SYNTHESIS AND CHARACTERISATION OF ZINC OXIDE NANOPARTICLES USING PHENOLIC RESINS

G.Annamalai[1], R.Shanmugapriya [2], J.Senthilkumaran[3], V.S.Sangeetha[4]

Assistant professor,

[1]Department of chemistry ,Dhanalakshmi Srinivasan College of Arts & Science for Women(Autonomous)

Perambalur

ABSTRACT

Phenolic gum or phenol formaldehyde (PF) tar containing distinctive level of zinc oxide (ZnO) nanoparticles was arranged and used to treat rubberwood. Three sorts of treatment arrangements were readied, in particular (1) low atomic weight phenol formaldehyde gum (LMwPF), (2) 1,5 wt % nano ZnO broke up in water (ZnO/H2O), and (3) blend of both LMwPF and 1,5 wt % nano ZnO (LMwPF/ZnO). The rubberwood tests were lowered into the treatment answers for 60, 90, and 120 min, before vacuum impregnation. The untreated rubberwood tests filled in as the controlled examples. The warm solidness conduct and opposition against white-decay parasites (Pycnoporus sanguineus) of the treated rubberwood tests were assessed. The outcomes uncover that the treated rubberwood had somewhat better warm steadiness contrasted with the untreated examples. As far as rot opposition, the rubberwood treated with LMwPF and LMwPF/ZnO have high obstruction against white-decay growths. Then again, the rubberwood treated with ZnO/H2O didn't accomplish comparable viability as the other two medicines, aside from the examples that were lowered in ZnO/H2O for 120 min. The outcomes demonstrate that 1,5 wt % nano ZnO could be adequate in giving better solidness than rubberwood given that more drawn out submersion time is embraced.

Catchphrases: Fungal obstruction, Hevea brasilensis, impregnation alteration; phenol formaldehyde sap; warm strength

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 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).

To improve wood toughness against biodeterioration specialists, one of the promising procedures is to impregnate the wood with either nano-sized zinc oxide (ZnO) or zinc borate, which permit the penetrants to enter the cell divider undeniably. ZnO nanoparticles have wide applications in different regions including drug for the assembling of sunscreens items (Jeon et al. 2016, Dao et al. 2016, Zuzanna et al. 2013), wastewater treatment (Wang et al. 2008), and as an antifungal and antibacterial specialist (Sawai, 2003, Sawai and Yoshikawa 2004, Jain et al. 2009). ZnO nanoparticles are known to have great antimicrobial capacity (Iždinský et al. 2018). Lykidis et al. (2016) impregnated Scots pine with nano ZnO and zinc borate utilizing the full cell measure and altogether improved the opposition of the impregnated wood against earthy colored decay growths, Serpula lacrymans. In an examination by Ghorbani-Kookandeh et al. (2014), beech wood impregnated with ZnO nanoparticles displayed huge improvement in opposition against white-decay organisms, Trametes versicolor. Plus, paper made with ZnO nanoparticles-treated mash filaments had prevalent antimicrobial impact against Escherichia coli and Staphylococcus aureus, a Gram-negative and Gram-positive bacterium, separately. Aside from parasites and microorganisms, the impregnation of nano ZnO likewise present the wood with better opposition against Subterranean termites (Akhtari and Nicholas 2013).

Phenolic tar is one of the notable wood surface defenders which is generally utilized in wood-based industry, because of its high adaptability, amazing water opposition, great mechanical properties, great protection from acids, minimal effort, and basic creation measure. It is additionally non-harmful and hard to light (Furuno et al. 2004, Dong et al. 2009, Huang et al. 2014). Changing the phenolic pitch properties utilizing ZnO nanoparticles as added substance ought to improve the degree of wood security particularly against rot growths and UVA radiation. ZnO nanoparticle is an inorganic material which has a wide band hole (3,37 eV) and huge excitation restricting energy of 60 meV. Subsequently, it can retain strike that matches or surpasses their band hole energy, which lies in the UV scope of the sunlight based range; hence it can work as an UV safeguard (Fangli et al. 2003). Meaning to improve the organic obstruction of the wooden composites, Gao et al. (2018) altered the watery phenol formaldehyde (PF) sap utilizing nano copper oxide (CuO). The PF pitch, alongside prevalent natural obstruction capacity, shown self-relieving properties that can remunerate the unfriendly impacts on mechanical strength. Nonetheless, hardly any examinations have been performed to evaluate the impact of ZnO nanoparticles as against wood rotting organisms (shape, sapstain, white-and earthy colored decay) (Mantanis et al. 2014).

Hence, this examination plans to assess the impact of ZnO nanoparticles in low atomic weight phenol formaldehyde (LMwPF) tar on the sturdiness of rubberwood towards white-decay growths under research center conditions. To accomplish the target of this examination, various convergences of ZnO nanoparticle were joined into the LMwPF tar plan for impregnation treatment. The cooperation between ZnO nanoparticle with LMwPF tar, the impact of restoring time, and a few properties were examined by Fourier change infrared spectroscopy (FTIR) and thermo gravimetric examination (TGA/DTG). The warm conduct of ZnO nanoparticles stacked LMwPF gum impregnated into the rubberwood was additionally described utilizing TGA/DTG. The morphology and dispersibility properties of ZnO/PF arrangement into the rubberwood structure were described utilizing SEM.

MATERIALS AND METHODS

Planning of materials

Fourier change infrared spectroscopy (FTIR) investigation

FTIR was utilized to describe the synthetic changes in LMwPF because of the expansion of ZnO nanoparticle prior to impregnating into wood. The compound changes of the relieved LMwPF pitch and LMwPF/ZnO (restored at 103 °C for 6 h in a stove) were estimated in the scope of frequencies somewhere in the range of 280 and 4000 cm−1 utilizing a Perkin Elmer FTIR instrument (1 cm−1 goal, 32 sweeps, KBr strategy). The examination was done at room temperature.

Warm strength

Warm security properties of the rubberwood treated with LMwPF/ZnO nanoparticles were examined utilizing a warm gravimetric investigation (TGA/DTG), SDT Q 600 exploration instrument at a warming pace of 10 ℃/min, from 25 to 1000 ℃ under nitrogen air. Mass of the example utilized was around 10-15 mg. Subsidiary warm gravimetric (DTG) was additionally acquired to decide the greatest pace of weight reduction.

Surface morphology

Morphology and microstructure of rubberwood treated with LMwPF/ZnO were seen by SEM, JEOL variable weight SEM (VP-SEM 1455). A little wood square of 10 × 10 × 12 mm was set up from the treated rubberwood tests. At that point, the focal point of the treated wood block was cut from the cross over area utilizing a microtome to get a 5-mm thick example. The dried cut examples were put on a conductive carbon sticky tape surface which was connected to the SEM stub, and afterward Pd/gold covered on the cutting surface and saw at a quickened voltage of 20 kV.

Growth test

Both treated and untreated rubberwood tests were tried for toughness as indicated by the systems determined in ASTM 2017 - 05 (Standard Test Method of Natural Decay Resistance of Wood). White-decay growth, Pycnoporus sanguineus was utilized as the test parasite. The feeder take from rubberwood with measurement of 3 × 29 × 35 mm were arranged and adapted. Malt remove agar (MEA) was utilized as a supplement vehicle for refined the growth. A measure of 2 wt % malt remove and 1,5 wt % weight agar was set up by blending it in with refined water in a container. The medium was sanitized at 121 °C for 20 min and permitted to cool before vaccinations. After the medium was cooled and cemented, the white-decay parasite was immunized on the outside of the media and brooded in a hatchery at 27 + 2 ℃ for around 4-5 days until the mycelium covered at leasttwo-third of the petri dish. At that point, a sterile test block was set on the feeder strips and moved into the way of life bottle. Preceding the moving test square and feeder strip into the way of life bottle, 150 g sieved soil and 70 ml refined water was added into the way of life bottle. After the test blocks were brought into the way of life bottles, they were left to brood for about four months. Toward the finish of the test, the test blocks were cleaned for eliminating all the mycelium on the surfaces. The test blocks were then stove dried until the consistent loads were reached and the level of weight reduction brought about by white-decay parasite was resolved.

Oven dried rubberwood (Hevea brasilensis) was gotten from a business market in Selangor. The rubberwood was cut into the element of 25 × 25 × 9 mm before they were adapted to a harmony dampness substance of 20% in a molding room. Novalac type low sub-atomic weight phenol formaldehyde (LMwPF) was bought from a nearby producer situated in Shah Alam, Selangor. The LMwPF (Mw 600) with 45% strong substance was utilized. Nano ZnO altered with octadecyl ammonium/silane utilized in this examination was acquired from Nanocor Inc.

Impregnation treatment

The rubberwood tests were treated with three sorts of treatment additives, specifically (1) 45% low atomic weight phenol formaldehyde sap (LMwPF), (2) 1,5 wt % nano zinc oxide broke up in water (ZnO/H2O), and (3) blend of 45% LMwPF and 1,5 wt % nano zinc oxide (LMwPF/ZnO). The arrangements were blended for 40 min. A bunch of untreated examples was set up to fill in as the controlled examples. All medicines were led at Forest Research Institute Malaysia (FRIM) in Kepong. Preceding vacuum impregnation, the rubberwood tests were lowered in the additives for 60, 90, and 120 min. Eight replications were ready for every treatment. From that point onward, the examples were vacuum impregnated for 1 hr and afterward, the weight was gradually delivered for 90 min from the vacuum chamber. The examples were then taken out and dried in a stove at 60 ℃ for 48 hr. The weight percent pick up (WPG) of the examples after impregnation were resolved.

RESULTS AND DISCUSSION

Compound property of LMwPF/ZnO

Figure 1 shows the FTIR spectra of unadulterated LMwPF and LMwPF/ZnO nanocomposite arranged utilizing distinctive convergence of ZnO nanoparticles. Band at 3461 cm−1 compares to the - OH useful gathering, while groups at 2920 and 2851 cm−1 relates to - CH extending. Groups at 1220 cm−1 are doled out to C-O extending vibrations of phenolic tar. The band at 3461 cm−1 for LMwPF/ZnO nanocomposite test shows a diminishing in power contrasted with that of the unadulterated LMwPF pitch, proposing that the - OH practical gatherings of phenolic tar were involved by the ZnO nanoparticles. The comparable perception was accounted for by Dhoke et al. (2009) when utilizing ZnO nanoparticle in the alkyd-based waterborne covering plan. The other assimilation pinnacles of phenolic gum containing 0; 0,5; 1; 1,5; 2, and 2,5 wt % ZnO didn't change essentially, showing that the structure of the LMwPF gum was unaltered by the expansion of ZnO nanoparticles. Be that as it may, LMwPF/ZnO nanocomposite combination arranged utilizing 1,5 wt % ZnO nanoparticles was picked for additional examination.

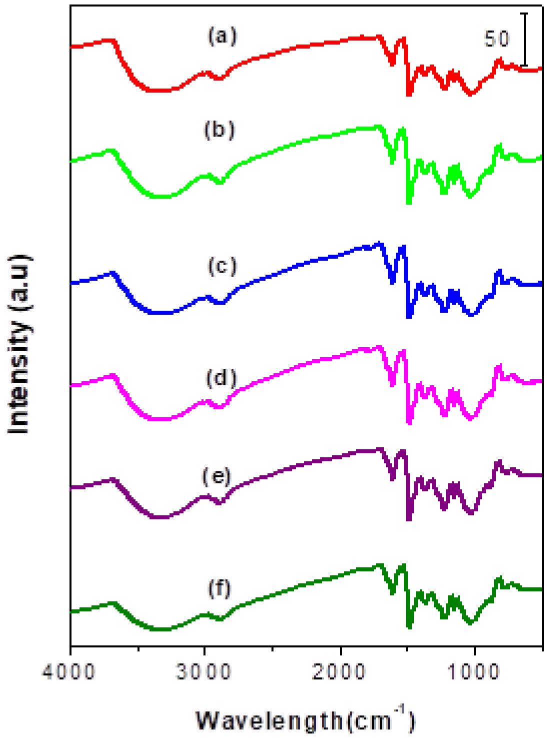

Figure 1: FTIR spectra of (a) pure LMwPF resin, LMwPF containing (b) 0,5 wt %, (c) 1,0 wt %, (d) 1,5 wt %, (e) 2,0 wt %, and 2,5 wt % of ZnO nanoparticles.

Weight percent pick up (WPG)

The WPG of the rubberwood treated with various sorts of arrangement are appeared in Table 1. The WPG is an element of submersion time where the more extended the submersion time, the higher the WPG of the examples. The rubberwood treated with ZnO/H2O recorded the most reduced WPG going from 1,07% to 1,54%. In the interim, the rubberwood treated with LMwPF/ZnO has the most noteworthy WPG (6,30%-7,13%) contrasted with that of the examples treated with LMwPF exclusively (4,19%-4,52%). As indicated by Dungani et al. (2014), PF sap could just infiltrate the wood cell lumen and has high inclination of filtering out from the lumen. Then again, expansion of nanoparticles could help the obsession and polymerisation of PF pitch after impregnation and consequently brought about higher WPG contrasted with the wood impregnated with PF gum exclusively.

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

Warm conduct

The TGA/DTG thermograms of ZnO nanoparticles, unadulterated LMwPF sap, LMwPF/ZnO nanocomposite treated and untreated rubberwood are introduced in Figure 2. Table 2 shows the TGA/DTG information of ZnO nanoparticles, unadulterated LMwPF, LMwPF/ZnO treated and untreated rubberwood. TGA/DTG thermograms for all examples unmistakably show that the mass misfortune was actualized in two stages. The main mass misfortune was performed at temperatures between room temperature and 120 °C because of the vanishing of water. The water misfortune for every example happened at under 100 °C. The DTG of rubberwood treated with nano ZnO has a high amount of water than those of the untreated rubberwood, rubberwood treated with LMwPF pitch, and rubberwood treated with LMwPF/ZnO. High water content in the rubberwood treated with nano ZnO is because of the presence of water utilized as ZnO transporter during treatment measure.

Figure 2 likewise shows that the example displayed further debasement ventures at the reach from 150 to 470 °C. The debasement wonders of the examples are for the most part ascribed to the corruption of cellulose and lignin of the rubberwood. Be that as it may, the debasement responses of the examples here were diverse regarding their energies of initiation, contingent upon the kind of treatment utilized. In light of DTG, the corruption of the untreated rubberwood was higher (68,5%), trailed by ZnO-treated rubberwood (67,5%), LMwPF-treated rubberwood (67,5%), and LMwPF/ZnO-treated rubberwood (66,6%). This implies that LMwPF/ZnO polymer marginally improved the warm dependability of rubberwood. This wonder might ascribe to the higher WPG came about by the LMwPF/ZnO arrangement as a higher measure of materials has been impregnated into the rubberwood and prompted an all the more thermally stable structure (Dungani et al. 2014).

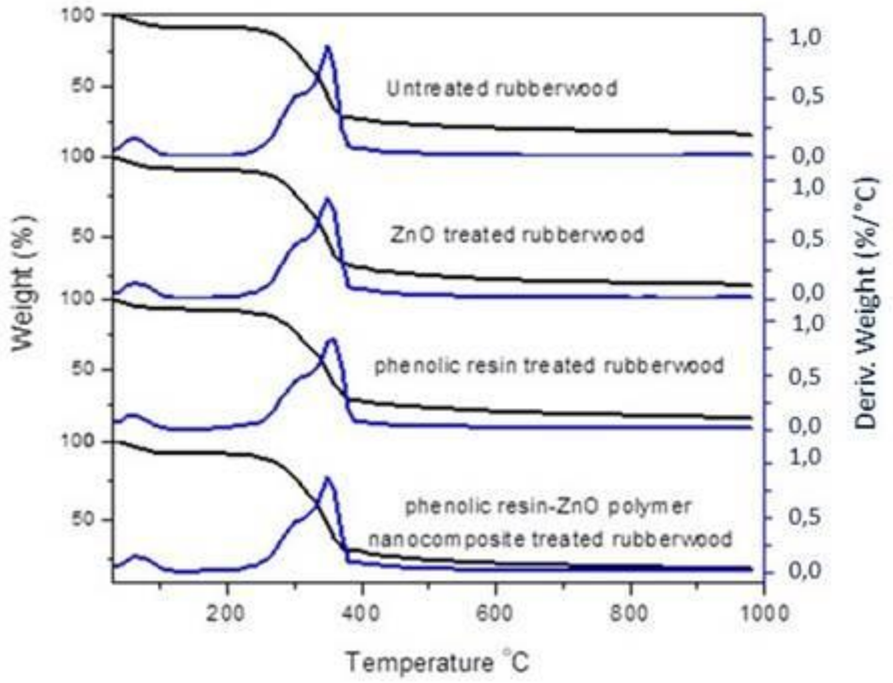

Figure 2: TGA/DTG thermograms of ZnO nanoparticles, pure LMwPF resin and LMwPF/ZnO-treated rubberwood.

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.

Growth test

Table 3 sums up the level of weight reduction and opposition class of the treated and untreated rubberwood following two months openness to the white-decay growth. The opposition classes were grouped dependent on the weight reduction of tests as indicated by American Society for Testing and Materials ASTM D2017. As per the norm, the untreated rubberwood with 26,7% weight reduction falls into the class of moderate opposition (Class 3) towards P. sanguineus. For the examples treated with nano zinc oxide broke up in water (ZnO/H2O), huge improvement in organism obstruction was noticed and the improvement expanded with expanding lowering occasions. Tests that were lowered in ZnO/H2O for 60 min before the vacuum impregnation treatment fall into Class 2 of opposition, with a weight reduction of 15,0% after openness to the parasite. Then again, the weight reduction of the examples lowered in ZnO/H2O for 90 and 120 min before the vacuum impregnation treatment were 9,9% and 1,6%, separately, which is profoundly opposition (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	$26,7 \pm 3,5^{d}$	3
LMwPF	60	$0,29 \pm 0,12^{a}$	1
	90	$0,25 \pm 0,10^{a}$	1
	120	$0,15 \pm 0,10^{a}$	1
LMwPF/ZnO	60	$0,26 \pm 0,20^{a}$	1
	90	$0,21 \pm 0,17^{a}$	1
	120	$0,10 \pm 0,12^{a}$	1
ZnO/H_2O	60	$15,0 \pm 2,9^{c}$	2
	90	$9,9 \pm 10,5^{bc}$	1
	120	$1,6 \pm 0,5^{ab}$	1

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

Concerning the examples treated exclusively with LMwPF pitch, 0,15%-0,29% weight reduction was recorded, showing extremely high obstruction gave by the LMwPF treatment (Class 1). Then again, 0,10%-0,26% weight reduction was seen after the expansion of nano ZnO into LMwPF. From the outcomes, the toughness of ZnO/H2O treated rubberwood (1,6%-15,0%) was fundamentally improved contrasted with that of the untreated examples (26,7%). In spite of the fact that the upgrades were generally little when contrasting and LMwPF and LMwPF/ZnO medicines, opposition Class 1 was accomplished when the examples were lowered in the ZnO/H2O answer for a long enough time before impregnation (≥90 min).

Then again, LMwPF and LMwPF/ZnO medicines demonstrated comparative viability against white-decay growths. The actual obstruction framed by the LmwPF and nano ZnO could keep the wood from debased by the stomach related compound delivery by the organism (Zanatta et al. 2017). What's more, decrease in the water retention limit of the wood because of diminished accessible void spaces is likewise a primary factor that prompts the improvement in parasitic obstruction (Leemon et al. 2015). Reasonable developing climate supported by the parasite was forestalled as the water diffusivity in the wood was decreased (Nabil et al. 2016). Subsequently, the mix of the two medicines brought about the wood with exceptionally high obstruction against contagious rot. The wood treated with LMwPF shows higher protection from organisms since phenolic has a 3-dimensional organization that is hard to break down and debase (Gusse et al. 2006). Clausen et al. (2010) additionally detailed that the utilization of nano ZnO upgraded the obstruction of wood against organisms and termites just as shields the wood from UV debasement and forestalls filtering. Improved rot obstruction of particleboard treated with nano ZnO against Trametes versicolor and Coniophora puteana were accounted for by Marzbani et al. (2015). The creator ascribed the improvement to the antifungal properties of nano ZnO.

The best an ideal opportunity to lower wood tests into all additive treatment (ZnO/H2O, LMwPF, LMwPF/ZnO) was 120 min. The hour of submersion into wood additive influenced the opposition of wood to organisms. Longer submersion period will improve the maintenance and in this manner prompts higher opposition against organisms assault (Brelid et al. 2000). Notwithstanding, there was no critical distinction between the submersion time for LMwPF and LMwPF/ZnO. Subsequently, the submersion season of 60 min for the two medicines is adequate while the nano ZnO/H2O carefully requires submersion season of 120 min to accomplish critical improvement in rot opposition.

CONCLUSIONS

ZnO nanoparticles was effectively blended in with LMwPF and impregnated into rubberwood. The most elevated WPG was recorded from the rubberwood treated with LMwPF/ZnO as the nanoparticles could encourage the polymerisation and obsession of LMwPF gum following impregnation. Well scattering of the treatment arrangement and infiltration into the rubberwood was seen as proposed by SEM picture. Better warm soundness was seen in the treated rubberwood tests as lower mass misfortune was recognized toward the finish of the TGA test, likely due to the higher WPG achieved. Concerning rot obstruction, the rubberwood treated with LMwPF and LMwPF/ZnO had high opposition against the white-decay parasite assessed. The wonder may be ascribed to the actual hindrance framed by the LMwPF and nano ZnO that keep the wood from corrupted by the stomach related chemical delivery by the organism. What's more, the hydrophobic trait of the wood after treatment likewise represses the development of growth that favor a high dampness climate. In any case, the rubberwood impregnated with ZnO/H2O didn't show comparative adequacy, aside from the examples that were lowered in the treatment answer for 120 min before impregnation

ACKNOWLEDGMENTS

The creators are appreciative to the Forest Research Institute Malaysia (FRIM) and Higher Institution Centers of Excellence (HICoE) for giving the examination materials and offices.

REFERENCES:

Browne, F.G. 1961. The biology of Malayan Scolytidae and Platypodidae. Malayan Forest Record No. 22. Forest Department: Kuala Lumpur. (Accessed from) (Accessed from) http://www.avocadosource.com/papers/Research_Articles/BrowneFG1961.pdf (consulted: 1 October 2018) [Links]

Dungani, D.; Islam, M.N.; Abdul Khalil, H.P.S.; Davoudpour, Y.; Rumidatul, A. 2014. Modification of the Inner Part of the oil palm trunk (OPT) with oil palm shell (OPS) nanoparticles and phenol formaldehyde (PF) resin: physical, mechanical, and thermal properties. *BioResources* 9(1): 455-471. [Links]

Fangli, Y.; Peng, H.; Chunlei, Y.; Shulan, H.; Jinlin, L. 2003. Preparation and properties of zinc oxide nanoparticles coated with zinc aluminate. *Journal of Materials Chemistry* 13(3): 634-637. [Links]

Furuno, T.; Imamura, Y.; 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 Science and Technology* 37(5): 349-361. [Links]