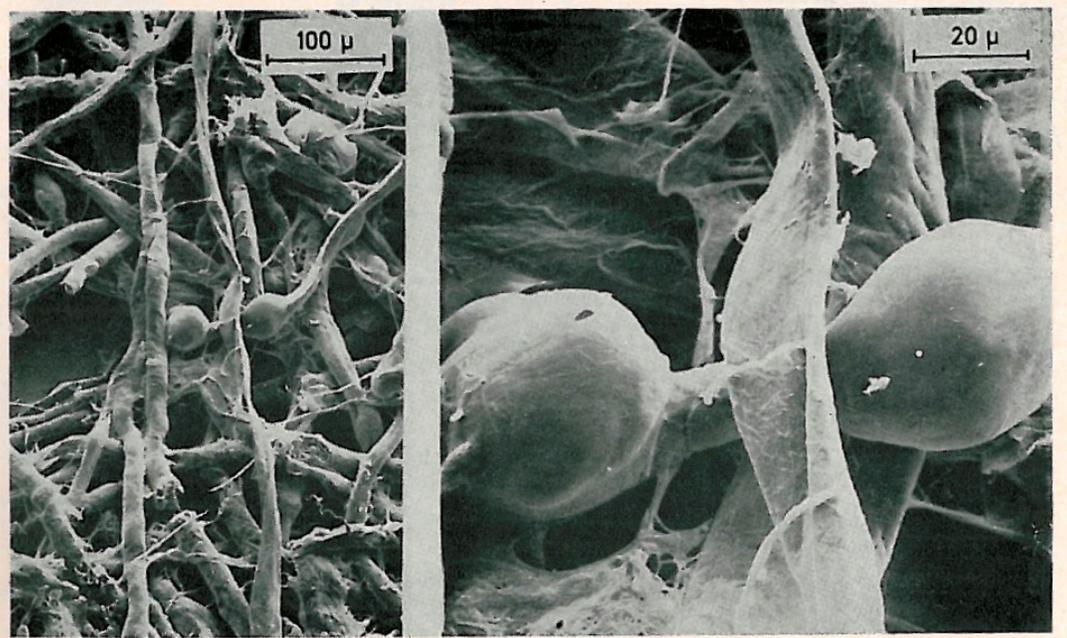


Figure 2.7: SEM images at two different magnifications of a cotton linter paper, which has passed the laser beam. Note the formed bubbles have lost their fibrillar structure. Used with the permission of Rightslink Copyright Clearance Center, Textile Research Journal, 1974. [32]

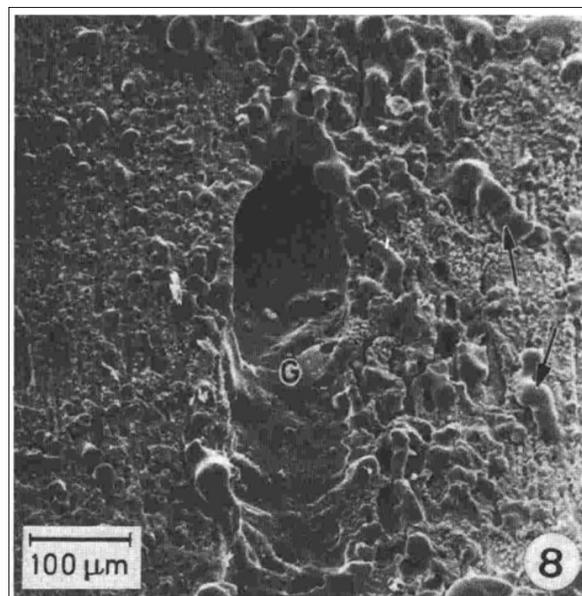


Figure 2.8: Suggested Evidence of bubble formation after laser irradiation. Used with the permission of Rightslink Copyright Clearance Center, Applied Surface Science Journal, 1998. [33]

Although the cellulose fibers were modified, lignin more effectively absorbed the laser energy. A similar change was also seen by Parameswaran in plywood veneer, seen in Figure 2.9 highlighting changes in the cell wall of wood.

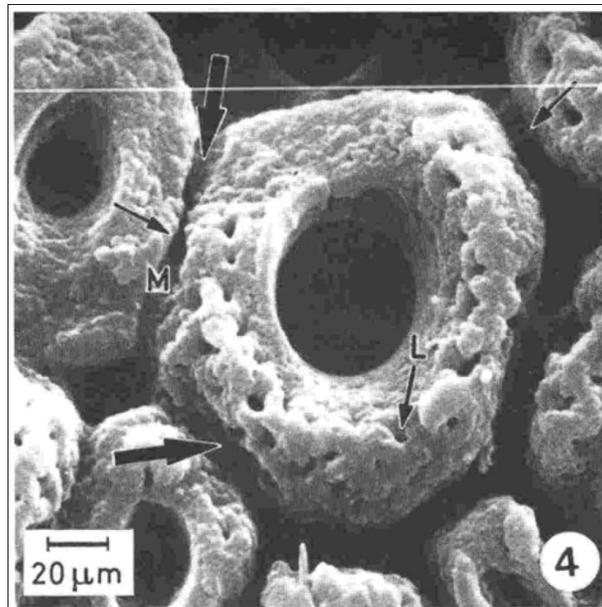


Figure 2.9: End grain of laser modified veneer pine plywood. Used with the permission of Rightslink Copyright Clearance Center, Holz als Roh- und Werkstoff Journal, 1982. [25]

Figure 2.9 shows fibers with holes (L) with highly degraded middle lamella (arrows) in veneer plywood [25]. This is further evidence that lignin more effectively absorbed the laser energy than other materials.

Another study investigated the surface of wood after laser irradiation using a variety of post treatment steps, such as exposure to dioxane (lignin solvent), sodium hydroxide (lignin and hemicellulose solvent), sulfuric acid (cellulose hydrolysis agent), and acid chlorite (bleaching procedure to generate holocellulose) [34]. The analysis revealed that the hypochlorite significantly removed the glassy like material, while other treatments caused the surface to remain grainy with consistent coverage of the glassy material. The authors attributed the material at the surface to be mostly lignin, but it is unclear from the translation why the lignin

solvents do not cause drastic changes to the surface appearance. A recent FTIR analysis reported that laser modified wood surfaces contain lignin partially depolymerized, but condensation of aromatic rings also occurs, along with changes to the hemicellulose components[35].

Further research indicates that out of the three primary components of wood, cellulose is least changed by laser modification. Haller's theory that components other than cellulose more effectively absorb laser light was supported by an SEM image of CO₂ laser ablated wood, seen in Figure 2.10.

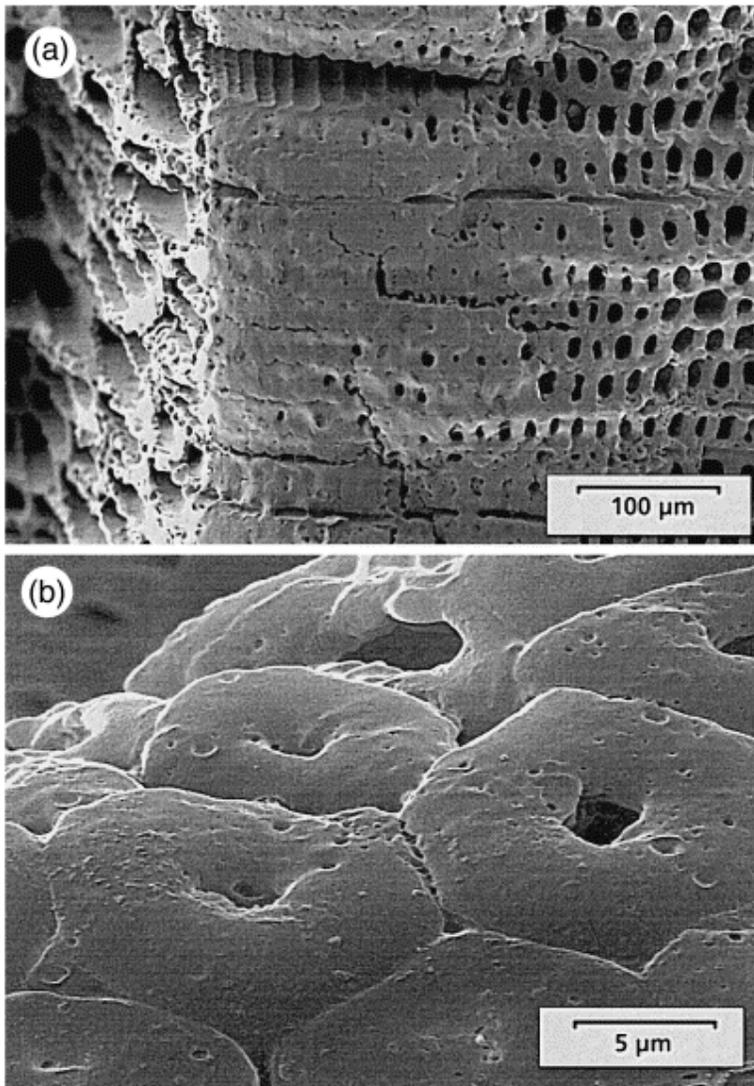


Figure 2.10: Laser ablated surfaces. (a) Pine, cross cut, CO₂-TEA laser (b) beech, cross cut, XeCl excimer laser. Used with permission of the US Forest Products Laboratory, Forest Products Journal, 1975. [33]

2.5 Laser Applications for Wood: Machining, micromachining, and cleaning

Lasers have been used in numerous wood-related applications including cutting, laser cleaning, pyrolysis and surface improvement modification. Although attempts were made to cut wood with lasers in the 1960s, laser cutting of wood was not common commercially until the 1970s. 1963 marked the first time that a laser was used with a wood substrate.[36] Utilizing a pulsed ruby laser, Bryan was only able to create holes 0.03” diameter that were 0.06” deep, due to the lower power output and short pulsed duration of the laser [36].

Currently, the primary type of laser utilized for laser cutting of wood is currently carbon dioxide lasers with growing application of fiber lasers[37, 38]. This latter fact is because fiber lasers have higher efficiencies, higher quality beams, flexible delivery systems and smaller physical sizes [39]. A body of research for the optimization and understanding of carbon dioxide lasers cutting wood exists, including computer modeling, design of experiment analysis, and testing on variety of woods [39-41]. Laser cutting advantages over mechanical cutting methods include no tool wear providing consistent cutting, no downtime from tool changing, low noise emissions, lower material loss (a smaller kerf), less dust, and the ability to cut intricate patterns [3, 5, 42, 43].

Typical methods of machining wood involve mechanical contact. This mechanical contact with wood causes damaged to the wood, specifically a layer of crushed trachieds that is difficult to penetrate with adhesives or coatings [42, 44]. This lack of penetration greatly diminishes the ability of the coating or adhesive to work properly. A comparison of laser-irradiated wood versus band saw cut wood is seen below in Figure 2.11.



Figure 2.11: SEM comparison of band saw cutting (top of image) and laser irradiation (bottom of image) Used with the permission of Rightslink Copyright Clearance Center, Applied Surface Science Journal, 1998. [33].

The upper part of Figure 2.11 shows the damaged layer of wood created by the band sawed while the bottom side shows clean, open wood vessels that are easily penetrable by coatings or adhesives. Either by cutting the wood by lasers instead of mechanical methods, or adding a laser post treatment to remove the damaged layer, the wood structure is opened up allowing the adhesive or coating to penetrate deeper into the cells thereby improving the final properties of the complete system.

Microtoming wood is a method that utilizes mechanical forces to lay bare the anatomical structure of wood for numerous applications. Several researchers have demonstrated that lasers can also lay bare the anatomical structure of wood, without any mechanical forces on the structure, often leaving a structure that is more intact than mechanical Microtoming methods as seen in Figure 2.12[4, 28, 44].

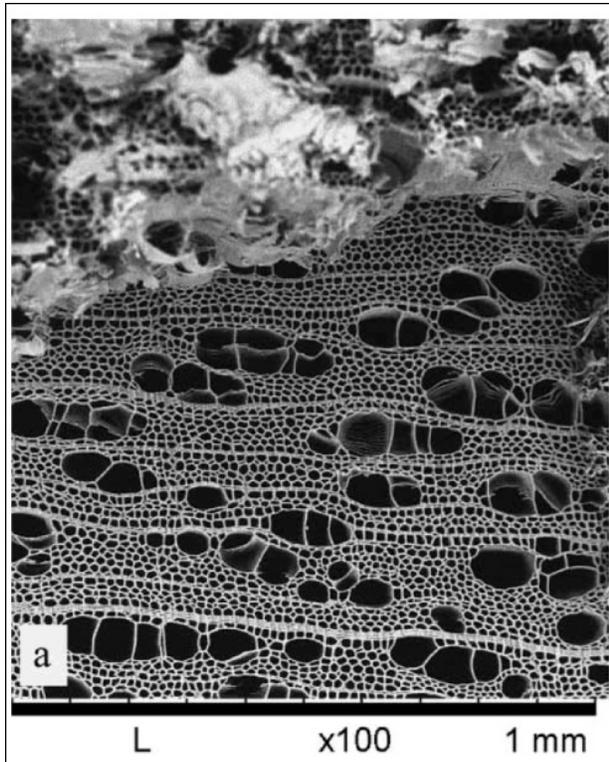


Figure 2.12: Micrograph showing UV laser ablated zone (the lower three-quarters) of heat-treated birch. Used with the permission of Rightslink Copyright Clearance Center, Wood Material Science and Engineering Journal, 2009.[28]

Lasers have been employed for cleaning lignocellulosic materials, including historical documents as well as ancient wooden objects[45]. The technique is based on that lower energy doses can be applied that removes non-lignocellulosic species at the outer most surface, while leaving lignocellulosic materials unaltered. Wood absorbs certain wavelengths better than others, so researchers have utilized lasers with wavelengths in the non-optimal wood absorption ranges (outside of the UV range) to remove oil/lime paints, plaster, dirt, etc [4]. Many of these impurities absorb laser energy and are ablated during the cleaning process, by lasers such as XeCl lasers (308nm, absorbed by wood), as well as Nd:YAG lasers (532 and 1064nm) [4, 31]. Nd:YAG lasers, at 1064nm, is minimally absorbed by wood, made the cleaning process self-limiting; one that removed unwanted material like graphite and soil, materials that absorb the 1064 wavelength of light, while leaving the wood unmodified at the energy dose [4].

2.6 Variables Important in Laser Processing

Several areas of research to better understand laser light interaction with wood surfaces can be categorized into variables that either relates to the laser set-up or the substrate characteristics. Significant variables for the former include: gas assistance, interaction time, laser fluence, wavelength, laser type, heat affected zone, beam geometry, and laser speed [39, 46, 47]. For the latter, wood species, earlywood/latewood, laser/wood orientation, wood moisture content, wood specific gravity, thermal conductivity, among a few others [5, 46]. Below is a discussion about important parameters that have been previously studied.

Gas Assist/Gas Jets

Addition of a gas jet, or assisted gas jet system, to a laser system has many benefits when working with wood substrates[39]. Dependent upon gas type surface oxidation is minimized, adherence of particulates are avoided, the plasma plume and vaporized materials are removed; sample cooling is obtained providing reduction in the heat affected zone, and can extend the life of the laser[14].

The type of gas, the pressure of the gas, and the number of nozzles were all found significant for wood/laser interaction in laser processing [5, 43, 48] By using an inert gas such as nitrogen, oxidation of the wood is minimized [5]. When using compressed air during laser cutting of wood, severe burning and charring occurs, which leads to a larger kerf, over cuts, all leading to a larger material loss [40].

Particulate/plasma plume removal is important as it interferes with the laser's ability to modify the wood, may increase the heat-affected zone (HAZ), and could re-adhere materials to the substrate [4, 5]. It was found that 5 ms after a 6ns laser pulse, a plasma plume was present. This plume was suggested as an insulator for the surface increasing the HAZ, while also partially blocking future laser pulses[4] . A 25% reduction in the HAZ was seen when increasing from one to two gas jets, Figure 2.13 [39]. Re-adherence to the substrate was non-optimal, as it would diminish the qualities of the newly irradiated surface.

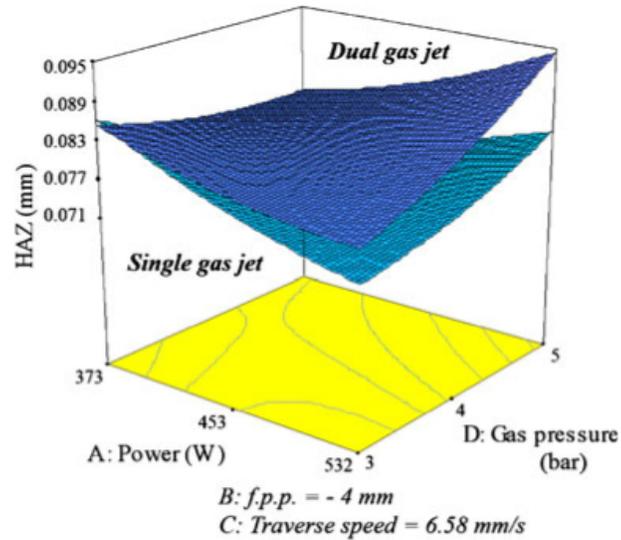


Figure 2.13: DOE results indicating effects of power, gas pressure, and the number of nozzles on the HAZ. Used with the permission of Rightslink Copyright Clearance center, International Journal Advanced Manufacturing Technology, 2010. [39]

One area where literature diverges: whether or not the addition of gas works as a coolant, or if it extends the energy of the laser. Peters suggested that the gas jet extends the energy of the laser, but acted as a coolant to reduce thermal damage [43]. All other literature in this area showed that the gas acted solely as a coolant [39, 40, 48].

Interaction Time

If a large quantity of energy is applied over very short periods of time at high heating and cooling rates, non-ideal laser modification is minimized. Non-ideal laser modification is defined as charring or burning, while ideal laser modification typically results in the ablation of the irradiated area. The interaction time is dependent on the laser pulse duration, the time between pulses, the pulse rate, and the speed of the laser [21].

During laser modification of wood three events can happen: charring, melting, and/or ablation[4]. Charring typically occurs at lower speeds. Increasing laser speed leads to melting, and eventually ablation, or vaporization [43], assuming a high enough laser fluence. Typically

melting/softening and flow occurs simultaneously with melting. If melting a surface is the goal, then the lowest amount of energy that will melt the surface but not ablate significant amounts of material is best, as material removal equals cost.

Shorter interaction time at high fluence leads to instantaneous modification or vaporization, as there is no time for heat transfer to the uncut [unmodified] material, which yields wood with minimal charring, and a slight darkened, glazed appearance [43]. In the late 1990s a femtosecond (10^{-15} s) titanium sapphire laser was used to modify wood, and did so without any cell damage or charring [49]. Although no charring or cell damage is optimal for wood modification, the titanium sapphire laser had a low average power and therefore was not useful, especially on an industrial scale.

The effect of speed on the depth of wood modification, specifically cutting, is outlined in Figure 2.14 below.

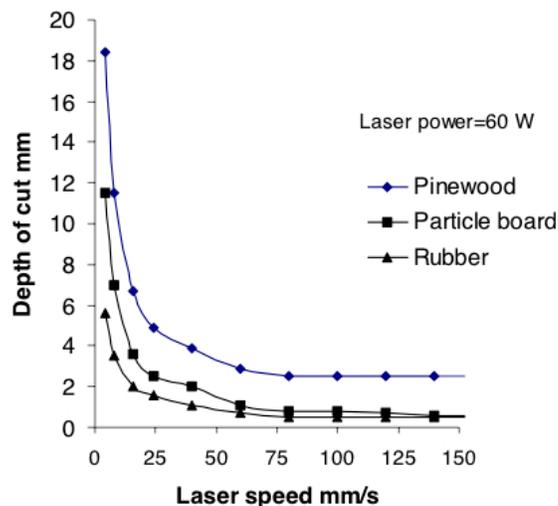


Figure 2.14: Carbon dioxide laser speed and corresponding depth of cut for pinewood, particleboard, and rubber. Used with the permission of Rightslink Copyright Clearance Center, Journal of Materials Processing Technology, 2004. [41]

Above 75 mm/s the cutting depth levels out, but below that speed the depth of cut increases exponentially. In order to melt or glaze, with minimal material removal via ablation or burning, higher speeds are therefore optimal to limit energy loss below the surface.

Fluence

Fluence or power density is the laser power per unit area; therefore it is both a measure of the power of the laser, and the spot size of the focused beam when imparted to the wood substrate [4]. The variable that most closely interacts with fluence is speed. Increasing fluence and speed leads to less charring, more melting and ablation [4, 27]. At a high enough combination of speed and fluence melting will occur, while higher quantities of material will be vaporized via ablation [27]. By changing the laser fluence, many changes become evident, including a change in surface roughness, wood color, reduction in crystallinity, woody polymer degradation, and in some cases more charring and carbonization [14]. With increasing laser fluence, melting and ablation occurs, leading to an increase in surface roughness and in damage [5]. The surface roughness is due largely impart to variations in wood structure [5]. High levels of fluence totally destroy the wood structure. With the combination of mechanical forces and laser modification of cellulose it was found that intensities of 19 W/mm^2 led to decomposition to ash [26].

Low levels of fluence is important in the application of laser cleaning of historical documents and wood substrates. It was found that at 1064nm with a Nd:YAG laser 183×10^6 to $283 \times 10^6 \text{ W/cm}^2$ was the optimum range for the self-limiting cleaning of wood panels [4]. By utilizing a laser wavelength that is not highly absorbed by wood, one can apply enough energy to remove the dirt/unwanted coatings at fluences that, if in the absorption range of wood, may cause unwanted modification (in the sense of historical preservation)[45].

Wood Variable: Earlywood vs Latewood

Temperate climate trees have annual growing cycles with the wood cells showing different growth patterns at the beginning and ending stages of the cycle. Wood cells at the beginning of the growing season are termed earlywood and in many species have relatively thin secondary walls. As the growing season advances, growth rate is reduced and the cell walls for many species have thicker cell walls (although they remain chemically equivalent). The variations in the effect of laser interaction with earlywood and latewood are both structural and chemical.

Previous research has indicated that when both the latewood and earlywood were laser modified, the HAZ was greater in earlywood, ablation rate is higher in earlywood, and light emissions during the process is greater, which further show differences in ablation. It was noted that the “less regular structured earlywood” incurred more damage from laser modification than latewood [5]. This difference was initially discovered by Parameswaran, as seen in Figure 2.15.

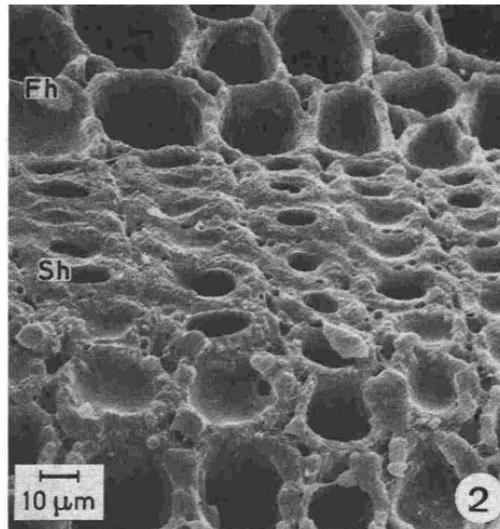


Figure 2.15: Laser ablated wood. The center of the image is latewood while the top and bottom are earlywood. Used with the permission of Rightslink Copyright Clearance Center, European Journal of Wood and Wood Products, 1982. [25]

The difference in ablation is largely due to the ratio of free space and cellular structure between early wood and late wood.

Further evidence of greater laser modification in earlywood vs latewood was found by Panzer, both through microscopy and high speed imaging of the laser modification process. High-speed photograph showed significant differences in the brightness of light emitted between earlywood and latewood during laser ablation. This brightness, due to the burning of gases exiting the wood surface, changed depending on early wood or late wood.

Laser movement to Grain Orientation

The direction in which the laser is traveling is significant in both the surface modification and cutting of wood[48]. This factor is significant as the thermal properties of the wood depend

on structure, which varies with cell orientation. When moving a laser with the grain the heat transfer is greater in the fiber direction, due to the inherent geometry of the material[48]. When moving the laser perpendicular to the grain the heat transfers most readily in the grain direction. Moving the laser perpendicular to the grain leads to increased heat affected zone (HAZ), lower yield and quality of laser cutting, decreased process efficiency, slower cutting speeds, and increased creation of micro-cracks[5]. Barcikowski measured the HAZ and determined that the HAZ smallest to largest was laser direction parallel to grain/fiber direction, then diagonal to grain, then lastly perpendicular to the grain [5]. Peters tested grain and laser direction and found that with southern pine there was a 33% decrease in cutting speed to achieve the same depth of cut when cut perpendicular to the grain direction [43]. Due to this increased HAZ and reduction in cutting speed, a lower yield, process efficiency and quality of finished surface were found [39]. Lastly, micro cracks, approximately 1mm wide have been discovered when moving the laser perpendicular to the wood [48]. All of these results support the claim that optimal laser movement to grain orientation should be parallel whenever possible.

Wood variable: specific gravity

The wood variable of specific gravity for laser processing has overall been found to be a significant factor. Peters and Yusoff both indicate that the specific gravity of wood or wood density changes the cutting requirements of that particular wood [40, 43]. The only counter argument, where specific gravity is unrelated to cutting speed was determined by Mcmillin. Mcmillin found that when cutting wet wood “the max feed speed was unrelated to specific gravity”[42]. This might be due to the fact that increase moisture content has far more significant effect on laser requirements than the density, although both are interrelated. The porosity of wood, which plays into specific gravity, was also found to be significant. This significant variable is seen with beech compared to pine. It was found that beech ablation rates were 50% lower than pine[4].

The thermal conductivity of wood plays a vital role in laser cutting of wood, as it determines how well, or poorly the wood transfers the laser energy away from the cut/modified portion. It was determined that low thermal conductivity of wood was undesirable as it leads to carbonization as it cannot cool quickly[4]. Thermal conductivity is linked to specific gravity as

Walinder showed that the thermal conductivity increases with density and ambient temperature[28].

Wood Variable: Moisture Content

Moisture content was found to increase the required amount of laser energy or slow down the rate of laser ablation [30, 41-43]. This reduction in cutting efficiency occurred because water highly absorbs energy from carbon dioxide laser irradiation[40]. Laser cutting of wood efficiencies drop 70% when increasing the moisture content of southern yellow pine from 6% to 63%[42]. Meanwhile when just modifying the surface it was found that a 20% higher ablation rate was required when increasing the moisture content of beech from 12% to 30%.

Wood Variable: Plane of orientation

The cutting plane determines what face of the wood structure is facing the laser. The ablation depth of the laser depends on the anisotropy of the wood structure. If applying the laser on the cross sectional face, a large part of the incident power gets “lost” in the interior of the tube like cells with minimal modification[4]. This was found to be more pronounced with coniferous wood.

2.7 Wood adhesives

Bonding lignocellulosic substrates together

Applications of wood require it to have dimensions and isotropic strengths that are not naturally found. The most abundant natural resource, wood, has been modified industrially in such a way to create wood-based composite materials that have the dimensions and strengths required for diverse applications. Wood composites typically consist of a wood substrate, often a veneer, chip, or strand, combined with a synthetic adhesive. The wood composites industry relies predominately on petroleum-based adhesives, such as phenol formaldehyde (PF), urea formaldehyde (UF), and polymethylenediphenyldiisocyanate (pMDI)[50]. Wood composites for structural applications (such as sheathing, roofing, and flooring) contain PF or a combination of PF and pMDI because of the stability and durability of these adhesives when exposed to wet

environments. The PF technology is one of the oldest synthetic polymer chemistries and has proved to be very economical over the years[51]. PF replaced many of the protein-based adhesives after World War II, which were the work-horse for panel-based products. Other wood-based composite materials such as particleboard, medium-density fiberboard, and furniture plywood predominately contain UF adhesives[50]. UF adhesives are low cost and can be tailored to a wide range of woody materials[2]. However, these adhesives contain added formaldehyde that can emit into the atmosphere. Most people have been exposed to formaldehyde when opening the packaging of ready to assemble furniture, as an odor is immediately detected. Since the year 2000, the general public's sensitivity toward environmentally harmful practices has drove governmental regulations for synthetic adhesives, creating a need for more environmentally friendly adhesives, or wood composite manufacturing practices[1]. The two categories eco-friendly bonding practices fit into are biobased adhesives and wood welding.

Alternative bio-based adhesives

Alternative bio-based adhesives are broken into categories based on base material, with most bio-based adhesives fitting into tannins, lignins, proteins, and carbohydrates.

Tannin Adhesives

As of 2006, two primary tannin adhesive methods, tannin autocondensation and hexane hardening were ready for industrial use but have not been accepted commercially[1].

Lignin Adhesives

The lignin adhesives area chemistries rely on the phenolic nature of the material, as well as the abundance and low cost of lignin as a by-product in the paper industry[1]. The primary issue with lignin adhesives is a lower reactivity towards formaldehyde, even compared to phenol, this translates to long processing times, specifically during pressing and therefore higher processing costs. Although there have been attempts to activate the lignin chemistry via enzymes, as of 2006 the method was too slow. There is only one successful system that utilizes lignin as of 2006, for the processing of high density fiberboard.

Protein Adhesives

Alternative bio-based adhesives began to fulfill new governmental requirements for wood composite adhesives[52]. Adhesives that incorporate raw agricultural materials that require little fractionation are viable substitutes, with an example based on the commercialized adhesive containing soy protein [53]. In 2006, specifically a soy based adhesive, developed by researchers at Oregon State, funded by the American United Soybean Board, and commercialized by multiple companies. Although bio based, the soy based adhesives still contains components that are derived from petroleum products. Further research has investigated developing soy-based adhesives that eliminate all petroleum additives [1, 52].

Carbohydrate Adhesives

Carbohydrate adhesives are categorized into: 1. UF/PF modifiers, 2. degraded compounds utilized as precursors to adhesives, and 3. used individually. Although there may be some commercial success with these methods, none are as well-known as the soy based adhesive [1].

Unsaturated Oils

Unsaturated oils, one example source being cashew nut shell liquid, have been researched but have not reached market due to cost. Although epoxidated unsaturated oil yields acceptable results, the cost is currently too high[1].

Wood Welding

Historically adhesives, primarily of the phenol or urea formaldehyde chemistries, have been the primary wood adhesive for wood composites [2]. As the chemistries relied on petroleum, a non-renewable resource with fluctuating prices, a more renewable resource with more stable cost was desired. Wood welding, typically refers to wood composites that utilize thermoplastic polymers as joining devices[54, 55]. Wood welding was originally developed by the automobile industry but most scientific knowledge gained from the research remains trade secrets and not followed up. The research area of wood welding technologies (WWT), since 1993, has been growing. WWT utilizes thermoplastic polymers such as polyamides and

polycarbonates. These thermoplastics are bonded to the wood using ultra sonic energy, vibration welding, spin welding, and lasers [22]. WWT works on the principle of applying energy in such a way to melt the thermoplastic and create an intimately bond with the wood, optimally causing the thermoplastic material to enter the vacancies of the wood, creating a "root network" [56]. These bonds can be utilized to create numerous wood composite materials, with applications including furniture, windows and doors, stress skin floors, and structural applications such as trusses and glulam. WWT advantages include the economical usage of wood (less wood moulding), clean and repeatable processing (no liquids, no PF/UF adhesives), which result in impervious, dense joints [57, 58].

In ultrasonic WWT, an ultra-sonic energy is focused on the thermoplastic dowel/wood interface, combined with pressure and speed. The ultrasonic vibrations are created by an ultrasonic power supply and convertor, which together generates mechanical vibrations from electricity. These vibrations are then sent through a booster and horn then are transmitted to the substrate[54]. By controlling the speed, weld time, and hold time a good bond is formed.

The energy required to fuse the thermoplastic to the wood in vibrational welding is acquired by friction. By causing vibrations parallel to the joint, either linearly or orbitally, enough energy is created to fuse the thermoplastic to the wood. The vibrations are created by the response of tensional springs to an electromagnetic field. The primary machine variables are the pressure between the parts, welding time, amplitude, and hold time[55].

Spin welding technology is a WWT similar to vibrational welding as the energy required for fusing the wood and thermoplastic is pulled from friction. Spin welding works by spinning the thermoplastic piece against the wood substrate. The amount of energy imparted to the interface is controlled by the rotational speed, time of process, and the pressure applied.

In an attempt to improve the limitations of WWT, the thermoplastic was substituted with wood, creating the technology know as wood-wood welding.

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Chapter 3: Controlled modification of wood surfaces with laser light

Manuscript for Consideration in Holzforschung

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Abstract

Applying concentrated energy to wood surfaces causes a variety of different responses, dependent upon the energy density. White oak, *Quercus alba*, was exposed to a CO₂ laser, an open flame, as well as heated in a vacuum oven and the samples were comparatively analyzed. Surface analysis of the wood included chemical analysis using photoacoustic Fourier Transform infrared spectroscopy and x-ray photoelectron spectroscopy. Differences in cellular topology were analyzed through the aid of a stereomicroscope and scanning electron microscope. Finally, material isolated from the surface was analyzed with differential scanning calorimetry. Both flame treatment and oven heating caused darkening of the wood surface, resulting in severely damaged cellular structure. CO₂ laser-treatments caused the wood surface to undergo flow, reducing the microscopic surface roughness of wood. Corresponding chemical analysis revealed polymeric degradation based on energy source with the laser treatment drastically impacting polymer scission and modification of the repeat units. Isolated material from the surface of laser treated wood showed a softening transition that is similar to reported glass transition of milled wood lignin for oak. The work illustrates the fundamental differences of wood degradation when interacting with energy of varying power densities.

Keywords: laser, wood surface modification, photoacoustic infrared spectroscopy, rapid heating,

Introduction

Wood surfaces are complex arising from the destruction of the cell wall material, migration of water and extractive components to the surface, and the contamination of the surface with dust and other air-borne materials. Additionally, heat is generated at the surface during cutting operations and subsequent elevated temperatures during drying can alter the type and quantity of functional groups at the surface[1]. This phenomenon has shown to impact the bondability of wood [2]. Moreover, wood surfaces can be purposefully modified through exposure to different forms of energy [3, 4]. One of the oldest and classic examples is the flame treatment of wood for storage of food and drink [5, 6]. While sterilization of wood occurs when exposed to open flame, the treatment also leads to a complex interaction between the container and contents. Coopers have perfected the flame treatment of wood in order to assist in the development of some of the world's most expensive beverages [7, 8].

Flame treatment of wood exposes the surface to approximately $18\text{-}55\text{ kW}\cdot\text{m}^{-2}$ heat flux. This input of energy causes the surface of wood to reach temperatures of $300\text{-}400^\circ\text{C}$ [9]. The temperature is clearly higher than the thermal degradation temperature, as well as the glass transition temperature of the woody polymeric components [9]. Wood is known to thermally degrade at temperatures above 200°C and can continue to auto-ignite if raised above 300°C [10]. Thermal transport properties of wood are such that wood is highly insulating and at the edge of the char zone, the temperature is approximately 200°C [10]. Hence, centimeters away from the flame source, the poor conductivity of wood and char layer, leaves the bulk of the wood unmodified, making the process clearly a surface modification technique.

Current understanding of the flame treated wood surface is centered on the response of the polymeric components. Cellulose, lignin, and heteropolysaccharides each have a unique, but perhaps synergistic response to the energy resulting in a variety of degradation products such as phenols, acetaldehydes, and hydroxymethyl furans [11, 12]. Clearly, there is polymer backbone degradation, such as chain scission, pendant group bond breakage, such as loss of acetyl groups, and dehydrogenation. Acidic side groups or free radicals can help further catalyze the depolymerization, but at the same time aromatic lignin residues have relatively higher thermal stability and can serve to scavenge degradative radicals with their resonance stabilizing

structure. Hence, there is a complex array of products after flame treatment of the surface that arises from the intimate mixture of the polymeric components [13].

Flame treatment of wood is not the only method to expose the surface to concentrated amounts of energy. Other methods have centered on light, such as high intensity infrared or ultraviolet lamps, or plasma and arc discharges[14]. The former has been used primarily for accelerating aging studies, where UV light is shown to interact strongly with the lignin polymeric components, resulting in the erosion of high lignin content zones of the wood cell wall [15]. Plasma and arc discharges have been used to generate reactive species at the surface leading to gas phase modification or to assist in the adhesion of laminate coatings [16-18].

The power density of such treatments reaches approximately to $0.1 \text{ J}\cdot\text{cm}^{-2}$, providing enough energy to degrade the surface [15]. If energy is delivered at a higher power density, such as 100's to 1000's of $\text{J}\cdot\text{cm}^{-2}$, extremely rapid heating of the surface occurs [4, 19]. This power can be delivered by assistance of laser radiation, typically in the UV or IR wavelength. Previous work has shown the ability to machine wood and wood-composite materials with minimal residual char at the surface [20, 21]. Energy is concentrated enough to cause ablation of the wood surface transforming it from a solid to gas and aerosol degradation products [22]. This processing method has been applied as a technique for the incision of wood materials to enhance the treatment of wood with low permeability values [23]. Other work has shown that wood surfaces can become modified in such a way that the wood surface after treatment can actually cause the appearance of an amorphous-like layer to form on the surface disrupting the cell structure [24].

Building from this previous work, we compare changes to the wood surfaces as a result of a number of different levels of energy treatment. It is expected that these results will have potential impact on wood utilization in the areas of coatings, biomass conversion technologies, and alternative methods for barrel toasting.

Materials and Methods

Mature, rough-cut and kiln-dried White Oak (*Quercus alba*) was obtained at a lumberyard in Southwest Virginia, USA. The flatsawn white oak was planed to a 0.32 cm thickness, cut into a disc 8mm in diameter, 2mm thick and conditioned to 12% moisture content in an environmental chamber. The size was optimized to fit in the PA-FTIR chamber. Cellular orientation was such that the planes

parallel to the surface of the disc correspond to the tangent plane of orientation relative to the growth rings, parallel with the stem axis. After planing the wood, no other surface treatment was performed prior to exposure to the varying energy sources.

Wood was modified using a 60 Watt Universal Laser Systems V460 with a maximum vector speed of 0.48 m/s, and a high power density focusing optics attachment, yielding spot sizes between 50 to 100 μm (size changes because alteration of the focus plan based on the microscale roughness of wood). The samples were treated at 5 (low exposure), 10 (medium exposure), and 30 Watts (high exposure) at maximum vector speed, for one pass, utilizing vectors to raster the surface at a separation distance of 25 μm . Other treatments of wood included, a) heat treatment in an oven at 200 °C for a dwell time of 4 h; b) with a propane torch at a separation distance of 20 cm for 5 min and 10 minutes; and c) modified in a vacuum oven (10 mTorr) at 200 °C for a dwell time of 4 hours.

For photoacoustic FTIR, X-Ray Photoelectron spectroscopy (XPS) and Scanning Electron Microscopy (SEM) analysis, wood samples were dried in a vacuum oven at 60 °C and 10 mTorr for 48 h, as typical in previous literature[15]. XPS was carried out on a PHI Quantera SXM photoelectron spectrometer. The spectrometer was equipped with a scanning monochromatic X-Ray source, 26eV pass energy with a spot size of 200 μm and a take-off angle of 45°. CasaXPS software was utilized to deconvolute the peaks. A Shirley correction was utilized to create the proper background while the peaks were fitted utilizing the peaks found for red oak in previous research constrained to ± 0.5 eV while utilizing 2 ± 1 for FWHM values [25].

Photo acoustic Fourier Transform infrared spectroscopy (PAS-FTIR) was carried out on an 8700 Nicolet Thermo Electron Spectrometer with a MTEC 300 photoacoustic attachment. The test settings were 64 sample scans, a mirror velocity of 0.1581 cm^*s^{-1} , aperture of 150.00, a KBr beam splitter, resolution of 8 cm^{-1} and a sample gain of 2. The PA cell was purged with high purity helium, data was normalized with carbon black background spectra. Note for PA-FTIR experiments, samples needed to be extremely dry to ensure good signal to noise ratio because of water vapor contamination. Finally, differential scanning calorimetry (DSC) of the isolated surface sample was carried out on a TA Instruments Q100 DSC, with a heat cool heat ramp from -10 to 180°C at a ramp rate of 10°C*min⁻¹ in a hermetically sealed pan. Modifications in surface morphology were observed utilizing a Nikon SMZ1500 light microscope and a NeoScope JCM-5000 SEM. For the SEM, samples were coating with approximate 10nm thick layer of gold-

palladium prior to analysis.

Results and Discussion

Microscopy Analysis of Treated Wood

In Figure 3.1, light microscopy images indicate a distinct difference between laser modified wood and wood modified within the oven, both with and without the presence of atmosphere, as well as flame degradation. The horizontal lines seen on most samples are check marks from wood planing. With increasing laser power, in Figure 3.1,A-C, the samples appear to have a glossy, reflective surface. Also, across these samples there is increased surface roughness due to the density variations in the wood, as cell wall thickness directly impacts the laser ablation process [26, 27]. The oven (Fig. 1D&E) and flame (Fig.1,F) samples show that wood modified via those methods does not become glossy, but darkens similar to what is seen in charring process. These samples all appear similar with tan, dark brown, and black colors.

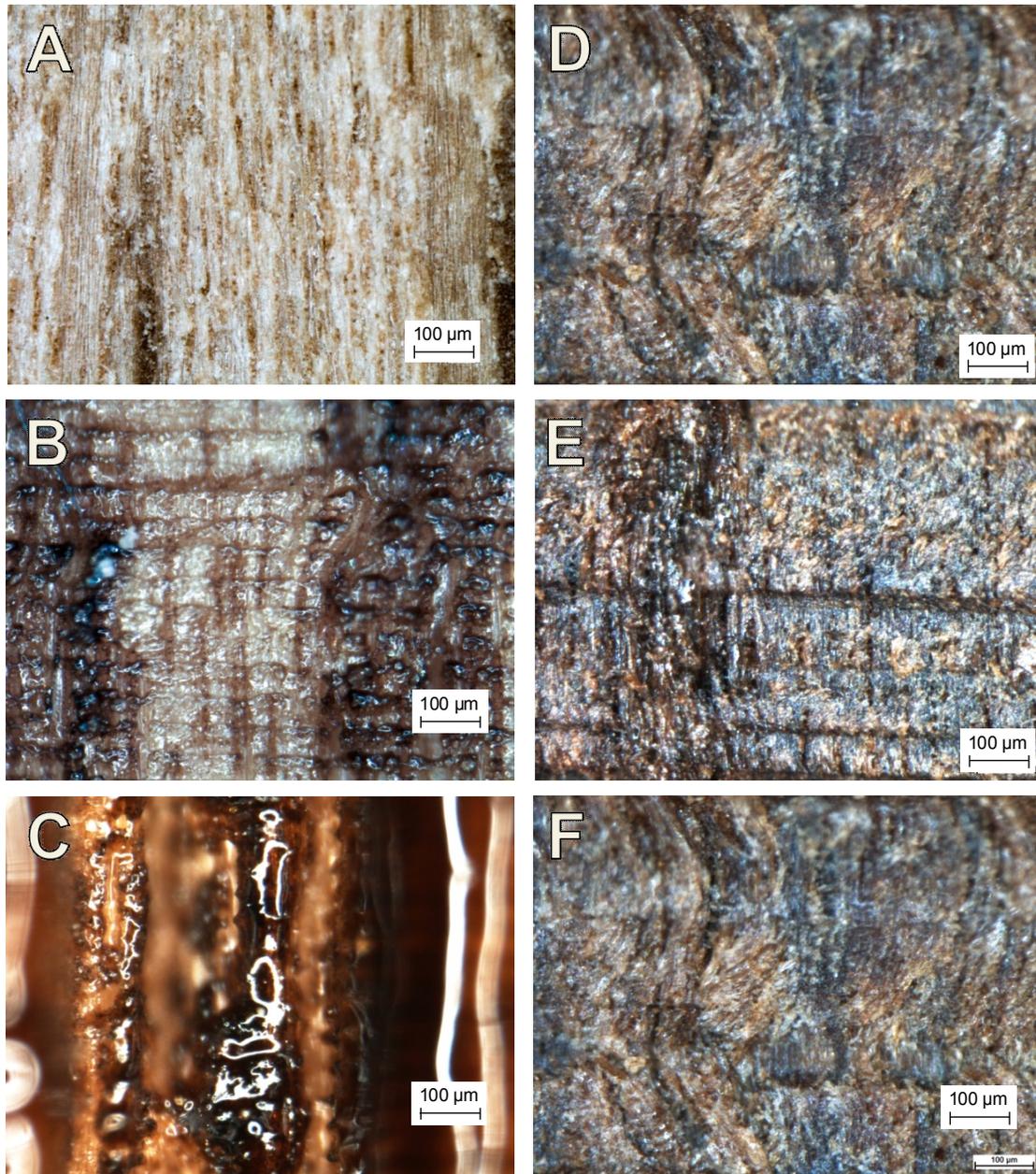


Figure 3.1: Light Microscopy of modified White Oak (tangential plane). (A) Control, (B-C) Laser degraded samples. (B) “Low Exposure” [5W]. (C) “Heavy Exposure” [60W]. (D) Oven degraded [200°C, 2h] (E) Vacuum oven degraded [200°C, 2h] (F) Flame degraded [propane, 17.5kW/cm², 5m]. Horizontal lines in samples arise from planing knife.

SEM images of the wood surfaces modified with the different treatments reveal distinct changes to the anatomic cellular structure (Fig. 2). The control sample surface with no additional modification to the planar cutting contains macerated cells that have some mechanical degradation such as fracture is evident (Fig. 2a). Laser modified wood for both medium (Fig. 2B) and high exposure (Fig. 2C) levels

have distinct changes to the surface topology. Cells are no longer clearly evident, but the cell structures have appeared to undergo flow. This change is reflected in the light microscopy images of the glossy characteristic surface. SEM analysis of the laser modified surface indicates similarities between the laser modified samples with different exposure levels. Although, the high exposure laser treated sample (C) has five times more energy imparted to the surface than the medium exposure sample (B), the surface topology of the material is very similar with the only difference being the appearance of greater surface roughness for the high exposure sample. This result indicates that the surface structure at both laser modification levels is very similar; with the only difference being more material ablation occurring has occurred at higher power inputs. Evident in the other modification methods (flame and oven) these surfaces have increased roughness but do not have any responses that appear similar to the laser treated wood. Hence, degradation because of flame treatment is occurring that appears only to show the results of a charring process. Typically, charring results in severe checking as a result of chain scission of the polysaccharide polymers and then severe shrinkage.

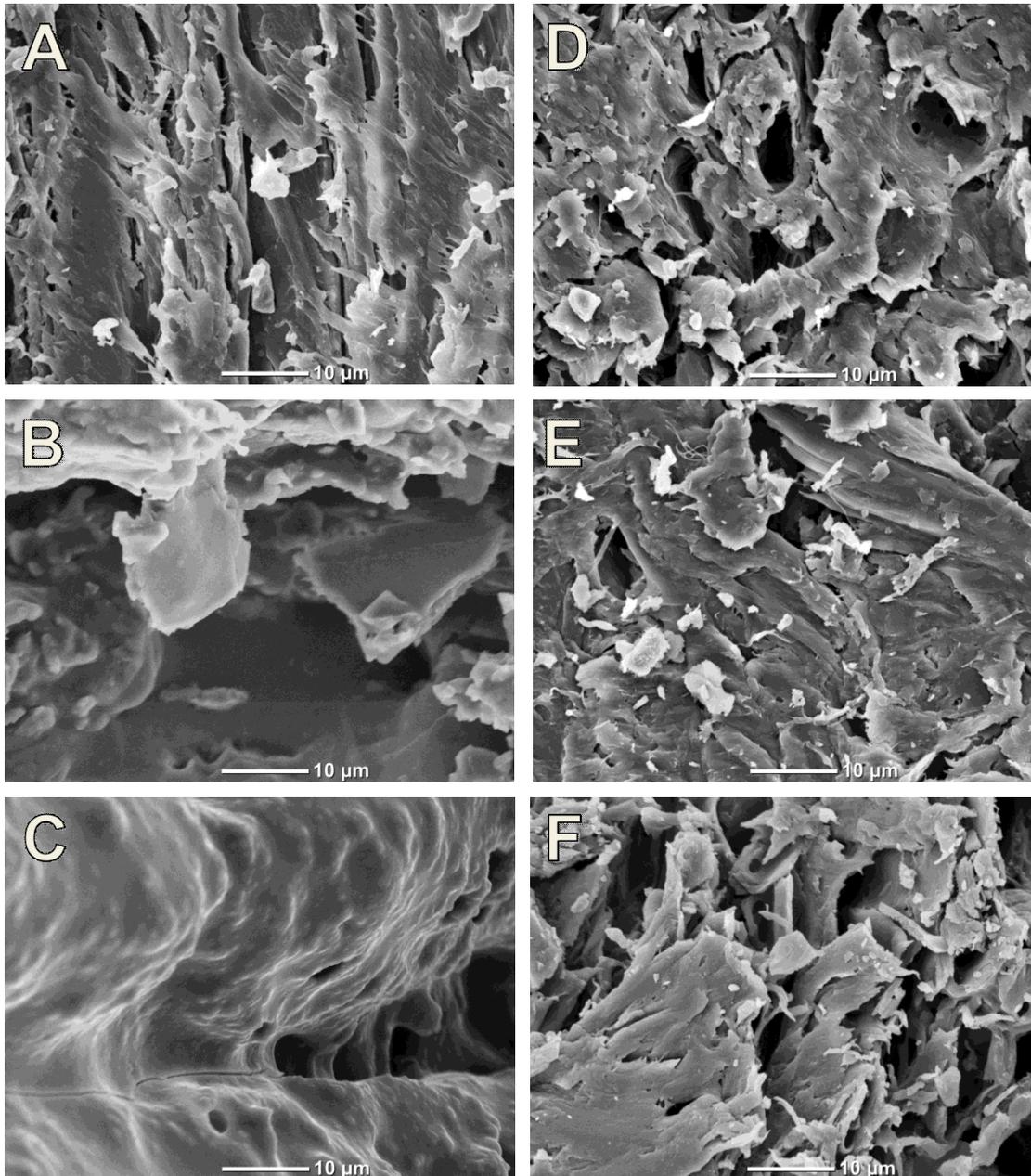


Figure 3.2: Scanning Electron Microscopy of modified White Oak (tangential plane). (A) Control, (B-C) Laser degraded samples. (B) “Low Exposure” [5W]. (C) “Heavy Exposure” [60W]. (D) Oven degraded [200°C, 2h] (E) Vacuum oven degraded [200°C, 2h] (F) Flame degraded [propane, 17.5kW/cm², 5m]. Horizontal lines in samples arise from planing knife.

The visual inspection of the treated surfaces clearly shows that concentrated irradiation creates a unique surface—woody material appears to have undergone significant flow without the same type of degradation found with the other energy treatments. In addition, the laser treated

surfaces appear to have similarities between the medium and high exposure levels. This observation suggests that there is an optimum amount of laser irradiation to modify the surface, and with subsequent increase in exposure energy, the morphology changes little most likely just causing more material to be directly transformed into gaseous by-products.

Photo-acoustic Fourier Transform Infrared Spectroscopy analysis of treated wood

PA-FTIR spectra indicate differences in surface chemistry, probing to an approximate 20 μm depth, amongst unmodified wood samples verse modification via oven, flame, and laser treatment (Fig. 3). Based on assignments by Faix [28] and Capretti and Focher [29], noteworthy differences of the treated samples relative to the control are found in shifts in the carbonyl ester stretching, 1741cm^{-1} shifted to 1730cm^{-1} ; induction of carbonyl stretching when attached to aromatic compounds, as 1600cm^{-1} shifted to 1610cm^{-1} ; change in the aromatic vibration by the loss of methoxy substituents, 1504cm^{-1} shifted to 1511cm^{-1} ; and increase in condensed structures shown by increased relative peak intensity at 1330cm^{-1} combined with a shift at 1225cm^{-1} (especially for flame treatment). Minimal changes occur in the peaks associated with polysaccharide glycosidic and hydroxyl groups (1160 to 950cm^{-1}). When wood is heated to 200°C , the surface is significantly discolored. Changes associated with the hemicellulose substituents such as loss of acetyl moieties from the hemicellulose and changes to the aromatic structures of the lignin by the induction of carbonyl compounds would lead to the noted discoloration. The presence of atmospheric air during high temperature exposure affects the chemistry within the carbonyl stretching region, while other areas of the spectra for both the oven and vacuum oven overlay each other (Fig. 3). Flame treatment does show greater shifts in wavenumbers from the control specimen, relative to the oven specimens; this change is seen at the carbonyl peak at 1725cm^{-1} , in the aromatic stretching regions of 1600 and 1511cm^{-1} , and evidence of condensed lignin structures at 1330 combined with shifts at 1225cm^{-1} . Similar peaks were identified as being sensitive to thermal treatment in white oak heated to higher temperatures 350°C [30].

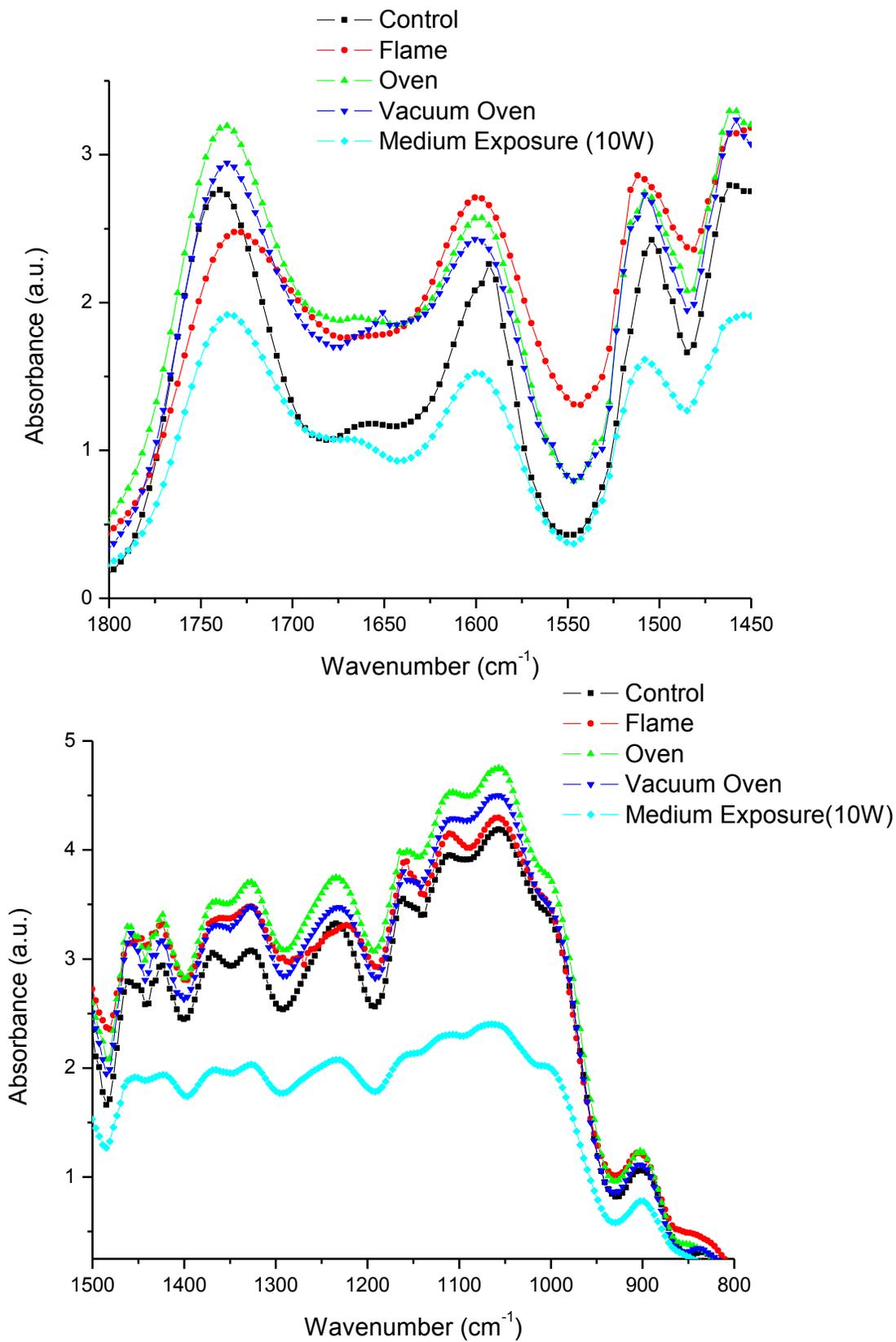
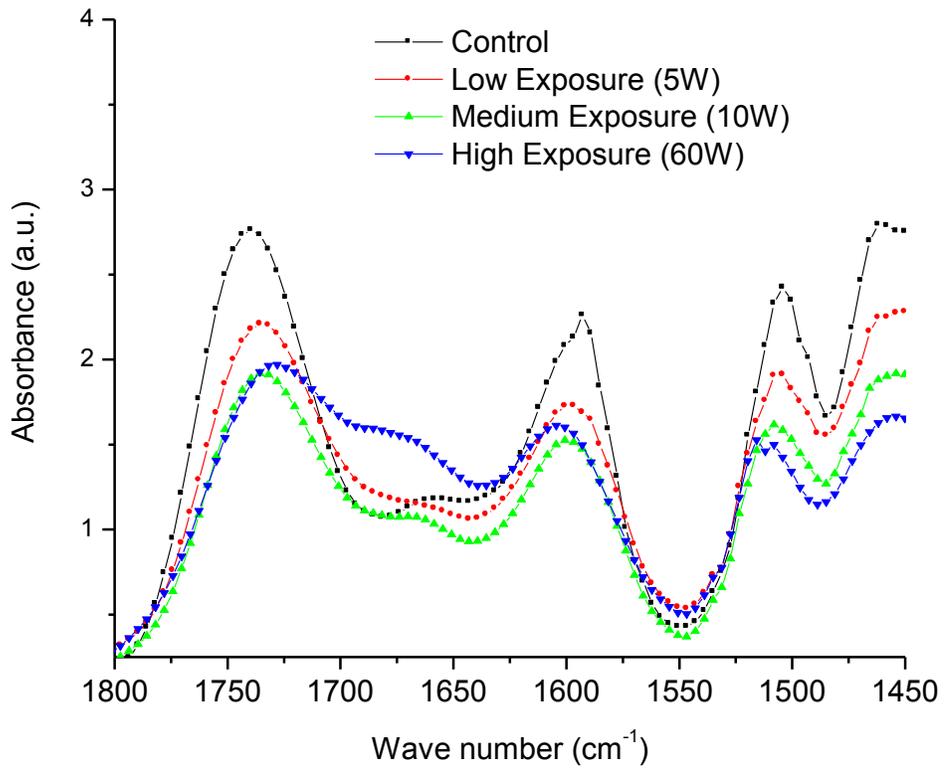


Figure 3.3: PA-FTIR of white oak modified by flame, oven 200°C, vacuum oven 200°C, and laser modification, A) 1450-1800 cm^{-1} and B) 800-1500 cm^{-1} .

Significant differences arise in the laser treatment of white oak relative to the control (Fig. 4A&B). Overall, absorption intensity is reduced for the samples and this may be due to the topological changes indicated in the microscopy section. IR light most likely is reflected and scattered differently because of the surface treatment reducing the corresponding signal. However, if the data is compared based on the degree of exposure, significant changes arise. The shifts described above are minimal for low-exposure levels, but are greater with the high-exposure levels. The peak intensity of the polysaccharide hydroxyl bending region and glycosidic stretching (1160 to 950cm^{-1}) changes dramatically relative to the aromatic and carbonyl stretching region. This relative change in intensity indicates a reduced polysaccharide presence at the irradiated surface. At 900cm^{-1} , a peak correlated to cellulose's C1 hydrogen, decreases then disappears with increasing laser modification (Fig. 4B). C1 is involved in the glycosidic bonds of cellulose, indicating that modification to cellulose occurred with laser exposure. The degradation may create levoglucosan, previously found as a common byproduct of cellulose pyrolysis [31]. Previous research indicates that cellulose requires more energy than hemicellulose to degrade, and this is reflected by the fact that lignin and hemicellulose peak assignments change more readily at lower laser fluences.



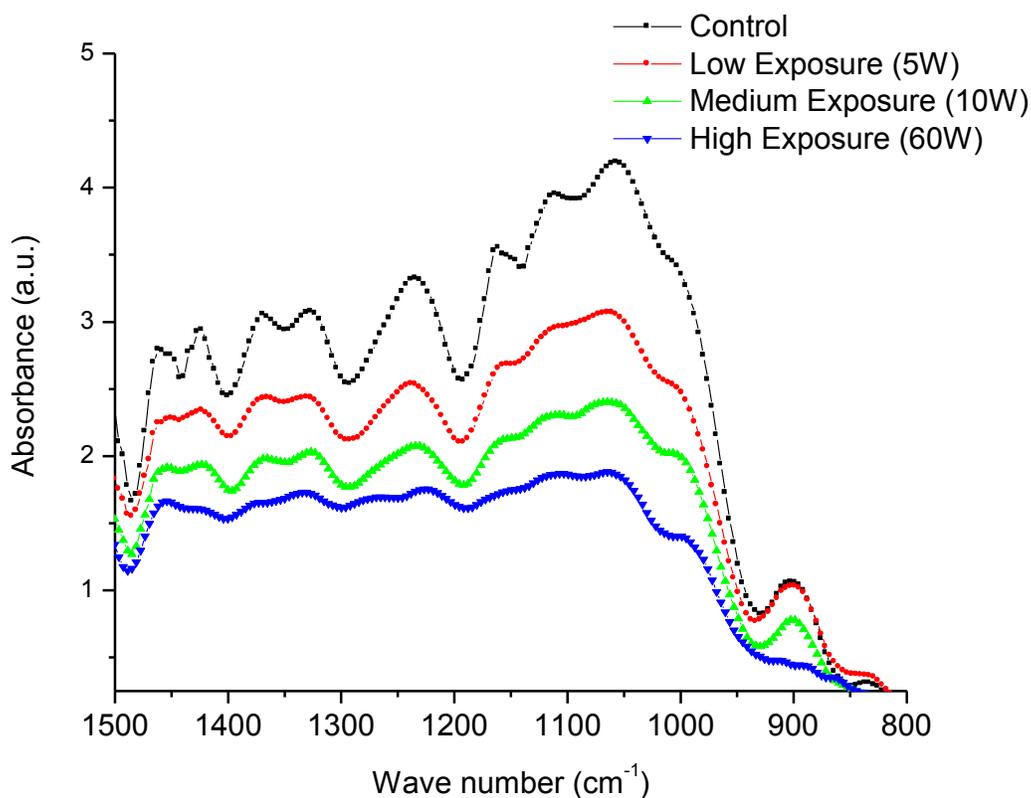


Figure 3.4. PA-FTIR of white oak modified by various levels of laser irradiance, A) 1450-1800 cm^{-1} and B) 800-1500 cm^{-1} .

Chemical modification may be catalyzed by degradation products liberated by the laser treatment, as there is evidence at 1741cm^{-1} of decreasing concentrations of acetate groups, forming acetic acid, which further degrade the polysaccharide components. Additionally, photons have been shown to interact strongly with lignin aromatic units, generating radicals in this polymer component. As a result, quinone methides are formed [32] that are highly reactive and would quickly react available hydroxyl rich compounds, including acidic side groups that were liberated. Reaction of the lignin components with the organic acid would provide one of the paths towards the development of additional carbonyl compounds on the aromatic substituents (especially noted in increased peak intensity between 1700 and 1675 cm^{-1}). In addition to acetic acid, formaldehyde and other organic acids liberated from heated wood, simple compounds of hydrogen, water, and carbon dioxide products are often evolved during the pyrolysis of woody material.

X-Ray Photoelectron Spectroscopy

Because there was a sharp reduction of polysaccharide signals indicated in the FTIR section, laser treated samples were further analyzed using XPS (Fig. 5). Elemental analysis of carbon (C1s) and oxygen (1s) at the surface was quantified and the carbon peak was deconvoluted into four carbon peaks: C1 being predominately associated with lignin (C-C) linkages, C2 related to C-O linkages, C3 associated with both C=O carbonyl and O-C-O linkages, and C4 being associated with linkages of O-C=O bonds [25, 33](Table 3.1). The total carbon to oxygen ratio does not change significantly from the control value. In light of the reduced polysaccharide signal from the FTIR spectra this data is surprising. However, significant changes in chemistry have occurred at the surface. The ratio of the C1 to the C2 increased dramatically after laser treatment. For the high exposure sample, the C1/C2 ratio actually decreases along with an increase in C3 relative to the low exposure sample. This change would be predicted by the FTIR spectra with increased carbonyl adsorption in the high exposure sample. This change in ratios do not arise from the migration of the polymeric components, as hydrolytic lignin was reported to have an experimental O/C ratio of 0.39 and C1/C2 ratio of 1.11, while cellulose has an experimental O/C ratio of 0.74 and C1/C2 ratio of 0.22 [1]. Hence the material at the surface does not resemble the polysaccharide components. Instead, there is a large amount of material on the surface with C-C bonds. Extractives such as tannins are reported to have a high C1/C2 ratio [34]. At the surface, wood modification by the laser may either allow transport of the extractive materials to the surface as the material is rapidly heated (as seen by the wood cells that have undergone some type of flow Fig. 2) or the laser energy is causing a condensation amongst the aromatic lignin units, combined with loss of methoxy, phenolic, and aryl ethers. To place the laser treatment in perspective to other samples, a previous report on a hardwoods heated to 200°C after 2 hours indicated a decrease in O/C ratio to 0.23 and increase in

C1/C2 to 3.26. It appears that the surface of the wood is unique after laser treatment.

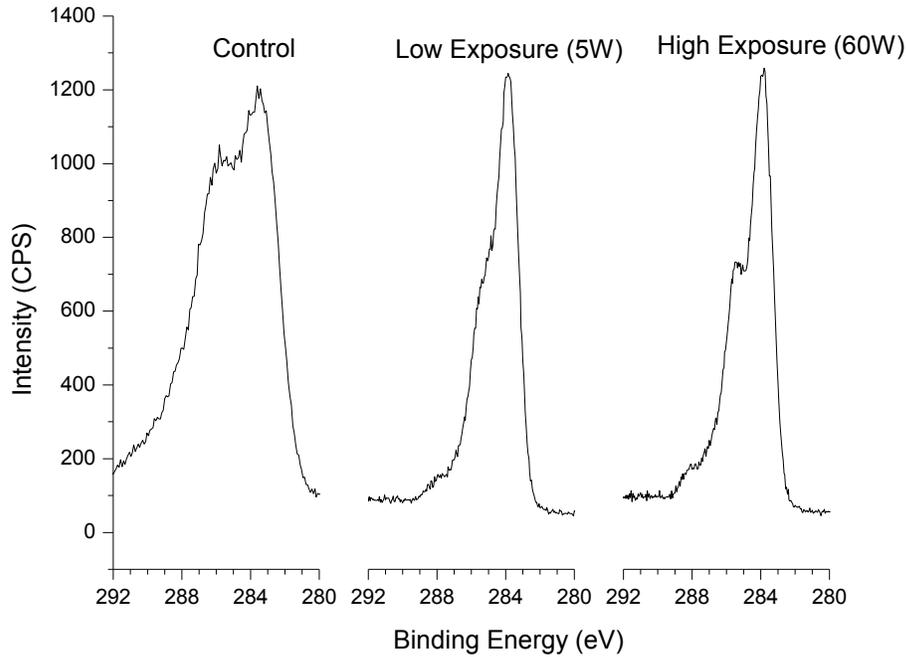


Figure 3.5. XPS of oak modified by increasing fluences of laser energy.

Table 3.1. Deconvoluted XPS peaks showing a shift from c1 to c2 due to laser modification.

Sample	C1	C2	C3	C4	C1/C2 Ratio
Control	58.06	32.62	7.88	1.44	1.8
Low Exposure (5W)	82.17	11.3	6.54	0	7.3
High Exposure (60W)	76.71	14.67	8.62	0	5.2

Table 3.2. XPS data showing the ratio of carbon to oxygen in the control, low and high laser exposure.

Sample	C1s	O1s	O/C Ratio
Control	75.78	24.18	0.32
Low Exposure (5W)	77.25	21.1	0.27
High Exposure (60W)	76.06	23.94	0.31

Differential Scanning Calorimetry

Mechanically isolated material from the high exposure laser sample surface and unmodified

samples were analyzed using DSC. For the second heating ramp, there was a consistent, albeit somewhat broad, change in baseline centered at 130°C arising from a change in the heat capacity during the glass transition (T_g). The control material did not show any change in the baseline at these temperatures, although there was always a consistent fluctuation at 50°C. While the surface material is heavily modified, it does coincide with the reported T_g value of milled wood lignin from red oak and other hardwoods, as determined with DSC [35]. Hence, the surface material of laser-modified wood can undergo some type of flow post-laser treatment if exposed to temperatures greater than 130°C.

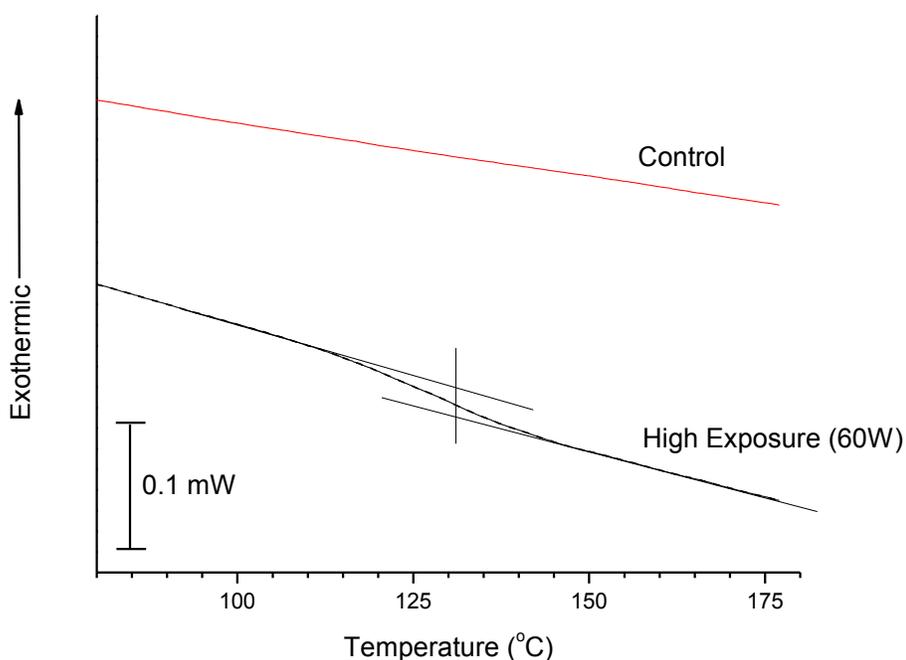


Figure 3.6. DSC comparing the unmodified control sample to the modified surface found after laser modification, showing the clear addition of a glass transition temperature at 130°C.

Conclusions

Wood surfaces were analyzed after they were exposed to varying quantities of energy from elevated temperatures in an oven, flame treatment, and laser treatment. In all cases there was discoloration of the surface after exposure to these different energy levels. Light microscopy of the wood surfaces revealed the beginning stages of charring of the wood from the oven and flame treatment. Moreover, there was a significant color change for the laser-modified wood that was accompanied by a change in the glossiness of the surface. Further microscopy studies of the wood

surface revealed a distinct surface topology; it appeared that wood cells had undergone softening and flow. Chemical analysis of the surfaces revealed changes in the carbonyl and aromatic regions indicating modification of the hemicellulose and lignin components with the different energy treatments. Moreover, many of the chemical changes were maximized for the medium and high exposure levels of the laser with the latter providing a unique C1/C2 ratio for solid wood surfaces. Isolated surface material of the laser treated sample had a glass transition temperature at 130°C after heating to elevated temperatures post-laser treatment. Taken together, laser modification of wood provides a unique surface in both morphology and chemistry that may provide a path towards designing wood surfaces with particular functionality.

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Chapter 4: Laser Activated Bonding of Wood and Initial Optimization

ABSTRACT

Laser activated bonding of wood is a new method of bonding two wood substrates. Irradiating the surface of wood with laser light, within an optimal set of parameters, causes the wood surface to flow. Subsequently, two wood samples that have modified surfaces are hot-pressed together creating a wood composite. Laser light modified wood composites were tested in tensile shear for mechanical strength, using a design of an experiment (DOE) approach to optimize both hot-pressing and laser irradiation parameters. It was found via screening and DOE experiments that laser power and focus as well as hot press pressure were significant factors to optimize tensile strength values. Samples with the optimized conditions had performance values that were comparable to control samples created using phenol formaldehyde resins. The data suggests that laser-activated bonding of wood can yield a wood composite requiring no liquid adhesives as the wood itself serves the dual role of adhesive and substrate. This novel bonding technique has potential to be a disruptive technology in the mature market of wood composites.

INTRODUCTION

The most common adhesives utilized in wood composites are petroleum-based and emit gases during production and product life that are classified as carcinogenic and can be nauseating upon significant exposure [1]. Since 2000, governmental restrictions on wood composite adhesives has led researchers to look for wood adhesives that are sustainable, emit no harmful gases, economical, and yield performance on par with current formaldehyde wood composites [2]. Although there is research in a wide variety of renewable adhesives including tannins, carbohydrates, soy protein, and wood welding, there is only a single commercial alternative to phenol formaldehyde (PF) adhesives which is soy-based [2]. While significant progress has occurred in addressing critical issues of renewable and sustainable adhesives, the soy-based adhesive still requires some petroleum-based additives [2].

With thermoplastic and metallic substrates, adhesion for the same materials can easily occur via heat as the liquid like surfaces achieve intimate contact and form a ridged joint upon cooling. A developing area of work is in the area of laser welding that is applied industrially. Laser technology is used in many industrial materials applications for precision machining in addition to joint welding. Previous research on the laser modification of lignocellulosic materials has focused on automated machining and cutting, with other studies demonstrating utility of lasers for cleaning historical documents and wood surfaces, pyrolysis, accelerated weathering, and microtoming [3-7]. As the polymeric components of wood are sensitive to high energy levels it is logical that these studies have focused in the above applications. However, the earliest studies on the interaction of laser light and wood indicated that laser irradiation causes the wood surface to undergo flow [8-10]. The laser modified surfaces appear to have a glossy reflective surface as seen in light microscopy images. At higher magnification using an SEM, cells were no longer clearly evident and appear to have undergone flow (Holzforschung, under review). Interestingly, the studies suggest that the wood surface reach a liquid-like, rubbery state during the process of laser irradiation, dependent upon the laser energy.

The novel observation that wood can be auto-adhered using frictional heat was demonstrate in a number of studies that explored how adhesive joints could be formed without added adhesive. Pizzi and co-workers applied pressure and oscillatory vibration creating heat from friction to bond wood substrates [11-14]. These studies identified lignin and hemicelluloses underwent softening and flow while cellulose fibers entangle, creating an entanglement network in a matrix of lignin and hemicellulose.

Because there is evidence that the wood surface reaches a liquid, rubber-like state during laser irradiation and that this surface can undergo thermal softening when heated, adhesion between laser-modified substrates is investigated in this current study. Significant variables identified in previous studies understanding laser modification of wood included laser wavelength [6, 9], laser fluence [ref [4]], laser movement to wood grain orientation [3, 15, 16], moisture content [16, 17] species [18] and specific gravity [3, 4] In this research we investigated laser technology for bonding wood, screening a host of variables to optimize the bond strength. Multiple initial screening tests helped identify significant factors in this new process. Within this study variables

related to laser parameters (laser power and focus) and hotpress variables (time, temperature, and pressure) were investigated via a design of experiment (DOE) to maximize bond strength.

MATERIALS AND METHODS

Materials

3.2 mm thick “Grade A” Yellow-poplar (*Liriodendron tulipifera*) and southern yellow pine (*Pinus* spp.) rotary-peeled veneer were obtained from a southeastern US laminated veneer mill. The as-received 60x60cm samples were conditioned to 12% moisture content in a walk-in environmental humidity controlled room.

Methods

Wood veneer samples were cut into 5cm squares and modified utilizing a ULS-V460 60W carbon dioxide laser with high power density focusing optics, resulting in a circular spot size with a diameter of approximately 50 μm . For the design of experiment testing, laser wattages of 3 to 15W were utilized, with the laser moving at a constant 0.5 m/s, at 40,000 pulses per meter. Specific parameters utilized in the ULS print driver included a maximum image density of 6, tuning of zero, while utilizing vector mode. The trajectory of the laser was designed in AutoCAD, using the smallest resolution usable by the laser between lines, 0.002 in (50.4 μm) to irradiate the surface.

Laser modified samples were placed in contact matching their irradiated surfaces and subsequently hot pressed together utilizing a MP2000 mini hot press. Press conditions were the following: time ranged between 3-12 min; pressure between 0.7-2.4 MPa; and temperatures between 140-190°C, controlled by a TC2 Temperature controller (both instruments made by Micromet Instruments, Inc.). The time between laser modification and hot pressing ranged from 5 m to 3 days; with no detectable difference in bond strength. A diagram of the design and laser modification process is shown in Figure 4.1.

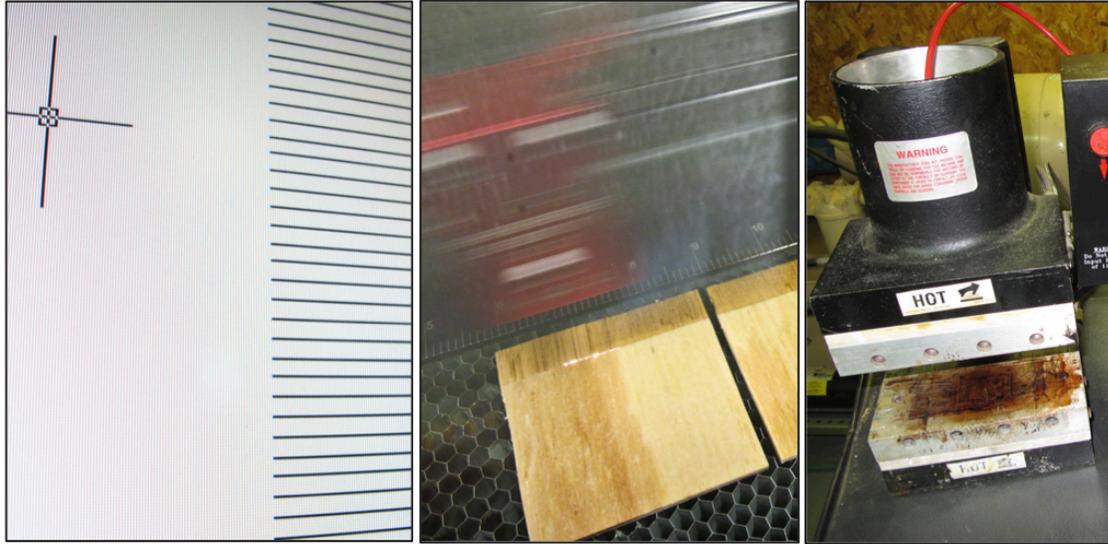


Figure 4.1: Illustration of method (a) screen shot of AutoCAD design (b) laser transferring design wood (c) mini hot press.

Control samples were made with a commercial phenol formaldehyde adhesive. A PF resol resin for veneer applications from Georgia Pacific containing 59.93 corn cob residue (CCR) with a total mixture weight of 800.1 grams was applied at a spread rate of 0.442 kg/m^2 . The samples were immediately hot pressed at 1.03MPa (150PSI), for 10m at 200°C .

Mechanical testing

Samples were tested via a modified version of the EN 204 shear tensile test, differing only in sample size. A band saw was used to notch the specimen to the bondline, being careful to ensure consistency in cutting depth (overcuts were removed, while undercuts were recut). Samples were hand tightened in a MTS test frame and strained in tensile mode at a rate of 0.1 in/min monitored with a 30,000 Newton load cell. Samples were measured with microcalipers to determine area between notches. A modified version of the ASTM D 3043 3 point bending for flexural strength was used for comparisons to PF industrial adhesives, modified in accordance to Figure 4.2 below, differing in sample size. Three-ply samples were created using the optimized laser and press conditions. Displacement of the specimen was measured using a linear voltage differential transformer (LVDT) and load recorded with a 30,000 Newton load cell. Tensile

shear strength test specimen's grain direction was parallel to the long side of the test specimen. Flexural strength test specimen's grain directions of outer plies were parallel to the long side of the specimen, while the inner ply was perpendicular. For each treatment, X samples were tested from at least two different boards. 10 samples were tested for each combination, each set cut from one 30.5 cm square 3 ply composite.

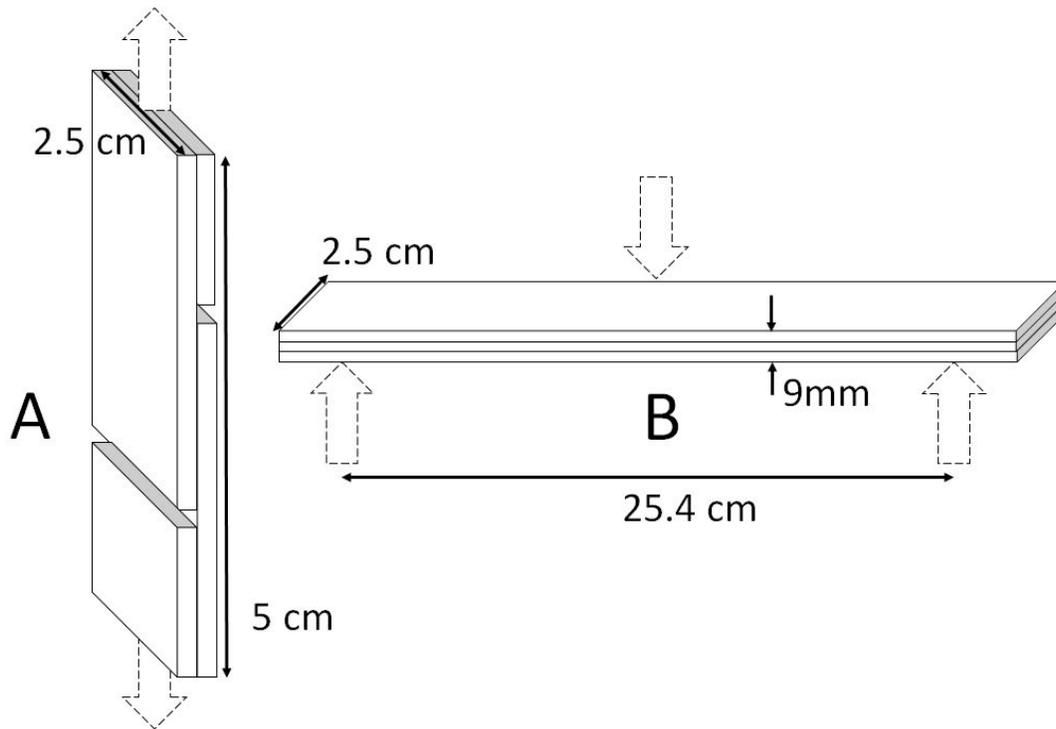


Figure 4.2: Diagrams of mechanical test methods. (a) Tensile Shear Strength (b) Flexural Strength

Design of Experiment Method

Initial screening and knowledge about the process to optimize is vital for choosing appropriate variables, known as factors, and the associated levels for each factor. The factors and associated levels hypothesized as significant were then entered into JMP8 DOE software, specifically a custom design, using the response surface method, resulting in a matrix of tests to run. A

fractional factorial design was chosen over a full factorial design in order to conduct fewer experiments. After completing the experiment, which included 4 test runs, the resulting mechanical test data was compiled for the DOE analysis. When analyzing the DOE, the most significant main level factors and interactions were included while less statistically significant variables were systematically excluded. The DOE was analyzed by running a model that investigated the effect of more significant variables, with a model "personality" of standard least squares and an "emphasis" on effect screening (two options in JMP). By removing the less significant factors the estimations of optimal significant factors were improved.

RESULTS

Earlier results indicated that after irradiating wood with a laser, the modified wood surface underwent flow after being heated above 130°C [19]. After laser modification, even after a few days, the wood surfaces adhered to another modified wood surface under time, temperature, and pressures typically found in normal wood composite manufacturing. Images of the modified surface and bonded specimen are displayed in Figure 4.3.

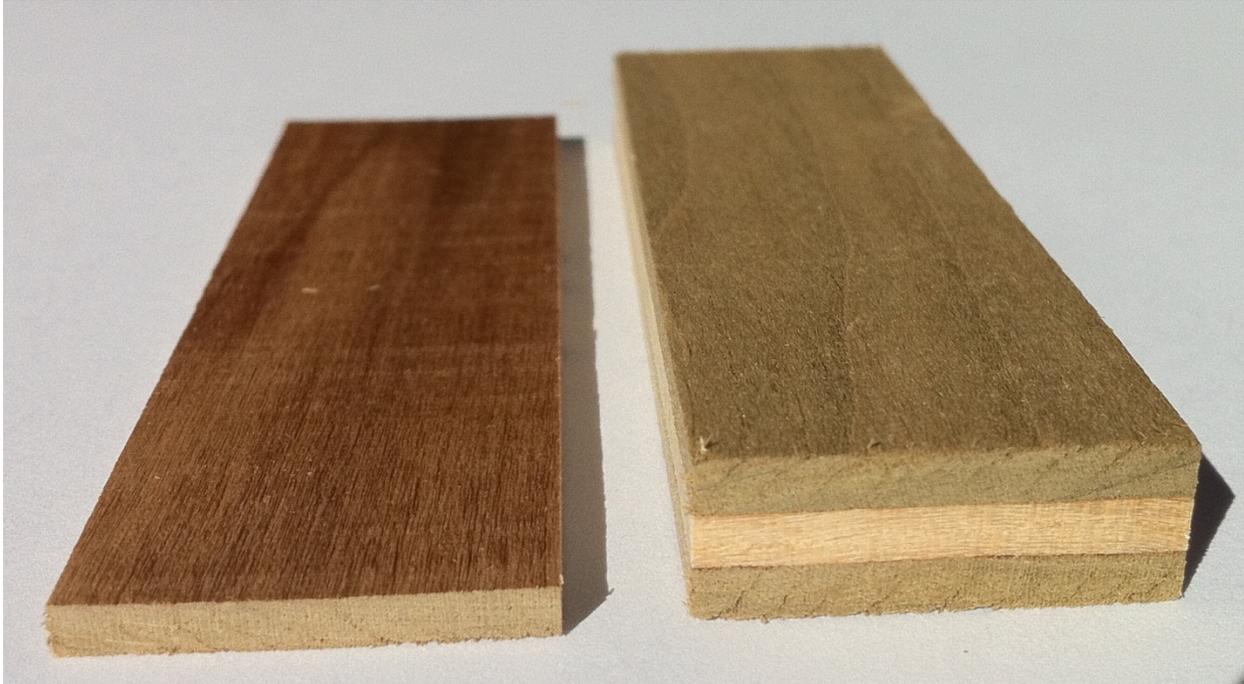


Figure 4.3: Photo of laser modified poplar (left) and 3-ply bonded poplar after hotpressing (right)

Figure 4.3 shows the laser-modified poplar veneer and laser-modified poplar that has been bonded into a 3 ply wood composite. In comparison to unmodified poplar (top surface of wood composite), the laser modified surface is darker, and upon light microscopy, appears to have flowed and melted (Holzforschung, under review). Various ladder studies were undertaken, some without mechanical testing, in order to understand the factors that affect laser activated bonding of wood, and levels of the factors that were significant. Because of the dearth of literature in this area, all tests are described below in the initial screening section, providing insight and justification for the parameters chosen for the DOE experiments.

Initial Screening

Laser Speed

Previous research indicated that in order to cause wood to flow with minimal degradation, the heating and cooling must occur in a very short period of time [4, 9]. The maximum laser speed of the equipment for vector scans was utilized in this experiment to minimize the amount of time the substrate was irradiated with the laser. Figure 4.4 shows the surface irradiated with the laser

as a function of laser speed (maximum and half maximum) and laser focus (in-focus to 2.5cm out of focus).

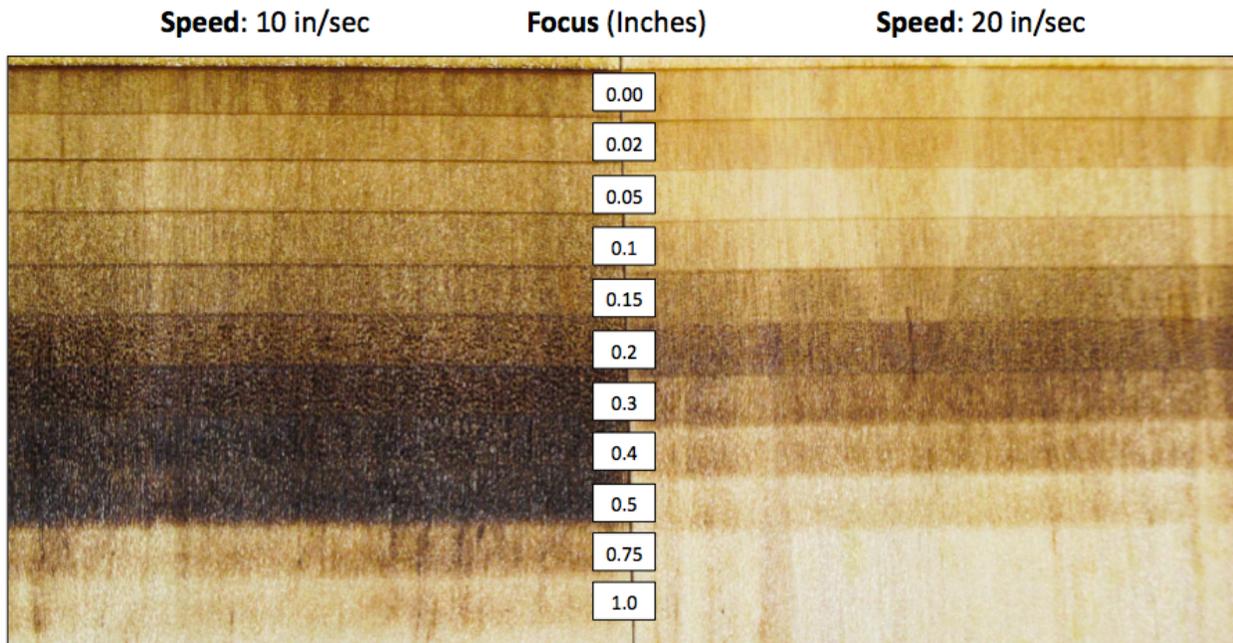


Figure 4.4: Comparison of two different laser speeds changing the focal plane. The top number indicates the sample is in focused and the focal plane moves out of focus from top to bottom

Figure 4.4 revealed that at a lower laser speed, a darker area is seen through a greater range of focal plane increments, indicating that the additional amount of laser exposure in any one area leads to extended time at high temperatures resulting in charring. The sample moving at higher speed did not show any degree of charring, while charring was seen when the focal plane was moved 0.3 and 0.5 inches out of focus. This image is in congruence with previous research indicating that shorter time periods minimize charring [19]. Moving beyond a critical focal plane, the beam is so divergent that the radiation is not concentrated enough to modify the wood to any appreciable degree.

Laser Movement to Grain Orientation

Due to the orthotropic nature of wood, heat transfer varies depending whether the laser passes parallel or perpendicular to the grain, with previous research indicating more charring occurring when moving the laser perpendicular to the grain [3]. Based on microscopic observation in a stereomicroscope, grain orientation had a minor effect on the degree of char and ablation relative to the large changes that were observed between focal planes, as seen in Figure 4.4. For simplicity, all tests in the DOE utilized laser passes in the direction of the grain, to minimize variation, and charring.

Laser Power

Keeping the laser speed and focus of the laser constant, the amount of power was evaluated. It was found that the surface modification, relative to its bulk appearance appeared to stay the same between 15 and 30W, with higher laser fluences resulting only in more material removed via the ablation process (Figure 4.5). As seen in the Figure there is increased material removed as the power was increased beyond 10 watts.

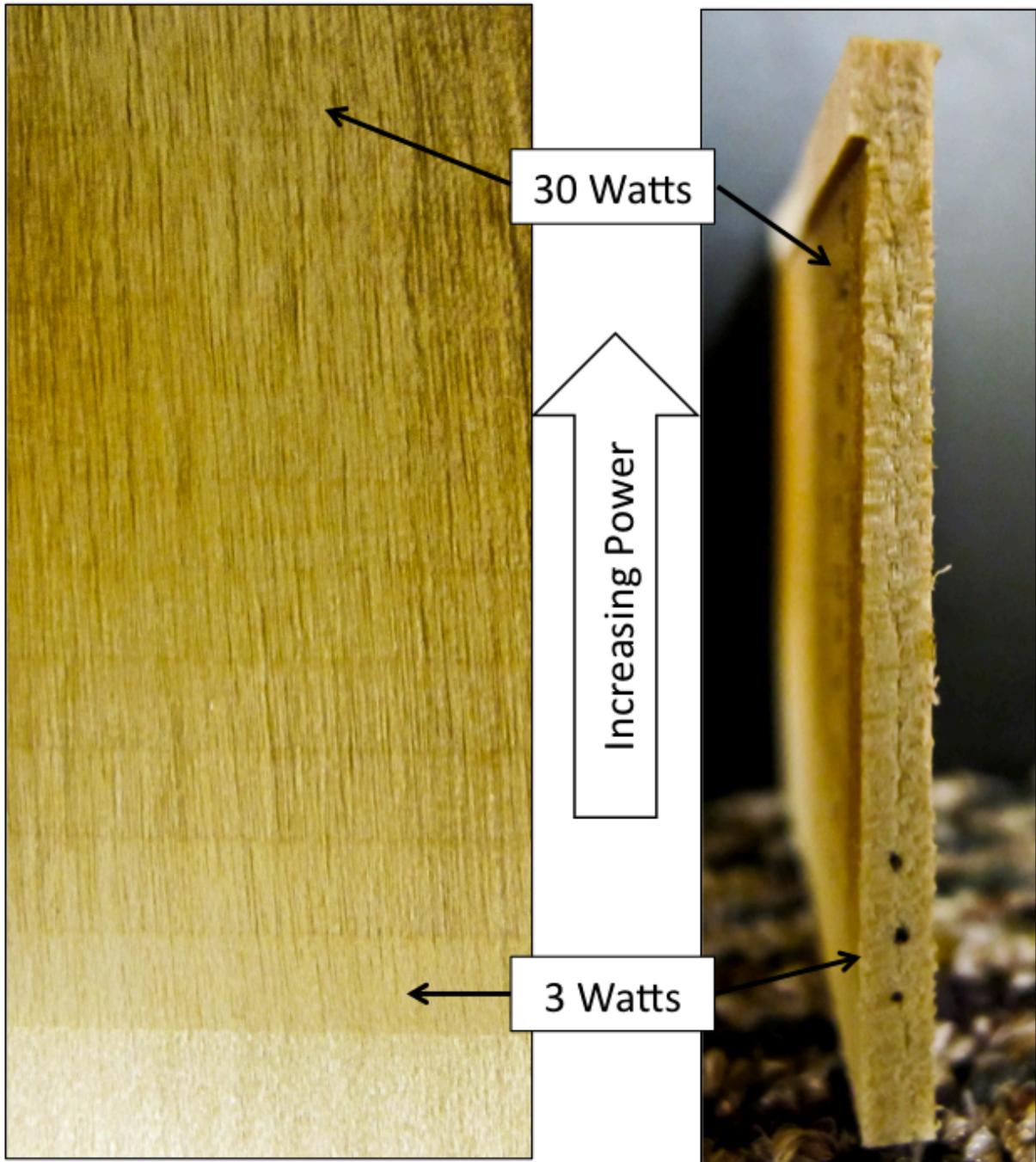


Figure 4.5: Images showing the effects of increasing laser power on poplar Left: Front View. Right: Side View

Figure 4.5 is a front and edge view of poplar wood, laser modified in $\sim 3\text{W}$ steps from 3 to 30 Watts. Increasing power within this range, the modified surface starts to appear more consistent

in color, while more material is removed via ablation. This upper 30W clearly indicates the fact that the optimum laser power must not erode significant volume of the wood in order to minimize material loss. Therefore 3 to 15 Watts was the chosen range for the factor of power in the DOE. Consistently after laser modification, the poplar samples would lose on average 3% and 20% in thickness for 3W and 15W, respectively.

Ridges Created by Laser

As the in-focus laser spot size was smaller than the resolution of the laser's motion system, ridges develop between laser lines during laser modification. In addition the Gaussian shape of the power of the laser beam creates a spot size with additional energy in the center. This is known to create “V” like grooves in micromachined polymethylmethacrylate [20]. As mechanical interlock of ridges may promote adhesion, the presence of the ridges may have a substantial effect on the bond strength, either negative or positive related to the orientation and the amount of surface contact. Two possibilities for positive effects of ridges include an increase in modified material and/or mechanical interlock. Since ridges increase the surface area, more modified material is at the surface versus a modified surface that is flat. The increased amount of modified wood may allow for more intimate contact while in the hot press. Mechanical interlock may increase the strength of the bond if enough ridges become interlocked. Figure 4.6 contains light microscopy images showing examples of ridges as a function of power and separation of raster lines (100 microns vs. 40 microns).

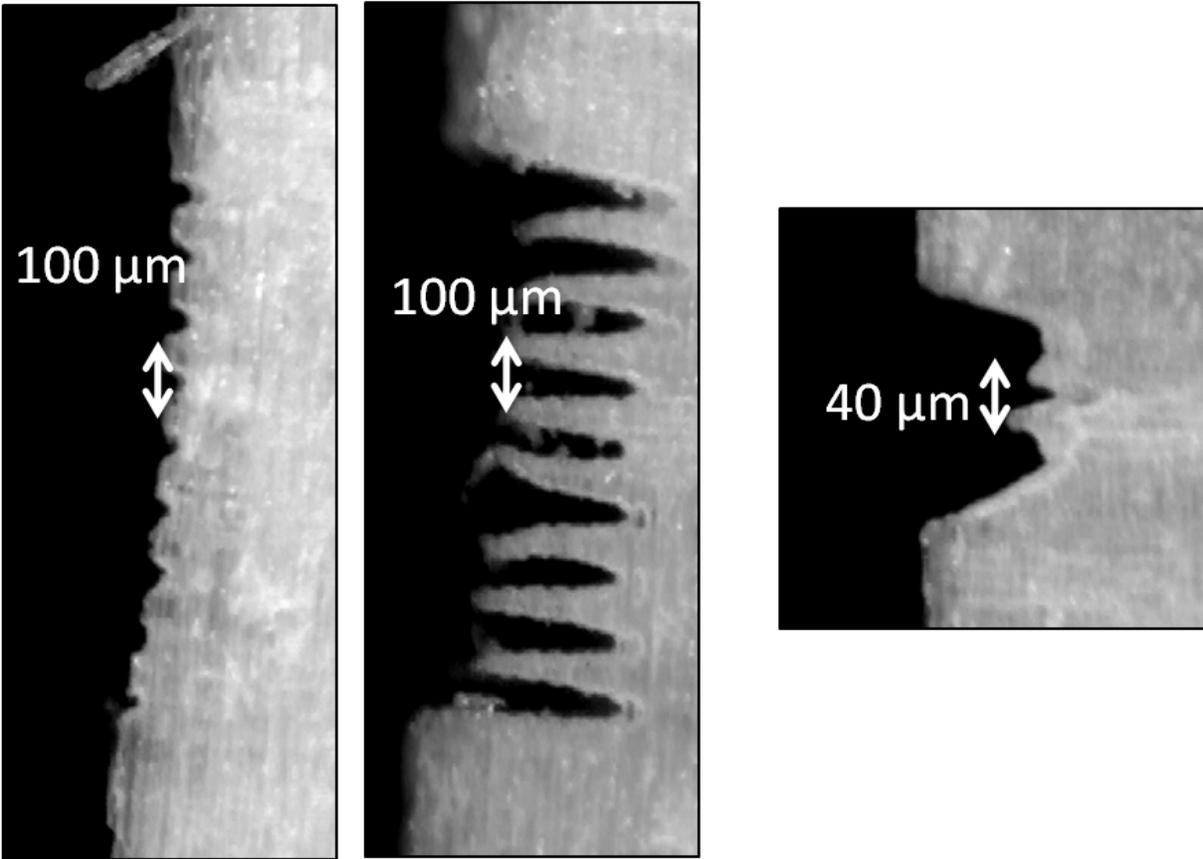


Figure 4.6: Light microscopy images of ridges during the laser ablation of wood. Left: 3 W laser power; center: 15 W laser power; right: evidence of resolution limitations of equipment as line spacing was reduced to 40 microns.

Above in Figure 4.6 are light microscopy images illustrating ridges with the top portion showing the increased depth with increasing laser power, the right showing the resolution limitations of the laser system. These images display the significance of the ridges, appearing as micro finger-joints. Screening tests were done testing variables such as ridges/no ridges, ridges parallel, ridges perpendicular, and effect of grain direction.

Moisture content of wood

Laser ablation tests were performed on wood samples soaked in water for 24 hr. The surfaces of the wood were fully saturated after the water treatment relative to the conditioned samples. Both

the conditioned samples and the fully saturated samples could be adhered together after laser modification. Qualitatively, it was observed that more energy is most likely required to laser modify wood with the higher moisture content. The result agrees with previous literature that indicated higher amounts of energy is required to achieve the same depth of ablation in wood with higher moisture contents [7, 9]. This result is related to the change of heat transfer properties of the material and the absorption of infrared light by the water. For these wet samples bonding still occurred, showing the possibility that wood does not need to be dried during laser processing. In the DOE experiment, the moisture content was kept at 12%, which is a few percent higher than the normal in service moisture content. It should be highlighted that reduced drying requirements of the veneer saves energy and lowering operational costs, while the relative to adhesives that require dry substrate for bonding [21]. The moisture content may also change the chemistries of the surface of the wood (via wet –air oxidation process), possibly altering final chemistry of the laser modified wood.

As received surface roughness of wood

Laser activated wood bonding process is applied to plywood composites, issues with wood surface roughness, both from natural heterogeneity to surface features created by the peeling process, known as knife checks, create surface roughness. Without a thick adhesive bond layer, surface roughness most likely has higher consequences on the final bond strength due to less intimate contact between each wood ply. Although an important feature, only “Grade A” poplar veneers were utilized in this experiment. Surface roughness of wood was minimized by utilizing higher grade veneer irradiating the tight side of the veneer. In screening tests, the loose side could easily become bonded, but caused wider variance in the test data; this limited the identification of important parameters and all samples were subsequently irradiated on their tight side.

Growth rings/plane of irradiation

Previous research found a 50 to 200 percent difference in ablation depth between earlywood and latewood, showing that the local structure of the wood is a significant in laser modification. The amount of early wood and late wood on a surface can be altered by how the wood is cut, i.e. quarter sawn versus flat sawn. In the case of the wood veneers utilized, all wood was peeled

and therefore the plane that was irradiated with the laser was tangential to the growth rings. It was observed that the grain pattern appeared as a photo-negative of the original piece for the southern yellow pine veneers. The earlywood appeared to be darker than the latewood. While this factor cannot be controlled, it is noted as a potential cause of variance within the system.

Design of Experiment Results

DOE is an experimental system that tests multiple factors for statistical significance, as well as testing factors for interaction effects, while reducing the amount of tests. Table 4.1 contains the values for all test specimens used in the DOE experimentation. As can be noted in the data, the range in average tensile strength values are from 0 MPa to 2.82 MPa. Some combination of parameters causes the samples to completely fail prior to testing.

Table 4.1: Yellow-poplar shear strength data for DOE analysis, triplicate tests averaged.

Power (Watt)	Pressure (MPa)	Temperature (°C)	Time (m)	Focus (inch)	Average Shear Strength (MPa)
3	0.7	140	12	0	0.97 ± 0.32
3	0.7	165	3	0.2	0.00 ± 0.00
3	1.6	140	7.5	0.2	0.00 ± 0.00
3	1.6	190	12	0.2	0.00 ± 0.00
3	2.4	140	3	0.2	0.00 ± 0.00
3	2.4	140	12	0.2	0.00 ± 0.00
3	2.4	190	3	0	2.79 ± 0.64
3	2.4	190	12	0	2.31 ± 0.43
9	0.7	140	12	0.2	1.22 ± 0.12
9	0.7	190	7.5	0	1.71 ± 0.37
9	1.6	165	3	0	2.19 ± 0.35

9	1.6	190	3	0.2	2.14 ± 0.48
9	2.4	140	7.5	0	2.73 ± 0.46
9	2.4	165	7.5	0.2	2.32 ± 0.17
15	0.7	140	3	0	1.42 ± 0.23
15	0.7	165	7.5	0.2	1.04 ± 0.07
15	1.6	165	12	0	1.75 ± 1.53
15	2.4	140	3	0.2	2.12 ± 0.36
15	2.4	190	3	0	2.79 ± 0.03
15	2.4	190	12	0.2	2.82 ± 0.52

Table 4.1 outlines the levels of various factors in combinations utilized for the DOE, 20 different set points, 3 replicates of each point. Several conclusions can be made with raw data. Lower laser powers of 3 watts tend to have a higher tendency to result in no shear strength, or low shear strength values. This lack of shear strength shows that 3 Watts of laser power may not be adequate for optimal laser modification for bonding. Also, aside from the combination of 190°C and 3 Watts, tests including 190°C platen temperatures resulted in higher shear strengths. The higher temperature may allow the modified wood surface to flow more than at lower temperatures, as well improve the thermal conductivity of the wood therefore increasing the efficiency of heat transfer from platen to bond line. It is clear when low wattage is used it must be completely in focus; else the power delivered at the surface is not great enough for modification to achieve bonding.

The significance of each factor or interaction is described by the probability of the variable or interaction among variables, outlined in the probability table 2.

Table 4.2: P Values from DOE model for shear strength of yellow-poplar samples

Parameter Estimates	P Value
Pressure	<.0001
Power	<.0001
Focus	<.0001
Power*Power	<.0001
Power*Focus	<.0001
Pressure*Temperature	0.0006
Power*Pressure	0.0142
Power*Temperature	0.0381

The P values in table 4.2 include all the parameters that are significant, or have a P value of less than 0.05. The chart indicates that several factors are significant as well as interactions between factors. The Power*Power term being significant indicates that there is a second order interaction occurring. This second order interaction is indicative of the first order curvature, in this case negative, verifying that the first order curve is concave down as seen later in the prediction profiler. Statistical proof of a concave down verifies that the maximum laser power is within the constraints utilized in the DOE. Additionally, the DOE was conducted with a pine species as well as poplar. Similar trends among all 5 factors tested were observed for pine, along with a DOE modeled maximum strength approximately 30% higher than found for poplar. When the DOE model is created using the significant variables, bond shear strength is reported to be a maximum of 3.5 MPa.

While the screening tests did determine significant variables and levels, 2 of the 5 main variables appeared to have optimal values outside of the chosen limits. Figure 4.7 below contains the prediction profiler that illustrates each factors effect on strength and the optimal value of the factor within the constraints of the DOE.

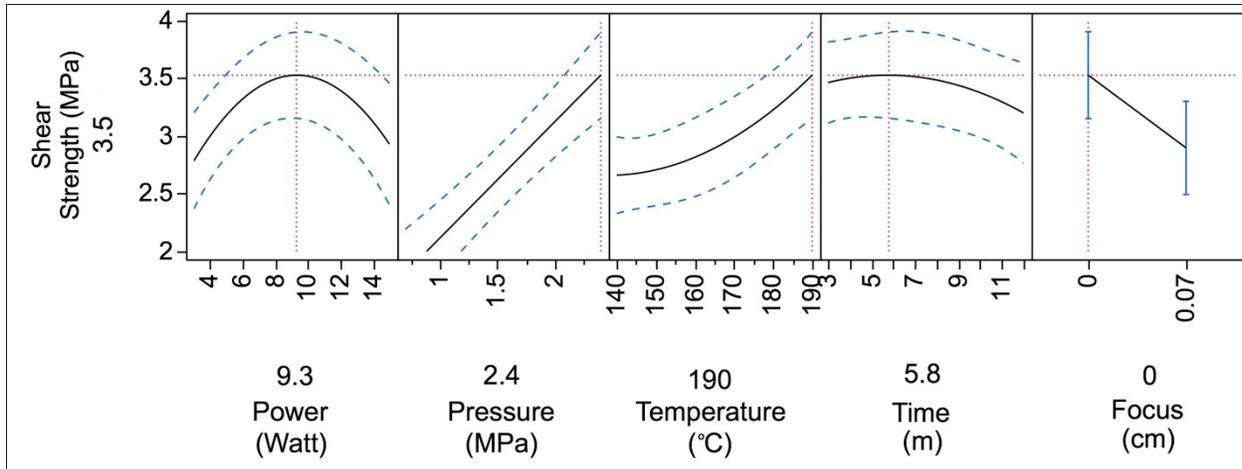


Figure 4.7: Prediction profiler indicating estimations of factors and their effect on shear strength for yellow-poplar substrates.

Figure 4.7 prediction profiler shows that when ignoring interactions, the optimum laser power and press time were found to be within the limits of the DOE, at 9.5 W and 6.4 m. The time prediction profiler illustrates that although the maximum strength is achieved at 6.4 minutes; similar strengths can be achieved between 3 and 6 minutes, while the strength of the bond decreases after 6 minutes, possibly indicative of thermal degradation of the modified wood.

As evident from the DOE prediction profiler in Fig 7, pressure and temperature profiles appear to indicate that the optimal values may lie outside of the limits placed upon those particular factors in this DOE. These limits approach physical limitations of the system. Higher strengths may be achieved as long as the wood or modified wood is not crushed by increased pressure. However, this factor may provide justification into investigating the laser treatment for strand composites, as wood typically is densified during hotpressing of particle board and oriented strand board. Exposure to higher temperatures will lead to thermal degradation of woody components, potentially impacting performance, dependent upon weight loss. In summary, though both temperature and pressure appear to have maximums outside the testing region, only pressure should be increased for possible improvements in strength.

The laser focus shows a slight improvement in shear strength when in focus, than when out of focus. Both levels of modification and the possibility of interlocking grain could be factors

contributing to this difference. However, it was not observed via visible inspection of the failed surface that wood became interlocked. It is more likely the differences are related to contact area.

As is common with many processes, interactions between factors, positive or negative, occurs. The most significant interaction found with the five variables tested in the DOE was between press temperature and pressure, as seen in Figure 4.8.

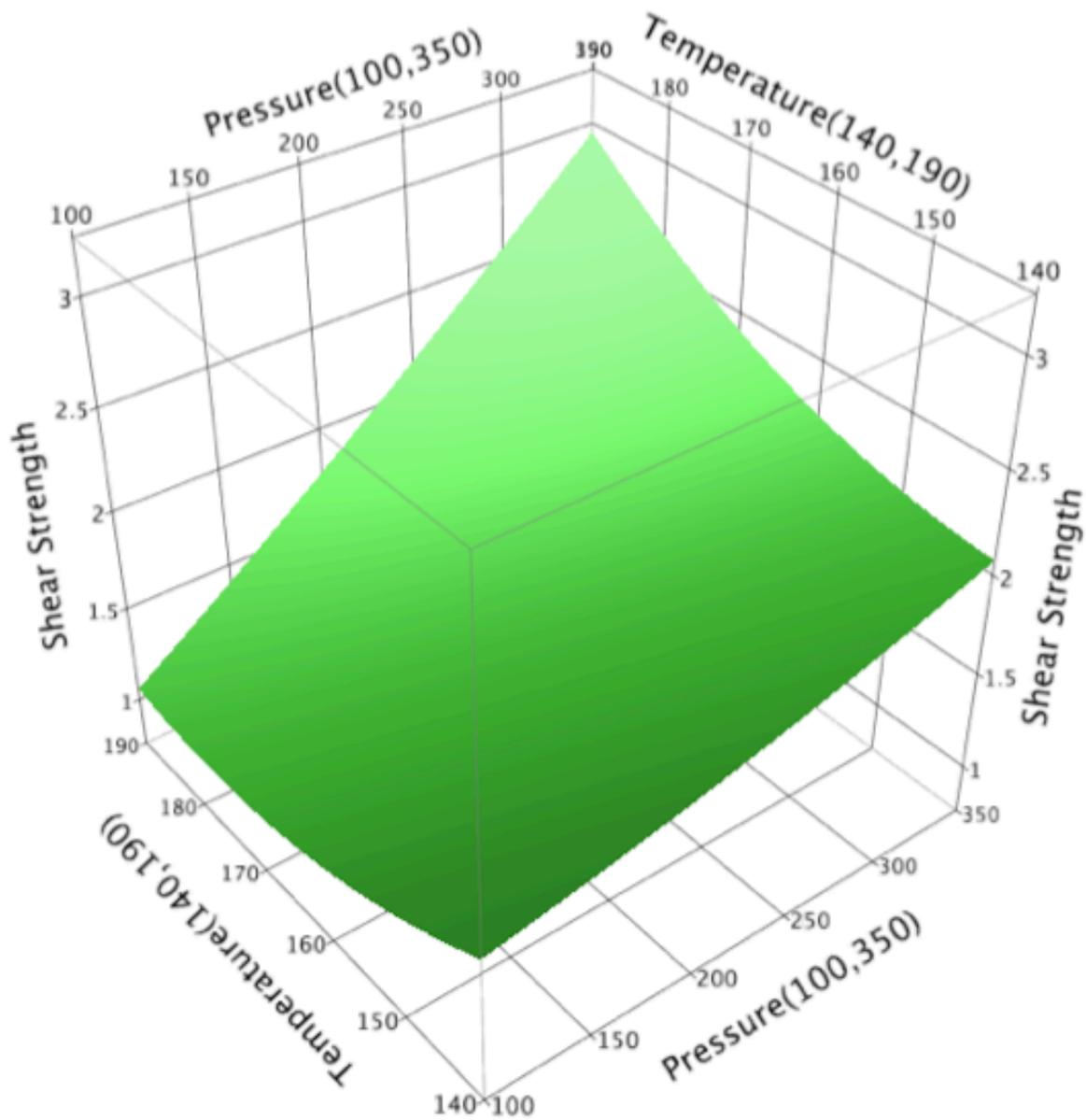


Figure 4.8: Surface profiler illustrating the interaction between temperature and pressure

The surface profile in Figure 4.8 displays the interaction between temperature and pressure indicating a synergistically positive effect when increasing both pressure and temperature. Higher temperatures allow the bonding material to be increased further above the softening temperature of the modified wood, while the pressure allows this material to achieve greater contact between surfaces.

Visual inspection of the fractured surface was performed on the samples for the DOE tests. Typically low strength failures resulted in wood failures of less than 5%. Failures at shear strengths above 2 MPa exhibited wood failures on the order of 5-50%. There were no test specimens that had 100% wood failure out of the bonding plane.

Comparison to Industrial Adhesives

Tensile shear strength tests were performed on both pine and poplar samples bonded with a commercial PF adhesive. The result of the tensile strength for poplar bonded with the PF resin was that it had average values of 1.7 MPa. Pine samples had slightly lower shear strength at 1.4 MPa. These values fell within the range of values tested for the laser-modified shear tests (Table 4.3).

Table 4.3: Tensile shear strength values of southern yellow pine and yellow-poplar bonded by laser modification or PF resin

Wood Species	Bond Method	Shear Strength (MPa)	Average Wood Failure (%)
Pine	PF Adhesive	1.4 ± 0.2	20
Pine	Laser	1.0 ± 0.4	4
Poplar	PF Adhesive	1.7 ± 0.4	27
Poplar	Laser	0.6 ± 0.2	0

Flexural tests using a 3-point bending set-up were performed on both pine and poplar that were laser modified using optimal values found in the DOE or bonded via PF resin. The results for bending modulus (MOE) and bending strength (MOR) for each sample type are seen below in Table 4.4.

Table 4.4: Results of 3 point bending tests of southern yellow pine and yellow-poplar bonded by laser modification or PF resin

Wood Species	Bond Method	Flexural Strength (MPa)			Flexural Modulus (GPa)		
Pine	Laser	62	±	19	10.6	±	2.5
Pine	PF	46	±	16	10.1	±	1.2
Poplar	Laser	81	±	9	7.1	±	1.1
Poplar	PF	101	±	7	10.8	±	1.0

For pine samples adhered with the laser-modified surface, both strength and stiffness values are slightly greater than the samples bonded with the commercial PF adhesive. However, there seems to be a species effect seen in the tensile shear specimens, as the poplar samples bonded using the laser process has lower values than what is reported for the pine samples and PF samples. The higher strengths seen with the pine may be attributed to the higher bond strength, or inherent material properties of pine.

The table 4.4 above indicates that bonding laser modified pine together achieves flexural mechanical properties similar to that of wood bonded by PF resin. The Wood Handbook lists typical plywood sheathing values in the range of 20.7 to 48.3MPa for flexural strength and 6.89 to 13.1GPa for flexural MOE. Hence, laser modified wood bonded falls in the performance range for MOE and exceeds the MOR values for both species.

Discussion

Optimization of DOE parameters

Increased pressure typically results in better bonding in plywood manufacturing utilizing PF adhesives due to enhanced intimate contact between wood and adhesive, up to a certain point before the crushing of wood structure and subsequent strength loss occurs [21]. It was revealed that higher pressure correlated with the bond strength, suggesting that the higher pressure facilitated intimate contact of bondlines. With rough cut surfaces, as occurs with rotary peeled veneers, it is intuitive that the higher pressure would enhance adhesion.

A previous report (chapter 3) revealed the laser-modified wood from a hardwood species undergoes a thermal transition at 130°C. As the laser-modified wood samples are raised to higher temperatures above its T_g , the surface can undergo flow and behave like a thermoplastic material. It was noted in previous experiments that the glass transition temperature shifts to higher temperatures with heating the isolated layer of laser-modified wood material to 180°C. This response is a hallmark of thermosetting materials, indicating “curing” of the adhesive. As temperature appeared as a factor in the DOE response, it appears that it impacts the bonding mechanism. However, there was no strong effect of time, or interaction between time and temperature, suggesting that the kinetics of a thermochemical reaction occurred by three minutes or did not occur in this system. While no specific mechanism has been identified within this study, the friction welding of wood indicated in the introduction section, reports that frictional heating can crosslink degraded polysaccharide components (like hydroxymethyl furfural) with lignin fragments. In those studies it was hypothesized that the bonding occurs when amorphous polymeric materials, primarily lignin but also some hemicelluloses flow, causing a partial detachment of long wood cells and fibers. Once heat is removed the system solidifies, thereby creating a wood cell fiber entanglement network whose matrix is composed of once molten woody polymers [22, 23]. Utilizing SEM and ^{13}C NMR verified both the network composite structure and its components. We hypothesize that bonding occurs under a similar mechanism for laser activated wood bonding, but with perhaps more polymer flow and less fiber entanglement combined with potentially some mechanical interlock of ridges.

Based upon empirical observations it is suggested that adhesion between wood surfaces occurs because the laser-modified surface layer is able to undergo flow at the above temperatures; subsequently, heating the samples and pressing together two rubbery surfaces, intimate contact is established and bonding occurs. The samples have mechanical integrity when removed from the hotpress. Preliminary tests show some water resistance (data not shown) suggesting chemical bonding occurs. This point will further be evaluated in future studies.

Conclusion and Future Work

Wood surfaces were laser modified and subsequently hotpressed together creating wood composites without any added adhesive. A combination of screening tests and a Design of Experiment furthered the understanding of the laser activated wood bonding method, yielding significant parameters for both the laser modification (power and focus) and subsequent bonding (hotpress pressure, and a pressure/temperature interaction parameter). By modeling the DOE data, it was determined that the maximum strength within the parameter limits chosen for the DOE will result in shear strengths of 3.5 MPa. There was a minimum energy density required which was controlled by the laser wattage and focus spot size. Both the shear strengths as well as flexural strengths of the laser modified wood bonding method were comparable to strengths of PF bonded specimens. Taken together, a new method of bonding wood is reported that has some performance characteristics of traditional wood adhesives, but does not require any additives.

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Chapter 5: Conclusion

1. Laser modification of wood results in a unique surface that is different from other heat treated wood surfaces.
2. Microscopy showed that the laser modified surface appears to have flowed or softened due to a smoother surface topology, with a change in color.
3. Laser modification of wood results in a surface that can flow/soften when heated above 130-150°C.
4. Chemical analysis showed changes in the carbonyl and aromatic regions indicating that the modified surface is primarily hemicellulose and lignin. For heavy levels of modification, cellulose was also modified by the laser.
5. The C1/C2 ratios from XPS revealed that one or more of the following occurred: more extractives have moved to the surface, condensation reactions among lignin units, and the loss of methoxy and breakage of aryl ether linkages.
6. Factors that influence laser modification of wood include laser parameters (power and focus) as well as hot press parameters (temperature, pressure).
7. The optimal laser parameters for southern yellow pine within the constraints of the DOE include a laser parameters of power at 10.2 Watts, laser with the focal plane on the wood surface, and press parameters: Temperature of 180°C, Pressure of 350 PSI (2.4 MPa), and a time of 10.4 minutes, yielding hypothetical max strength of 4.5 MPa.
8. The optimal laser parameters for yellow-poplar within the constraints of the DOE include a laser parameters of power at 9.5 Watts, laser in focus, and press parameters: Temperature of 190°C, Pressure of 350 PSI, and a time of 6.4 minutes, yielding hypothetical max strength of 3.5 MPa.
9. Plywood composites were created with the laser bonding method under optimized conditions. Southern yellow pine samples had flexural modulus and strength comparable to plywood samples bonded with phenol-formaldehyde resins. Yellow-poplar samples had flexural modulus values that were lower than the phenol formaldehyde bonded samples, but the flexural strength for the laser-modified samples were greater.

Appendix A: Experimental work related to wood bonding

Because the laser modification of wood for bonding was not previously reported, there were a number of studies that were performed to understand the variables that impact this phenomenon. For archiving purposes these studies are reported. Most of these studies are single experiments with limited replication. The studies were performed purposely in this manner so the experiments could be used to screen a greater host of variables, answering many questions that arose during the initial experimentation. Almost all samples were made using materials and methods outlined in chapter 4. Specifically, rotary peeled yellow-poplar and southern yellow pine were used, conditioned to 12% moisture, unless noted, and modified with the Universal Laser system. These various screening studies, listed below, are reported in the following pages:

1. Bonding of Wood-to-Wood without Laser Modification
2. Does Bonding Laser Modified Wood Require One or Both Surfaces to be Modified?
3. Instead of Laser Light, can Infrared Light from a Heat Lamp be used to modify the Surface of Wood for Bonding?
4. Effect of Moisture Content during Laser Modification
5. Effect of Moisture Applied Prior to Bonding Laser Modified Wood
6. Low Bonding Temperatures and Short Bonding Times
7. Focus Related to Depth of Field and Type of Laser
8. Type of Laser

1. Bonding of wood-to-wood without laser modification

Background

An experiment was run to test the possibility of two wood surfaces bonding together without any laser modification of either surface, to see if bonding would occur. While not expected, it was necessary to demonstrate that heat, pressure, and moisture alone without modification would be unable to form a stable bondline.

Test

Both yellow-poplar and southern yellow pine samples were tested. Samples were wetted as described in the "moisture content during bonding method", and then hot pressed at 300 PSI and 180°C for 10 minutes. Limited adhesion occurred for these samples.

Although some bonding occurred, both pine and poplar samples debonded within 10 minutes after exiting the hot press and therefore preventing mechanical testing. It was hypothesized that the thermal stresses of cooling combined with atmospheric hydration caused dimensional changes reducing the intimate contact between the two samples resulting in debonding of the plys.

Impact

The study demonstrates that under the conditions used, wood does not form bondlines with integrity when no adhesive is added to the system. Results from previous chapters demonstrate that adhesion is derived from the laser-modification process.

2. Does bonding laser modified wood require one or both surfaces to be modified?

Background

Initial experiments of laser activated wood bonding worked under the concept that both surfaces need to be laser modified for bonding to occur. If it was possible to bond wood while only laser modification of one of the two surfaces in the bond, the energy costs of the laser could be cut in half, processing time reduced, etc. A test was carried out to test this concept.

Test

One sample was laser modified within the optimal parameters while one sample remained unmodified. The samples were pressed together for 10 minutes, at 300PSI and 180°C. No bonding occurred. This initial experiment indicated that for two surfaces to bond, they must both be laser modified.

Impact

Although the result of this experiment could be considered a negative outcome, the knowledge that both surfaces must be similar chemically and/or morphologically for bonding could lead to a better understanding the bonding mechanism. Two hypotheses for lack of bonding that remain untested involve amount of material available and possible mechanical interlock. One possibility may be the lower amount of laser modified wood available to flow at the surface. This lower amount of material may not be able to create optimal intimate contact between the surfaces. Also, if the bond requires mechanical interlock from the ridges created during laser ablation, then ridges would not be on both sides of the bond, if only one surface was modified, leading to poor bonding/no bonding. However, plywood specimens with veneers bonded perpendicular readily form bonds, indicating that mechanical interlock is not the main mechanism. Note: the reduced area of irradiated surface may still be a variable investigated in future studies to limit processing time and energy by reducing overall exposure on adherend surfaces.

3. Instead of laser light, can infrared light from a heat lamp be used to modify the surface of wood for bonding?

Background

As a carbon dioxide laser used in the previous studies has a wavelength infrared region, the hypothesis that other infrared light sources such as a heat lamp could yield similar surface modification of wood was tested [1]. A test was set up utilizing a hot press and the same samples utilized for the design of experiment. The motivation is related to the challenge of upscaling the laser modification method or modifying larger samples at higher rates. Heat lamps irradiate larger areas than lasers, but at lower power densities[2].

Test

In this experiment a 250W R40 5" reflector lamp with a filter to minimize visible light irradiance was placed 2.5 cm from 2x2x1/8" pine and oak samples, as seen in figure A.1. The samples were irradiated for 3 minutes, then immediately placed in a hot press at 300 PSI and 180 C for 10 minutes.

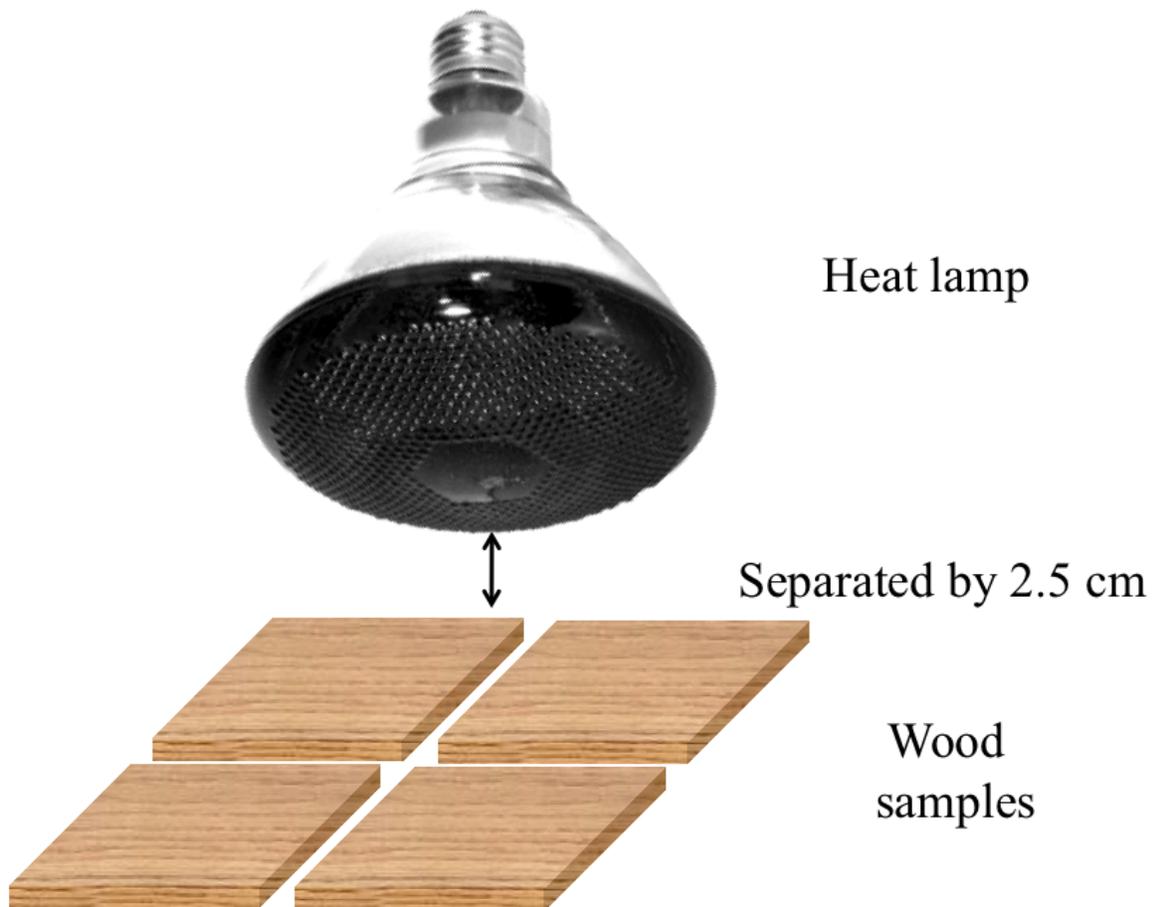


Figure A.1: Diagram of heat lamp experimental setup

No bonding occurred with any of the samples. The surfaces before bonding appeared to be primarily charred, but the charring was inconsistent across the surface, with some severe charring, and some areas having very little degradation, as seen in figures A.2 and A.3.

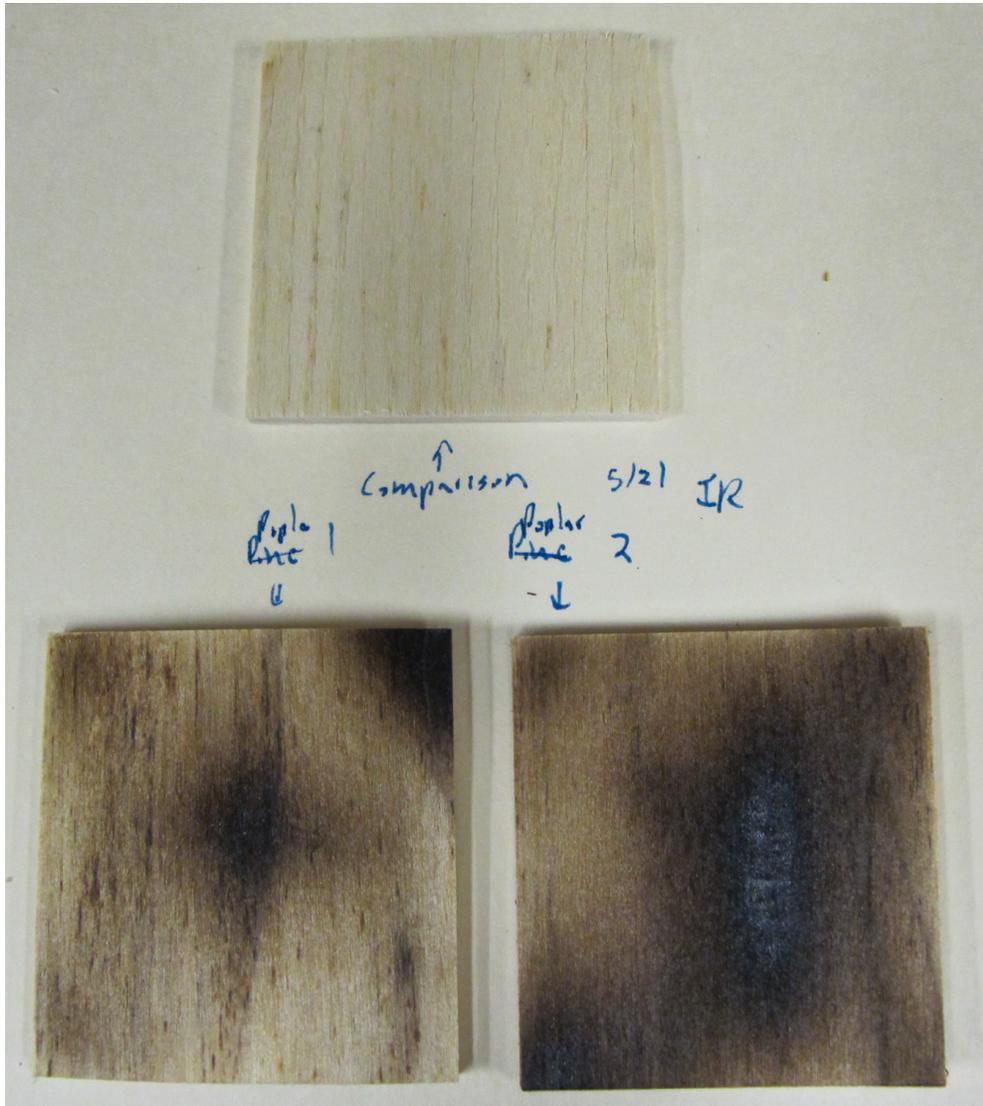


Figure A.2: Yellow-poplar sample (top) modified by IR lamp (bottom left) 2.5 min (bottom right) 5 min. Modification results in charring of the surface.

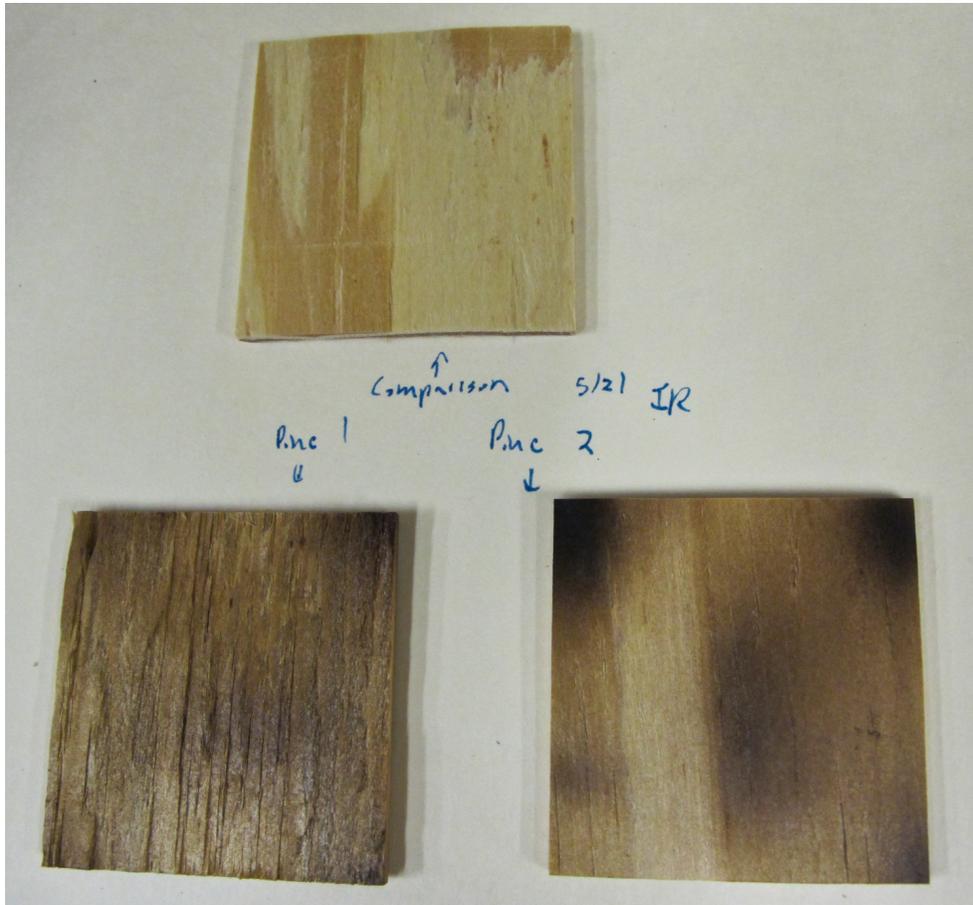


Figure A.3: Southern yellow pine samples (top) modified by IR lamp (bottom left) 2.5 min (bottom right) 5 min. Modification results in charring of the surface.

Three main reasons are suggested as contributing factors for the failure of heat lamps to modify wood surfaces in a similar fashion as the laser. Compared to the carbon dioxide laser, the heat lamp has inherent differences that may cause non-optimal wood surface modification, including a combination of lower fluence, longer interaction time, and a wider wavelength range. It was found that laser fluences below the lowest settings of the laser (3W @ 20in/sec in focus at 50 micron spot size) did not supply enough energy for the laser modification of the wood.

Likewise, the fluence of the light emitted from the heat lamp was not high enough to optimally modify the material. It would be logical to increase the time of interaction between the wood and the heat lamp in order to apply enough energy for surface modification. However, this time increase is not possible due to the destruction of the wood surface via charring. Laser modification makes the optimal modification of the surface possible as the interaction time is

small enough to not cause the prolong heating, which induces carbonization, therefore increasing the time with the IR lamp led to increased carbonization. The interaction time and energy density are the most significant difference between lasers and heat lamps. Lastly, carbon dioxide lasers have a much narrow wavelength range than IR lamps. Relative to the IR lamp, as of this time, the carbon dioxide laser produced the most optimal wavelength for laser modification. It is suggested that as certain wavelengths interact optimally with certain wood components, that a wider wavelength range could lead to non-optimal reactions in wood. Since the heat lamp has a significantly larger range of light wavelengths, it is less optimal for modification. A chart illustrating absorptivity of beech and pine at different wavelengths is below in figure A.4.

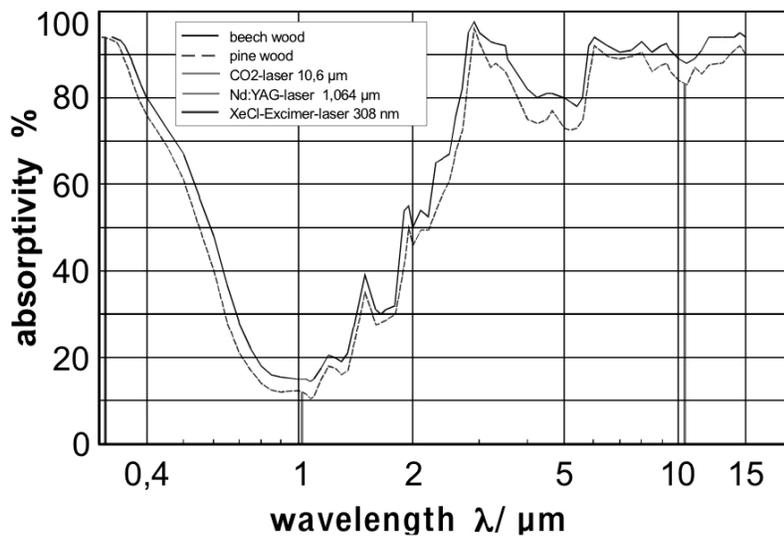


Figure A.4: Absorptivity of wood at various wavelengths. Used with the permission of Rightslink Copyright Clearance Center, Applied Surface Science Journal, 2007. [1]

Impact

Current heat lamp technology does not allow for photons generated in a heat lamp to modify the surface of wood for adhesion. Surface modification via heat lamp may still be possible by increasing the fluence, decreasing the interaction time, and decreasing the range of light wavelengths. Heat shields for space vehicles have been tested utilizing heat lamps that achieved 300kW/m^2 [2](or 300W/cm^2), The laser achieves up to 600 kW/cm^2 , or 3 orders of magnitude higher than the most powerful heat lamps created. If heat lamps existed with high enough

fluences for time periods more similar to the laser/wood interaction time, it may be possible by utilizing methods to minimize the range of wavelengths and to modify wood with heat lamps in a similar fashion to laser modification.

4. Effect of moisture content during laser modification

Background

The anatomical structure of wood is naturally optimized for transport of liquids in order for the tree to transfer water and other essential nutrients throughout its complex structure [3, 4]. In plywood manufacturing, as well as other wood composite operations, the wood must achieve a low enough moisture content before adhesive application to allow great enough adhesive cure; leading to eventual bond strength of the material [3]. To achieve this low moisture content, energy is required to remove water from the wood. If laser bonding of wood could bond wet wood together, a large reduction in the energy required to dry wood would be possible.

It is hypothesized that during laser ablation or hot pressing that the chemistry at the surface of the wood may be different as the water allows for transport of extractives that may not previously be located at the surface of the wood. These chemistries may help or hinder both the laser modification of the wood as well as the bond process undergone at the hot press.

Test

The moisture content of wood before laser modification was 12 %MC, induced by a minimum of 24h in an environmental chamber set at 65% RH (relative humidity) and 25 °C. The moisture content of wood before laser ablation, as well as during hot pressing, was testing for multiple theories/reasons, including reduction in energy costs in eventual production, possible transport of chemistries during laser ablation and hot pressing, plasticization of wood and modified wood surface during hot pressing, minimized unwanted degradation, as well as a variable in laser modification.

Pine wood samples of the standard size (peeled cut, grade A, 2'x2'x1/8"), were separated into two groups. One group was weighed then placed in an environmental chamber to achieve 12%

moisture content. The other group was soaked for 24h in tap water. Both samples were laser modified at a laser power of 10 Watts at a spacing of 0.002" inches, with the laser in focus.

Once laser modified, samples were hot pressed, in 2 ply, with grains aligned, at 180°C and 300 PSI for 10 minutes.

Although not quantified, there was visibly less surface modification on the samples that were soaked for 24h than the samples conditioned to a MC of 12%. This observation agrees with previous research that shows moisture content increases the density and thermal conductivity of wood. Due to increased water content, density, and thermal conductivity, more energy is required to remove excess water and ablate the more dense material while the increased thermal conductivity transfers the energy away from the wood's surface. All three of these factors minimize the surface modification via laser.

Impact

The above study demonstrated that wet wood can be laser modified and still be bonded together. This result suggests that the extreme of utilizing green wood, wood that has never been dried, may be amendable for this application.

5. Effect of moisture applied prior to bonding laser modified wood.

Background

Water is a known plasticizer of wood lowering the glass transition of dry wood by 60 to 100°C [3]. Because the mechanism of bonding is suggested to be related to softening of the laser modified wood layer it was thought that plasticization of the laser modified wood surface may enhance local flow and intimate contact. By plasticizing the wood and/or modified wood, the material may become more pliable therefore allowing for more intimate contact resulting in a better bond.

Tests

Laser modification and hotpressing were conducted as described elsewhere. Prior to hot pressing

samples were sprayed with water. Tensile shear tests were conducted on both samples that were sprayed with water and without water. Shear strengths were within 20% of one another. However, as this was only used as an initial screening test, the data demonstrated that both types of samples could undergo bonding.

Impact

No improvement in the water plasticized wood surfaces were recorded with the addition of water. However, it should be noted that moisture from the wood veneers may aid in the plasticization of the surface material as the wood is heated and moisture is initially driven towards the bondline. Also, further experimentation should be performed to determine the softening temperature of the laser modified surfaces as a function of plasticizer content.

6. Low bonding temperatures and short bonding times

Background

DSC tests indicated that the laser modified surface does not pass through a glass transition temperature until 130-150°C. The samples were tested to determine if bonding below the softening temperature occurs as well as if bonding can occur for samples pressed at the temperature conditions indicated previously, but with the times reduced below 3 minutes.

Tests

The hypothesis that the bonding of samples may be possible with pressure alone or at lower temperatures was tested. Laser modified samples were pressed at room temperature (22°C) as well as at 100°C for 10 minutes at 300 PSI. Bonding did not occur at either temperature, verifying that temperatures at or above the glass transition of the modified surface are required for bonding to occur.

Impact

The fact that bonding did not occur at room temperature or at 100°C is a negative outcome in terms of energy costs but a positive outcome in terms of understanding the bond method. Since

the bond cannot occur at lower temperatures it dictates the energy costs required for bonding. The fact that temperatures above 100°C (most likely above the glass transition temperature at 130-150°C) is required for bonding verifies that softening of the modified surface must be induced in order for bonding to occur.

7. Focus related to depth of field and type of laser

Background

As is typical with most applications that utilize light and optics to focus the light, there is a particular depth of field for a given laser and optics set up. Within that depth of field, typically at the center of the depth of field, the laser is in focus, yielding the highest laser fluence due to the laser beaming being at its smallest "waist" or diameter. As one changes the optics, or more typically, moves out of focus by changing the distance between the optics and the work piece, the laser fluence decreases. Previous research indicates that at lower fluences with lasers reduces wood ablation and more wood is carbonized. Below is a diagram of fluence and the associated result of irradiating wood with the respective fluence.

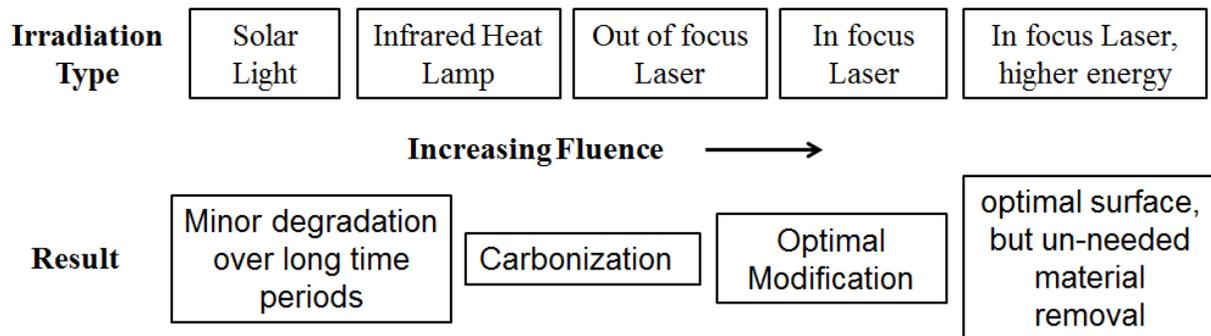


Figure A.5: Diagram of various light sources and resulting materials after irradiating wood

The above diagram conveys the result of various light sources irradiating wood. Optimal surface modification for laser activated bonding of wood is achieved with an in focus laser.

Impact

The application of light energy to wood can create a variety of products. Understanding the proper way to apply laser energy is vital to optimally laser modifying a wood surface for bonding.

8. Type of Laser

The only type of laser utilized so far in this research is a 10.6 micron wavelength 60W carbon dioxide laser. The type of laser requires optimization on two fronts, the wall plug efficiency and the efficiency of energy transfer to wood.

Wall plug efficiency is a measurement of the amount of energy that the laser uses and the associated laser energy output. Since a large majority of lasers utilize electrical energy in their process, typically entering the system through a wall plug, wall plug efficiency is the term used. (Note: manufacturers will sometimes refer to the wall plug efficiency as the energy entering the diode lasers utilized to pump a laser, often ignoring the energy used by the power supply and cooling systems.) There are other areas of efficiency in lasers, including pumping efficiency, but wall plug efficiency summates all of these into an easily comprehensible number. Wall plug efficiencies are typically in the range of 10-20% for carbon dioxide lasers, while pure diode lasers have been reported to reach efficiencies of over 60% [5].

Previous research indicates that wood absorbs certain wavelengths of light better than other wavelengths. For this research, the assumption can be made that a laser with a wavelength optimal for adsorption by wood would allow for the optimal energy transfer. Figure A.4 indicates the absorptivity of wood versus wavelength in the range of 0.3-15 microns. From the figure both a similarity between wood types and optimal laser types can be deduced. Beech and pine both have very similar absorptivity curves, lending to the hypothesis that most woods may have similar absorptivity. This hypothesis is significant as one laser system would be usable for most wood species, therefore simplifying widespread use.

Since the carbon dioxide laser optimally modified the wood material, then lasers at the same

wavelength, and perhaps lasers at similar wood absorptivity values, 85% and higher, would yield better results. Therefore an optimal laser would be a laser that emits a wavelength of 10.6 microns more efficiently than a carbon dioxide laser. If that type of laser does not exist, then lasers with the same high absorptivity at other wavelengths would be probable to have the next highest efficiency. Those wavelengths resulting in absorptivity above 85% include below 0.4 microns, the peak at 3 microns, and 6 microns and above. A sacrifice in wood absorptivity may be possible if the laser wall plug efficiency is high enough, as with laser diodes, which have the highest efficiency, but typically have wavelengths in the lower absorptivity values of 0.4 to 2.6 microns.

Future Work

Future work for this project can be broken down into 2 main sections, pilot scale testing and the science of the bondline chemistry. Researching both areas at the same time will be beneficial to the project as a whole, for example a certain wavelength of a laser may be optimally absorbed by the wood, and therefore dictate the laser utilized in pilot scaling. The reciprocal relationship may be true, for example the pilot scale testing may find a maximum speed at which the wood can be modified by a laser, which may give a better understanding of the science involved in the energy transfer from the laser to the wood.

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