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ORIGINAL RESEARCH

Testing the durability of copper based preservative treated bamboos in ground-contact for six years

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Abstract In this study, durability of bamboo samples in terms of the variability of location along culm height (top, middle and bottom) were evaluated in a ground-contact field test for six years in comparison to Scots pine and beech wood samples. Bamboo and wood samples were treated with Wolmanit-CB (CCB) and Tanalith-E (Tan-E) solutions, and then were installed in a field located in the North-West of Turkey. The decay resistance of samples was assessed by weight loss, and compared by SEM observations and FTIR analysis. Furthermore, chemical leaching from the samples was detected by ICP-OES after the test. Results showed that un-treated bamboo and wood samples had a very low durability such that weight losses were found as 64–80% for bamboo and 57–63% for wood samples. The SEM micrographs showed the characteristics decay patterns of soft-rot type I and brown-rot fungi in the parenchyma cells, vessels and fibers in vascular bundles. Fungal hyphae within the cell walls resulted in the gradual breakdown of the cell wall layers. FTIR analysis revealed the mechanism of the biodegradation, which indicates the reduction of carbohydrate content. The weight loss in CCB and Tan-E treated bamboo samples was reduced as 20–45% depending on bamboo height parts, but the wood preservatives did not ensure sufficient resistance for six years against soil degrading organisms since more than half of the chemical amount leached out from the bamboos to soil. Weight losses were well confirmed by chemical leaching rates for both CCB and Tan-E. It was observed that the lower parts of the culm were more durable, which was also in accordance with ICP-OES and SEM analysis. Copper-based preservatives seemed to be more efficient in pine and beech wood samples than bamboos since the impregnability of bamboo was much lower than that of wood.

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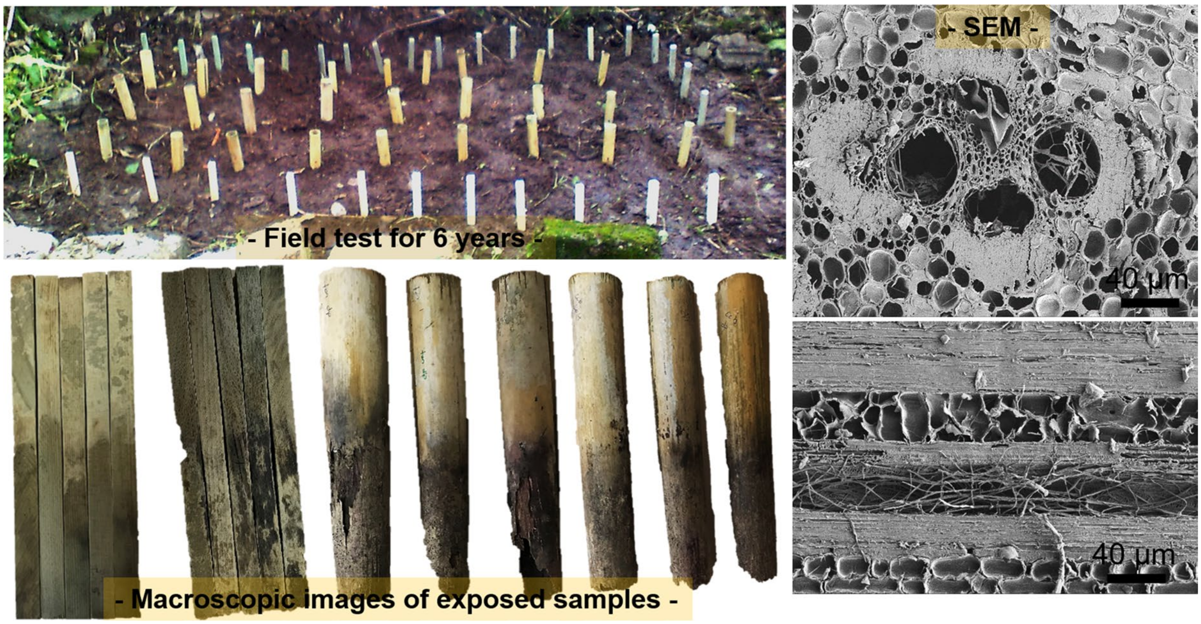
Graphical abstract



Keywords Ground-contact · Bamboo · Copper-based preservatives · Decay · Leaching

Introduction

There is an increasing demand for the limited forest resources in various applications, thus novel researches are needed to investigate new materials that can be an alternative to wood. Bamboo with high fiber content is the fastest growing woody plants in the world, which reaches maturity in 3–5 years (Sun et al. 2012; Li et al. 2017; Ju et al. 2021). However, the products of bamboo are susceptible to environmental degradations such as ultraviolet (UV) rays (Baysal et al. 2016; Topaloglu 2019), mould (Sun et al. 2011, 2012; Li et al. 2017) and decay fungi, and insect attacks (Schmidt et al. 2011, 2013; Wei 2014; Kaminski et al. 2016; Tang and Trinh 2019; Gauss et al. 2021a) during storage, transport and final utilization areas (Wei et al. 2013). Those factors shorten service life of the bamboo products, and reduce its value in market, and lead wastage of bamboo resources (Sun et al. 2011, 2012; Li et al. 2017).

The bamboo culms comprise about 50% parenchyma, 40% fibers and 10% vessels and sieve tubes (Kumar et al. 1994). Fungi and insects easily degrade the bamboos in hot and humid environment due to the parenchyma cells which are filled a high amount of starch (2–6%), sugar (2%), protein (1.5–6%), fat (2–4%) and low contents of resin, wax and tannin (Kumar et al. 1994; Sun et al. 2011; Ju et al. 2021; Gauss et al. 2021a). Certain beetles are attracted by the starch in bamboos, and the larvae fed along the culm. Termites and fungi are also attracted by the starch in bamboos, and break down the cellulose by enzymes (Kaminski et al. 2016). Bamboos have lower durability compared with wood (Liese 1980). Variation in durability of bamboos depends on the length of the culm and the thickness of the wall. The lower parts of the culm are considered more durable, while the inner part of the wall degrades faster than the outer parts, which is probably related to the anatomical and chemical nature of the cells (Liese 1980; Kumar et al. 1994). Laboratory decay tests indicated that bamboos are more prone to both soft rot and white rot attack than to brown rot (Liese 1980; Kumar et al. 1994; Wei 2014; Mehramiz et al. 2021). It was reported that un-treated bamboo has a service life of only 2–5 years (Kaur et al. 2016a). Therefore, bamboos require essential preservation treatments before their final usage as a structural building material (Gauss et al. 2019).

Several traditional and simple treatment options such as soaking for several weeks in water (which leaches out some of the starch), smoking (which provides a light protective layer) and surface coating (which provides some protection against water) are used. Unfortunately, all these methods have limited effect to ensure durability (Kaminski et al. 2016). Various bamboo treatments such as chemical and natural preservatives, heat, and oleo-thermal treatments have been demonstrated in both academic and industrial levels (Wang et al. 2018; Gauss et al. 2021b). Many researchers have extensively investigated treatments of bamboo with different chemicals such as ZnO (Li et al. 2017), chitosan-copper complex and organic fungicides (Sun et al. 2012), ZnO/graphene (Wang et al. 2018), chitosan-copper complex (Tang and Trinh 2019), citric acid, formic acid, propionic acid and sorbic acid (Tang et al. 2009) against mould fungi, silver (Ju et al. 2021), tannin-boron based preservative (Gauss et al. 2021a), propiconazole (Mehramiz et al. 2021) against decay fungi, cashew nut shell liquid (Falemara et al. 2018), various plant extracts and oil based formulations such as organic acids, essential oils and eco-friendly chemical based formulations (Kaur et al. 2016a) against decay fungi and termite attacks. Ammoniac-copper-quaternary (ACQ), borax-boric acid (BBA) and copper-chrome arsenate (CCA) were examined with unsterile soil laboratory burial tests by Razak et al. (2007). Beside these laboratory tests, field exposure tests were also performed to examine the durability of bamboos for exterior purposes. Decay and termite resistance of bamboo were studied after 32 months of field exposure in Hilo, Hawaii, and bamboos were found to be unsuitable for exterior exposure without some type of supplemental treatment by Morrell (2011). Razak et al. (2002) exposed the bamboos in a field for 24 months, and found that un-treated and in-effectively treated culms decayed extensively. Wei (2014) exposed the bamboos to soil in field for 3.5 years, and reported that a soft-rot decay was outer layer while a white rot was assumed in the center. A field-test of chitosan-copper complex (Tang and Trinh 2019), copper based wood preservatives (AC450) and borax/boric acid (Odour et al. 2010) treated bamboos, and an oil heat treated bamboos (Razak et al. 2004) were also performed. Kaur et al. (2016b) reported that the traditional water leaching method and smoking method, and plant extract treatments of bamboo were able to provide better protection than un-treated bamboo but full protection in field was not achieved with these methods. Un-treated bamboos were damaged up to 60% within 3 months, and completely destroyed within 6 months of exposure to termites.

Ground-contact field tests are one of the most important ways to understand the durability of wood in end use applications (Mattos et al. 2014). Furthermore, field tests which ensure more realistic conditions (Meyer et al. 2014) such as climatic conditions and soil microflora can influence the durability of wood in-ground-contact (Brischke et al. 2014). Therefore, field tests are required to draw a comprehensive conclusion regarding bamboo durability (Mehramiz et al. 2021). As detailed above, literature offers some studies dealing with the durability of treated bamboos in field exposure tests (Razak et al. 2002; Razak et al. 2004, 2005; Odour et al. 2010; Morrell 2011; Wei 2014; Kaur et al. 2016b; Tang and Trinh 2019). The large body of literature data is not always consistent due to the variability of the bamboo species and microorganisms. Moreover, sampling, the cutting season, moisture content and the age of the plants influence the results (Schmidt et al. 2011).

Based on the above considerations, the present study is aimed to investigate the durability of CCB and Tan-E treated bamboos in ground-contact field test for 6 years. Weight losses were evaluated for three parts (top, middle and bottom) of bamboo culms along with height. The exposed samples were characterized by scanning electron microscopy (SEM), inductively coupled plasma (ICP-OES), and Fourier transformation infrared (FTIR) spectroscopy. Two wood species (a soft and a hardwood) were also studied to determine their differences in durability in terms of weight loss. To the best of our knowledge, there has been no prior comprehensive study dealing with 6 years field performance of CCB and Tan-E treated bamboos which are taken from 3 portions along culm height.

Table 1 Dimensions of bamboo culms without node section

Bamboo parts	Length (mm)	Diameters (mm)	Wall thickness (mm)
Bottom	295.3 (27.3)*	41.90 (1.24)	4.54 (0.82)
Middle	275.5 (10.4)	37.34 (1.40)	3.76 (0.46)
Top	270.2 (10.8)	32.78 (2.45)	3.10 (0.38)

*Values in parenthesis are standard deviations

Materials and methods

Preparation of samples and impregnation process

Bamboo (*Phyllostachys bambusoides* Sieb. et. Zucc.) culms, and Scots pine (*Pinus sylvestris* L.) and beech (*Fagus orientalis* L.) sapwood were obtained from Trabzon located in the North-East Black Sea region of Turkey. The bamboo culms with bottom diameters (D) of 45 mm and top diameters of 30 mm were cut at about 10 cm above the ground and 8–9 m was taken from the remaining upper portion. Subsequently, it was subdivided into three portions (approximately 3 m at each portion) containing both nodes and internodes along with the diameters of the culms labeled as bottom (D: 41–45 mm), middle (D: 36–40 mm), and top (D: 30–35 mm). Node sections of the culms were removed because the nodes have a complex structure and decrease mechanical properties (Tomak et al. 2012). Average dimensions of bamboo culms without node sections are shown in Table 1. Sapwood of Scots pine and beech was sawn into 20×20×300 mm (R, T, L) dimensions. Bamboo and wood samples were then conditioned in a conditioning room at 20 °C and 65% relative humidity for 4 weeks.

Copper based wood preservatives with low toxicity and high efficiency are widely used in worldwide. They are well-fixed into the bamboo, and can be used in ground-contact applications (Kaminski et al. 2016). The CCB (Cu/Cr/B) is one of commercial preservatives used to impregnate wood in utilization class of HC-4. It is composed of copper sulfate ($CuSO_4{\cdot}5H_2O$, 12.2%), copper II oxide (CuO, 1%), boric acid (H_2BO_3, 25%), chromium (VI) oxide (CrO_3, 5.5%), natriumdichromat ($Na_2Cr_2O_7{\cdot}2H_2O$, 30.3%), and water (7.2%). Tan-E (copper azole) is also one of the widely used copper based wood preservatives in utilization class of HC-4 that replaced instead of CCA (Cu/Cr/As). It is composed of copper carbonate (22%), copper hydroxide 2-aminoethanol (47%), triazole derivative (< 1%) and boric acid (< 5%). CCB and Tan-E were obtained from Emsan Company and Hemel Company in Turkey, respectively. Aqueous solutions of 3% wood preservatives were prepared using distilled water at a room temperature. Ten replicate bamboo and wood samples were used for each treatment.

Table 2 Climatic parameters of Biga, Canakkale between the years of 2013–2019

Parameters	2013	2014	2015	2016	2017	2018	2019/Jan
Frosty days (temp. < -0.1 °C)	26	12	31	37	33	14	4
Stormy day	7	5	6	8	2	3	0
Rainy day	98	121	98	89	91	116	16
Avg. total rainy (mm = kg/m^2)	48.43	71.77	52.42	45.59	58.87	71.52	123.10
Avg. min. temp. (°C)	9.51	10.21	10.04	9.86	9.16	10.90	3.20
Avg. max. temp. (°C)	21.07	20.89	20.63	22.34	21.62	22.06	11.60
Min. temp. (°C)	3.88	4.38	3.80	2.87	3.30	5.38	-4.60
Max. temp. (°C)	27.78	28.17	28.15	30.46	29.53	28.02	18.90
Avg. temp. (°C)	14.88	15.15	14.88	15.72	14.92	16.05	6.70
Min. relative humidity (%)	14.83	23.83	26.25	26.83	26.25	33.00	41.00
Max. relative humidity (%)	99.67	99.92	99.67	100.00	100.00	99.75	100.00
Avg. max. relative humidity (%)	94.51	97.88	94.72	94.65	94.88	95.68	96.80
Avg. min. relative humidity (%)	48.78	54.88	52.82	47.68	50.99	57.28	66.50
Avg. relative humidity (%)	75.99	83.74	77.93	74.73	76.52	80.17	86.20

The samples were immersed in the solutions for 336 h at atmospheric pressure. Samples were weighted for the chemical uptake after removing any excess solution from the surfaces. Then, samples were wrapped in plastic bags for one week at the room conditions to complete the fixation of copper based preservatives into samples. Samples were conditioned again at 20 °C and 65% relative humidity for 3 weeks.

Field test

The field exposure was started in January 2013, and was finished in January 2019. The test field (27°15′ E and 40°13′ N) located in Biga, Canakkale, Turkey where the climate is warm and temperate with a high humidity rates. Climatic parameters of the location were obtained by Turkish State Meteorological Service, and are summarized in Table 2. Ten replicate samples for each group were inserted in the soil to approximately half of their length at a distance of 300 mm from each other, in accordance with EN 252 (1990). The distribution of the samples per group was made randomly. Weight loss of the samples (%) after the test were recorded based on the initial dry weights of samples at the end of the test.

Chemical leaching during the field test

The chemical content of both exposed and un-exposed samples was measured using Inductively Coupled Plasma (ICP) analysis, using an ICP spectrometer (ICP-OES, Pelkin Elmer) after the microwave digestion. For this purpose, samples were taken from each sample at 4 cm above the groundline and 2 cm below the groundline (AWPA E7, 1993), and milled in a Wiley mill with a mesh size of 0.5 mm (IKA MF10) for the analysis. Chemical leaching rate (%) from the samples during the field exposure of 6 years was calculated after ICP analysis.

ATR-FTIR spectroscopic analysis

FTIR of samples was measured on wood powder by an ATR detector of FTIR equipment. The FTIR spectra were recorded between 400 and 4000 cm^{-1} wavelengths and with a 4 cm^{-1} resolution (32 spectra averaged) using a Bruker ATR-FTIR spectrometer. The spectra were baseline corrected and smoothed using the OPUS software (Bruker Optics GmbH, Ettlingen, Germany).

Morphological analysis by SEM

Morphological changes of the samples were investigated by using an (E) SEM device (Quanta 200 FEG, FEI Instruments, Hillsboro, OR, USA) with a large field detector (LFD) operated at 5 kV with a 8–12 mm sample-detector distance and a 3.0-nm spot size. Surfaces of samples were smoothed by microtome (LEICA RM2125 RTS, Wetzlar, Germany) cut and Pt/Au sputtered before measurement.

Statistical analysis

Preservative uptakes and weight losses of samples were statistically analyzed with Ona-way Anova test in IBM SPSS Statistic 25, followed by a Duncan's post hoc test.

Results and discussion

Preservative uptake of bamboo and wood samples

Table 3 shows the preservative uptake values (%) of the samples. Depending on bamboo height parts, preservative uptakes of bamboos were found to be 34.58–42.23% and 37.35–43.43% for CCB and Tan-E, respectively. In the case of S. pine and beech samples, uptakes were 53.04 and 41.15% for CCB, and 59.56 and 49.02% for Tan-E, respectively. There was a significant difference between the uptake values of

Table 3 Preservative uptake (%) of bamboo and wood samples

Wood preservatives		Bamboo	Scots pine	Beech
CCB	Bottom	34.58^{c*} (1.71)	53.04^{a} (2.07)	41.15^{b} (1.77)
	Middle	42.23^{b} (5.96)		
	Top	41.51^{b} (4.71)		
Tan-E	Bottom	37.35^{d} (2.75)	59.56^{a} (3.21)	49.02^{b} (2.25)
	Middle	42.99^{c} (2.18)		
	Top	43.43^{c} (2.39)		

*Different letters (a–d) within a line indicate significant difference by Duncan's homogeneity groups, $P < 0.05$

the samples according to Ona-way Anova test in IBM SPSS Statistic 25 ($P<0.05$).

Bottom parts of the bamboos absorbed less preservative than other parts of the bamboos, probable due to the cell wall thickness of the culms in bottom part. The reason may be also related to differences in the microstructure and chemical composition of different bamboo parts (Ju et al. 2021). The preservative penetration into a culm occurs preferentially in the longitudinal direction from both ends through the vessels. To a small extent, penetration also occurs through the intercellular cavity and the sieve tubes of the vessels (Liese 1980). Top parts of the bamboos have higher fiber and vessel amounts than bottom parts (Zakikhani et al. 2017), and so that the preservatives may diffuse more in top parts of culms. Middle and top parts absorbed statistically similar amount of preservatives. Higher uptakes were recorded for wood samples in comparison to bamboos such that S. pine had the highest uptake values. Sun et al. (2012) and Gauss et al. (2019) reported that bamboos have different structure and anatomy than wood has, and bamboos have not radial transport systems, which are very important for preservative absorptions. Kumar et al. (1994), Kaur et al. (2016a, b), Falemara et al. (2018) and Chi et al. (2020) also reported that the outer surface of bamboo is rich in wax layer and silica content, and the interior is lack of transverse conduction tissue such as xylem rays, which restricts preservative flow into the round culms. Similar findings were also reported by Lee et al. (2001), Baysal et al. (2016), Chen et al. (2018, 2021), Falemara et al. (2018) and Gauss et al. (2019). The bamboo used in this study has higher density than Scots pine and beech, (Tomak et al. 2012) which limits the maximum amount of solution that can be absorbed by the bamboos (Gauss et al. 2019). Tan-E was absorbed much than CCB for both bamboos and wood samples, which is the same as the previous research results for fir wood by Cavdar (2014).

Weight loss of bamboo and wood samples during field test

Figure 1 shows the weight loss of samples during the 6 years of field conditions including the combined effect of sun, rain, snow, weathering, and microbial and insect attack etc. Bamboos were more susceptible to decay than wood in accordance with a previous study (Kaminski et al. 2016). Weight loss caused by degradation factors in the field was found to be 35.93–58.83% and 39.53–56.10% for CCB and Tan-E treated bamboo samples, and 64.39–79.87% for un-treated (control) bamboo samples, respectively. Weight loss of CCB treated wood, Tan-E treated wood and control wood was 13.37, 14.02 and 56.69% for S. pine, and 20.13, 30.29 and 63.18% for beech, respectively. The above-groundline of the samples revealed a slight observable attack while the below-groundline areas showed a great degradation for both un-treated and treated bamboos. Razak et al. (2004) investigated strength and durability of an oil cured bamboos after 12 months of ground-contact test, and they found that 48, 40 and 4–34% weight loss

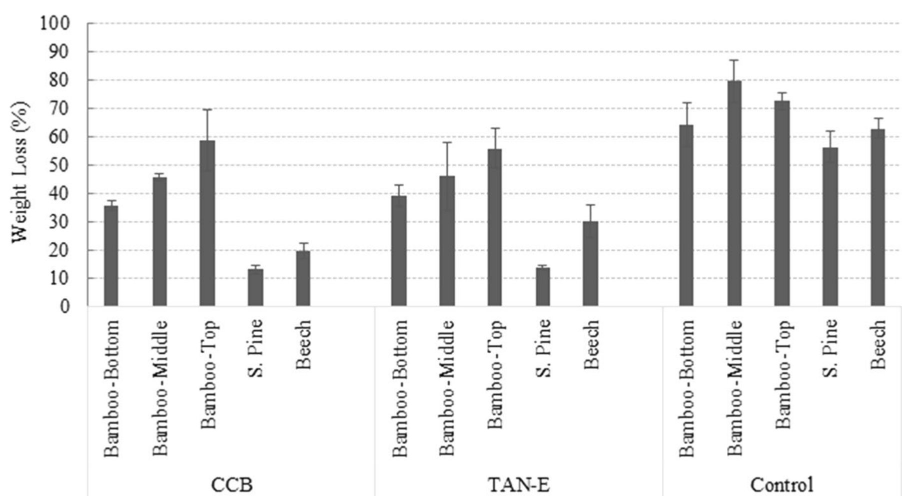


Fig. 1 Weight loss of bamboo and wood samples during 6 years of field test

for un-treated bamboo, rubberwood and oil-cured bamboos, respectively. Similar weight losses were also reported in another study by Razak et al. (2005). Singha and Borah (2017) found that 67.66% weight loss for un-treated (control) bamboos and 25.99% for treated bamboos (traditional methods) after field test.

Obviously, wood samples had greater decay resistance than bamboo samples. Lower decay rate in wood samples might be probably related to higher uptake of the preservatives in wood in comparison to that of bamboos. As been reported before by Liese (1980), preservatives diffuse from the vessels, and the vessels occupy only a small portion about 5–10% of the cross section of culms. Even when the vessels are completely filled by the preservative, the bamboo culms can be degraded by biological organisms if the preservative does not diffuse into the fibers and parenchyma cells enough, the main portion of the culm being left un-treated (Liese 1980). Sun et al. (2011) also reported that the preservatives are mainly distributed on the surface of bamboo due to refractory properties of bamboos, and this might not protect bamboos against degrading organisms in field. In addition, the nutrients such as starch, sugar, protein and fat etc. are believed to be main factors on decaying process of bamboos (Sun et al. 2011). Fungal attack was influenced by the free glucose in bamboos (Okahisa et al. 2006). Liese (1980) and Singha and Borah (2017) reported that the degradation caused by biological organisms has been proportional to the starch content of the bamboo, and their attack was more in field conditions.

Decay resistance of the bamboos decreased from bottom to top despite higher preservative uptake was found in the upper parts than bottom parts of the culms. Wall thickness of the bamboos probably played an important role on decay resistance. It is expected that as the wall thickness of the bamboos decreases, decaying can occur more quickly. More durability property in the lower parts of the culm was also reported by Jiang (2008) and Tomak et al. (2013). Chemical and anatomical structure of the woody constituents differ a long with bamboo culms. Fiber percentage and vascular bundle concentration increase in the upper part of the culms (Liese 1998; Li 2004). It was also proved that more woody components (hemicellulose, cellulose and lignin) exist in upper parts in comparison to bottom parts (Tomak et al. 2013). The higher durability in bottom parts were attributed to presence of lower holocellulose content in the bottom portion of bamboo culms than in the middle and top portions (Suprapti 2010). Furthermore, glucose and starch contents might be higher in the top portion than in the portion of culms. Samples from young culms and from top parts of culms, respectively, decay extensively than older ones and those from the bottom parts since top parts of culms have the highest starch content (Suprapti 2010; Schmidt et al. 2011), and free glucose content (Okahisa et al. 2006).

Treated samples exhibited better resistance than controls, and the results indicate that the importance of preservative treatment in samples to field biodegradation. A significant difference was not found between the preservative type in terms of weight losses of bamboos ($P > 0.05$), meaning both preservatives exhibited similar protection against degradation factors during the field test. In all cases, weight loss of CCB and Tan-E treated samples was found to be lower than that of controls. Copper is the main fungicide used for treating wood in soil contact since it is the only biocide that shows a high efficiency against soft rot fungi and other soil-borne fungi (Civardi et al. 2015). Cu^{2+} causes generation of highly active free radicals which damage fungal proteins and DNA (Stirling and Temiz 2014).

Weight losses of samples were analyzed by One-way Anova test in IBM SPSS Statistic 25, and it was found a significant difference between the weight losses of the samples ($P < 0.05$). Weight losses of samples treated with CCB were found to be in following order by Duncan's homogeneity groups in One Way Anova: bamboo-middle-control ≥ bamboo-top-control ≥ bamboo-bottom-control ≥ beech-control ≥ bamboo-top-CCB ≥ S. Pine-control ≥ bamboo-middle-CCB > bamboo-bottom-CCB > beech-CCB = S. Pine-CCB. Weight losses of samples treated with Tan-E were found to be in following order by Duncan's homogeneity groups in One Way Anova ($P < 0.05$): bamboo-middle-control ≥ bamboo-top-control ≥ bamboo-bottom-control = beech-control ≥ bamboo-top-Tan E = S. Pine-control ≥ bamboo-middle-Tan E ≥ bamboo-bottom-Tan E > beech-Tan E > S. Pine-Tan E.

Chemical leaching during the field exposure test

Figure 2 shows the leaching rate (%) of boron (B), chromium (Cr) and copper (Cu) of CCB treated

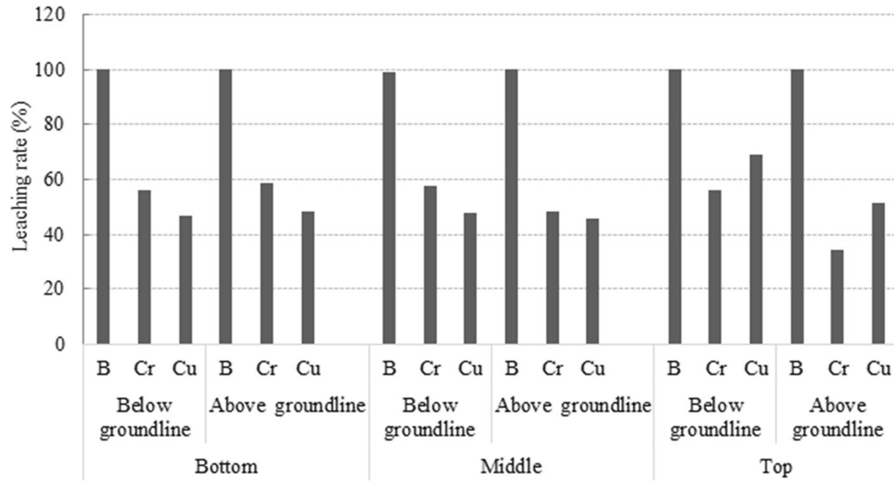


Fig. 2 Leaching rate (%) of chemical components (B, Cr, Cu) of CCB treated bamboo samples after field test

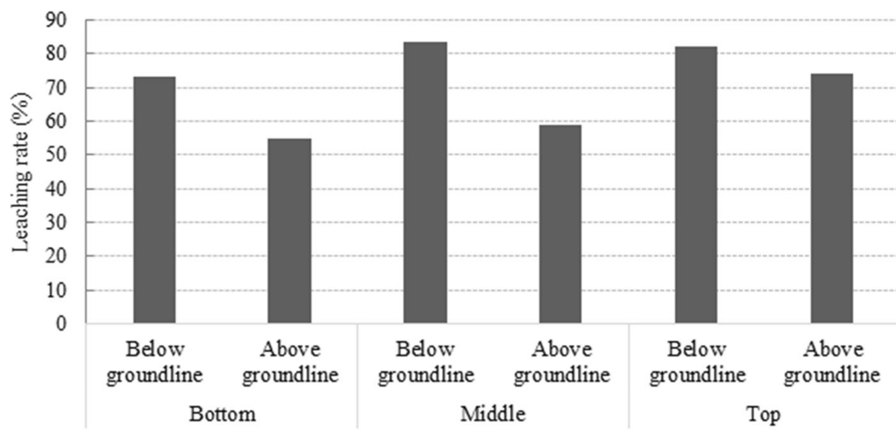


Fig. 3 Leaching rate (%) of copper of Tan-E treated bamboo samples after field test

bamboo samples (relative to un-exposed samples treated at the same concentration levels of the preservatives), and Fig. 3 shows copper leaching rate (%) from Tan-E treated bamboo samples following field test.

As seen in the figures, nearly all the boron was removed in CCB treated bamboo samples during the field test. Lima et al. (2021) also found 100% boron leaching in CCB treated eucalyptus wood in field exposure after 2 years. The high solubility of boron in water ensures that they can easily leach from treated wood without suitable additional protection (Tomak et al. 2011; Kaminski et al. 2016; Gauss et al. 2021a). Regardless of the bamboo height parts, nearly 55% chromium leached from bamboos in below groundline, such that all parts of the bamboos exhibited similar chromium leaching rate. Copper was leached as 47% in bottom and middle parts of bamboos while it was 70% for the top part of bamboos in below groundline. Bamboo parts had a great impact on chromium leaching for above groundline samples while they had a slight impact on copper leaching. Chromium leaching was increased from top (34%) to bottom parts (59%) in above groundline. Copper leaching was found as an avg. 48% for above groundline samples. Samples from the below groundline had greater leaching rates of chemicals than samples from the above groundline. The high moisture content of soil and decomposition of samples by microorganisms in soil may have an effect on the high leaching rates of the chemicals. Migration of woody elements to soil also confirms the leaching rates of chemicals (Lima et al. 2021).

Copper leaching in Tan-E treated bamboos was found as 73% for bottom parts of the bamboos while it as 82% for top parts in below groundline. In the case of above groundline samples treated with Tan-E, it was ranged from 55 to 74% for bottom and top parts of culms.

In all cases, upper parts of bamboo culms had greater copper leaching rates. This finding is in accordance with the high weight losses in upper parts of culms. High leaching rates of the chemicals might imply that the preservatives did not diffuse into the bamboo tissue enough. In addition, the preservatives might mainly distribute on the surface of bamboo after impregnation. Leaching of copper being an important fungicide among the wood preservatives had an impact on weight loss of bamboos. The remaining copper is supposed to be not sufficient to control decaying organisms in soil. Weight losses were well confirmed by copper leaching rates for both CCB and Tan-E. Edlund and Nilsson (1999) found 85% chemical loss for Wolmanit CX-S and 69% chemical loss for Tanalith MCB treated wood after exposure in unsterile forest soil during 12 months.

Morphological analysis by SEM

Figures 4, 5, and 6 show the morphology of bamboo samples with different sections (radial and cross sections) exposed to field test. The SEM micrographs of top and bottom parts of bamboo samples from the below groundline were taken since the most prominent properties were observed in these parts.

Bamboos were observed to be very sensitive to decay in soil in accordance with weight loss results of bamboos. White-rot, brown-rot and soft-rot fungi as well as bacteria may be found in most soils, but

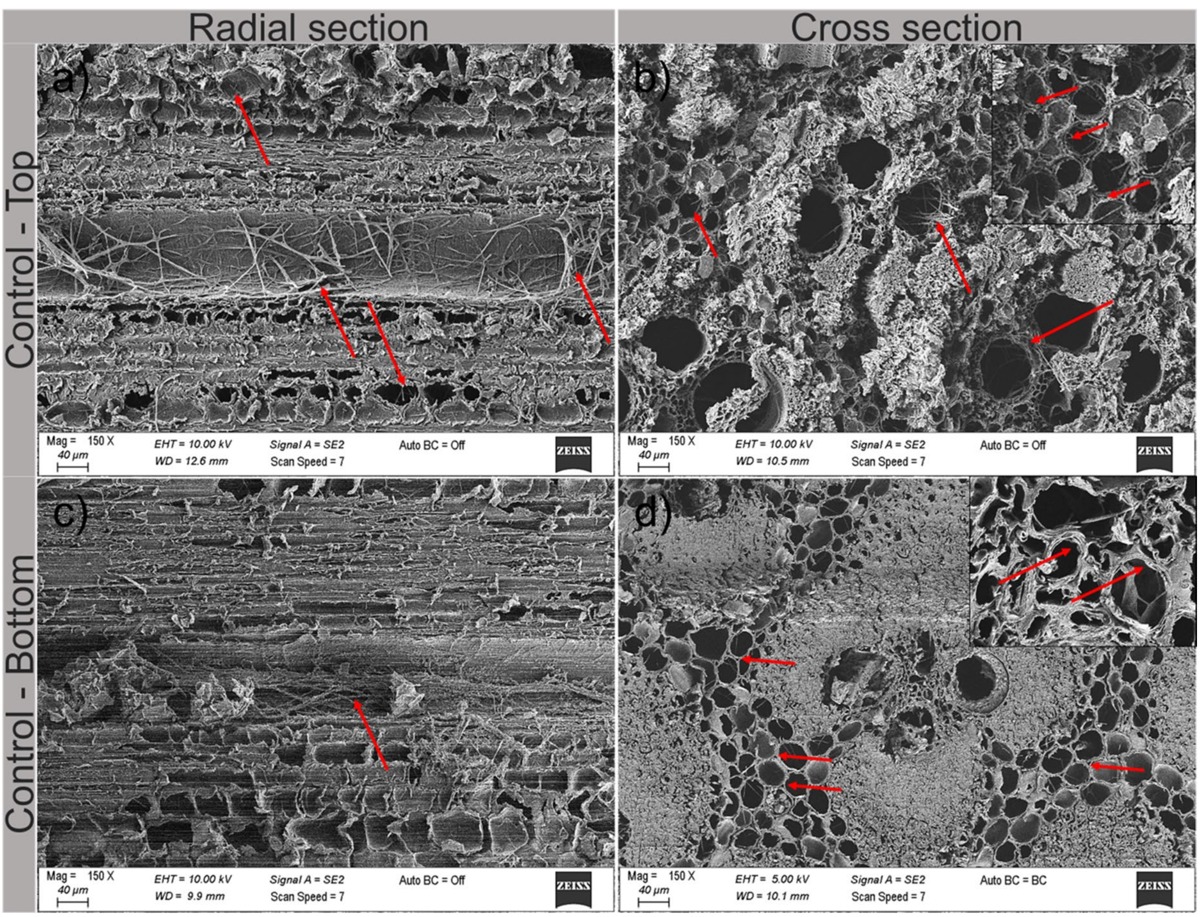


Fig. 4 **a**, **b** Radial and cross section of top part of exposed control bamboo samples **c**, **d** Radial and cross section of bottom part of exposed control bamboo samples

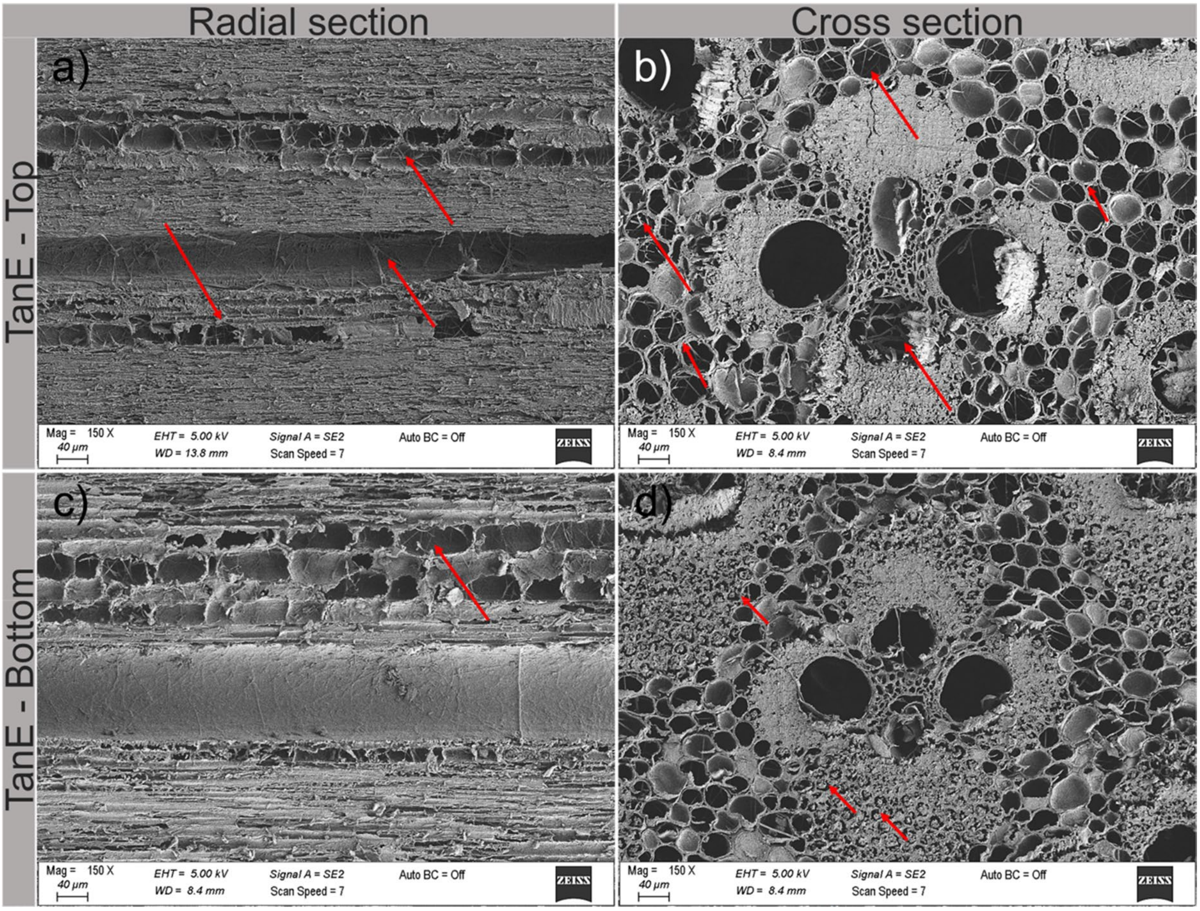


Fig. 5 **a**, **b** Radial and cross section of top part of exposed Tan-E treated bamboo samples **c**, **d** Radial and cross section of bottom part of exposed Tan-E treated bamboo samples

their activities differ in different type of soils (Edlund and Nilsson 1999). Especially soft-rot fungi are most common in soils, and they can be distinguished from other decaying fungi by the decay patterns such as producing cavities within the secondary walls of wood cells (Type I attack) and eroding the secondary wall completely (Type II attack) leaving a relatively intact middle lamella (Hamed 2013). Brown-rot fungi primarily attack the cell-wall carbohydrates, leaving a modified lignin at the end of the decay process (Zabel and Morrell 1992). In the study, characteristics decay patterns of soft-rot fungi and brown-rot fungi were observed. Cell wall erosion in addition to the cavities formed by soft-rot fungal hyphae within the cell walls (Figs. 4b, d, 5b, d, 6b, d), and cell wall degradation was probably formed by brown-rot fungal hyphae within the cell walls (Figs. 4b, d, 5b, d, 6b, d) resulted in the gradual breakdown of the cell wall layers. Little of the cell wall remained un-affected, and extremely weak decayed cells easily fragmented.

Microstructure of un-treated samples showed that a large number of hyphae were in the parenchyma cells and in the vessels, and cracks were observed along the grain direction probably due to enlarge and merge of the pits on vessels by hyphal perforation (Fig. 4). Cell wall of top parts damaged more than that of bottom parts (Figs. 4a, c, 5a, c, 6a, c). In the case of treated samples, a large number of hyphae appeared in the parenchyma cells and few of them appeared in the vessels (Figs. 5b, d, 6b, d), but the structure damaged less than controls (Figs. 4b, d). Vessels and fibers in vascular bundles were less destructed than parenchyma cells for treated samples. Razak et al. (2002) found extensive white and soft-rot decay in

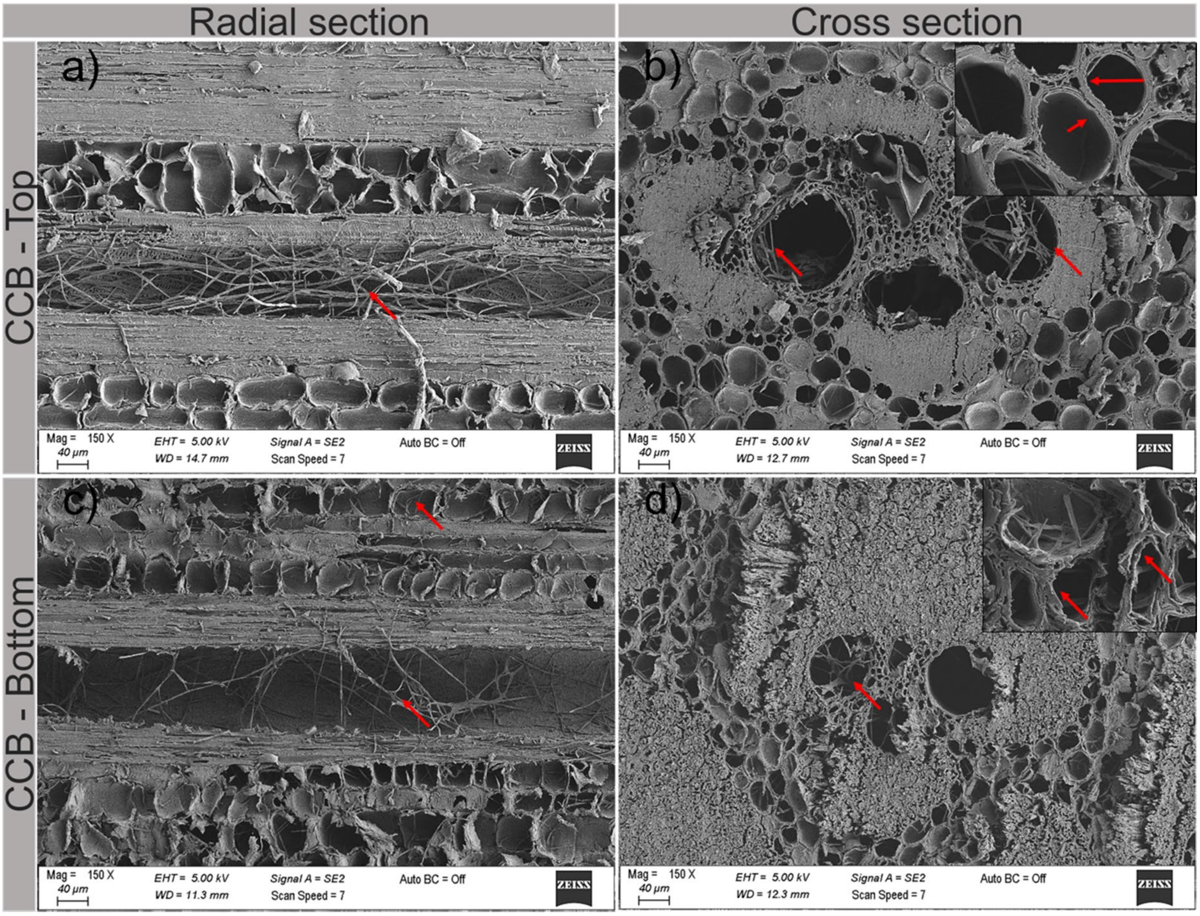
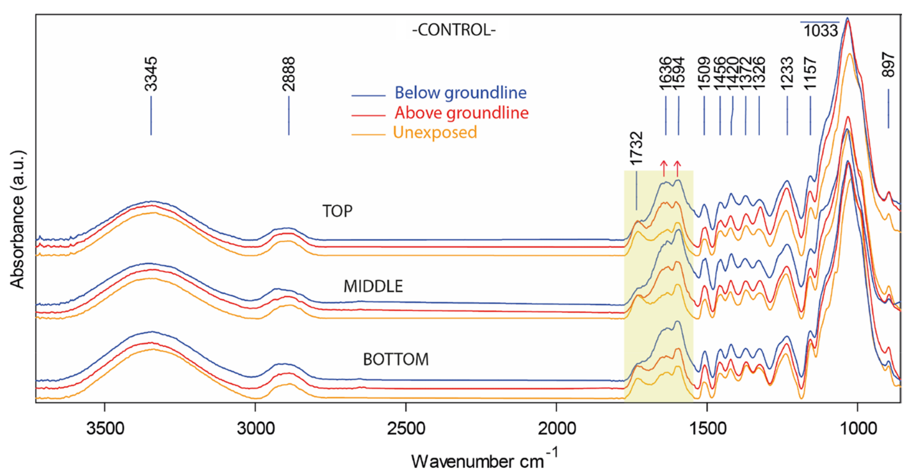


Fig. 6 **a**, **b** Radial and cross section of top part of exposed CCB treated bamboo samples **c**, **d** Radial and cross section of bottom part of exposed CCB treated bamboo samples

Fig. 7 FTIR spectra of top/middle/bottom part of bamboo control samples exposed/un-exposed to soil for 6 years



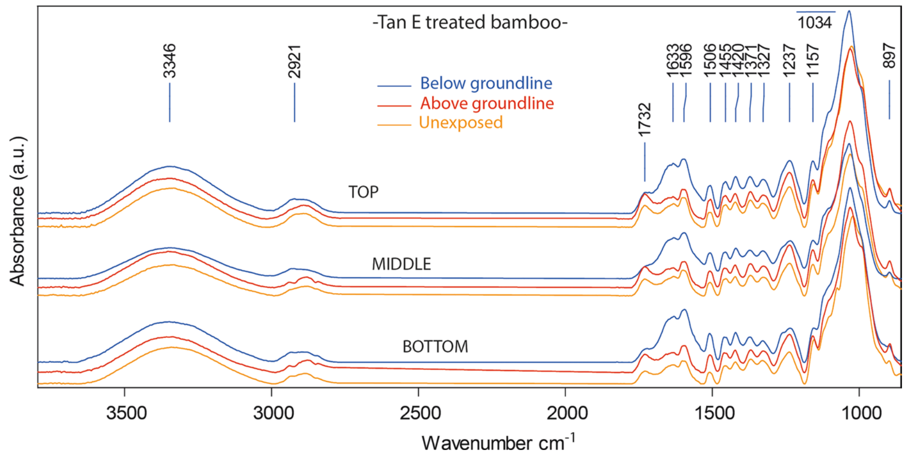


Fig. 8 FTIR spectra of top/middle/bottom part of Tan-E treated bamboo samples exposed/un-exposed to soil for 6 years

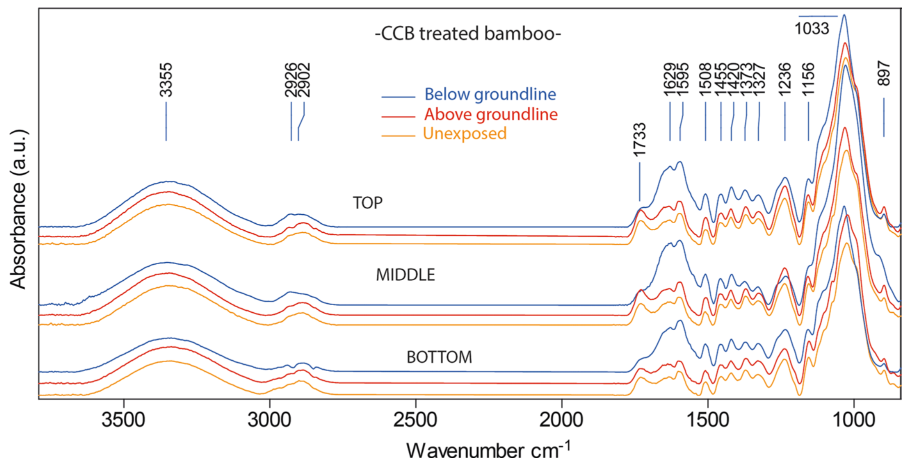


Fig. 9 FTIR spectra of top/middle/bottom part of CCB treated bamboo samples exposed/un-exposed to soil for 6 years

untreated and ineffectively treated culms after field exposure for 24 months, and fungi was observed in the cell lumina, in cell walls and in the intercellular spaces. In contrast, the tissues of culms with effective preservative treatments showed restricted hyphal colonization, infrequent hyphal invasion into cells via pits, or no cell wall degradation.

Chemical analysis with FT-IR spectroscopy

FT-IR studies were carried out to determine the extent of structural changes in the spectra of exposed bamboo samples, and to reveal degradation mechanism with respect to the parts (top/middle/bottom) of the bamboo samples. FTIR spectra of control, Tan-E and CCB treated bamboo samples both before (unexposed) and after 6 years of field exposure (exposed) are shown in Figs. 7, 8, and 9. In the FTIR study, the spectra of the samples which were taken from above the groundline were also provided. In the spectra of un-exposed/exposed control samples as shown in Fig. 7, the basic structural components of bamboo can be observed clearly. The unconjugated C=O stretching of hemicelluloses (xylans) can be found at 1732 cm^{-1}, C=C stretching of aromatic skeleton of lignin can be found at 1507 cm^{-1}, asymmetric bending of C–H in CH_3 of lignin can be found at 1455 cm^{-1}, aromatic skeletal vibrations of lignin and C–H deformation in plane of cellulose can be found at 1421 cm^{-1}, C–H deformation in cellulose and hemicelluloses can be found at 1372 cm^{-1}, syringyl nuclei of lignin and C–O stretching in xylan can be found at 1237 cm^{-1}, C–O–C stretching of cellulose and hemicellulose can be found at 1158 cm^{-1}, and C–H deformation of cellulose can be found at 898 cm^{-1} (Pandey and Pitman 2003; Xu et al. 2013).

From the spectra of un-exposed and exposed control samples, it can be clearly observed that top/middle/bottom parts of bamboo have very similar degradation trend. Besides, it can be seen at first glance that the above-ground section of the samples are less degraded than below-ground section of bamboo samples. We can observe the chemical change due to the biodegradation by increase of the band intensities at 1636 and 1594 cm^{-1} (Fig. 7). These bands belong to the stretching vibrations of conjugated C=O and stretching vibrations in aromatic structure C=C in the lignin structure (Moosavinejad et al. 2019). Significant changes in FTIR spectra can be attributed to the soft-rot type I and/or brown-rot fungi, which have ability to modify lignin structure and also degrade hemicellulose and cellulose (Zabel and Morrell 1992). In parallel, it was observed a reduction the intensity of 1732 cm^{-1}, which belongs to C=O stretching of hemicelluloses. The decrease of the hemicellulose content implies the biodegradation of the samples both soft-rot and brown-rot fungi (Pandey and Nagveni 2007).

On the other hand, Tan-E and CCB treated bamboo samples have very similar spectra at the below ground section of the samples, which implies similar biodegradation trend (Figs. 8, 9). Interestingly, it can be said that the above ground part of the treated samples shows different spectra than the controls. There is no difference in the spectra of exposed or un-exposed samples above ground section after 6 years, which implies contrary to controls, lignin modifying fungal activity was not took place for treated samples above ground. However, the spectra of the below ground section of the bamboo show increase of the band intensities at 1636 and 1594 cm^{-1} similar to controls. In the spectra of treated and exposed samples below ground shows significant decrease in the intensity of 1732 cm^{-1} carbonyl band (unconjugated C=O in hemicelluloses) is also correlates with the increase in weight loss of samples.

To resolve further the biodegradation mechanism and to make a semi-quantitative evaluation of hemicellulose, cellulose and lignin amounts, we calculated intensity ratios of carbohydrate bands (hemicellulose, I_{1732} and cellulose, I_{1375}, I_{1158}) with respect to lignin-associated band (I_{1509}) both for exposed and un-exposed samples below ground (Table 4). As shown, for control, Tan-E or CCB treated bamboo samples the intensity ratio of carbohydrate bands with respect to lignin (I_{1732}/I_{1509}, I_{1375}/I_{1509}, I_{1158}/I_{1509}) reduced considerably after 6 years of exposure. In addition to lignin modification by the soft rot attacks, it can be concluded that the significant reduction of the carbohydrate content implies brown-rot attack (Zabel and Morrell 1992).

Table 4 Average ratios of the intensity of lignin associated band (1509 $cm.^{-1}$) with carbohydrate bands for exposed and un-exposed samples

ID/Below groundline	I_{1732}/I_{1509}	I_{1375}/I_{1509}	I_{1157}/I_{1509}
Control			
Top			
Exposed	0.5	1.25	1.75
Un-exposed	1.45	2	2.9
Middle			
Exposed	0.36	1	1.16
Un-exposed	1.3	1.7	2.4
Bottom			
Exposed	0.66	1.11	1.77
Un-exposed	1.2	2	3.2
Tan-E treated bamboo			
Top			
Exposed	0.75	1.25	1.83
Un-exposed	1.4	1.8	2.8
Middle			
Exposed	0.5	1.05	1.44
Un-exposed	1.2	1.5	2.2
Bottom			
Exposed	0.45	0.84	1.15
Un-exposed	1.2	2	3.2
CCB treated bamboo			
Top			
Exposed	0.58	1.08	1.42
Un-exposed	1.75	2.25	3
Middle			
Exposed	0.5	0.75	1.25
Un-exposed	1.5	2	2.75
Bottom			
Exposed	0.43	1.06	1.5
Un-exposed	1.3	1.85	2.7

Conclusion

Bamboo and wood samples were installed in a field, where the climate was warm and temperate with a high humidity rates for 6 years, and as a result of long exposure time and the environment, a great destruction was observed in the samples that was well confirmed by weight loss, FTIR and SEM micrographs. Bamboos were more susceptible to decay than wood, due to their typically thin walls, and their different anatomical and chemical compositions. Treatment with copper based preservatives ensured better durability to bamboos in comparison with controls, but they did not inhibit the degradation caused by soft-rot fungi and brown-rot fungi attack since a great amount of chemical leached out from the bamboos to soil. These findings also supported by FTIR analysis, which indicates the structural change in lignin due to the soft-rot fungi and decrease in carbohydrate content implies brown-rot fungal decay. Both preservatives exhibited similar durability in field in terms of weight loss of bamboos. Bamboo samples taken from the upper parts of culms showed less biological resistance than dipper parts in field exposure test which was also in accordance with ICP-OES and SEM analysis. Fungal hyphae within the parenchyma cells, vessels and fiber walls resulted in the gradual breakdown of the cell wall layers.

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Declarations

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