Natural Weathering's Effect on Mechanical Properties of Short Cycle Coconut Trunk Lumber Impregnated Using Kraft Black Liquor

Rudi Dungani,[a,*] Tati Karliati,[a] Anne Hadiyane,[a] Takashi Tanaka,[b] Masaaki Yamada,[b]
Sri Hartati,[c] Mustika Dewi,[a] and Jamaludin Malik [d]

The weathering resistance properties of short cycle coconut trunk lumber (SC-CTL) were evaluated in response to impregnation using kraft black liquor (BL) and black liquor/phenol formaldehyde (BL/PF) resin. Concentrations of 10, 15, 20, and 25% w/w kraft BL and PF resin with BL were impregnated into SC-CTL using a vacuum-pressure method. Natural weathering tests lasting 6 and 12 months were performed according to ASTM D1435 (1999). After the prescribed testing period, samples were analyzed for their morphological changes *via* FT-IR and SEM. Mechanical tests were conducted to analyze changes caused by natural weathering in impregnated SC-CTL. The results showed that BL with PF resin impregnation into SC-CTL improved the resistance against natural weathering. The SEM study confirmed that fungi could not colonize the treated samples. The results also suggested that addition of 20% BL in PF resin was sufficient to inhibit weathering. Thus, it was concluded that impregnation of PF resin with BL is a good method to improve the mechanical properties of SC-CTL.

Keywords: Natural weathering; Black liquor; Coconut wood; Mechanical properties; Morphological

Contact information: a: School of Life Sciences and Technology, Institut Teknologi Bandung, Bandung 40132, Indonesia; b: Faculty of Agriculture, Shizuoka University, Shizuoka 422-8529, Japan; c: Faculty of Agriculture, Universitas Padjadjaran, 45363 Bandung, Indonesia; d: Forestry Products Research and Development Center, Ministry of Environment and Forestry Indonesia, Bogor, 16610 Indonesia;
** Corresponding author: rudi@sith.itb.ac.id*

INTRODUCTION

According to the Indonesian Pulp and Paper Association (2018), Indonesia's paper production capacity was 16 million tons per year, while 11 million tons of pulp was produced per year. From the production of the pulp, lignin production from black liquor was estimated to be approximately 3.16 million tons/year in 2019. It is conventional practice to evaporate black liquor and incinerate it to recover the pulping chemicals. If this is not done, the black liquor pollution poses a serious threat to the environment.

The utilization of lignin from black liquor, such as for adhesives, will give added value to the material. Previous studies have shown the success of lignin precipitated from black liquor as a component in formaldehyde-based adhesives, such as phenol-formaldehyde (PF) resin (Gothwal *et al*. 2010; Santoso and Sutigno 2003). Kraft lignin produced as a byproduct in the pulping/paper industry also can use in phenolic resin composites for the production of abrasive components (Siddiqui *et al*. 2017). Furthermore, Karliati *et al*. (2018) reported that the addition of kraft lignin could make it possible to reduce phenol formaldehyde use in the manufacture of plywood. They also reported that black liquor is a potential material for reducing the use of formaldehyde-based adhesives for plywood. Previous studies reported that lignin precipitated from black liquor can replace up to 30% of the phenol present in the phenol formaldehyde resins used for plywood preparation, with no major changes in plywood strength properties (Kouisni *et al*. 2011).

However, the presence of salts, alkalinity, and soaps in the black liquor would be expected to interfere with resin during and properties in hard-to-predict ways. When some of these solids dissolve in water and reach a certain concentration, they begin to precipitate and interfere with the action of dispersants for solid–liquid mixtures. Furthermore, BL components are surface active agents that often cause foaming problems in solution (Alwadani and Fatehi 2018).

Coconut wood (*Cocos nucifera*), which is used for building materials, is usually cut down at age greater than 18 years. However, when harvested, coconut wood is still young (short cycle), so the short cycle coconut wood has low mechanical and physical properties such as stability dimension, strength, and resistance to wood-damaging organisms. One effort that can be made to address such issues is modification with phenol-formaldehyde resin to obtain better properties. At present, the use of short cycle coconut wood is not limited to building materials but is also used for furniture and craft products (Rana *et al*. 2015). Therefore, it is necessary to improve the quality of short cycle coconut wood as a substitute for wood for optimal performance.

Improvement of wood quality, especially mechanical strength and dimensional stability, has been achieved using resin impregnation (Furuno *et al*. 2004; Abdul Khalil *et al*. 2012; Dungani *et al*. 2013, 2016; Ma *et al.* 2016). According to these researchers, impregnation of phenol formaldehyde into wood, especially oil palm, results in higher physical, mechanical, and dimensional stability properties. Resistance towards degradation when in contact with the environment is an important issue, where it is exposed to a variety of conditions (Islam *et al*. 2013). Conditions including moisture, sunshine, and microbial attack are factors that contribute to composite degradation. Several types of degradation have been recognized in coconut wood, *viz.* weathering degradation. Degradation by weather include the effects of ultraviolet (UV) light and water (Nikafshar *et al.* 2017; Zhoa *et al.* 2017). Therefore, short cycle coconut wood can be impregnated with resins to improve its properties. In impregnation treatment, formaldehyde-based resin is expensive, and to reduce the use of phenolic-based resin, black liquor can be used instead.

Accordingly, it may be possible to improve the degradation resistance by impregnation of kraft black liquor into coconut wood. To the authors' knowledge, no prior report has assessed the weathering resistance properties of kraft black liquor impregnated lumber. Thus, the aim of this study is to demonstrate the effects of kraft black liquor impregnation on the natural weathering properties of short cycle coconut trunk lumber. Mechanical and morphological properties of kraft black liquor impregnated short cycle coconut trunk lumber are analyzed to investigate the effects.

EXPERIMENTAL

Materials

Black liquor (BL) was obtained as a by-product of pine pulp processing in the pulp digesting kraft process sampling from a paper mill in Bandung City, West Java Province, Indonesia. The compositions were as follows: total solids was 48.6%, lignin was 251.8 g/L, pH was 12, and mass density (20 °C) was 1.232×10^3 g/m^3.

Coconut wood (*Cocos nucifera*) was obtained from a 15-year-old local plantation in Sumedang, West Java, Indonesia. The diameter of the coconut wood used for this study was 400 mm, with a density of 0.24 to 0.35 g/cm^3. The coconut wood was sawn to make it into 50 × 50 × 500 mm^3 size (for the thickness, width, and length, respectively). The coconut wood was sawn to 50 × 50 × 500 mm^3 size (for the thickness, width, and length, respectively). Coconut wood was re-sawn to obtain a sample with a size of 30 × 50 × 300 mm^3 (short cycle coconut trunk lumber, SC-CTL), then dried (105$\pm$2 ºC) in a kiln (Monica Shui Henan Taiguo Boiler Manufacturing Co., Ltd., Henan, China) to a moisture content of 13 to 15%.

Methods

Preparation of mixture of PF-resin and kraft BL

Phenol-formaldehyde (PF) resin was prepared at high molecular weight with a concentration of 15% w/w, where the amount of 150 g PF was dissolved in 1000 g normal water. Exactly 10% w/w, 15% w/w, 20% w/w, and 25% w/w kraft BL were added to the PF resin to obtain different concentrations. The mixtures (PF resin and kraft BL) were compounded using a mechanical stirrer at 3000 rpm for 15 min. Monitored mixing made certain that PF resin was mixed well and avoided agglomerating in the mixture.

Impregnation process

The impregnation process was completed according to Abdul Khalil *et al.* (2012) and was applied to two treatments, namely kraft BL with concentrations of 10, 15, 20, and 25% and BL kraft with the same concentration added to the PF resin of concentration 15% w/w. The impregnated process was completed through the following steps. The SC-CTL was placed into the steel impregnation chamber (Automatic, Sentosa Teknik Co., Ltd., Bogor, Indonesia) for vacuum process at 3 bar pressure for 15 min. Then, it underwent the pressure process at 5 bar pressure for 60 min. The mixture of resin and kraft BL was evacuated from the chamber, and the vacuum process was undertaken with 3 bar pressure for 10 min. Short cycle coconut trunk lumber impregnated using kraft black liquor was noted as SC-CTL impregnated.

After impregnation, the samples were dried at 150 °C for the curing process for 2 h. Dried weight of all samples was determined to calculate the WPG. The average WPG was calculated for each treatment of experimental samples.

Natural weathering test

The weathering test was performed based on the ASTM D1435 (1999) method with specimens sized at 300 × 50 × 20 mm^3. The specimens were oven-dried for 3 days at 60 °C, and then weighed before weathering (W_1, g).

Weathering was conducted on the roof of a building at Northeast School of Life Sciences and Technology, Institut Teknologi Bandung, West Java Province, Indonesia. The building is 10-m high and its roof is wide with no shadow from a neighboring obstruction (Fig. 1). Samples were placed vertically on the roof and exposed to variable weather factors, such as precipitation, sunlight, temperature, moisture, and wind for 6 and 12 months.

Climate data at the site was available from the official weather stations. Measurements of the average temperature, relative humidity, UV intensity, annual rainfall, and long radiation were 25.90 °C, 81.74%, 856.5 cal/m^2, 1570 mm, and 67.16%, respectively, through one year.

Fig. 1. Natural weathering test area

Characterization of test samples degraded

Characterization of degraded SC-CTL samples was completed by visual observation, using Fourier transform infrared (FT-IR) spectroscopy (Nicolet Avatar 360; Welltech Scientific, Inc., Chantilly, VA, USA). IR spectra were taken from the sample powder of SC-CTL impregnated at various exposure times in order to reveal the gradual changes resulting from 0, 6, and 12 months exposure. The absorbance bands showed the reactive groups on sample surface.

Scanning electron microscope (SEM) was used to analyze the morphological images of SC-CTL impregnated after natural weathering testing. Testing by SEM was carried out using a Scanning Electron Microscope (SEM) model ZEISS (EVO MA10; Carl *Zeiss* SMT, Oberkochen, *Germany*). A thin section of samples was mounted on an aluminum stub using a conductive silver paint. The sample was sputter-coated with gold prior to morphological examination. The specimens were analyzed directly at 5 kV.

Mechanical properties testing

Tests of tensile properties (strength and modulus) were carried out according to ASTM D3039 (2000) standard with using an Instron Universal Testing Machine (Model 5582; Shanghai HESON Instrument Technology Co., Ltd., Shanghai, China). The samples with dimension 120 mm (length) x 15 mm (width) x 3 mm (thickness) were prepared for each testing. The samples were tested at a cross-head speed of 5 mm/min and a gauge length of 60 mm. Flexural properties (strength and modulus) were tested using Instron Model 5582 Universal Testing Machine (Model 5582; Shanghai HESON Instrument Technology Co., Ltd., Shanghai, China) based on the ASTM D790 (2003) standard. The samples with dimension 160 mm (length) x 20 mm (width) x 10 mm (thickness) were prepared for each testing. The specimen lies on a support span and the load is applied to the center by the loading nose producing three points bending at a specified rate. The parameters for this test are the support span, which the length of the support spans is 128 mm, the speed of the loading is 5 mm/min, and the maximum deflection for the test.

Data analysis

A one-way analysis of variance (ANOVA) and Duncan’s multiple range test was used to analyze the data by identifying the effect of weathering test of BL-impregnated SC-CTL. The A factor is the exposure time (A1 = 0 month, A2 = 6 months, and A3 12 months) and factors B has five levels of BL concentration (B1 = 0%, B2 = 10%, B3 = 15%; B4 = 20%; B5 = 25%). The results were analysed using the statistical package SPSS version 16.0 software (Hashmicro, Oxley Bizhub, Singapore).

RESULTS AND DISCUSSION

Visual Assessment of SC-CTL Impregnated

Visual observations of PF-impregnated SC-CTL without and with BL showed that the surface of the sample experienced a change of color that was darker after 9 and 12 months, respectively, of exposure in the weathering (Figs. 2 and 3). However, an increase in color occurred after 12 months of exposure to weathering. These results revealed the effect of weathering attack, especially UV and water, on the PF-impregnated SC-CTL with BL and showed that addition of BL resin reduced the effects of UV and water that lead to decay in SC-CTL.

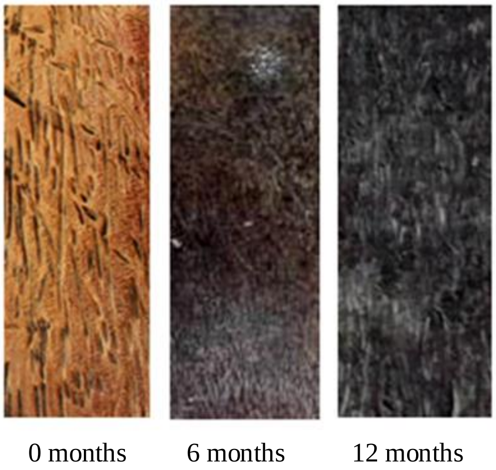
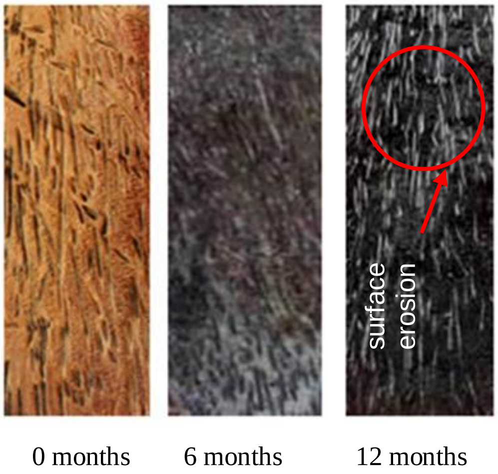

0 months 6 months 12 months

Fig. 2. PF-impregnated SC-CTL surfaces after exposure to weather from 0 to 12 months

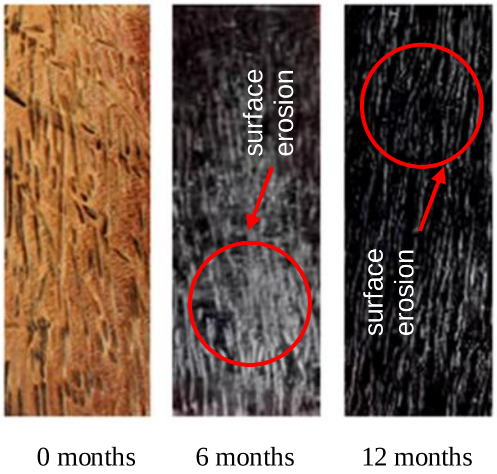
0 months 6 months 12 months

Fig. 3. PF-impregnated SC-CTL with 20% of BL surfaces after exposure to weather from 0 to 12 months



0 months 6 months 12 months

Fig. 4. BL-impregnated SC-CTL surfaces after exposure to weather from 0 to 12 months



0 months 6 months 12 months

Fig. 5. Dried SC-CTL surfaces after exposure to weather from 0 to 12 months

As shown in Fig. 3, there was a tendency towards lighter coloration in PF-impregnated SC-CTL with BL compared to the weathered PF-impregnated SC-CTL. As rain leaches the brown decomposition products of lignin, a silver-gray layer consisting of a disorderly arrangement of loosely matted fibers develops over the brown layer (Feist and Hon 1984).

Based on Figs. 4 and 5, after six months of exposure by weathering, the samples (BL-impregnated and SC-CTL dried) became more faded and darker due to weathering. Both samples showed the highest degree of degradation by weather after 12 months of exposure. Visual observations showed that the surface of the sample changed in color (darker), and gathered dirt and mildew (Oberhofnerová *et al.* 2017). The changes in sample color occur due to photochemical reactions, which are affected by UV and visible light (Teacă *et al.* 2013).

Surface erosion is an important finding in visual observation. Due to UV and water, there was decay observed in SC-CTL and this caused surface erosion to occur in the BL-impregnated SC-CTL, PF-impregnated SC-CTL with BL, and dried SC-CTL. However, it was not apparent in PF-impregnated SC-CTL specimens. According to Lopez *et al*. (2005), exposure to natural sunlight, wetting and drying cycles, and exposure to the wind caused the samples to rub against each other – on the edges as well as the faces. However, deterioration on PF-impregnated SC-CTL is lower compared to the impregnated SC-CTL other, where the PF-impregnated SC-CTL surface minimally exposed (Fig. 2).

The effects of climatic parameters on the weathering process were evaluated according to the climatic data obtained from the Meteorological, Climatological, and Geophysical Agency weather stations of Sumedang, Indonesia for one year. Recorded climatic data of the test site during exposure periods indicated that the test site had annual average temperature, relative humidity, UV intensity, rainfall, and long radiation values of 25.9 °C, 81.74%, 856.5 cal/m^2, 1570 mm, and 67.16%, respectively. The natural weathering test area was situated 325 m above the sea level. According to meteorological data of the site, it can be said that both the humidity and the temperature increased from the 6th to 12th month. However, the temperature was constant during the 1-year exposure. The rainfall (mm) tended to decrease. The number of rainy days was highest in June, July, and August. Under the climatic conditions, high weight loss values and degradation of surface were observed in the control stakes as expected. However, as reported before, decay played an important role in strength losses.

Infrared Spectra

Figure 6 shows the FT-IR spectra of BL-impregnated SC-CTL, PF-impregnated SC-CTL, and PF-impregnated SC-CTL with BL at 0, 6, and 12 months of exposure of the weathering condition, respectively. It was found that impregnation of PF or PF with BL caused changes in the FT-IR spectra of the SC-CTL.

The overall absorbance peak decreased with the increase of exposure duration. A strong absorbance peak was observed at 3419 cm^{-1}, 3415 cm^{-1}, and 3416 cm^{-1} for 0, 6, and 12 months exposure, respectively, for the BL-impregnated SC-CTL (Fig. 6a). However, these peaks were at 3412 cm^{-1}, 3414 cm^{-1}, and 3423 cm^{-1} for PF, and at 3740 cm^{-1}, 3412 cm^{-1}, and 3413 cm^{-1} for PF-impregnation with BL, respectively for 0, 6, and 12 months exposure. The IR spectrum in the range of 3423 to 3412 cm^{-1} represent the stretching vibrations of O-H bond in cellulose (Pandey and Pitman 2003). However, the absorbance peak appeared at 3740 cm^{-1} for PF-impregnated with BL before exposure was also assigned to hydrogen bond (O-H) stretching vibration (Van Daele *et al.* 2018).

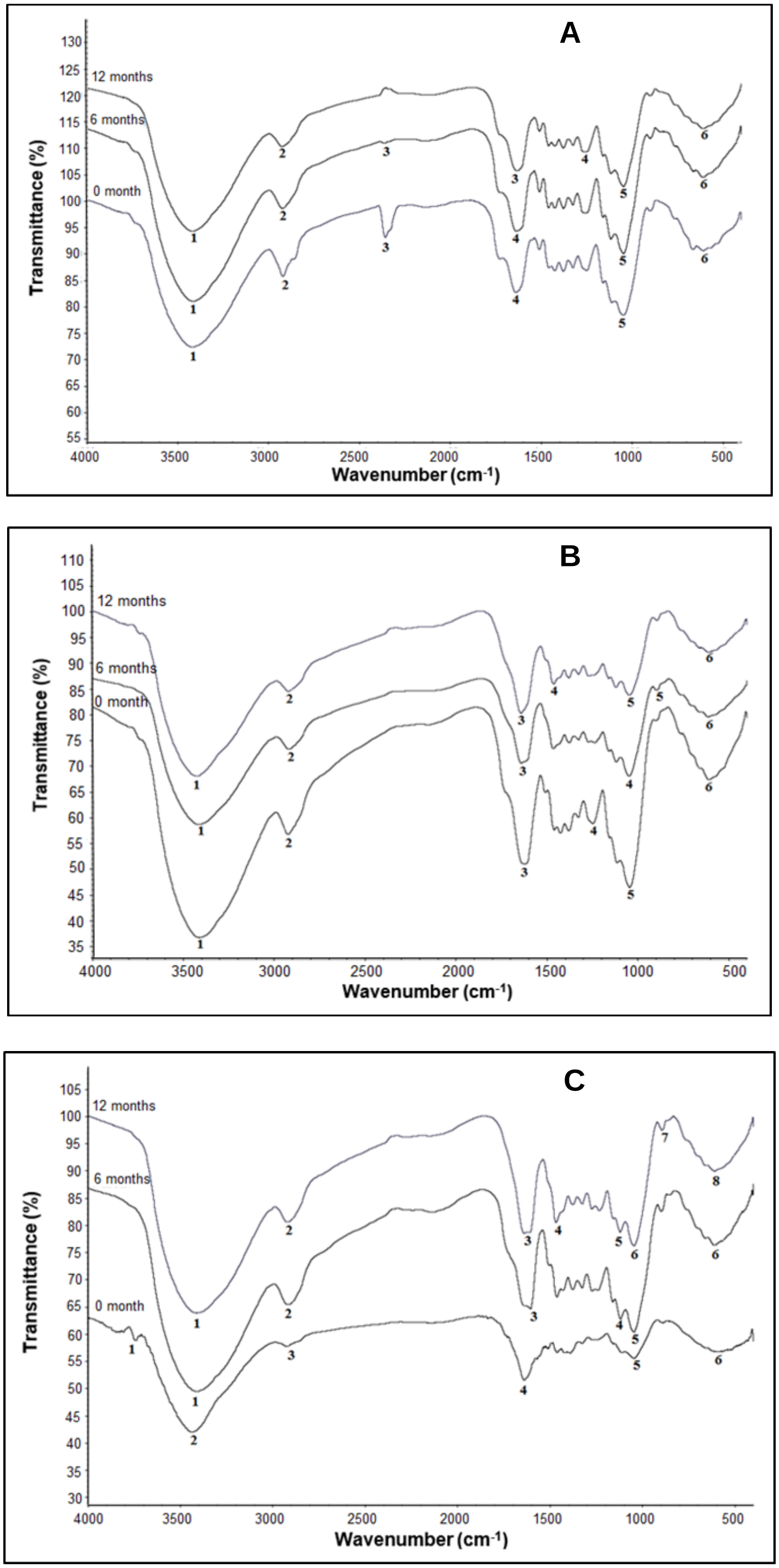


Fig. 6. IR spectra before and after exposure to natural weathering: (a) BL-impregnated, (b) PF-impregnated, and (c) PF/BL-impregnated

The spectra of 1047 to 1045 cm^{-1} represents silicate minerals (Si-O bonds) (Georgokapoulos 2003), which was not found in BL with PF-impregnated SC-CTL. The hydroxyl stretching bond of water (3435 cm^{-1}) (Pongjanyakul *et al*. 2009) was only found in PF-impregnation with BL before the exposure to weathering conditions. The peak for aromatic ring (C=C in plane) was only found at 1606 cm^{-1} for PF-impregnated with BL at 6 months exposure. The broad absorbance band at around 1120 cm^{-1} is attributed to a stretching vibration of Si-O-Si linkage (Pongjanyakul *et al.* 2009; Gautam *et al.* 2012).

After exposure to weathering conditions, various chemical reactions occurred, such as dehydration, hydrolysis, oxidation, decarboxylation, and transglycosylation, resulting in changes in the FT-IR spectra (Kocaefe *et al*. 2008). Photo-induced degradation of treated and untreated wood caused the main changes in the absorption intensity as reported by Temiz *et al*. (2007). However, the intensity of the changes of these bands was related to the change of functional groups and chemical structure of the samples.

Several peaks in the stretching vibrations of O-H bond in cellulose within the region of 3419 to 3412 cm^{-1} changed to peaks at regions of 3415 to 3414 cm^{-1} and 3423 to 3413 cm^{-1} after 6 and 12 months, respectively. These findings of decreased intensity at the peak with increasing exposure time were consistent with the study by Yildiz *et al*. (2011).

Hydroperoxides as a result of the reaction of free radicals with molecular oxygen under natural weather condition are important in the weathering process. In addition, hydroperoxides undergo photolysis in the presence of UV light, forming two free radicals that react with the samples to from two new peroxides. These chain reactions, according to Evans *et al.* (2002) lead to the rapid increase in the rate of polymer degradation on the surface of the wood polymers (Fig. 7).

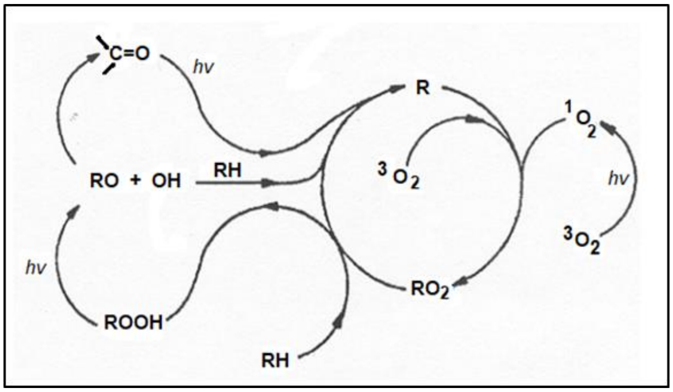


Fig. 7. Schematic diagram of polymer degradation on the surface of the SC-CTL-impregnated (Feist and Hon 1984)

Furthermore, these reactions also increase the swelling of the cell walls, increasing the access of both the peroxides and light to the cellulose and lignin (Feist and Hon 1984).

The absorbance peak changed with the increase of BL concentration and duration of exposure. The PF-impregnation with BL changed the chemistry of lignin and cellulose to something similar to that of acetylated wood, as studied by Deka and Petrič (2008). They suggested that the observed reduction in weathering (weight loss) of PF-impregnated with BL might be a result of polymerization of both resin and BL. The free radical process might be disrupted during weathering when these components were impregnated with polymer with the function as barrier and the weathering process was then retarded (Yousif and Haddad 2013).

Change of Morphological Properties

Distortion and erosion of fiber became more pronounced in the SC-CTL controls after 12 months of weathering (Fig. 8a), particularly the middle lamella and cell lumen. Similar findings were reported by Bhat *et al*. (2010); after one year of weathering, *Acacia mangium* wood showed holes in the middle lamella, distorted cell lumen, and some degradation of the cell wall. As mentioned earlier, the samples after 6 and 12 months of weathering exhibited decay fungi in the cell lumen. After 9 to 12 months of exposure, hyphal extension of fungi and damage increased in all areas. When the weathering process was extended to 12 months, hyphal of fungi increased, and hyphae were seen at greater distances from the exposed surfaces.

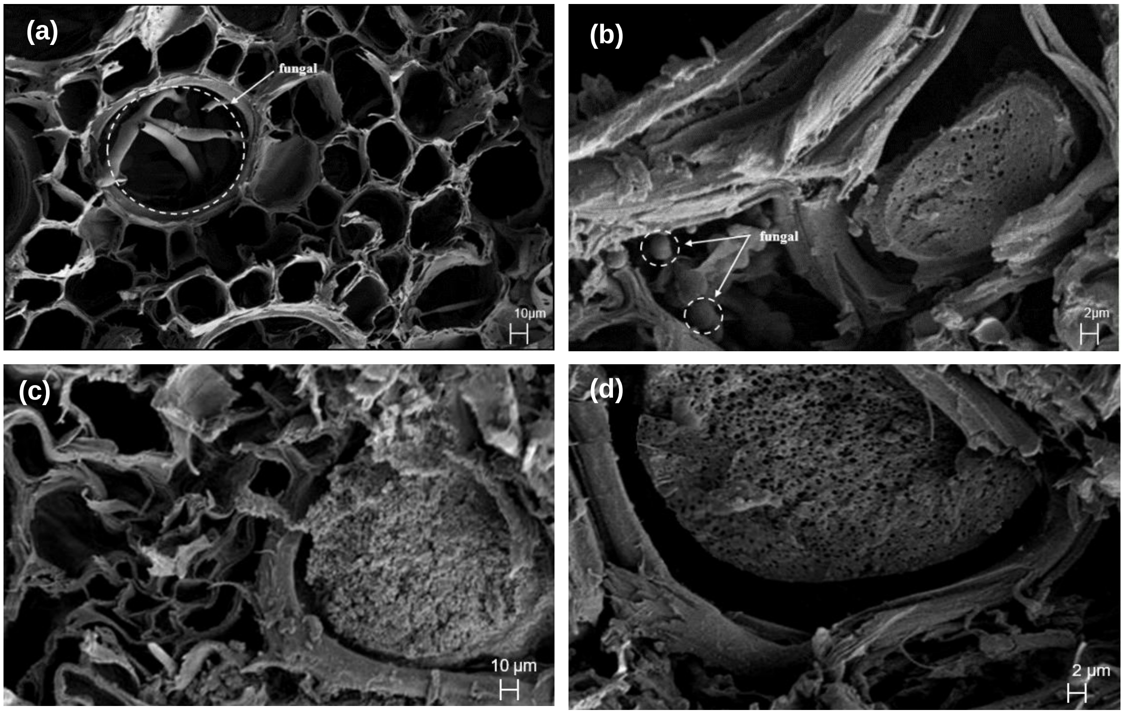


Fig. 8. Effect of prolonged natural weathering on the morphology SC-CTL: (a) Dried SC-CTL, (b) BL-impregnated SC-CTL, (c) PF-impregnated SC-CTL, and (d) PF/BL-impregnated SC-CTL

The changes of morphological properties of BL-impregnated SC-CTL after natural weathering showed that the middle lamella could still be clearly discerned in these samples after 6 months weathering (Fig. 8b). Some erosion of the middle lamella and delamination of the cell wall was apparent in samples after 12 months weathering, but overall the changes were less pronounced than in SC-CTL weathered samples. The effects of BL-impregnation could retard the formation of aromatic (lignin) radicals that initiate photo-oxidation. Alternatively, it was possible that the resin matrix in SC-CTL scavenged free radicals, preventing them from attacking lignin and cellulose. Such a suggestion is consistent with observations by Evans *et al*. (2002) that benzoyl groups in wood obstruct free radicals and photo-stabilize polymers.

The SEM micrographic images suggested that the PF-impregnated SC-CTL with BL reduced the rate of weathering, and thus removed from the SC-CTL first as a result of the weathering. Thus, the photodegradation and leaching of the matrix were important in weathering. Weight losses of samples also occurred due to these factors (Carol *et al*. 2010).

Accordingly, the ability of PF impregnation with BL to protect lignin from photodegradation might explain why weight losses of impregnated SC-CTL during natural weathering were lower than those of PF-impregnated SC-CTL.

Effects on Mechanical Properties Due to the Natural Weathering

As expected, mechanical properties (tensile and flexural) of all samples deteriorated due to the weathering effects. Generally, the highest decrease of mechanical properties occurred at 12 months of exposure to weathering conditions. Figures 9 to 12 show the change of mechanical properties due to weathering for different durations of exposure.

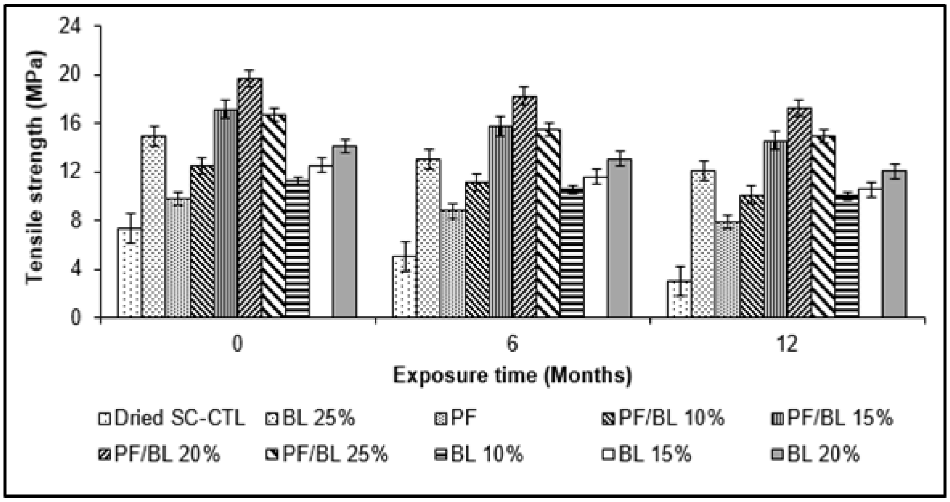


Fig. 9. Tensile strength of PF-impregnated SC-CTL with various LB levels, BL-impregnated SC-CTL, PF-impregnated SC-CTL, and dried SC-CTL after the weathering test from 0 to 12 months

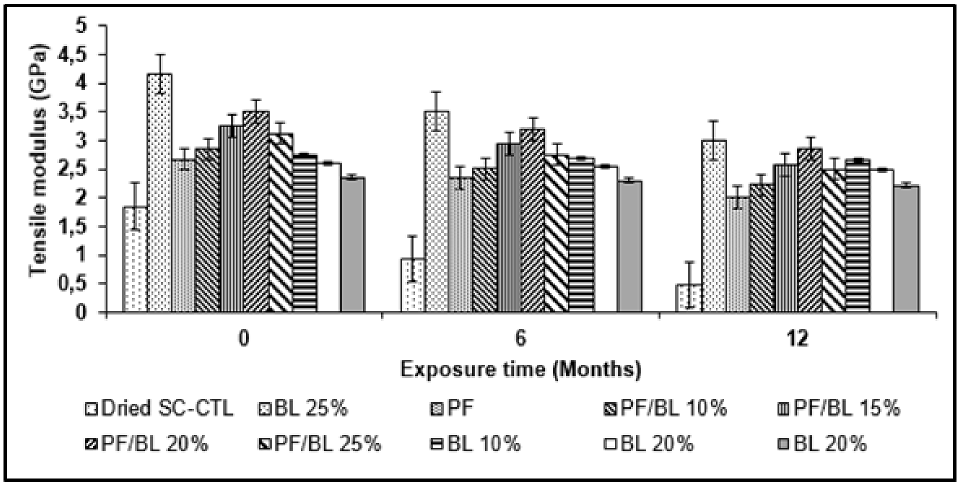


Fig. 10. Tensile modulus of PF-impregnated SC-CTL with various of LB levels, BL-impregnated SC-CTL, PF-impregnated SC-CTL, and dried SC-CTL after the weathering test from 0 to 12 months

The change of all these mechanical properties was significantly higher (F = 27.48, df = 4, $P < 0.05$) for untreated SC-CTL samples compared to the treated one. In general, the mechanical properties (tensile and flexural) decreased in both BL-impregnated SC-CTL and PF-impregnated SC-CTL with BL after the exposure to weathering, but PF-impregnated SC-CTL with BL were more resistant than BL-impregnated SC-CTL and PF-impregnated SC-CTL.

Generally tensile properties (such as tensile strength and modulus) for all samples showed reduction after exposure to the environment for 12 months. According to Fig. 9, tensile strength of PF-impregnation with 10%, 15%, 20%, and 25% BL concentration decreased 19.3%, 15.1%, 12.8%, and 11.1%, respectively, after 12 months of exposure to weathering conditions. Meanwhile, the BL-impregnation resulted in a tensile strength decrease of 20.0% at the same duration.

Figure 10 shows the change of tensile modulus properties due to weathering for different duration of exposure. Tensile modulus also decreased in PF-impregnation of SC-CTL with 20% BL, where the tensile modulus change was up to 18.8% in 12 months exposure time. This change was 10.5 to 25.1%, 7.7% to 21.8%, 7.7% to 20.6%, and 5.4% to 20.2% for 0%, 10%, 15%, and 25% of BL concentration, respectively.

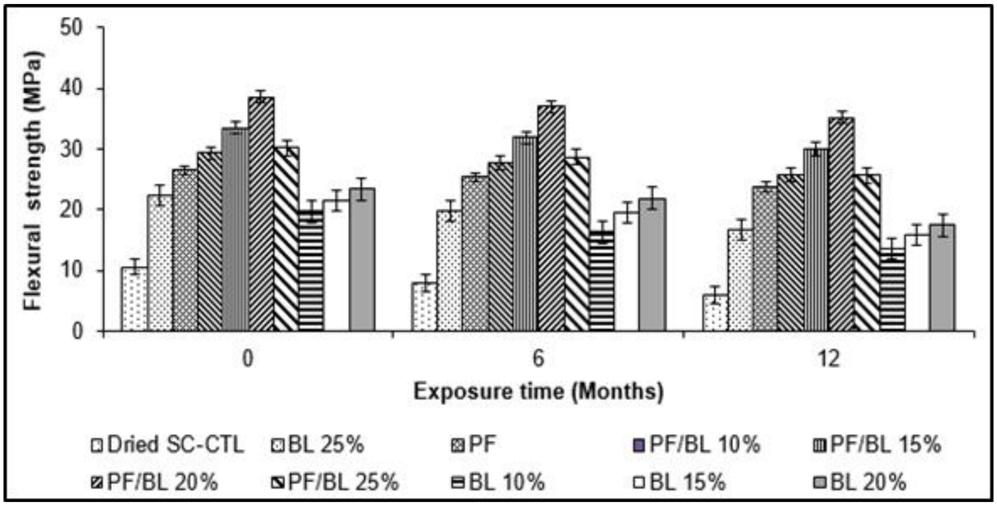


Fig. 11. Flexural strength of PF-impregnated SC-CTL with various LB levels, BL-impregnated SC-CTL, PF-impregnated SC-CTL, and dried SC-CTL after the weathering test from 0 to 12 months

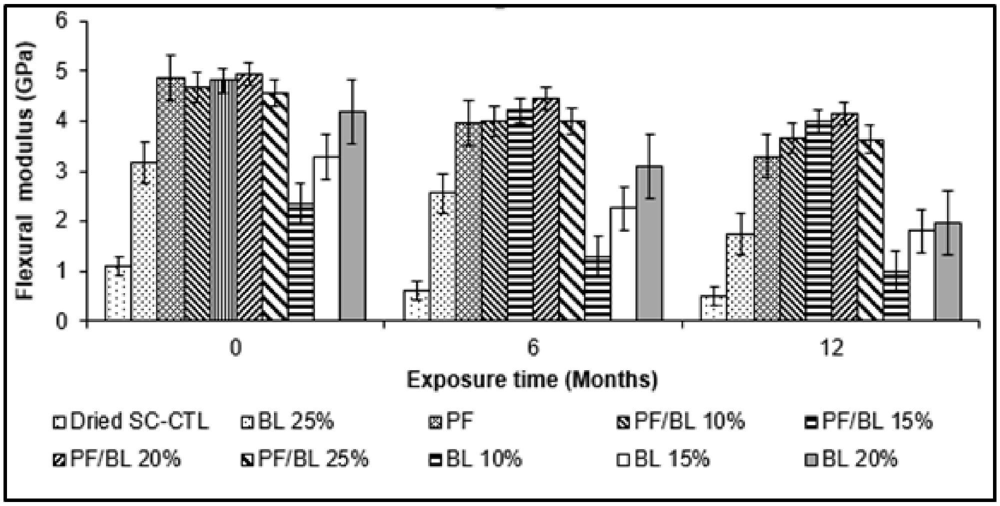


Fig. 12. Flexural modulus of PF-impregnated SC-CTL with various LB levels, BL-impregnated SC-CTL, PF-impregnated SC-CTL, and dried SC-CTL after the weathering test from 0 to 12 months

Figure 11 shows the flexural strength of BL-impregnation reinforcement, which was the highest degradation from 6.92% to 12.31% after 6 to 12 months of exposure. Meanwhile, for 20% of BL in PF resin, flexural strength showed deterioration from 2.6% to 6.2% at the same condition. This was followed by 20% of BL and 25% of BL with degradation to 7.5%, and 7.0% after 12 months of exposure, respectively. Impregnated SC-CTL with 10% BL showed higher degradation compared to the BL concentration, which was 8.9% degradation after 12 months of exposure.

In contrast, flexural modulus value for all samples showed degradation after 12 months exposure to the weathering condition. Flexural modulus decreased by up to 24.3% for BL-impregnated without PF resin. Meanwhile, for the 10% of BL it decreased 21.4%, for 3% BL it decreased 16.8%, and for 10% of BL decreased 20.4% after 12 months exposure (Fig. 12). Further, 20% of BL showed the lowest amount of decrease after 12 months (16.0%).

Polymer degradation is mainly caused by chemical bond scission reactions in a macro molecule. The natural fibers are susceptible to the moisture, temperature, high energy radiation, and attack from bio-organisms (Sreekala *et al*. 2002). This condition demonstrated that the SC-CTL showed higher deterioration compared to the SC-CTL after impregnation treatment once exposed to the environment. The PF resin and the BL filled the cell lumen to form a rigid cross-linked polymer that improved the strength and stiffness of the SC-CTL (Nur Izreen *et al*. 2011). Thus, treated samples had higher mechanical properties compared to the untreated ones even after weathering. Deka *et al.* (2003), Nur Izreen *et al*. (2011), and Evans *et al*. (2000) also reported similar mechanical properties losses due to natural weathering.

The SC-CTL tended to absorb moisture from the environment due to polar groups inside their fiber structure. Incorporation of these polar and non-polar characteristics creates compounding difficulties that lead to non-uniform dispersion of fibers within the matrix, which impairs the efficiency of the composite (John and Thomas 2008). Besides contributing to the high moisture absorption of the fiber, the polar nature also results in high moisture sorption in composites that leads to a void in the fiber matrix interphase, which would possibly reduce the mechanical properties of their composites. If moisture is not removed from natural fibers prior to compounding by drying, the products will become porous (Akil *et al*. 2011). However, for PF-impregnation with BL, good wetting between phenol formaldehyde matrixes with BL increased quality interface area and reduced the number of disfigurement (micro voids) into SC-CTL. The BL in PF play a positive role to generate polymerization during the impregnation process, which can improve the self-bonding strength of fiber cell lumen and cell wall impregnated. The mixture of BL in thermoset resin had interfacial adhesion that was better to prevent the absorption of water molecules to hydrophilic fiber. According to the study on weathering performance on plant fiber thermoplastic composite by Rowell *et al*. (2000), agro-based fibers undergo UV degradation through free radical reactions with the decomposition of the cellulose in the cell wall.

Statistical Analysis on Degradation by Weathering

Table 1 shows the change of mechanical properties due to weathering for different durations of exposure. In the subsequent statistical analysis of Duncan’s multiple range test, the tensile strength properties difference was highly significant ($P < 0.05$) at all concentrations of BL and exposure time, except after 6 months of exposure there was no difference between 20% and 25% of BL concentration.

Results of this analysis showed the differences in tensile modulus properties were not significant between BL concentrations 0% and 10%, as well as 15% and 25% at 6 months exposure. Moreover, BL concentration between 10% and 25% as well as 15% and 20% also showed no significant difference at 6 months exposure by weathering.

Table 1. Summary of Results from Duncan's Multiple Range Test for Tensile Properties of PF-impregnated SC-CTL with BL

PF/BL (%)	Tensile Strength (MPa)		
	Time Exposure (Months)		
	0	6	12
PF	9.81^{Aa}	8.22^{Ac}	6.70^{Ae}
PF/BL 10	12.51^{Ba}	11.44^{Bc}	9.75^{Be}
PF/BL 15	17.17^{Ca}	15.57^{CEc}	14.25^{Ce}
PF/BL 20	19.64^{Da}	18.69^{Dc}	17.38^{De}
PF/BL 25	16.72^{Ea}	15.13^{ECc}	13.50^{Ee}
PF/BL (%)	Tensile Modulus (GPa)		
	Time Exposure (Months)		
	0	6	12
PF	2.67^{ABab}	1.89^{ABc}	1.02^{Aed}
PF/BL 10	2.85^{BAab}	1.98^{BAcd}	1.33^{Bed}
PF/BL 15	3.25^{CEa}	2.62^{CDcbd}	2.10^{Cded}
PF/BL 20	3.51^{Da}	2.68^{DCcd}	2.00^{Dced}
PF/BL 25	3.12^{ECa}	2.12^{Ec}	1.57^{Eed}

Note: Values are means (n = 5); different capital and lowercase letters indicate significant differences within a column and a row, respectively ($p < 0.05$)

BL concentration between 10% and 25% did not significantly decrease for flexural strength at any weathering exposure times (Table 2). Therefore, there was no decrease in flexural strength at 6 and 12 months of exposure for 20% and 25% of BL concentration. Similarly, at 0%, 10%, and 15% BL concentration, after 6 months exposure there was no significant decrease.

Table 2. Summary of Results from Duncan's Multiple Range Test for Flexural Properties of PF-impregnated SC-CTL with BL

PF/BL (%)	Flexural Strength (MPa)		
	Time Exposure (Months)		
	0	6	12
PF	14.46^{Aab}	13.49^{Acd}	12.62^{Ae}
PF/BL 10	29.35^{BEa}	28.21^{BEcb}	27.35^{BEed}
PF/BL 15	33.51^{CDabe}	32.72^{Ccd}	31.68^{Ceab}
PF/BL 20	38.55^{DCab}	37.62^{Dcde}	36.84^{Decd}
PF/BL 25	30.12^{EBa}	28.76^{EBcde}	28.02^{EBecd}
PF/BL (%)	Flexural Modulus (GPa)		
	Time Exposure (Months)		
	0	6	12
PF	4.35^{Aa}	3.65^{ABc}	2.95^{Ae}
PF/BL 10	4.67^{Bea}	3.94^{BACc}	3.12^{BCEe}
PF/BL 15	4.81^{Cda}	3.89^{CBEc}	3.20^{CBEe}
PF/BL 20	4.95^{DCa}	4.16^{Dc}	3.55^{De}
PF/BL 25	4.57^{EBa}	3.85^{Ecc}	3.19^{EBCe}

Note: Values are means (n = 5); different capital and lowercase letters indicate significant differences within a column and a row, respectively ($p < 0.05$).

Similarly, for flexural modulus, there was no significant decrease between 0% and 10% as well as 15% and 25% BL concentration after 6 months exposure. Moreover, there was no significant decrease for 0 and 10% as well as 15% and 20% of BL concentration at 6 months exposure. Further, at 12 months exposure to weathering there was no significant difference between 15% and 20% BL concentration.

CONCLUSIONS

1. The phenol-formaldehyde (PF)-impregnated short cycle coconut trunk lumber (SC-CTL) with black liquor (BL) showed that addition of BL reduced the effects of ultraviolet light (UV) and water decay in SC-CTL.
2. Overall, erosion of the middle lamella and delamination of the cell wall were less pronounced on PF-impregnated SC-CTL with BL than in SC-CTL weathered samples. PF resin and BL, which are located in the fiber lumen, were slightly better compared to the PF resin only.
3. BL-impregnated SC-CTL showed the highest degradation compared to the PF-impregnated with 10%, 15%, 20%, and 25% of BL samples.

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REFERENCES CITED

Abdul Khalil, H. P. S., Amouzgor, P., Jawaid, M., Hassan, A., Ahmad, F., Hadiyane, A., and Dungani, R. (2012). "New approach to oil palm trunk core lumber material properties enhancement *via* resin impregnation," *J. Biobased Mater. Bio.* 6(3), 299-308. DOI: 10.1166/jbmb.2012.1212

Akil, H. M., Omar, M. F., Mazuki, A. A. M., Safiee, S., Ishak, Z. A. M., and Abu Bakar, A. (2011). "Kenaf fiber reinforced composites: A review," *Mater. Design* 32(8-9), 4107-4121. DOI: 10.1016/j.matdes.2011.04.008

Alwadani, N., and Fatehi, P. (2018). "Synthetic and lignin-based surfactants: Challenges and opportunities." *Carbon Resour. Convers.* 1, 126-138. DOI: 10.1016/j.crcon.2018.07.006

ASTM D790 (2003). "Standard test methods for flexural properties of unreinforced and reinforced plastics and electrical insulating materials," ASTM International, West Conshohocken, PA, USA.

ASTM D1435 (1999). "Standard practice for outdoor weathering of plastics," ASTM International, West Conshohocken, PA, USA.

ASTM D3039 (2000). "Standard test methods for tensile properties of polymer matrix composite materials," ASTM International, West Conshohocken, PA, USA.

Bhat, I. H., Abdul Khalil, H. P. S., Khairul, B. A., Bakare, I. O., and Issam, A. M. (2010). "Effect of weathering on physical, mechanical and morphological properties of chemically modified wood materials," *Mater. Design* 31(9), 4363-4368. DOI: 10.1016/j.matdes.2010.03.045

Carol, A. C., Green, F., and Nami Kartal, S. (2010). "Weatherability and leach resistance of wood impregnated with nano-zinc oxide," *Nanoscale Res. Lett.* 5, Article Number 1464. DOI: 10.1007/s11671-010-9662-6

Deka, M., Das, P., and Saikia, C. N. (2003). "Studies on dimensional stability, thermal degradation and termite resistant properties of bamboo (*Bambusa tulda* Roxb.) treated with thermosetting resin," *Bamboo Rattan* 2(1), 29-41.

Deka, M., and Petrič, M. (2008). "Photo-degradation of water borne acrylic coated modified and non-modified wood during artificial light exposure," *BioResources* 3(2), 346-362. DOI: 10.15376/biores.3.2.346-362

Dungani, D., Abdul Khalil, H. P. S., Islam, N., Sumardi, I., Aditiawati, P., and Hadiyane, A. (2016). "Soil burial degradation of oil palm shell (OPS) nanofiller and phenol formaldehyde (PF) resin-impregnated oil palm trunk lumber (OPTL): Dimensional stability and mechanical properties," *J. Biobased Mater. Bio.* 10(4), 258-264. DOI: 10.1166/jbmb.2016.1585

Dungani, R., Jawaid, M., Abdul Khalil, H. P. S., Jasni, J., Aprilia, S., Hakeem, K. R., Hartati, S., and Islam, M. N. (2013). "A review on quality enhancement of oil palm trunk waste by resin impregnation: Future materials," *BioResources* 8(2), 3136-3156. DOI: 10.15376/biores.8.2.3136-3156

Evans, P. D., Owen, N. L., Schmid, S., and Webster, R. D. (2002). "Weathering and photostability of benzoylated wood," *J. Polym. Degrad. Stabil.* 76(2), 291-303. DOI: 10.1016/S0141-3910(02)00026-5

Evans, P. D., Wallis, A. F. A., and Owen, N. I. (2000). "Weathering of chemically modified wood surface. Natural weathering of scots pine acetylated to different weigh gain," *Wood Sci. Technol.* 34(2), 151-165. DOI: 10.1007/s002260000039

Furuno, T., Imamura, Y., and Kajita, H. (2004). "The modification of wood by treatment with low molecular weight phenol-formaldehyde resin: A properties enhancement with neutralized phenolic-resin and resin penetration into wood cell walls," *Wood Sci. Technol.* 37(5), 349-361. DOI: 10.1007/s00226-003-0176-6

Feist, W. C., and Hon, D.N.-S. (1984). "Chemistry and weathering and protection," in: *The Chemistry of Solid Wood*, Advances in Chemistry Series 207, R.M. Rowell (ed.), pp. 349-370: American Chemical Society, Washington D.C.

Gautam, C., Yadav, A. K., and Singh, A. K. (2012). "A review on infrared spectroscopy of borate glasses with effects of different additives," *ISRN Ceramics* 2012(428497), 1-17. DOI: 10.5402/2012/428497

Georgokapoulos, A. (2003). "Study of low rank Greek coals using FTIR spectroscopy," *Energy Source* 25(10), 995-1005. DOI: 10.1080/00908310303390

Gothwal, R. K., Mohan, M. K., and Ghosh, P. (2010). "Synthesis of low cost adhesive from pulp & paper industry waste," *J. Sci. Ind. Res.* 69, 390-395.

Islam, N., Dungani, R., Abdul Khalil, H. P. S., Alwani, M. S., Wan Nadirah, W. O., and Fizree, H. M. (2013). "Natural weathering studies of oil palm trunk lumber (OPTL) green polymer composites enhanced with oil palm shell (OPS) nanoparticles," *SpringerPlus* 2, Article Number 592. DOI: 10.1186/2193-1801-2-592

John, M. J., and Thomas, S. (2008). "Biofibres and biocomposites," *Carbohyd. Polym.* 71(3), 343-364. DOI: 10.1016/j.carbpol.2007.05.040

Karliati, T., Sumardi, I., Darwis, A., and Rumidatul, A. (2018). "Incorporation of phenol-formaldehyde-based black liquor as an adhesive on the performance of plywood," *J. Biol. Sci.* 18(7), 346-353. DOI: 10.3923/jbs.2018.346.353

Kocaefe, D., Poncsak, S., and Boluk, Y. (2008). "Effect of thermal treatment on the chemical composition and mechanical properties of birch and aspen," *BioResources* 3(2), 517-537. DOI: 10.15376/biores.3.2.517-537

Kouisni, L., Fang, Y., Paleologou, M., Ahvazi, B., Hawari, J., Zhang, Y., and Wang, X.-M. (2011). "Kraft lignin recovery and its use in the preparation of lignin-based phenol formaldehyde resins for plywood," *Cell. Chem. Technol.* 45(7-8), 515-520.

Lopez, J. L., Sain, M., and Cooper, P. (2005). "Performance of natural-fiber-plastic composites under stress for outdoor application: Effect of moisture, temperature and ultraviolet light exposure," *J. Appl. Polym. Sci.* 99, 2570-2577. DOI: 10.1002/app.22884

Ma, Q., Zhao, Z., Yi, S., and Wang, T. (2016). "Modification of fast-growing Chinese fir wood with unsaturated polyester resin: Impregnation technology and efficiency," *Results. Phys.* 6, 543-548. DOI: 10.1016/j.rinp.2016.08.017

Nikafshar, S., Zabihi, O., Ahmadi, M., Mirmohseni, A., Taseidifar, M., and Naebe, M. (2017). "The effects of UV light on the chemical and mechanical properties of a transparent epoxy-diamine system in the presence of an organic UV absorber," *Materials* 10(2), 180-197. DOI: 10.3390/ma10020180

Nur Izreen, F. A., Zaidon, A., Rabia 'tol Adawiah, M. A., Bakar, E. S., Paridah, M. T., Mohd Hamami, S., and Anwar, U. M. K. (2011). "Enhancing the properties of low density hardwood *Dyera costulata* through impregnation with phenolic resin admixed with formaldehyde scavenger," *J. Appl. Sci.* 11(20), 3474-3481. DOI: 10.3923/jas.2011.3474.3481

Oberhofnerová, E., Pánek, M., and García-Cimarras, A. (2017). "The effect of natural weathering on untreated wood surface," *Maderas. Cienc. Tecnol.* 19(2), 173-185. DOI: 10.4067/S0718-221X2017005000015

Pandey, K. K., and Pitman, A. J. (2003). "FTIR studies of changes in wood chemistry following decay by brown-rot and white-rot fungi," *Int. Biodeter. Biodegr.* 52(3), 151-160. DOI: 10.1016/S0964-8305(03)00052-0

Pongjanyakul, T., Khunawattanakul, W., and Puttipipatlehachor, S. (2009). "Physicochemical characterizations and release studies of nicotine–magnesium aluminum silicate complexes," *Appl. Clay Sci.* 44(3-4), 242-250. DOI: 10.1016/j.clay.2009.03.004

Rana, M. N., Das, A. K., and Ashaduzzaman, M. (2015). "Physical and mechanical properties of coconut palm (*Cocos nucifera*) stem," *Bangladesh J. Sci. Ind. Res.* 50(1), 39-46. DOI: 10.3329/bjsir.v50i1.23808

Rowell, R. M., Lange, S. E., and Jacobso, R. E. (2000). "Weathering performance of plant-fiber/thermoplastic composites," *Mol. Cryst. Liq. Crys. A* 353(1), 85-94. DOI: 10.1080/10587250008025650

Santoso, A., and Sutigno, P. (2003). "Effect of dried cassava flour and dextrin as urea formaldehyde extender against stickiness of kapur plywood," *Int. J. Prod. Res.* 22(2), 61-68.

Siddiqui, H., Mahmood, N., Yuan, Z., Crapulli, F., Dessbesell, L., Rizkalla, A., Ray, A., and Xu, C. (2017). "Sustainable bio-based phenol-formaldehyde resoles using hydrolytically depolymerized kraft lignin," *Molecules* 22, 1850-1868. DOI: 10.3390/ijms18061224

Sreekala, M. S., George, J., Kumaran, M. G., and Thomas, S. (2002). "The mechanical performance of hybrid phenol-formaldehyde-based composites reinforced with glass and oil palm fibers," *Compos. Sci. Technol.* 62(3), 339-353. DOI: 10.1016/S0266-3538(01)00219-6

Teacă, C. A., Roşu, D., Bodîrlău, R., and Roşu, L. (2013). "Structural changes in wood under artificial UV light irradiation determined by FTIR spectroscopy and color measurements-A brief review," *BioResources* 8(1), 1478-1507. DOI: 10.15376/biores.8.1.1478-1507

Temiz, A., Terziev, N., Eikenes, M., and Hafren, J. (2007). "Effect of accelerated weathering on surface chemistry of modified wood," *Appl. Surf. Sci.* 253(12), 5355-5362. DOI: 10.1016/j.apsusc.2006.12.005

The Indonesian Pulp and Paper Association (2018). "The pulp and paper industry grows 5% next year," Retrieved from (https://www.kontan.co.id/tag/asosiasi-pulp-dan-kertas-indonesia-apki), Accessed 2 Dec 2019.

Van Daele, M., Detavernier, C., and Dendooven, J. (2018). "Surface species during ALD of platinum observed with *in situ* reflection IR spectroscopy," *Phys. Chem. Chem. Phys.* 20(39), 25343-25356. DOI: 10.1039/C8CP03585G

Yildiz, S., Yildiz, U. M. C., and Tomak, E. D. (2011). "The effects of natural weathering on the properties of heat-treated alder wood," *BioResources* 6(3), 2504-2521. DOI: 10.15376/biores.6.3.2504-2521

Yousif, E., and Haddad, R. (2013). "Photodegradation and photostabilization of polymers, especially polystyrene: Review," *SpringerPlus* 2013(2), 398-429. DOI: 10.1186/2193-1801-2-398

Zhoa, J., Cai, G., Cui, L., Si Larbi, A., and Tsavdaridis, K. D. (2017). "Deterioration of basic properties of the materials in FRP-strengthening RC structures under ultraviolet exposure," *Polymers* 9(9), 402-413. DOI: 10.3390/polym9090402

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