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RESISTANCE IMPROVEMENT OF RUBBERWOOD TREATED WITH ZINC OXIDE NANOPARTICLES AND PHENOLIC RESIN AGAINST WHITE-ROT FUNGI, *Pycnoporus sanguineus*

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ABSTRACT

Phenolic resin or phenol formaldehyde (PF) resin containing different percentage of zinc oxide (ZnO) nanoparticles was prepared and used to treat rubberwood. Three types of treatment solutions were prepared, namely (1) low molecular weight phenol formaldehyde resin (LMwPF), (2) 1,5 wt % nano ZnO dissolved in water (ZnO/H_2O), and (3) combination of both LMwPF and 1,5 wt % nano ZnO (LMwPF/ZnO). The rubberwood samples were submerged into the treatment solutions for 60, 90, and 120 min, before vacuum impregnation. The untreated rubberwood samples served as the controlled samples. The thermal stability behaviour and resistance against white-rot fungi (*Pycnoporus sanguineus*) of the treated rubberwood samples were evaluated. The results reveal that the treated rubberwood had slightly better thermal stability compared to the untreated samples. In terms of decay resistance, the rubberwood treated with LMwPF and LMwPF/ZnO possess very high resistance against white-rot fungi. On the other hand, the rubberwood treated with ZnO/H_2O did not attain similar effectiveness as the other two treatments, except for the samples that were submerged in ZnO/H_2O for 120 min. The results indicate that 1,5 wt % nano ZnO could be sufficient in imparting superior durability to rubberwood provided that longer submersion time is adopted.

Keywords: Fungal resistance, *Hevea brasilensis*, impregnation modification, phenol formaldehyde, resin, thermal stability.

INTRODUCTION

Rubberwood (*Hevea brasiliensis*) is a very important plantation crop in Southeast Asian countries, particularly Malaysia. However, it is a non-durable wood which is very prone to the attack by fungi and insects that starts almost immediately after the tree is felled. Blue stain fungi, ambrosia beetles, and powder-post beetles are among the fungi and insects that invade rubberwood and render it non-usable (Browne 1961, Hong *et al.* 1980, Norhara 1981). Owing to this, rubberwood is mainly used interiorly such as furniture where its light colour and good appearance are certainly adding value to the designated application (Ratnasingam *et al.* 2011). In order to enhance the biological durability of rubberwood, preservative treatment must be carried out. Fortunately, rubberwood is very amenable to preservatives and very easy to be treated. Application of conventional wood preservative such as chromated copper arsenate (CCA) and boron is a common practice in treating rubberwood (Yang *et al.* 2006). However, both preservatives impose adverse effects to the environment and has fixation problem in wood. Hence, alternative preservative like copper chromate borate (CCB) is a potential candidate (Gallio *et al.* 2018). Apart from that, various green preservation techniques have been proposed. For

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instance, plant essential oils such as lavender oil, lemon grass oil, and thyme oil were found very effective in protecting the wood from fungi attack (Bahmani and Schmidt 2018). Heat treatment with the application of vegetables oil as heating medium is also a promising method to enhance the biological durability of wood (Lee *et al.* 2018).

In order to enhance wood durability against biodeterioration agents, one of the promising techniques is to impregnate the wood with either nano-sized zinc oxide (ZnO) or zinc borate, which allow the penetrants to penetrate the cell wall to a greater extent. ZnO nanoparticles have wide applications in various areas including pharmaceutical for the manufacturing of sunscreens products (Jeon *et al.* 2016, Dao *et al.* 2016, Zuzanna *et al.* 2013), wastewater treatment (Wang *et al.* 2008), and as an antifungal and antibacterial agent (Sawai, 2003, Sawai and Yoshikawa 2004, Jain *et al.* 2009). ZnO nanoparticles are known to have good antimicrobial ability (Iždinský *et al.* 2018). Lykidis *et al.* (2016) impregnated Scots pine with nano ZnO and zinc borate using the full cell process and significantly improved the resistance of the impregnated wood against brown rot fungi, *Serpula lacrymans*. In a study by Ghorbani-Kookandeh *et al.* (2014), beech wood impregnated with ZnO nanoparticles exhibited significant improvement in resistance against white-rot fungi, *Trametes versicolor*. Besides, paper made with ZnO nanoparticles-treated pulp fibres possessed superior antimicrobial effect against *Escherichia coli* and *Staphylococcus aureus*, a Gram-negative and Gram-positive bacterium, respectively. Apart from fungi and bacteria, the impregnation of nano ZnO also bestow the wood with better resistance against Subterranean termites (Akhtari and Nicholas 2013).

Phenolic resin is one of the well-known wood surface protectors which is widely used in wood-based industry, due to its high flexibility, excellent water resistance, good mechanical properties, good resistance to acids, low cost, and simple production process. It is also non-toxic and difficult to ignite (Furuno *et al.* 2004, Dong *et al.* 2009, Huang *et al.* 2014). Altering the phenolic resin properties using ZnO nanoparticles as additive should improve the level of wood protection especially against decay fungi and UVA radiation. ZnO nanoparticle is an inorganic material which has a wide band gap (3,37 eV) and large excitation binding energy of 60 meV. Therefore, it can absorb light that matches or exceeds their band gap energy, which lies in the UV range of the solar spectrum; thus it can function as a UV absorber (Fangli *et al.* 2003). Aiming to improve the biological resistance of the wooden composites, Gao *et al.* (2018) modified the aqueous phenol formaldehyde (PF) resin using nano copper oxide (CuO). The PF resin, along with superior biological resistance ability, displayed self-curing properties that can compensate the adverse effects on mechanical strength. However, few studies have been performed to assess the effect of ZnO nanoparticles as anti-wood decaying fungi (mold, sapstain, white- and brown-rot) (Mantanis *et al.* 2014).

Therefore, this study aims to evaluate the effect of ZnO nanoparticles in low molecular weight phenol formaldehyde (LMwPF) resin on the durability of rubberwood towards white-rot fungi under laboratory conditions. To achieve the objective of this study, different concentrations of ZnO nanoparticle were incorporated into the LMwPF resin formulation for impregnation treatment. The interaction between ZnO nanoparticle with LMwPF resin, the effect of curing time, and several properties were investigated by Fourier transform infrared spectroscopy (FTIR) and thermo gravimetric analysis (TGA/DTG). The thermal behaviour of ZnO nanoparticles loaded LMwPF resin impregnated into the rubberwood was also characterised using TGA/DTG. The morphology and dispersibility properties of ZnO/PF solution into the rubberwood structure were characterised using SEM.

MATERIALS AND METHODS

Preparation of materials

Kiln dried rubberwood (*Hevea brasilensis*) was obtained from a commercial market in Selangor. The rubberwood was cut into the dimension of 25 × 25 × 9 mm before they were conditioned to an equilibrium moisture content of 20% in a conditioning room. Novalac type low molecular weight phenol formaldehyde (LMwPF) was purchased from a local manufacturer located in Shah Alam, Selangor. The LMwPF (Mw 600) with 45% solid content was used. Nano ZnO modified with octadecyl ammonium/silane used in this study was obtained from Nanocor Inc.

Impregnation treatment

The rubberwood samples were treated with three types of treatment preservatives, namely (1) 45% low molecular weight phenol formaldehyde resin (LMwPF), (2) 1,5 wt % nano zinc oxide dissolved in water (ZnO/H_2O), and (3) combination of 45% LMwPF and 1,5 wt % nano zinc oxide (LMwPF/ZnO). The solutions were mixed for 40 min. A set of untreated samples was prepared to serve as the controlled samples. All treatments were conducted at Forest Research Institute Malaysia (FRIM) in Kepong. Prior to vacuum impregnation, the rubberwood samples were submerged in the preservatives for 60, 90, and 120 min. Eight replications were prepared for each treatment. After that, the samples were vacuum impregnated for 1 hr and then, the pressure was slowly released for 90 min from the vacuum chamber. The samples were then taken out and dried in an oven at 60 °C for 48 hr. The weight percent gain (WPG) of the samples after impregnation were determined.

Fourier transform infrared spectroscopy (FTIR) analysis

FTIR was used to characterise the chemical changes in LMwPF due to the addition of ZnO nanoparticle before impregnating into wood. The chemical changes of the cured LMwPF resin and LMwPF/ZnO (cured at 103 °C for 6 h in an oven) were measured in the range of wavelengths between 280 and 4000 cm^{-1} using a Perkin Elmer FTIR instrument (1 cm^{-1} resolution, 32 scans, KBr method). The analysis was carried out at room temperature.

Thermal stability

Thermal stability properties of the rubberwood treated with LMwPF/ZnO nanoparticles were analysed using a thermal gravimetric analysis (TGA/DTG), SDT Q 600 research instrument at a heating rate of 10 °C/min, from 25 to 1000 °C under nitrogen atmosphere. Mass of the sample used was around 10-15 mg. Derivative thermal gravimetric (DTG) was also obtained to determine the maximum rate of weight loss.

Surface morphology

Morphology and microstructure of rubberwood treated with LMwPF/ZnO were observed by SEM, JEOL variable pressure SEM (VP-SEM 1455). A small wood block of 10 × 10 × 12 mm was prepared from the treated rubberwood samples. Then, the centre of the treated wood block was sliced from the transverse section using a microtome to obtain a 5-mm thick specimen. The dried sliced samples were put on a conductive carbon adhesive tape surface which was attached to the SEM stub, and then Pd/gold coated on the cutting surface and viewed at an accelerated voltage of 20 kV.

Fungus test

Both treated and untreated rubberwood samples were tested for durability according to the procedures specified in ASTM 2017 - 05 (Standard Test Method of Natural Decay Resistance of Wood). White-rot fungus, *Pycnoporus sanguineus* was used as the test fungus. The feeder strip from rubberwood with dimension of 3 × 29 × 35 mm were prepared and conditioned. Malt extract agar (MEA) was used as a nutrient medium for culturing the fungus. An amount of 2 wt % malt extract and 1,5 wt % weight agar was prepared by mixing it with distilled water in a bottle. The medium was sterilised at 121 °C for 20 min and allowed to cool before inoculations. After the medium was cooled and solidified, the white-rot fungus was inoculated on the surface of the media and incubated in an incubator at 27 + 2 °C for about 4-5 days until the mycelium covered at leasttwo-third of the petri dish. Then, a sterile test block was placed on the feeder strips and transferred into the culture bottle. Prior to the transferring test block and feeder strip into the culture bottle, 150 g sieved soil and 70 ml distilled water was added into the culture bottle. After the test blocks were introduced into the culture bottles, they were left to incubate for 16 weeks. At the end of the test, the test blocks were cleaned for removing all the mycelium on the surfaces. The test blocks were then oven-dried until the constant weights were reached and the percentage of weight loss caused by white-rot fungus was determined.

RESULTS AND DISCUSSION

Chemical property of LMwPF/ZnO

Figure 1 shows the FTIR spectra of pure LMwPF and LMwPF/ZnO nanocomposite prepared using different concentration of ZnO nanoparticles. Band at 3461 cm^{-1} corresponds to the -OH functional group, while bands at 2920 and 2851 cm^{-1} corresponds to –CH stretching. Bands at 1220 cm^{-1} are assigned to C–O stretching vibrations of phenolic resin. The band at 3461 cm^{-1} for LMwPF/ZnO nanocomposite sample shows a decrease in intensity compared to that of the pure LMwPF resin, suggesting that the -OH functional groups of phenolic resin were occupied by the ZnO nanoparticles. The similar observation was reported by Dhoke *et al.* (2009) when using ZnO nanoparticle in the alkyd-based waterborne coating formulation. The other absorption peaks of phenolic resin containing 0; 0,5; 1; 1,5; 2, and 2,5 wt % ZnO did not change significantly, indicating that the structure of the LMwPF resin was unaltered by the addition of ZnO nanoparticles. However, LMwPF/ZnO nanocomposite mixture prepared using 1,5 wt % ZnO nanoparticles was chosen for further study.

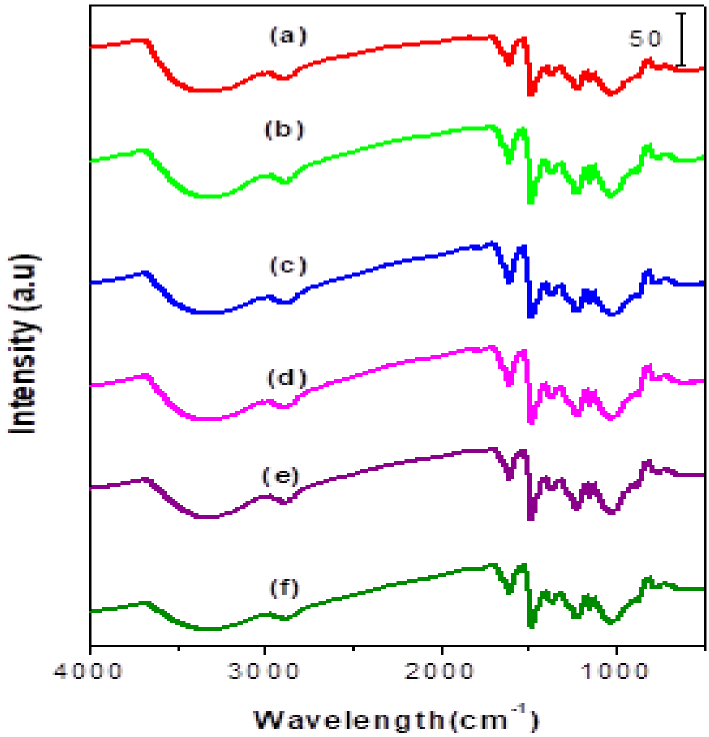

Figure 1: FTIR spectra of (a) pure LMwPF resin, LMwPF containing (b) 0,5 wt %, (c) 1,0 wt %, (d) 1,5 wt %, (e) 2,0 wt %, and 2,5 wt % of ZnO nanoparticles.

Weight percent gain (WPG)

The WPG of the rubberwood treated with different types of solution are shown in Table 1. The WPG is a function of submersion time where the longer the submersion time, the higher the WPG of the samples. The rubberwood treated with ZnO/H_2O recorded the lowest WPG ranging from 1,07% to 1,54%. Meanwhile, the rubberwood treated with LMwPF/ZnO has the highest WPG (6,30%-7,13%) compared to that of the samples treated with LMwPF solely (4,19%-4,52%). According to Dungani *et al.* (2014), PF resin could only penetrate the wood cell lumen and has high tendency of leaching out from the lumen. On the other hand, addition of nanoparticles could assist the fixation and polymerisation of PF resin after impregnation and subsequently resulted in higher WPG compared to the wood impregnated with PF resin solely.

Table 1: The WPG of the rubberwood samples treated with different types of solution.

Type of treatment	Submersion time (min)	Weight percent gain (%)
Untreated	0	-
LMwPF	60	4,19
	90	4,37
	120	4,52
LMwPF/ZnO	60	6,30
	90	6,87
	120	7,13
ZnO/H_2O	60	1,16
	90	1,07
	120	1,54

Thermal behavior

The TGA/DTG thermograms of ZnO nanoparticles, pure LMwPF resin, LMwPF/ZnO nanocomposite treated and untreated rubberwood are presented in Figure 2. Table 2 shows the TGA/DTG data of ZnO nanoparticles, pure LMwPF, LMwPF/ZnO treated and untreated rubberwood. TGA/DTG thermograms for all specimens clearly show that the mass loss was implemented in two steps. The first mass loss was performed at temperatures between room temperature and 120 °C due to the evaporation of water. The water loss for each specimen occurred at below 100 °C. The DTG of rubberwood treated with nano ZnO has a high quantity of water than those of the untreated rubberwood, rubberwood treated with LMwPF resin, and rubberwood treated with LMwPF/ZnO. High water content in the rubberwood treated with nano ZnO is due to the existence of water used as ZnO carrier during treatment process.

Figure 2 also shows that the specimen exhibited further degradation steps at the range from 150 to 470 °C. The degradation phenomena of the specimens are generally attributed to the degradation of cellulose and lignin of the rubberwood. However, the degradation reactions of the samples here were different in terms of their energies of activation, depending on the type of treatment used. Based on DTG, the degradation of the untreated rubberwood was higher (68,5%), followed by ZnO-treated rubberwood (67,5%), LMwPF-treated rubberwood (67,5%), and LMwPF/ZnO- treated rubberwood (66,6%). This means that LMwPF/ZnO polymer slightly improved the thermal stability of rubberwood. This phenomenon could possibly attribute to the higher WPG resulted by the LMwPF/ZnO solution as a higher amount of materials has been impregnated into the rubberwood and led to a more thermally stable structure (Dungani *et al.* 2014).

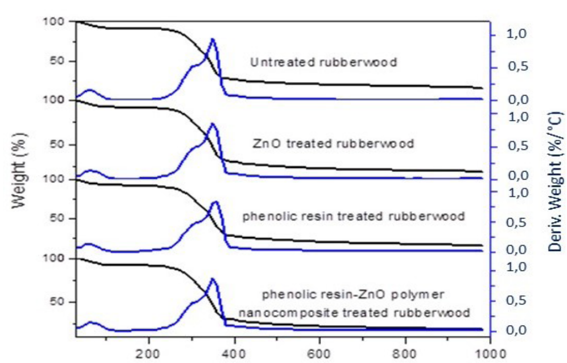

Figure 2: TGA/DTG thermograms of ZnO nanoparticles, pure LMwPF resin and LMwPF/ZnO-treated rubberwood.

Table 2: TGA/DTG data of ZnO nanoparticles, pure LMwPF resin and LMwPF/ZnO-treated rubberwood.

Samples	TGA degradation of interval step 1 (°C)	DTG peak of step 1 (°C)	Percent mass loss (%)	TGA degradation of interval step 2 (°C)	DTG peak of step 2 (°C)	Percent mass loss (%)
Untreated	30-120	60,3	3,9	150-470	352	68,5
ZnO-treated	30-120	60,3	3,9	150-470	352	67,5
LMwPF-treated	30-120	56,9	3,3	150-470	352	67,5
LMwPF/ZnO-treated	30-120	62,8	3,5	150-470	352	66,6

Morphology of treated rubberwood

SEM was used to characterise the surface morphology of rubberwood treated with LMwPF/ZnO solution. The SEM image of the treated rubberwood is presented in Figure 3. The experiments were carried out to study the dispersibility of nano ZnO and LMwPF resin in wood cells structure. As shown in Figure 3, the ZnO nanoparticles (white) and LMwPF resin (black) were well dispersed in the wood cells structure. From Figure 3, the LMwPF/ZnO admixture has deposited on the cell wall and cell lumen, indicating good penetration of the solution.

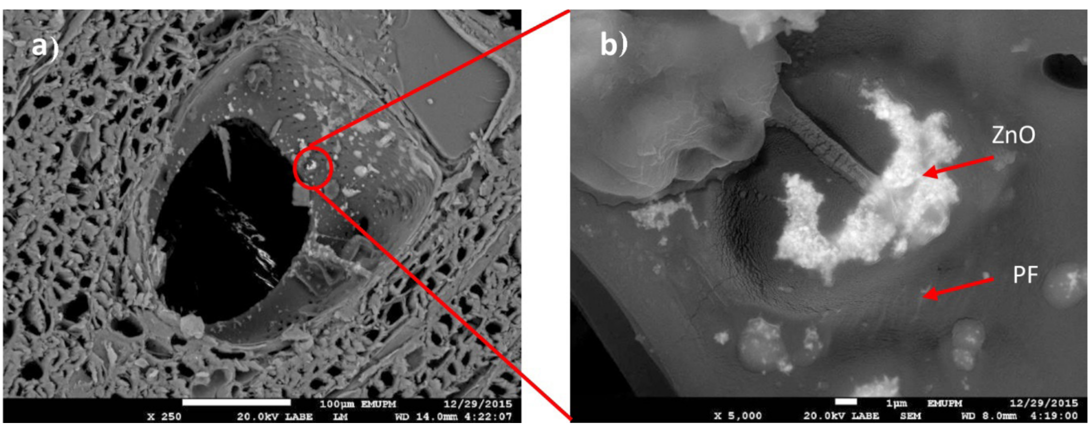

Figure 3: SEM images of LMwPF/ZnO-treated rubberwood: a) magnificent 250× and b) magnificent 5000×.

Fungus test

Table 3 summarises the percentage of weight loss and resistance class of the treated and untreated rubberwood after 8-weeks exposure to the white-rot fungus. The resistance classes were classified based on the weight loss of samples according to American Society for Testing and Materials (ASTM) ASTM D2017. According to the standard, the untreated rubberwood with 26,7% weight loss falls into the class of moderate resistance (Class 3) towards *P. sanguineus*. For the samples treated with nano zinc oxide dissolved in water (ZnO/H_2O), significant improvement in fungus resistance was observed and the improvement increased with increasing submerging times. Samples that were submerged in ZnO/H_2O for 60 min before the vacuum impregnation treatment fall into Class 2 of resistance, with a weight loss of 15,0% after exposure to the fungus. On the other hand, the weight loss of the samples submerged in ZnO/H_2O for 90 and 120 min before the vacuum impregnation treatment were 9,9% and 1,6%, respectively, which is highly resistance (Class 1) towards *Pycnoporus sanguineus*.

Table 3: Percentage of weight loss and resistance class of the treated and untreated rubberwood after 8-weeks exposure to *Pycnoporus sanguineus*.

Type of treatment	Submersion time (min)	Mass loss (%)	Resistance Class
Untreated	0	26,7 ± 3,5^{d}	3
LMwPF	60	0,29 ± 0,12^{a}	1
	90	0,25 ± 0,10^{a}	1
	120	0,15 ± 0,10^{a}	1
LMwPF/ZnO	60	0,26 ± 0,20^{a}	1
	90	0,21 ± 0,17^{a}	1
	120	0,10 ± 0,12^{a}	1
ZnO/H_2O	60	15,0 ± 2,9^{c}	2
	90	9,9 ± 10,5^{bc}	1
	120	1,6 ± 0,5^{ab}	1

Note: Mean value followed by different letters a,b,c,d are significantly different at $p \leq 0.05$.

As for the samples treated solely with LMwPF resin, 0,15%–0,29% weight loss was recorded, indicating very high resistance bestowed by the LMwPF treatment (Class 1). On the other hand, 0,10%-0,26% weight loss was observed after the addition of nano ZnO into LMwPF. From the results, the durability of ZnO/H_2O treated rubberwood (1,6%-15,0%) was significantly improved compared to that of the untreated samples (26,7%). Although the improvements were relatively small when comparing with LMwPF and LMwPF/ZnO treatments, resistance Class 1 was achieved when the samples were submerged in the ZnO/H_2O solution for a long enough time before impregnation (≥90 min).

On the other hand, LMwPF and LMwPF/ZnO treatments showed similar effectiveness against white-rot fungi. The physical barrier formed by the LmwPF and nano ZnO could prevent the wood from degraded by the digestive enzyme release by the fungus (Zanatta *et al.* 2017). In addition, reduction in the water absorption capacity of the wood as a result of decreased available void spaces is also a main factor that leads to the improvement in fungal resistance (Leemon *et al.* 2015). Suitable growing environment favored by the fungus was prevented as the water diffusivity in the wood was reduced (Nabil *et al.* 2016). Thus, the combination of both treatments resulted in the wood with very high resistance against fungal decay. The wood treated with LMwPF shows higher resistance to fungi because phenolic has a 3-dimensional network that is difficult to dissolve and degrade (Gusse *et al.* 2006). Clausen *et al.* (2010) also reported that the application of nano ZnO enhanced the resistance of wood against fungi and termites as well as protects the wood from UV degradation and prevents leaching. Improved decay resistance of particleboard treated with nano ZnO against *Trametes versicolor* and *Coniophora puteana* were reported by Marzbani *et al.* (2015). The author attributed the improvement to the antifungal properties of nano ZnO.

The best time to submerge wood samples into all preservative treatment (ZnO/H_2O, LMwPF, LMwPF/ZnO) was 120 min. The time of submersion into wood preservative affected the resistance of wood to fungi. Longer submersion period will improve the retention and therefore leads to higher resistance against fungi attack (Brelid *et al.* 2000). However, there was no significant difference between the submersion time for LMwPF and LMwPF/ZnO. Hence, the submersion time of 60 min for both treatments is sufficient while the nano ZnO/H_2O strictly requires submersion time of 120 min to attain significant improvement in decay resistance.

CONCLUSIONS

ZnO nanoparticles was successfully mixed with LMwPF and impregnated into rubberwood. The highest WPG was recorded from the rubberwood treated with LMwPF/ZnO as the nanoparticles could facilitate the polymerisation and fixation of LMwPF resin immediately after impregnation. Well dispersion of the treatment solution and penetration into the rubberwood was observed as suggested by SEM image. Better thermal stability was observed in the treated rubberwood samples as lower mass loss was detected at the end of the TGA test, probably due to the higher WPG attained. As for decay resistance, the rubberwood treated with LMwPF and LMwPF/ZnO possessed very high resistance against the white-rot fungus evaluated. The phenomenon might be attributed to the physical barrier formed by the LMwPF and nano ZnO that prevent the wood from degraded by the digestive enzyme release by the fungus. In addition, the hydrophobic characteristic of the wood after treatment also inhibits the growth of fungus that favour a high moisture environment. However, the rubberwood impregnated with ZnO/H_2O did not display similar effectiveness, except for the samples that were submerged in the treatment solution for 120 min before impregnation.

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