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Corrosiveness of Thermally Modified Wood

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Abstract: Thermally modified wood is becoming commercially available in North America for use in outdoor applications. While there have been many studies on how thermal modification affects the dimensional stability, water vapor sorption, and biodeterioration of wood, little is known about whether thermally modified wood is corrosive to metal fasteners and hangers used to hold these members in place. As thermally modified wood is used in outdoor applications, it has the potential to become wet which may lead to corrosion of embedded fasteners. Here, we examine the corrosiveness of thermally modified ash and oak in an exposure test where stainless steel, hot-dip galvanized steel, and carbon steel nails are driven into wood and exposed to a nearly 100% relative humidity environment at 27 °C for one year. The corrosion rates were compared against control specimens of untreated and preservative-treated southern pine. Stainless steel fasteners did not corrode in any specimens regardless of the treatment. The thermal modification increased the corrosiveness of the ash and oak, however, an oil treatment that is commonly applied by the manufacturer to the wood after the heat treatment reduced the corrosiveness. The carbon steel fasteners exhibited higher corrosion rates in the thermally modified hardwoods than in the preservative-treated pine control. Corrosion rates of galvanized fasteners in the hardwoods were much lower than carbon steel fasteners. These data can be used to design for corrosion when building with thermally modified wood, and highlight differences between corrosion of metals embedded in wood products.

Keywords: modified wood; corrosion; stainless steel; hot-dip galvanized steel; heat treatments

1. Introduction

Wood is a sustainable biomaterial that has been used as a building material since the beginning of civilizations. Under proper conditions, wood can last for millennia, as exhibited by artifacts such as the Shigir Idol or the coffin of Tutankhamun [1,2]. However, in outdoor applications, it is susceptible to degradation from moisture cycling, ultraviolet radiation, and decay fungi [3].

Preservative treatments have been used for many years in North America to increase the durability of wood in outdoor applications [4]. Preservative treatments protect wood by impregnating it with chemicals that are either fungistatic or fungitoxic and inhibit fungal growth. Frequently, these chemicals are combined with an insecticide to further protect the wood against termites and other wood-boring insects. Waterborne wood preservative treatments are registered pesticides and their ability to be used in the United States is dependent on their ability to maintain their registration with the US Environmental Protection Agency [5].

Currently, there is an interest in using *modified wood* as an alternative to preservative-treated wood in certain outdoor applications. *Modified wood* is wood whose chemistry and/or structure is altered to achieve desired properties through thermal or chemical treatments [6]. In contrast to preservative-treated wood, the decay resistance in modified wood is a result of non-toxic changes to the wood structure which make the wood harder for the fungi to colonize. The mechanisms through which modified wood achieves its decay resistance are still not fully understood, although it is realized that all wood modifications affect how water is associated with the wood cell wall [7]. One current hypothesis is that wood modifications may inhibit diffusion of fungal decay agents through the cell wall [8–12].

Thermally modified wood is a modification process where the wood properties are changed by heating wood in a non-oxidizing environment. While many different thermal modification profiles have been used, typical treatment temperatures are between 160 °C and the char temperature of wood (300 °C). Thermally modified wood has been studied for over 100 years [13], however, it was not available commercially in North America until recently. In the thermal modification process, hemicelluloses and celluloses are degraded through pyrolysis and other chemical reactions. The amount of the induced chemical changes to the wood are typically measured through the mass loss that occurs during the thermal modification process. The degradation of cellulose and hemicelluloses causes a reduction in the mechanical strength of thermally modified wood [14]. However, the remaining, semi-pyrolyzed material has increased dimensional stability and lower equilibrium moisture content at a given relative humidity [15,16]. Thermally modified wood has also been shown to be more decay resistant than untreated wood [17–21].

Given that thermally modified wood has improved decay resistance and moisture properties, there is interest in using it in place of preservative-treated wood in certain outdoor environments. Prior to widespread commercial adoption, it is necessary to characterize the performance of thermally modified wood in laboratory tests. While much work has already been carried out on the decay resistance of thermally modified wood, there are few published data on the corrosiveness of modified wood to metal fasteners [22–24] and even less data on the corrosiveness of thermally modified wood [25]. While not typically considered a corrosive environment, when wood is above 15% moisture content, fastener corrosion can occur [26–28].

The corrosion of metal fasteners has been widely studied since a 2004 change in the registration of wood preservatives in the United States [5]. At that time, corrosion failures were seen in service as new wood preservatives entered the marketplace [29,30]. As a result of these corrosion concerns, an extensive test program was developed. It was found that wood moisture content has a large effect on the corrosion rate of embedded metals; below 15% corrosion does not occur. As the moisture content is increased, the corrosion rate increases until fiber saturation [26–28]. Corrosion of embedded fasteners was found to proceed at a constant rate with time [31,32]. Most of the previous corrosion testing was performed in an environment at 27 °C and near 100% relative humidity (RH) conditions [22,28,32–38]. It was found that the corrosion rates under these conditions were as high or higher than those measured in the fully saturated wood state [28]. Therefore, corrosion rates measured in service should be less than or equal to those measured in the 100% RH environment.

In this paper, we examine the corrosiveness of thermally modified hardwoods in a year-long exposure test at 27 °C and near 100% RH. The data are compared against controls of untreated and preservative-treated southern pine. In addition to providing new properties of thermally modified wood, the experiments also provide valuable information on the corrosivity of hardwood species, of which little data exists.

2. Materials and Methods

2.1. Thermally Modified Wood

The thermally modified wood was provided from a commercial supplier. The thermal modification followed the Finish Thermowood process [39,40]. Wood was equilibrated at 120 °C to facilitate drying and then heated to 190 °C for 3 h before being quenched with water. Two different species were tested, red oak (*Quercus rubra* L.) and white ash (*Fraxinus americana* L., Sp. Pl.). For each species, three different conditions were tested: "control", without thermal modification, thermally modified, and thermally modified wood with an oil coating. The oil coating is typically applied by the company to their commercial products; however, in this study we tested it to see if it had any effect on fastener corrosion. In addition to these six specimens, two additional groups were added for a comparison: untreated southern pine (*Pinus* spp.) and southern pine commercially treated with a common copper containing wood preservative, micronized copper azole, (MCA) treated to retention of 1 kg m^{-3} (suitable for above ground use).

2.2. Fasteners

Three types of fasteners were tested: hot-dip galvanized steel, plain carbon steel, and stainless steel 16d nails with a length of 90 mm. Ten replicates were tested for each fastener type and wood treatment. The average diameters of the steel, galvanized steel and stainless steel fasteners were 4.1, 3.6, and 4.2 mm respectively. The composition of the steel and stainless steel fasteners was obtained with optical emission spectroscopy, (Table 1). The composition of the carbon steel fastener was consistent with UNS G10180 carbon steel and the stainless steel fastener was consistent with UNS S30400 austenitic stainless steel. The galvanized coating thickness was measured at six different points along one of the fasteners from a scanning electron micrograph. The mean coating thickness was 91 μm with a standard deviation of 36 μm. The composition of the galvanized coating thickness was measured with an X-ray fluorescence analyzer (Table 1).

Table 1. Composition of the fasteners tested, or for the galvanized fastener, the composition of the galvanized coating. Composition is given as a weight percent.

	Carbon Steel	Stainless Steel	Galvanized Coating
Carbon	0.191	0.040	–
Silicon	0.130	0.419	0.415
Manganese	0.750	1.680	–
Phosphorus	0.007	0.025	–
Sulfur	0.007	0.020	–
Chromium	0.022	18.110	–
Nickel	–	8.830	–
Molybdenum	–	0.253	–
Copper	0.040	0.181	–
Cobalt	0.004	0.106	0.037
Tin	0.001	0.013	0.032
Bismuth	0.006	–	0.186
Zinc	–	0.018	balance
Iron	balance	balance	2.815

Prior to exposure, the surface areas of the fasteners were determined optically with the method of Rammer and Zelinka [41,42]. Fasteners were then cleaned in an ultrasonic cleaner with soap solution for 5 min, rinsed under deionized water, dried, and weighed to the nearest 0.1 mg.

2.3. Exposure

Fasteners were driven into holes predrilled in the wood with a diameter of 4.0 mm (5/32”). Given the extremely high densities of the hardwood species tested, it was impossible to drive the fasteners into the wood unless the entire length of the fastener was predrilled to a diameter near that of the fastener. The carbon steel and stainless steel fasteners could not be driven into holes smaller than 4.0 mm, therefore, this resulted in the galvanized fasteners being driven into slightly oversized holes. Fasteners were driven with a pneumatic palm nailer as opposed to a hammer. The pneumatic nailer was necessary to drive the fasteners into the high density hardwoods without bending the fasteners. For each treatment group, one board was tested; all three types of nails were driven into the same board with a space of at least 25 mm between fasteners. The sample geometry and location of replicates closely followed ASTM standard G198 [43]. Previous work has shown that the area of interaction of the fastener with the wood is localized to a region less than 1 mm from the fastener surface [44,45].

Once the fasteners were driven into the wood, the boards were placed in a sealed container for one year. The boards were placed above a reservoir of water, which created a local environment of close to 100% RH inside of the container; the temperature of the room was 27 °C. These conditions closely match previous corrosion tests on preservative-treated wood [28,33–36,38]. In this experiment however, the containers were inadvertently moved at some point during the exposure. As a result, some of the water from reservoirs made contact with the boards which increased the moisture content of some of the specimens. The moisture content was measured at the end of the experiment by cutting small cross sections of the board throughout its width and gravimetrically determining the moisture content. Moisture contents are listed in Table 2. Although the thermal modifications likely affect the hygroscopicity and thus equilibrium moisture content, the conditions of the corrosion tests involved condensation and, in some cases, splashing, and therefore the final moisture contents are more a result of the environment than the treatment. However, the corrosion rates of fasteners have been found to not vary from the 100% relative humidity condition to full saturation, so these differences are unlikely to affect the reported corrosion rates [28].

Table 2. Final wood moisture contents of the different wood species and treatments tested.

Species	Treatment	Final Moisture Content (Standard Deviation)
Ash	Untreated	36% (8%)
	Thermally Modified	25% (8%)
	Thermally Modified w/Oil Treatment	32% (4%)
Oak	Untreated	18% (3%)
	Thermally Modified	16% (1%)
	Thermally Modified w/Oil Treatment	16% (1%)
Pine	Untreated	27% (1%)
	Preservative-Treated	49% (6%)

The fasteners were originally set to be exposed for one year. However, due to the US Government shut down, the experiment could not be accessed. Instead, fasteners were exposed for slightly longer than 1 year (at most, 11,256 h of total exposure). However, the corrosion of metals in wood has shown to increase linearly with time (constant corrosion rate), so these slight differences in exposure times should not affect the reported corrosion rate [34,46,47].

2.4. Post-Test Cleaning Procedure

Following the exposure, the fasteners were removed from the wood. Fasteners were removed by making cross-cuts in the wood near the fastener. The thin amount of wood on both sides of the fastener could then easily be removed by hand. Larger sections between the fasteners were retained and used to measure the wood moisture content. Fasteners were then cleaned for 60 min in an ultrasonic cleaner with a 50:50 solution (volume ratio) of a proprietary chelating agent (EvapoRust™ Orison Marketing LLC, Abilene, TX, USA) and deionized water. Following the cleaning, the nails were wiped with a paper towel, allowed to air dry and weighed to the nearest 0.1 mg. The mass change caused by the cleaning process (m_c) itself was measured by cleaning uncorroded fasteners using the same process. The change in mass of the corroded fasteners (Δm) was calculated as

$$\Delta m = m_f - m_i + m_c, \tag{1}$$

where m_f and m_i were the initial and final masses, respectively.

2.5. Determination of the pH and Tannin Content

Water extracts of the wood were directly analyzed for pH and tannin concentrations. Since corrosion is an aqueous process, water extracts should mimic the corrosive environment near the fastener and several studies have shown good correlation between corrosion measurements in water extracts of wood and solid wood [48–50]. The extracts were made by the method of Zelinka, Rammer and Stone [50]. Wood was ground into sawdust and then mixed with reverse osmosis water in a 1:10 (wood:water) weight ratio and allowed to sit at room temperature for one week before filtration. The pH was measured in the extract using a pH probe.

Total phenolics and tannins were determined using a lab procedure published by The Food and Agriculture organization of the United Nations (FAO/IAEA) [51,52]. The method was largely based on the published work of Makkar, et al. [53]. This 2-step procedure first uses the Folin test to determine total phenols. Then, polyvinyl polypyrolidone (PVPP) is added to precipitate tannin-sized polyphenols. The Folin test is run again to measure remaining polyphenols, and tannins are calculated as the difference between total and remaining polyphenols (after PVPP precipitation).

In this study, 2 mL aliquots of the water extracts were taken and passed through a 0.45 uM centrifuge filter to remove particulates. A standard curve was prepared using Sigma-Tannic Acid (Sigma-Aldrich, 403040, Saint Louis, MO, USA) at 5 concentrations (including a blank). Then, the Folin test reagents: Distilled Water, Sodium Carbonate (Sigma-Aldrich, 791768, Saint Louis, MO, USA) and Folin & Ciocalteu's phenol reagent (Sigma–Aldrich, F9252, Saint Louis, MO, USA) were mixed together in test tubes for color development for 40 min. Aliquots of the filtered water extracts were treated identically. Sample concentrations were measured (at 725 nm) against the standard curve using a Thermo Scientific Gensys 180 UV-Vis spectrophotometer after subtracting a blank (consisting of dist. H_2O and Folin reagents). Afterwards, 100 mg of PVPP (Sigma-Aldrich, P-2472, Saint Louis, MO, USA) was weighed into fresh test tubes and dissolved in 1 mL of dist. water. A 1 mL aliquot of filtered water extract sample was added and thoroughly mixed. Samples were then placed in a 4 °C refrigerator for 15 min and then spun for 10 min at 10,000 rpm through a 0.45 μM centrifuge filter and analyzed using the Folin test as described above.

3. Results and Discussion

3.1. Stainless Steel Fasteners

The corrosion rate of the stainless steel nails was essentially zero. In all but one case, the corrosion rates were less than 0.3 μm year^{-1} and the standard deviations were bigger than the mean corrosion rate. In one case, the average corrosion rate measured was 1 μm year^{-1}. However, in this case, the standard deviation was 3 μm year^{-1}. Therefore, it can be safely concluded that stainless steel nails do not corrode in thermally modified ash or oak. This is in line with previous results that have shown that stainless steel fasteners exhibit little to no corrosion in preservative-treated and untreated softwoods [34].

3.2. Carbon Steel Fasteners

The corrosion rates of carbon steel fasteners and hot dip galvanized fasteners are presented in Figure 1. In general, the error bars showing the standard deviations are very large. The standard deviations are higher than our previous work on preservative-treated softwoods [35]; these differences are attributed to difficulties in driving the fasteners into the wood without causing splitting near the fastener or otherwise damaging the fastener. Despite the fact that error bars are too large to find statistically significant differences in most cases, the mean corrosion rate appears to exhibit some trends. For instance, for the untreated wood species, it appears that the corrosiveness of ash and pine are similar and that they are both less corrosive than oak.

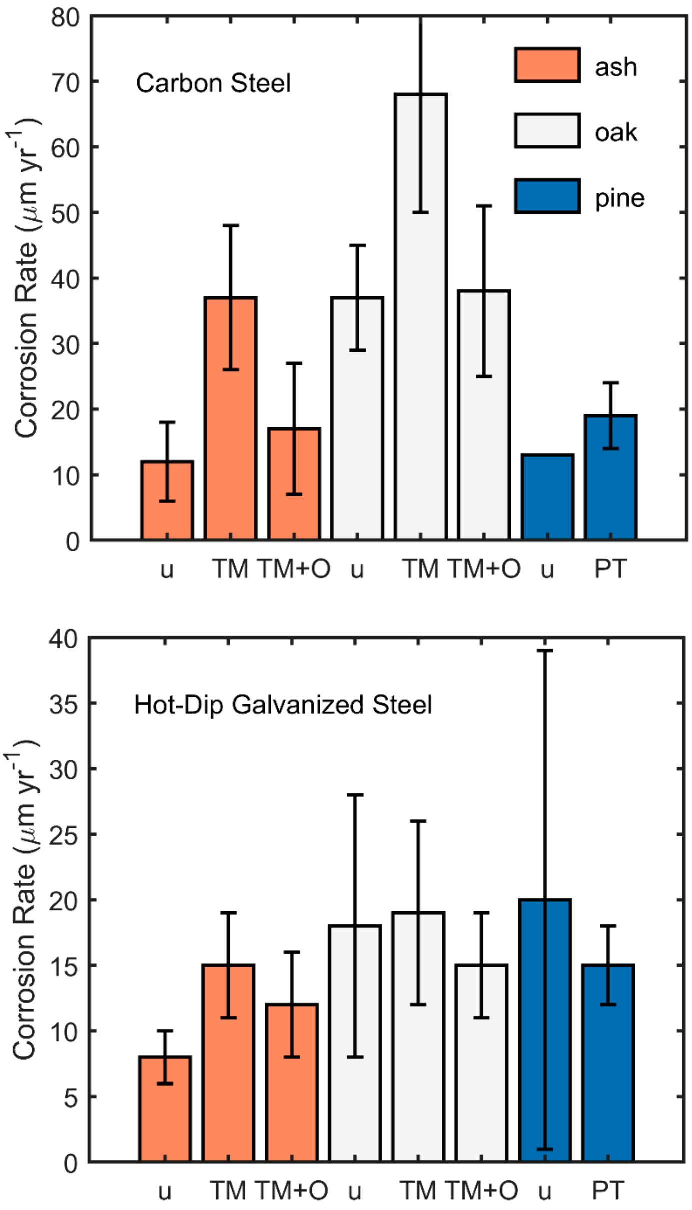


Figure 1. Corrosion rates measured for hot-dip galvanized and plain carbon steel fasteners in ash, oak, and pine. Legend: u = untreated, TM = Thermally Modified, TM + O = Thermally Modified with Oil treatment, PT = Preservative Treatment. The error bars represent the standard deviation. Note the different *y*-axis scales.

The measured values for corrosion of steel nails in untreated pine is slightly higher than previously measured in previous studies under the same conditions (13 µm year^{-1} as opposed to 5 µm year^{-1}) [22,46]. Likewise, the measured corrosion rate of 20 µm year^{-1} for the preservative-treated wood (a micronized copper azole) is higher than previously measured values of 11–13 µm year^{-1} for copper azole and micronized copper quaternary preservatives [35]. There are slight metallurgical differences in the carbon steel fasteners used in these studies; in the fasteners used in the present study, they contain more carbon than those used in the previous study (UNS G10180 as opposed to a UNS G10140). However, according to Kodama [54] different carbon steel alloys do not exhibit "remarkable (differences) in corrosion behavior". Therefore, it is likely that the corrosion differences are a result of different exposure conditions such as differences in moisture content, preservative treatment formulations, or preservative treatment retentions.

In addition to trends between wood species, the effect of thermal modification on corrosion can be observed by examining a single wood species. For both the ash and the oak, the thermal modification process increased the corrosivity of the wood. The mean corrosion rate of ash nearly tripled from 12 to 37 μm year^{-1} when comparing the untreated and thermally modified wood. Likewise, the corrosion rate of the oak also increased by more than 50% from 37 to 68 μm year^{-1}. The post-thermal modification oil treatment also appears to have an effect on the corrosivity of the fasteners, decreasing the measured corrosion rates of both the ash and the oak. The mean corrosion rates for the oil-treated specimens are 17 and 38 μm year^{-1} for the ash and oak specimens, respectively. These corrosion rates are very close to the mean values of the corrosion rates measured for the untreated ash and oak specimens.

3.3. Hot-Dip Galvanized Fasteners

The corrosion rate data for the hot-dip galvanized fasteners are also presented in Figure 1. Similar trends can be observed across the species and treatments as for the carbon steel fasteners; however, their effects are less pronounced. Similar to the carbon steel fasteners, the measured corrosion rate of untreated ash is less than that of oak. Furthermore, the oil treatment results in reducing the corrosiveness of the thermally modified wood. However, unlike the steel fasteners, the galvanized fasteners show less of an increase in corrosion with the thermal modification treatment. The mean corrosion rate of ash increased from 8 to 15 μm year^{-1} between the untreated and thermal modification treatment. In oak, the mean corrosion rates of the galvanized fasteners were 19 μm year^{-1} for both the untreated and thermal modification treatment.

3.4. Comparison of the Corrosion Rates of Hot-Dip Galvanized Fasteners and Carbon Steel Fasteners

In previous work on preservative-treated softwoods, it has been observed that galvanized fasteners exhibit a higher corrosion rate than carbon steel fasteners [34,35,46,50,55]. This is in contrast to atmospheric corrosion where hot-dip galvanized products corrode much more slowly than steel. The local environment makes a large difference in whether or not galvanized products corrode more slowly than carbon steel. For atmospheric corrosion, drying cycles allow a passive film to form which protects the remaining zinc coating from rapid corrosion [56,57]. In previous corrosion testing of galvanized fasteners in softwoods, these corrosion products were not found, and galvanized fasteners corroded more rapidly than steel [35].

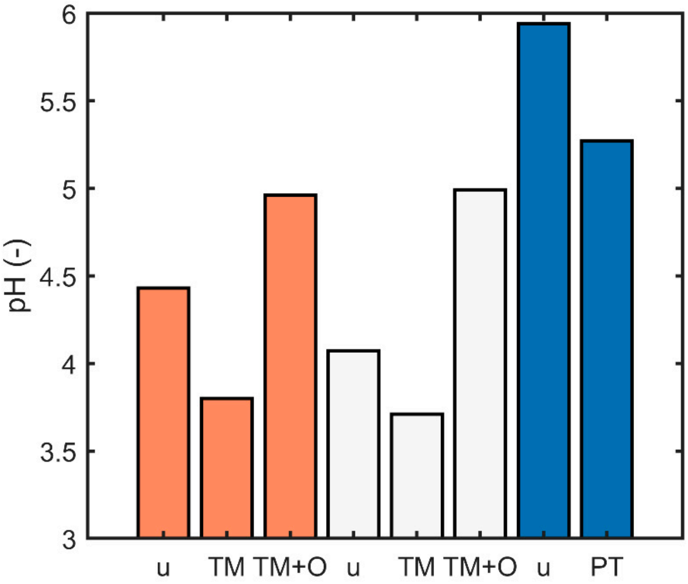
It appears in the hardwoods that galvanized steel corrodes more slowly than carbon steel. This can be seen most clearly for oak, where the corrosion rate for carbon steel (37 μm year^{-1}) was nearly double that of galvanized steel (19 μm year^{-1}). Galvanized steel also corroded more slowly than carbon steel across the thermal modification and oil treatments (Note that in this study, the mean corrosion rate of galvanized steel was slightly lower than that of carbon steel, however, the results are not statistically different and contradict the previous literature. The remainder of the discussion comparing the different treatments and species compares the results to the literature values in treated pine). Therefore, one important finding of this study is that galvanized steel corrodes more slowly than carbon steel in hardwoods whereas it generally corrodes more rapidly in preservative-treated wood. The corrosion mechanism in treated wood involves the reduction of cupric ions from the wood preservative. Since zinc is less thermodynamically stable than steel in the presence of cupric ions, it could be that this larger driving potential is accelerating the kinetics in preservative-treated wood. Limited data has shown that galvanized steel also corroded more rapidly than carbon steel in untreated pine, however, the absolute values of these corrosion rates were small, the error bars high, and the results statistically uncertain. This study has highlighted how little is known about our understanding of the corrosion rates in different metals in untreated wood species. Beyond scientific importance, quantifying the relative corrosion rates of different metals is incredibly important for materials selection, as materials that work well in pressure-treated pine may not work well in hardwoods.

3.5. Comparison of the Wood Species and the Effect of pH and Tannins

Zelinka and Stone [48] developed a model to explain differences in the corrosion of metals embedded in untreated wood of different species. Their model was based on corrosion rates measured electrochemically in water extracts of wood. While this method was shown to give similar corrosion rates to those measured in solid wood for preservative-treated wood, corrosion rates in the extracts are much higher in untreated wood. Despite this, Zelinka and Stone developed a model that could predict the *relative* corrosiveness of the wood species from the total amount of tannins in the wood and the pH of the wood, as measured by the pH of the extract. Tannins were included in the model because they were shown to act as corrosion inhibitors. The model treated the effects of tannins and pH as orthogonal and showed that the pH only increases the corrosion rate below a pH of 5.

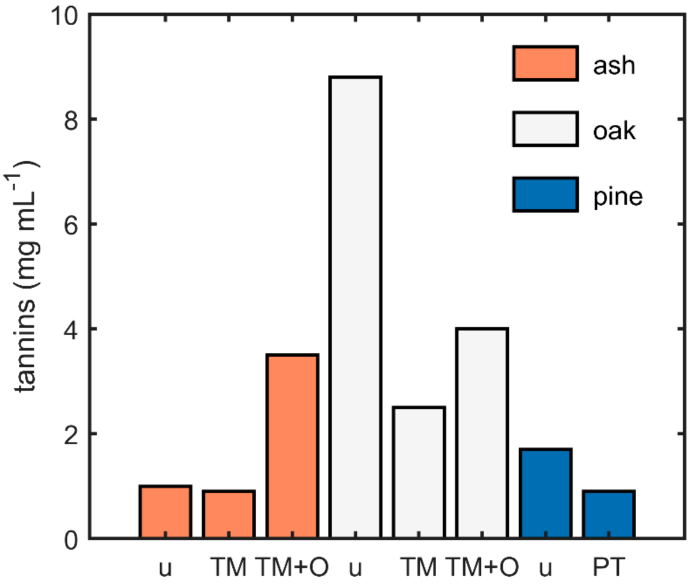
Both the pH and tannin concentrations were measured on water extracts of the different wood species and treatments; results are shown in Figure 2. For the unmodified woods, oak was more acidic than the ash but also contained more tannins. The increase in the corrosiveness of the oak compared to the ash can be explained by the lower pH.

The pH and tannin concentrations also correlated nicely with the corrosion data across the thermal modification and oil treatments. The thermal modification results in the wood becoming more acidic and at the same time, removes or destroys some of the soluble tannins available in the untreated wood. Both of these would be expected to create a more corrosive environment towards embedded fasteners, which was observed for both steel and galvanized steel in both wood species (Figure 1). Furthermore, the oil treatment greatly raised the pH of both the oak and the ash so that the pH was higher than the unmodified wood. The oil treatment also appears to raise the tannin level of the wood, either through solubilizing polyphenols in the thermally modified wood or the oil treatment which contains tannins itself. As a result, the pH of both the ash and oak was higher than the modified wood and the observed amount of tannins were much greater than the thermally modified material. As expected, this correlates with a decrease in the observed corrosion rates with the oil treatments (Figure 1).



(**a**)

Figure 2. *Cont.*



(**b**)

Figure 2. pH (**a**) and concentration of tannins (**b**) found in the different wood treatments. Legend: u = untreated, TM = Thermally Modified, TM + O = Thermally Modified with Oil treatment, PT = Preservative Treatment.

Beyond the aforementioned study, it is difficult to place the corrosion data collected in this study in the broader literature as very little quantitative corrosion data has been published for hardwoods. Smith [58] published a table ranking wood species from "most corrosive" to "least corrosive but did not list corrosion rates or a methodology of how the table was constructed. Similar qualitative rankings were developed by Farmer [59] and Bartel-Kornacka [60]. Knotkova-Cermakova and Vlckova [61] did compare the corrosiveness of oak and ash; however, in their study, they did not examine the corrosion of embedded metals. Instead, they examined the corrosion of metals in sealed containers with high humidity and wood veneers. They found that in these conditions, the corrosion rate of steel in oak vapors was 120 µm year^{-1} and that of ash was 35 µm year^{-1}. The ratio between the corrosion rates of these two species (3.5) was similar to the ratio of the corrosion rates measured in this study (2.9). Given that the results of [61] were attributed to acid vapors produced by the wood, and similar results were observed between the two species groups in both studies, it suggests that the acidity of the wood may play a large role in the corrosiveness of embedded fasteners.

4. Conclusions

This paper examined the effect of a thermal modification and oil treatment on the corrosion of embedded fasteners for their potential use in outdoor structures. The data show that thermal modification makes the wood more acidic and increases the corrosiveness of both ash and oak. However, the post-thermal modification oil treatment reduces the corrosivity of the wood of the thermally modified wood by raising the pH and increasing the water soluble tannin content. For galvanized steel, the range of corrosion rates in thermally modified wood was similar to those measured in pressure-treated southern pine. However, carbon steel fasteners in thermally modified oak and ash exhibited higher corrosion rates than in pressure-treated wood.

In all wood species and treatments, stainless steel fasteners exhibited negligible corrosion. It is likely that stainless steel fasteners will not corrode in thermally modified wood in service. For the hardwoods, galvanized steel fasteners exhibited lower corrosion rates than steel fasteners, regardless of the thermal modification or oil treatments. This is in contrast to previous studies on preservative-treated wood where galvanized fasteners corroded significantly faster than steel fasteners. From a materials selection standpoint, if stainless steel fasteners cannot be used, hot-dip galvanized fasteners are preferable to carbon steel fasteners.

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