Effect of Nano-Zinc Oxide on Decay Resistance of Wood-Plastic Composites

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The aim of this study was to investigate the decay resistance of wood-polypropylene composites (WPCs) treated with nano-zinc oxide against the white rot fungus *Trametes versicolor* and the brown rot fungus *Coniophora puteana*. WPCs containing different loadings of nano-zinc oxide, namely 0, 1, 2, and 3 percent (by weight), were made. The composites were subsequently exposed to a decay test according to a modified ASTM D1413 standard. Nano-zinc oxide distribution in the composite was studied by scanning electron microscopy (SEM) combined with energy dispersive analysis of X-rays (EDAX). No clear evidence of nano-zinc oxide agglomeration at a loading of 3% (w/w) was obtained using SEM-EDAX. The results showed that nano-zinc oxide improved the decay resistance of the composite against the fungi.

Keywords: Nano-zinc oxide; Wood-polypropylene composites; Coniophora puteana; Trametes versicolor

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INTRODUCTION

The decay resistance of wood-plastic composites (WPCs) is important in exterior applications. The performance of WPCs in some studies has shown that WPCs are susceptible to decay (Mankowski and Morrell 2000; Morrell *et al.* 2006; Lomelí-Ramírez *et al.* 2009; Farahani and Saffarzadeh 2011). Wood is solely responsible for WPCs' susceptibility to fungal decay. In contrast to wood, plastics are generally resistant to fungal attack (Klyosov 2007; Lopez *et al.* 2005). Despite the fact that plastics are nearly non-porous and absorb little moisture, WPCs can be porous, depending on the wood flour content, and as a result of the porosity, fungi can access the wood in WPCs. Thus, WPCs need to be protected against fungi when they are used outdoors. Wood preservatives have been applied to protect WPCs against fungal decay (Klyosov 2007). In general, wood preservatives applied in WPCs must be thermally stable (Klyosov 2007). Therefore, not all wood preservatives can be used to protect WPCs against fungal attack.

Zinc is a metal that is a key component in some wood preservatives. In addition, zinc as zinc oxide has a long history as a preservative component in coatings (AWPA 2010). There are studies reporting the use of nano-zinc oxide as a UV stabilizer in coatings (Auclair *et al.* 2011; Saha *et al.* 2011) and as a wood preservative (Weichelt *et al.* 2010, Clausen *et al.* 2009; Kartal *et al.* 2009; Clausen *et al.* 2011). Nano-zinc oxide has also been used to impart UV resistance to plastics (Ammala *et al.* 2002; Yang *et al.* 2005; Zhao and Li 2006; Chen *et al.* 2011). The optical transparency of nanoparticulate zinc oxide permits its use in a wide range of applications. The screening efficiency of zinc oxide is also increased with reduced particle sizes, which allows for reduced loadings, when compared to larger particle sizes (Ammala *et al.* 2002). Nano-zinc oxide has the potential to be used in the preservation of WPCs because of its thermal stability at the temperatures used for manufacturing WPCs and because of its effectiveness against weathering (Clausen *et al.* 2009, 2010) and attack by white rot fungi (Clausen *et al.* 2009; Kartal *et al.* 2009). Nano-zinc oxide has been reported to be approximately as effective as its soluble counterparts at inhibiting brown rot fungi (Kartal *et al.* 2009).

No known study has evaluated the efficacy of nano-zinc oxide for protecting WPCs against fungal decay. Thus, the aim of this study was to examine the efficiency of nano-zinc oxide for improving the fungal decay resistance of WPC.

EXPERIMENTAL

Chemicals

Nano-zinc oxide (20 nm, 90 m^2/g), which was not surface modified, was supplied by Nano Pars Lima Co. Ltd., Tehran, Iran. The polypropylene and maleic anhydride grafted polypropylene (MAPP) used in this study were supplied by Marun Petrochemical Co., Ahwaz, Iran and Kimia Javid Co., Isfehan, Iran, respectively.

Wood

The wood was cottonwood (*Populus deltoides* 67/51) sapwood, which is a non-durable wood. The clone, which originated from Turkey, was planted in the north of Iran in 1986. Three logs cut from three trees were used for this study. The logs were manually debarked and then partially dried. The sapwood portions of the three logs were subsequently planed to produce shavings. After being dried, the shavings, were ground by a laboratory mill. The flour was then sieved through 40-mesh and 60- mesh sieves in sequence. The flour left on 60-mesh sieve was used to make WPC. Prior to WPC fabrication, the wood flour was oven-dried.

Wood-Plastic Composite

Each formulation of WPC (Table 1) was mixed using a Haake internal mixer at 190 °C with a rotor speed of 60 rpm . The mixed materials were then ground. The ground composite mixtures were subsequently pressed into boards with dimensions of 15 x 25 x 1 cm at 180 °C and at 29 bar for 10 min using a hydraulic press (OTT model, Waibligen, Germany). The boards were then cold pressed for 20 min to prevent from springback. After being edge cut, the boards, were cut to the samples used for decay and SEM EDAX studies. The samples were taken from the sides of the boards.

Table 1. Formulations of Wood-Plastic Composites Used in This Study

Wood content (% w/w)	Nano-zinc oxide loading (% w/w)	Polypropylene (% w/w)	MAPP (% w/w)
60	0	38	2
60	1	37	2
60	2	36	2
60	3	35	2

Decay Test

Composite samples with dimensions of 10 x 10 x 10 mm after sanding were exposed to the white rot fungus *Trametes versicolor* (Linnaeus) Lloyd (CTB 863 A) and the brown rot fungus *Coniophora puteana* (Schumacher ex fries) Karesten (BAM Ebw. 15) in a soil block decay test for three months in accordance with a modified ASTM D1413 test standard (ASTM 2002). The modification was that dimensions of 10 x 10 x 10 mm were used instead of those recommended in the standard. The replication was 4.

SEM- EDAX

Wood plastic composite samples were split in half and then sputter-coated with platinum (Echlin 2009). The SEM-EDAX of the split surfaces was carried out using an EDAX instrument (Genesis XM2 USA) set on a FE SEM S4800.

RESULTS AND DISCUSSION

Zinc was dispersed nearly evenly in the composite, and there was no clear evidence of agglomeration of zinc particles observed in the SEM-EDAX analysis (Fig. 1).

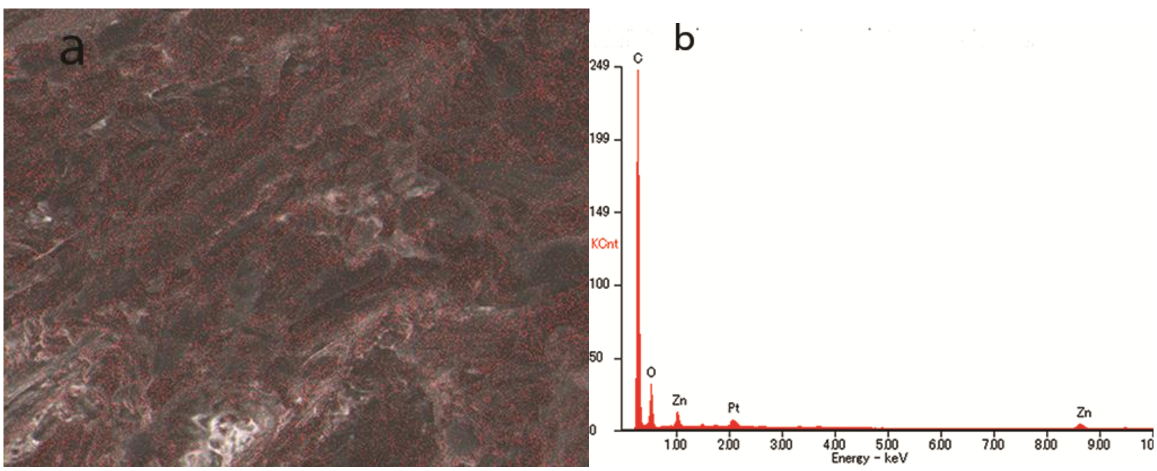

Fig. 1. SEM EDAX of WPC treated with nano-zinc oxide (magnification : × 250 and figure scale: 200 microns)**:** Zinc (red dots) mapping of wood plastic composite containing 3% (w/w) nano-zinc oxide (a) and the corresponding EDAX spectrum (b).

Nano-zinc oxide has been dispersed in polypropylene and high density poly-ethylene (Ammala *et al.* 2002). In this study, it was shown that nano-zinc oxide at loadings as high as 3% (w/w) did not agglomerate in the wood-polypropylene composite.

Weight losses (WL) due to the decay of the composites are given in Fig. 1. As can be observed, the weight loss of the composites decreased as the zinc oxide loading increased. No noticeable difference in weight loss due to decay was observed between the brown rot fungus *C. puteana* and the white rot fungus *T. versicolor* for the WPCs treated with nano-zinc oxide at different loadings; however, there was a noticeable difference observed for the untreated WPCs. It should be added that the average weight losses of cottonwood sapwood samples used as the virulence controls were 25.2% and 37.1% for *C. puteana* and *T. versicolor*, respectively. The WLs of the wood flour in the untreated composite were calculated to be 18.37 and 23.72 for *C. puteana* and *T. versicolor*, respectively. These values show the noticeable accessibility of the wood in the composite to the fungi.

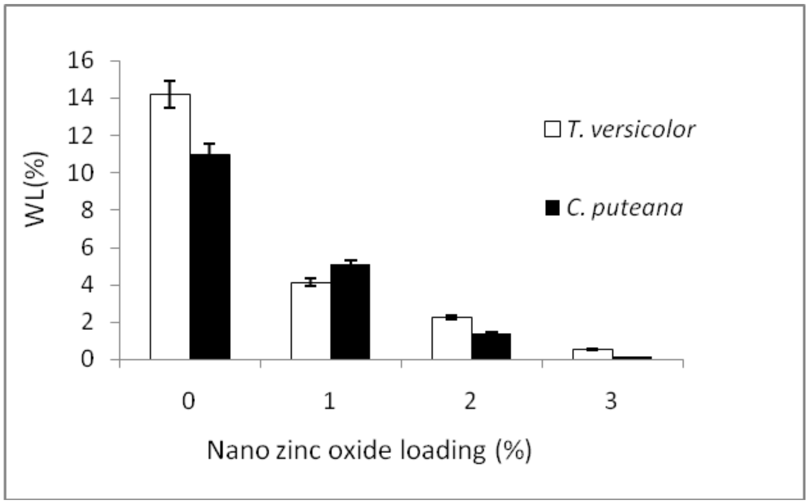

Fig. 2. Weight loss (WL) due to decay as a function of nano-zinc oxide loading

Nano-zinc oxide increased the decay resistance of the WPC for the two test fungi used in this study. The decay resistance against the fungi was achieved as a result of the toxicity of nano-zinc oxide toward the fungi. Reddy *et al.* (2007) reported the selective toxicity of nanomaterials, including metal oxides, to eukaryotes. Many brown rot fungi are heavy metal tolerant due to their ability to produce organic acids, notably oxalic acid. When in contact with wood preservatives containing heavy metals, these acids can form insoluble metal salts and detoxify the preservatives (Eaton and Hale 1993). However, *C. puteana* has been reported to be copper-sensitive (Green and Clausen 2003). In this study, the decay resistance against *C. puteana* was noticeably improved by nano-zinc oxide, suggesting that the brown rot fungus is not zinc-tolerant and that the nanometal oxide can be effective in protecting WPCs against *C. puteana*.

CONCLUSIONS

1. Nano-zinc oxide at loadings as high as 3% (w/w) were nearly evenly dispersed in WPCs.
2. Nano-zinc oxide improved the decay resistance of WPC against the fungi used in this study. The ability of the nanoparticle to improve the decay resistance against the brown rot fungus shows that the effectiveness of the nanometal is not restricted to white rot fungi only. Further studies are required to investigate the efficacy of nano-zinc oxide for improving the decay resistance against other brown rot fungi, *e.g.*, *Antrodia vaillantii*. Further studies are also required to investigate the leachability of the nano-zinc oxide during exterior exposure.

REFERENCES CITED

Auclair, N., Riedl, B., Blanchard, V., and Blanchet, P. (2011). "Improvement of photoprotection of wood coatings by using inorganic nanoparticles as ultraviolet absorbers," *Forest Prod. Soc.* 61(1), 20-27.

Ammala, A., Hill, A. J., Meakin, P., Pas, S. J., and Turney, T. W. (2002). "Degradation studies of polyolefins incorporating transparent nanoparticulate zinc oxide UV stabilizers," *J. Nanoparticle Res.* 4(1-2), 167-174.

ASTM D1413 (2002) "Standard test method for wood preservatives by laboratory soil-block cultures," *2002 Annual Book of ASTM Standards*, Vol. 4.10, American Society for Testing and Materials, Philadelphia, PA.

AWPA P22-10 (2010). "Standard for Ammoniacal Copper Zinc Arsenate (ACZA)" 2010 *American Wood Protection Association Book of Standards*, page 130, Birmingham, AL, USA.

Chen, S., Peng, Z., Wang, X., and Cheng, X. (2011). "The effect of nano-ZnO on corona aging and photo aging in low-density polyethylene," *IEEJ Trans. Elec. Electron. Eng.* 6(1), 7-13.

Clausen, C. A., Yang, V. W., Arango, R. A., and Green, F. (2009). "Feasibility of nano-zinc oxide as a wood preservative," *Proc. Am. Wood Protect. Assoc.* 105, 255-260.

Clausen, C. A., Green, F., and Kartal, S. N. (2010). "Weatherability and leach resistance of wood impregnated with nano-zinc oxide" *Nano scale Res. Lett*. 5(9), 1464-1467.

Clausen, C. A., Kartal, S. N., Arango, R. A., and Green, F. (2011). "The role of particle size of particulate nano-zinc oxide wood preservatives on termite mortality and leach resistance," *Nanoscale Res. Lett*. 6(1), 427-433.

Eaton, R. A., and Hale, M. D. C. (1993). *Wood: Decay, Pests and Protection*, Chapman and Hall, London.

Echlin, P. (2009). *Handbook of Sample Preparation for Scanning Electron Microscopy and X-ray Microanalysis*, Springer, New York.

Farahani, M. R. M., and Saffarzadeh, M. (2011). "Decay resistance of a commercial pistachio twig-plastic composite," *International Research Group on Wood Protection* IRG/WP 11-40554.

Green, F., and Clausen, C. A. (2003). "Copper tolerance of brown-rot fungi: Time course of oxalic acid production," *Int. Biodeter. Biodegr.* 51(2), 145-149.

Kartal, S. N., Green, F., and Clausen, C. A. (2009). "Do the unique properties of nanometals affect leachability or efficacy against fungi and termites?" *Int. Biodeter. Biodegr*. 63(4), 490-495.

Klyosov, A. I. (2007). *Wood-Plastic Composites*, John Wiley & Sons, Hoboken, New Jersey.

Lomelí-Ramírez, M. G., Ochoa-Ruiz, H. G., Fuentes-Talavera, F. J., García-Enriquez, S., Cerpa-Gallegos, M. A., and Silva-Guzmán, J. A. (2009). "Evaluation of accelerated decay of wood plastic composites by Xylophagus fungi," *International Biodeterioration & Biodegradation* 63(8), 1030-1035.

Lopez, J. L., Cooper, P. A, and Sain, M. (2005). "Evaluation of proposed test methods to determine decay resistance of natural fiber plastic composites," *Forest Prod. J.* 55(1), 95-99.

Mankowski, M., and Morrell, J. J. (2000). "Patterns of fungal attack in wood-plastic composites following exposure in a soil block test," *Wood and Fiber Science* 32(3), 340-345.

Morrell, J. J., Stark, N. M., Pendleton, D. E., and McDonald, A. G. (2006). "Durability of wood-plastic composites," *Wood Design Focus* 16(3), 7-10.
Reddy, K. M., Feris, K., Bell, J., Wingett, D. G., Hanley, C., and Punnoose, A. (2007). "Selective toxicity of zinc oxide nanoparticles to prokaryotic and eukaryotic systems," *Appl. Phys. Lett.* 90(21), 1-3.
Saha, S., Kocaefe, D., Krause, C., and Larouche, T. (2011). "Effect of titania and zinc oxide particles on acrylic polyurethane coating performance," *Prog. Org. Coat.*70(4), 170-177.
Weichelt, F., Emmler, R., Flyunt, R., Beyer, E., Buchmeiser, M., and Beyer, M. (2010). "ZnO-based UV nanocomposites for wood coatings in outdoor applications," *Macromol. Mater. Eng*. 295(2), 130-136.
Yang, R., Li, Y., and Yu, J. (2005). "Photo-stabilization of linear low density polyethylene by inorganic nano-particles," *Polym. Degrad. Stabil.* 88(2), 168-174.
Zhao, H., and Li, R. K. Y. (2006). "A study on the photo-degradation of zinc oxide (ZnO) filled polypropylene nanocomposites," *Polymer* 47(9), 3207-3217.

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