Effects of ozone treatment on fungal growth, chemical components and surface morphological characteristics of wood flooring materials

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SUMMARY
The effects of ozone treatment and extraction on fungal activities of bamboo and red-oak flooring materials have been investigated. One set of wood samples was extracted with cyclohexane and ethanol for 48 hours to remove extractable compounds. Another set of materials was exposed to ozone (2000 ppbv ± 63 ppbv) for five days. Solvent-extracted and ozone-treated samples were incubated in closed chambers at 85 % ± 2 % RH and 30 ^{o}C ± 1 ^{o}C. They were removed at regular intervals for fungal growth evaluation. Ozone treatment caused slight changes in chemical components of these two woods. For example, degradation of lignin components was observed as the decrease in IR bands in a region of 1450 cm^{-1} to 1610 cm^{-1}. Also, ozone-treated and control bamboo samples were slightly covered with mold after ten weeks of exposure to the humid environment, while no visual fungal growth is reported on extracted samples until two weeks after, probably because the extraction removed some components that limit fungal growth. Oak samples showed no evidence of mold growth during the same exposure period, suggesting that oak contains some inhibitory components to fungi.

IMPLICATIONS
Utilizing and investigating lignocellulose as renewable building materials are gaining increased public interest. However, color changes, physical and microbiological degradation can occur when woody materials are exposed to environmental conditions, such as ozone and humidity. The study objective is to assess the effect of ozone treatment and extraction on chemical components and morphological characteristics using various techniques in order to better understand the degradation processes on some common wood surfaces.

KEYWORDS
Fungi, Extractives, Ozone, Bamboo, Oak

INTRODUCTION
Selection of building materials depends on many criteria, for example, low volatile organic compound (VOC) emission, durability, and recyclability. For cellulose-based building materials, their susceptibility to mold growth is of significant concern. A number of studies have been shown mold growth on various products, e.g., plasterboards; cellulose insulation, cellulose containing ceiling tiles; particleboards, wood-based flooring materials [Herrera 2005; Dillavou et al. 2007; Karunasena et al. 2000]. A recent study by Hoang et al. 2010 pointed out the high susceptibility to mold growth of cellulose-rich materials after direct water exposure or following high humidity exposure. Their results illustrated that different woody materials supported mold growth at different levels and chemical composition of each material could be a major factor, as some wood contains natural antifungal compounds that prevent or minimize fungal growth. In fact, it is not easy to define chemical properties of

wood-based materials due to their complex heterogeneity of high molecular weight components, which principally contains cellulose (40 % to 50 %); lignin (15 % to 35 %); hemicellulose (20 % to 35 %), and solvent-soluble extractives (3 % to 10 %) such as terpenes, tannins, aromatic and aliphatic acids [MacDonald et al. 1969]. Recently, ozone has been promoted to disinfect buildings because it has been shown that high ozone levels (1000 ppm_v to 2000 ppm_v) can deactivate fungal spores [Currier et al., 2001; Palou et al., 2003]. However, reactions of ozone with material surfaces are of concerns as they are potential sources for secondary volatile organic compounds and particle formation [Poppendieck et al. 2007]. In the paper industry, ozone is usually used for deligninfication of wood products since it is seen as a strong reactant to break down lignin [Kobayashi et al. 2005].

Little information currently exists regarding the effect of ozone reaction and extraction on changes in surface chemistry and morphology of woody materials. The objectives of this study are:

- to investigate the fungal susceptibility of two different woody flooring materials: bamboo and oak hardwood.
- to determine the effect of wood extractives on fungal growth.
- to evaluate the fungal resistance of ozone treated wood surfaces.

METHODS

Bamboo and oak flooring materials were selected for this study. The materials were purchased from a local vendor and then stored in zip-locked bags before experiments. The materials were cut to identical sizes 2.3 cm x 2.3 cm and treated either with ozone or with a mixed solvent as described below:

Ozone treatment: material samples were placed in a 4-little glass flask which was ventilated continuously with the air containing 2000 $ppb_v \pm 63$ ppb_v for five days. Changes in functional groups on material surfaces by ozone were determined by using infrared spectra recorded using Attenuated Total Reflectance (ATR) spectroscopy. To avoid the spectral difference caused by external factors, such as contact pressures, all wood spectra were normalized to the 1030 cm^{-3} band, which is less likely to change during the treatment [Collom et al. 2003; Muller et al. 2003].

Solvent extraction: another series of material samples was treated with a mixture of cyclo-hexane and ethanol in a soxhlet extractor. The extraction procedure was adjusted from the ASTM D1105-96 standard with a slight modification of the solvent content (cyclo-hexane: ethanol = 2:1 by volume). The process was conducted for three days with about 12 cycles per day. When the extraction was completed, extracted specimens were used assessed for fungal resistance. The remaining solvent was collected and dried until a constant weight to determine the percentage of extractive in the products. Also component groups in extracts were analyzed using a GC/MS.

Both ozone treated and solvent extracted samples were then incubated in conditioning chambers with a relative humidity of 85 % ± 2 % and temperature of 30 ^oC in order to evaluate the effect of ozone treatment and extraction on the fungal resistance of wood materials. It is important to note that control samples, which were not treated with either ozone or cyclo-hexane/ethanol, were incubated in similar chambers. All materials were monitored periodically over a period of 3 months with a light microscope to detect fungal growth on material surfaces. In addition, to better understand the moisture sorption of both materials, IGASORP Sorption Analyser was utilized to determine the equilibrium moisture contents at each 10 % RH step. It is important to note that all experiments were conducted in duplicate or triplicate with the exception of moisture isotherm experiments. The moisture isotherm analyzer has a published accuracy of less than 5 % .

RESULTS

Figure 1 presents mold growth on back surfaces of bamboo materials for several incubation time steps (Week 0, Week 11 and Week 13). Visible fungal growth was observed after Week 10 on control and ozone-treated samples, while no fungi was detected on solvent-treated samples until Week 13. It also appears that more fungi grew on ozone treated samples than on control or solvent-extracted specimens. Further analysis is needed to verify this observation. Interestingly, none of oak specimens showed fungal growth on back surfaces (data not shown).

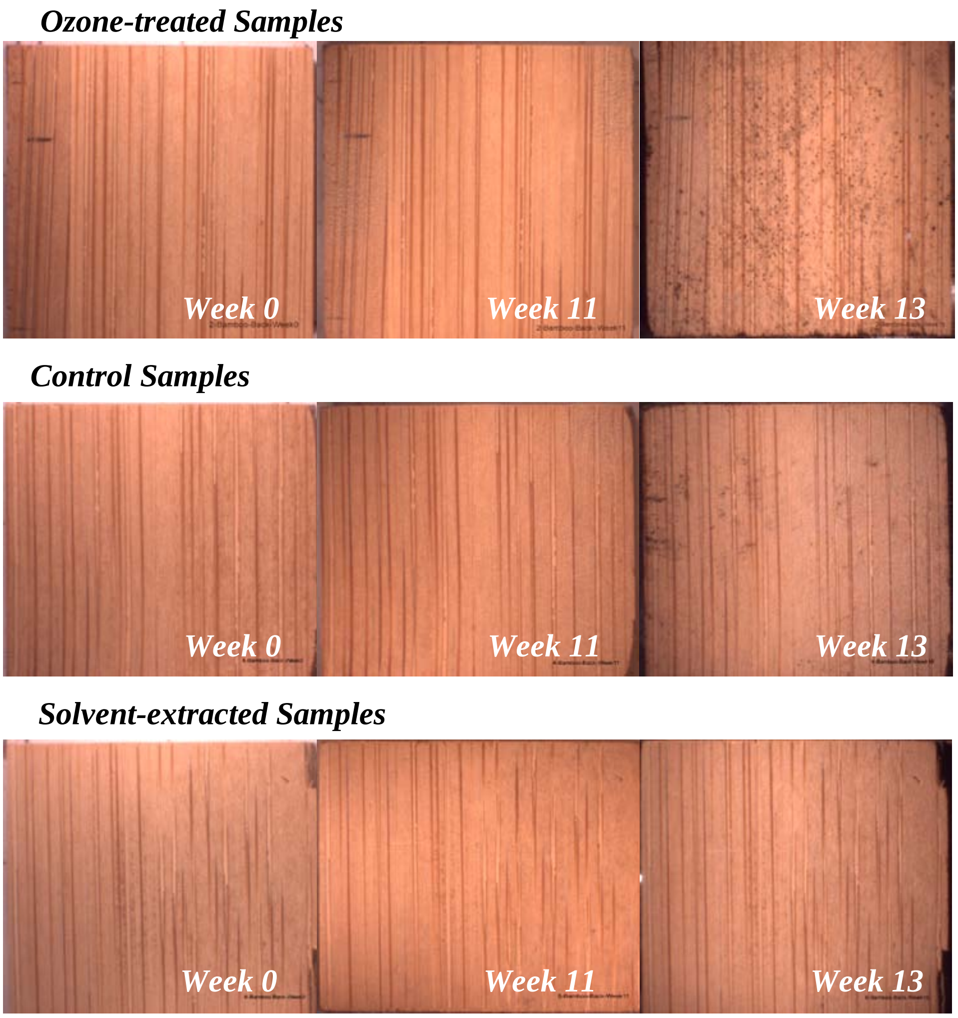

Figure 1: Fungal Growth Observation on Back Surfaces of Bamboo Flooring Materials

Water Uptake

The moisture adsorption isotherms of untreated oak and bamboo samples, measured at 30 ^{o}C and atmospheric pressure, are displayed in Figure 2. Both materials showed the same sorption pattern as a function of humidity. It is interesting to note that bamboo takes up less water than oak in the RH range between 0 % to 70 %. However, the rate of moisture uptake in bamboo is greater than that in oak with higher RH, ranging from 70 % to 90 %, which results in a crossover between the two sorption isotherms. This finding is important for indoor application, such as flooring, because water content in bamboo is less than that of oak in a typical indoor environmental condition. However, the opposite will be found in a very high humidity environment.

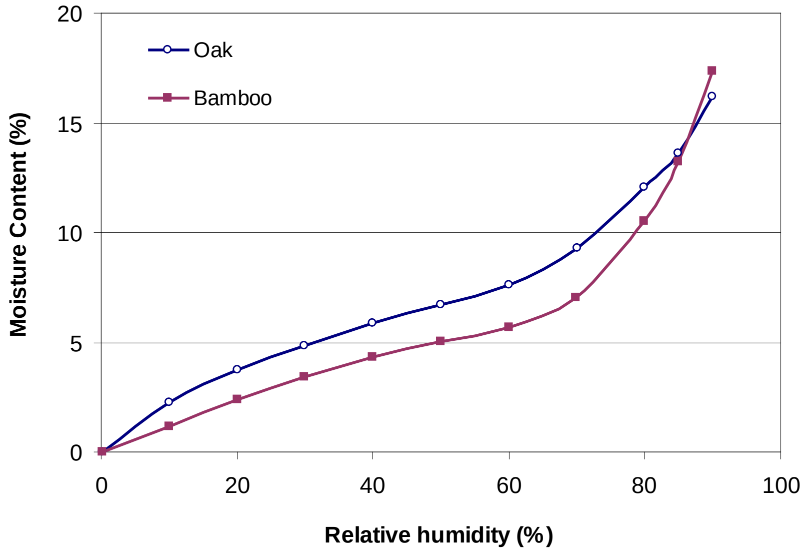

Figure 2. Isotherm Diagram at Temperature of 30°C.

Infrared Spectra of Wood Products

Figure 3 shows the IR spectra of untreated and ozone treated oak samples. The difference spectrum between two samples is shown with the bold line, with the positive peaks representing the increase and vice versa. The same observation was found for bamboo materials. It is quite clear that after ozone treatment, slight changes were observed on wood materials. An increase in intensity was shown on strong broad stretching in hydroxyl (OH) groups (3350 cm^{-1}), and C-H stretching in the 2920 cm^{-1} – 3000 cm^{-1} region. Bands in the region of 1750 cm^{-1} and 1040 cm^{-1}, in contrast, presented a reduction in intensity. This decay appeared to represent the degradation of lignin and cellulose components by ozone treatment.

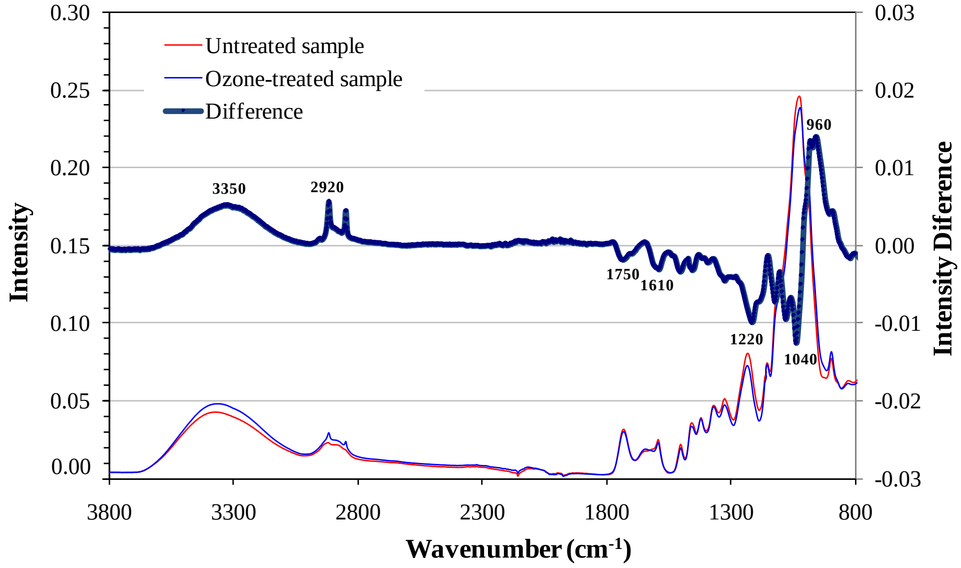

Figure 3. FT-IR Spectra of Untreated and Ozone-treated Oak

Extractive Components of Wood Products

The GC/MS results showed that extractives make up about 3.4 % ± 0.4 % and 2.6 % ± 0.3 of dried material mass for oak and bamboo respectively. Also, vanillin, furfural components, syringylaldehyde, and other phenolics were found in oak extractives while bamboo extractives include benzoic acid, decanal and other aldehydes.

DISCUSSION

Under favorable environmental conditions (e.g., RH = 80 % to 90 %; temperature = 30 ^{o}C), fungal spores will germinate if nutrients are provided (either from material components or external sources). It is clear that different materials support fungal growth at different level, as some materials provide "food" that are easily broken down by fungi while others contain toxic compounds that may inhibit fungal growth [Hoang et al. 2010]. In this study, fungal growth was evident on bamboo samples after 10 weeks of incubation in humid chambers, while oak, on the other hand, showed no support to fungal growth. A possible reason is that oak flooring materials contain vanillin and other phenolic components that can deactivate fungal spores [López-Malo et al. 1997]. Bamboo, however, is well known as susceptible to fungi due to its abundant starch and sugars [Li 2004, Zhang et al. 2010]. In addition, sorption isotherm shown in Figure 2 indicated that at the experimental condition (RH = 85 %; temp. = 30 ^{o}C), bamboo can uptake moisture faster and contain higher moisture content than oak. Hoang et al. 2010 presented the positive correlation of mold growth rate in the cellulose-based materials with their equilibrium moisture content [EMC]. In other words, materials with higher EMC appear to be more susceptible to mold growth. EMC may therefore be used as an indicator to evaluate the risk of mold growth in cellulosed-based materials.

Another interesting observation on fungal growth was found among different bamboo samples. Ozone treated specimens produce more visible fungal biomass than others under the same experimental condition. This finding suggests that ozone treatment may break down some wood components and produce more favorable compounds to fugal growth. For example, IR spectra in Figure 3 show lignin degradation after ozone treatment which may make the wood materials more susceptible to fungal attack. In addition, considerably less growth was observed on solvent extracted specimens; even it took longer for fungi to start germinating on these samples. It is possible that some fungi-favored component was extracted out. The same observation was seen in a recent study by Zhang et al. 2010. They found some different bamboo species contains extractives that could promote bamboo biomass infested by fungi No specific components are discussed at this point, suggesting further research is desirable.

CONCLUSIONS

The study has shown that internal components, e.g., extractives, play a key role on fungal resistance of wood materials. For instance, oak contained inhibitory compounds, such as vanillin, that increase the resistance to fungal growth. Ozone treatment slightly changes chemical components of materials by decomposing some high molecular weight compounds, such as lignin and cellulose. It is suggested that these impacts should be taken into account if ozone is selected as a building disinfectant. Further research is required to have a firm conclusion on the effect of ozone on the susceptibility of wood materials to fungal growth.

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