UNIVERSIDADE FEDERAL DE LAVRAS

CILENE CRISTINA BORGES

PERFORMANCE OF ZINC OXIDE AND TITANIUM DIOXIDE NANOPARTICLES ON WOOD PROTECTION

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Thesis submitted to the Federal University of Lavras in partial fulfillment of the requirements of the Graduate Program in Wood Science and Technology for the Degree of Doctor of Science.

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PERFORMANCE OF ZINC OXIDE AND TITANIUM DIOXIDE NANOPARTICLES ON WOOD PROTECTION

DESEMPENHO DE ÓXIDO DE ZINCO E DIÓXIDO DE TITÂNIO NA PRESERVAÇÃO DE MADEIRAS

Thesis submitted to the Federal University of Lavras in partial fulfillment of the requirements of the Graduate Program in Wood Science and Technology for the Degree of Doctor of Science.

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To my students.

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There are two possible outcomes: if the result confirms the hypothesis, then you've made a measurement. If the result is contrary to the hypothesis, then you've made a discovery.

(Enrico Fermi)

RESUMO

O uso da madeira apresenta inúmeras vantagens em relação a polímeros sintéticos, sendo o material preferido para diversas aplicações decorativas e de engenharia. Algumas madeiras, no entanto, apresentam baixa resistência natural a deterioração biológica e requerem tratamento. Através dos tempos, diversos tratamentos preservativos foram desenvolvidos, mas a busca por novas tecnologias de alta eficiência, baixa toxidade ao ambiente e à saúde humana continua sendo um desafio para pesquisadores. O uso de nanopartículas na proteção da madeira ainda é incipiente, mas a nanotecnologia tem avançado consideravelmente nos últimos anos, abrindo portas para novos experimentos e aplicações do conhecimento dentro da área de preservação de madeiras. O objetivo principal deste trabalho foi avaliar o desempenho de tratamentos à base de nanopartículas de óxido de zinco (ZnO) e dióxido de titânio (TiO_2) na proteção da madeira. Amostras de madeira provenientes de árvores de ~7 anos de idade foram tratadas à vácuo (45 min de vácuo a 550 mmHg) com seis tratamentos contendo diferentes concentrações de nanopartículas de ZnO e TiO_2 em dispersão aquosa, i.e., a) 1 (2% ZnO); b) 2 (1,5% ZnO, 0,5% TiO_2); c) 3 (1% ZnO; 1% TiO_2); d) 4 (0,5% ZnO; 1,5% TiO_2); e) 5 (2% TiO_2); f) 6 (não tratado). Após o tratamento, os corpos de prova foram submetidos a ensaios de apodrecimento acelerado, resistência à cupins subterrâneos e intemperismo. A retenção química foi avaliada por meio de espectroscopia de emissão com plasma indutivamente acoplado (ICP-AES) e a penetração na madeira foi qualitativamente avaliada por microscopia eletrônica de varredura com espectroscopia de energia dispersiva (SEM/EDS). O experimento foi realizado em delineamento inteiramente casualizado. Resultados mostraram que a retenção de ZnO decaiu com a diminuição da concentração de óxido das soluções. A retenção de TiO_2 nos tratamentos foi pouco detectável. A penetração do ZnO e TiO_2 pôde ser observada em todos os tratamentos. A perda de massa das amostras de madeira tratada expostos ao ensaio de apodrecimento acelerado diferiu de acordo com o fungo utilizado e tratamento aplicado. O ensaio com cupins subterrâneos permitiu detectar sinergia das soluções para o tratamento 2. Além deste, os tratamentos 1 e 3, considerados estatisticamente iguais, resultaram em perda de massa de 2,4% e 4,1%, respectivamente, valores considerados como baixos. A taxa de mortalidade média dos cupins foi avaliada após quatro semanas de ensaio, tendo como resultado três tratamentos ranqueados com 100% de mortalidade: tratamentos 1, 2, e 3. Em relação aos ensaios de intemperismo, o tratamento 5 resultou em madeira mais brilhante na face exposta enquanto os corpos de prova não tratados apresentaram menos brilho e tonalidade mais acinzentada em comparação aos tratados. Na face não exposta, o tratamento 1 resultou em madeira menos cinzenta e mais brilhante do que todos os outros tratamentos, incluindo amostras não tratadas. Com base nos resultados obtidos, pode-se concluir que tanto o óxido de zinco como o dióxido de titânio apresentam potencial para desempenhar um papel importante no futuro da proteção da madeira e podem ser incluídos como multicomponentes de uma nova geração de preservativos de madeira à base de nanopartículas.

Palavras-chave: madeira tratada, nanotecnologia, podridão, térmites, intemperismo.

ABSTRACT

The use of wood presents several advantages over synthetic polymers, being wood the preferred material for many decorative and engineering applications. Some wood species, however, have little or lack of natural resistance to biological deterioration, and need protection. Through the time, several preservative treatments have been developed, but the search for new technologies with high efficiency, low environment toxicity, and no risks to human health still have been a challenge for researchers. The use of nanoparticles on wood protection is still incipient; however, nanotechnology has advanced considerably in recent years, opening the door for new experiments and knowledge applications, in the field of wood protection. The main objective of this work was to evaluate the performance of zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles-based treatments on wood protection. *Eucalyptus urophylla* wood samples, made from ~7 years old trees, were vacuum-treated (45 min vacuum at 550 mmHg) with different concentrations of ZnO and TiO_2 nanoparticles in water dispersion, i.e., a) 1 (2% ZnO); b) 2 (1.5% ZnO, 0.5% TiO_2); c) 3 (1% ZnO; 1% TiO_2); d) 4 (0.5% ZnO; 1.5% TiO_2); e) 5 (2% TiO_2); f) 6 (untreated). After treatments, wood samples were subject to accelerated fungal decay, termite bioassay and weathering. Chemical retentions were analyzed by inductively coupled plasma emission spectroscopy (ICP-AES), and penetration into wood were evaluated by scanning electron microscopy with energy dispersive spectroscopy - SEM/EDS analysis. The experiment was set in a completely randomized design. Results of chemical retention showed that ZnO retention decreased according to the decreasing of the oxide concentration of each treatment. TiO_2 retentions of treatments were low detectable. Penetration of ZnO and TiO_2 nanoparticles could be observed for each treatment performed. Mass loss of treated wood samples exposed to rot fungal decay in soil-block tests presented different results, according to the fungus and treatment performed. Termite bioassay performed with subterranean termite had chemical synergy on treatment 2. Besides, other two treatments, 1 and 3, considered statistically equivalents, showed average mass loss of 2.4 and 3.1%, respectively, values considered as a low consumption. Average rating termite mortality were evaluated after four weeks, with three treatments rated at 100% of mortality: 1, 2, and 3. Regarding weathering tests, treatment 5 presented brighter than all other treatments in the exposed face, while untreated ones were less bright and grayer than all treatments performed. In the unexposed face, treatment 1 was less gray and brighter than all treatments, including untreated samples. Based on the results, we can conclude that both zinc oxide and titanium dioxide show potential to perform an important role on the future of wood protection, and could be included as multi-components of a new generation of nanoparticles-based wood preservatives.

Keywords: Treated wood, nanotechnology, fungal decay, termites, weatherability resistance.

CONTENTS

FIRST SECTION

1 PRESENTATION

Since the 1940-1950s, several synthetic polymers have been used as substitutes for a number of traditional materials. Despite that, natural materials, as wood, still been largely used in several applications, due to low cost, availability, and good life expectancy of wood. Wood is a primarily cellulosic material, the main natural polymer that makes up plants and trees, and offers unique sustainable credentials, as a natural and renewable product. Besides, in comparison to others materials, using wood reduces carbon emissions through the carbon dioxide stored in the timber product, and it is a biodegradable product.

Wood is a strength and lightweight material, with great diversity of color, texture, anatomical features and mechanical, chemical and physical properties, as well as natural resistance and beauty, among different species. Therefore, wood is an excellent candidate material to several applications, always considering the particular properties of each wood species, and its proper use. In the past, wood species of high durability were available. Through the time, these species became rare, or presenting high costs, and treated wood became an alternative to extend wooden structures service expectance and decrease the pressure over native forests.

In Brazil, traditional treatments based on arsenic, boron, chromium and cupper still have been utilized; however, beyond color changing, this kind of treatment could present environment and health risks. After 2015, the Environment Protection Agency (EPA) of United States of America is reevaluating all chromated arsenical products as part of the Registration Review Program (2015) to ensure it “can perform its intended function without unreasonable adverse effects on human health or the environment”. Thus, the search for new treatments with efficiency, low toxicity, no danger to human health, and viability of costs production is a challenge for researchers on wood protection.

Treated wood, regardless of the treatment applied have to present acceptable characteristics of service life, with resistance to several deterioration forms. Metals and metal oxides are traditionally used as biocide, but its use in nanoparticles scale shows the possibility of using low concentrations, maintaining the natural color of the wood, and controlled releasing of the active ingredient, besides less environmental impacts, increasing the effectiveness of wood treatments.

Among new solutions, treatments based on nanoparticles could have promising perspectives on wood protection. In order to prove this hypothesis, the main objective of this research is to evaluate the effects of different concentrations, and synergy, of zinc oxide and titanium dioxide nanoparticles-based treatments on wood protection. As specific objectives, treated wood samples were subjected to retention and penetration analysis, besides essays of accelerated fungal decay, subterranean termite attack, and weathering exposition in order to evaluate treated wood performance.

2 CONCLUDING REMARKS

The organization of this thesis was structured into papers, according to the new version of the Manual of standardization and academics works structures: undergraduate thesis, monographs, dissertations, and thesis of the Federal University of Lavras - Second edition (2016), been the concluding remarks the conclusion relative to each paper wrote.

Based on the review made on Paper 1 (Borges et. al, 2018), nanotechnologies applications on wood protection had good perspective for water repellency control, scratch resistance, durability, self-cleaning surfaces, wood biodeterioration, and can improve weatherability. Authors reported information about chemical retention and leaching of nanoparticles and weathering protection through nanoparticles, with good results. No significant differences between different nanoparticles sizes were reported for leach resistance and termites. White-rot fungus inhibition and termites control by using nanoparticles were reported; but no nanoparticles preparation was effective against brown-rot fungi *Meruliporia incrassate*, *Gloeophyllum trabeum* and *Tyromyces palustris*. However, control over decay caused by the brown-rot fungus *Mucor circinelloides* was reported.

Based on Paper 2, it was possible to conclude that zinc oxide retentions decreased according to the decreasing of the solution concentration of each treatment, while for titanium dioxide retentions most part of the treatments were low detectable. On fungal decay tests, for *Pycnoporus sanguineus* fungus (white-rot) attack control, treatment 1 (2% ZnO) had the more effective results. All treatments based on different concentrations of zinc oxide and titanium dioxide nanoparticles were effective to control wood damage caused by the white-rot fungus *Trametes elegans*. Treatment 2 (1.5% ZnO, 0.5 %TiO_2) performed the best result to control damage on termite bioassay. Wood consumption less than 4% on the termite bioassay is indicative of non-palatability or repellency caused by treatments 1, 2, and 3 (2% ZnO; 1.5%

ZnO, 0.5% TiO_2; and 1% ZnO; 1% TiO_2, respectively). Termite mortality for treatments 1 (2% ZnO), 2 (1.5% ZnO, 0.5% TiO_2), and 3 (1% ZnO; 1% TiO_2) was 100%. Regarding weathering, samples of all treatments were brighter and less gray than untreated wood. Samples of treatment 5 (2% TiO_2) presented brighter than other treatments in the exposed face, performing best weatherability protection to that situation. In the unexposed faces, samples of treatment 1 (2% ZnO) was less gray and brighter than samples of all treatments.

Nanoparticles-based wood preservatives have to be properly explored in future researches, focusing on the most promising results reported, as well as on other chemical substances with biocides activity, exploring the nanotechnology open issues. Nanoparticles-based treatments may perform an important role on the next generation of wood protection. These findings suggest that both zinc oxide and titanium dioxide should be considered as components of a new generation of multi-compounds wood preservatives, based on nanotechnology.

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BORGES, C. C.; TONOLI, G. H. D.; CRUZ, T. M.; DUARTE, P. J.; JUNQUEIRA, T. A. Nanoparticles-based wood preservatives: the next generation of wood protection? **Cerne**, v. 24, n. 4, p. 397-407, 2018.

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SECOND SECTION

PAPER 1 - NANOPARTICLES-BASED WOOD PRESERVATIVES: THE NEXT GENERATION OF WOOD PROTECTION?

BORGES, C.C.; TONOLI, G.H.D.; CRUZ, T.M.; DUARTE, P.J.; JUNQUEIRA, T.A. Nanoparticles-based wood preservatives: the next generation of wood protection? CERNE, v. 24, n. 4, p. 397-407, 2018.

Abstract

Wood is a natural material that shows a great variation of properties. Many treatments have been developed in order to extend the service life of wood products. Nowadays, products with low toxicity and economic viability are a challenge to researchers. Nanotechnology has been indicated as a solution to this issue, since wood preservatives can be utilized in low concentration, promoting satisfactory results in terms of protection with no color changes. The main objective of this review is to present nanotechnology advances on wood protection. Self-cleaning surfaces, scratch and weathering resistance, and biocides properties have been achieved through nanoparticles (NPs) applications. Studies evaluating the performance of NPs from silver (Ag), boron (B), copper (Cu), zinc (Zn), zinc oxide (ZnO), zinc borate ($B_2O_6Zn_3$), and titanium dioxide (TiO_2) on wood protections have reported promising findings. Tests performed against termites, rot, mold and stain fungi, and Ultraviolet (UV) degradation have demonstrated that some biocides have their properties improved in nanoscale. Controlled release and encapsulation technologies are another important matter once it can increase the effectiveness of wood treatments. NPs risk assessment for human health and the environment are still incipient. Despite that, some products as zinc oxide (nanoZnO) and titanium dioxide (nanoTiO_2) present encouraging potential. NanoZnO and nanoTiO_2 have been reported as promising antifungal, antibacterial, and antiviral agents; beyond their biocides properties, low ecotoxicity impacts to the environment are expected. Based on this review, we consider that wood treatments based on NPs may play an important role in the next generation of wood protection systems.

Keywords: wood deterioration, treatments, nanotechnology, biocides.

INTRODUCTION

Solid wood is a naturally created polymer composite, that results of the combination of cellulose, hemicelluloses and lignin naturally arranged into tubular structures that eventually forms a cylindrically layered composite (Csanády et al., 2015). Wood is a renewable material that has sustainable credentials. According to Food and Agriculture Organization of the United States (FAO, 2016), greater wood use can make a significant contribution to a societal desire for a more sustainable future. Using wood reduces carbon emissions, due to carbon dioxide stored in the timber products. Nowadays, carbon credits are traded as part of a voluntary market in the United States of America (USA), while Europe, which ratified the Kyoto Protocol, has a regulated carbon market (Ryan et al., 2010).

Timber has high strength to weight ratio, and is used efficiently in structures where it is carrying a lot of its own self-weight (Ramage et al., 2017). Since the earliest days of human civilization, wood has been a valuable and effective structural material for construction. However, lumber is not naturally durable, and to ensure durability it is necessary to make it resistant through treatments (Canadian Wood Council, 2018). Durability assessment is only based on the tree's heartwood, and not on its sapwood. Due to its extractives, heartwood has any appreciable degree of durability, while sapwood should be considered perishable.

Through the ages, lumber has been treated with preservatives in order to increase durability. However, there is increasing pressure to be environmentally friendly and reduce, restrict, or eliminate the use of wood preservatives because of the concern that toxic constituents may leach from the treated wood (Groenier and Lebow, 2006). Conventional wood preservatives, such as chromated copper arsenate (CCA), and chromated copper borate (CCB), are very effective to protect wood, however they may cause environmental pollution and some of them are hazardous to animals and human being (Venmalar, 2017). Due to the presence of arsenic, wood treatments based on CCA increase the environmental impacts and have limited commercialization, proving the necessity of development of new products for wood preservation (Santos et al., 2012).

In Brazil, traditional treatments based on CCA and CCB are the most utilized (Vidal et al., 2015); even if this kind of treatment causes undesirable wood color changing, and presents risks to environment and human health, they have a significantly higher performance than alternative copper-based preservatives. It has been shown that the percentage of copper removed during leaching tests was higher from wood treated with alternative copper-based preservatives than that of CCA treated wood (Temiz et al., 2014). For retentions of CCA-C greater than 6.8 $Kg.m^{-3}$ the expected lifetimes are over 50 years (Jankowsky et al., 2012). Since increasing life of a wood product implies less work related to replacement and lower cost for the user, this kind of treatment can give a positive environmental contribution because of the extended time of storage of carbon in each wood product, and the longer time to replacements, because every replacement results in an environmental impact (Alfredsen et al., 2017).

However, the Environment Protection Agency of United States (EPA) is reevaluating all chromated arsenical products as part of the Registration Review Program to ensure that chemicals can perform their function without adverse effects on human health or environment (EPA, 2015). CCA has been voluntarily phased out for most uses around residential areas and other areas where human contact with preservative-treated wood is common (Groenier and

Lebow, 2006). Thus, the searching for new treatments with efficiency, low toxicity, no danger to human health, and low costs production is a challenge for researchers on wood protection.

In this context, nanotechnology advance should be a key for the future of wood protection sciences, since nanoparticles (NPs) present the possibility of low concentration usage, maintaining the natural color of the wood and controlled releasing of the active ingredient. The main objective of this review is to present advances and possibilities of nanotechnology application on wood protection.

WOOD PROTECTION

Some species of wood have natural resistance to decomposition caused by microorganisms and insects, however, many of them are scarce or do not grow fast enough to attend the demand of the market (Lebow, 2010).

Natural resistance happens due to extractives that are substances formed on the tree, and naturally deposited into heartwood. Besides protection, extractives are responsible for the color of the heartwood, the wood part that presents natural durability (Lepage et al., 2017). In general, heartwood from some species is durable (Richardson, 2002), while sapwood from all species is very susceptible to decay (Lepage et al., 2017). Species with darker colored or denser woods are most durable, with high natural resistance. But, indeed, there is no wood that possesses natural resistance to all biodeterioration agents (Richardson, 2002).

Wood protection is a solution to this impasse. Wood protection science is the process of addiction of toxic or repellent substances called preservatives into wood, in order to increase resistance to decay and durability (Lepage et al., 2017). Preservative treatments can increase wood service life, reducing replacement costs and allowing efficient use of forest resources.

Through them, wood products can be protected against several attacks, as decay fungi, harmful insects, or marine borers (Lebow, 2010).

Regardless of the treatment received, some wood protection requirements have to be attended. To obtain long-term effectiveness, adequate penetration and retention are required for each wood species, chemical preservative, and treatment method. The degree of protection achieved depends on the product used and the proper penetration and retention of the chemicals, according to efficacy and adaptability to the use requirements (Lebow, 2010).

Leaching also affects the efficacy of the treatment, as well as, the potential impacts on human health and the environment. In the risk assessment of wood preservatives, it is important to know the preservative leaching rates under different exposure scenarios (Waldron et al., 2004).

Considering nanotechnology approaches, the releasing of wood preservatives is another important question. Encapsulation technologies and controlled release methods have revolutionized the use of pesticides and herbicide (Joseph and Morrison, 2006) and may do the same to the wood protection in the near future.

Nowadays, several studies present applications of nanotechnologies on wood protection. In the next sections, they will be properly discussed, looking for high efficiency, low risks to human health, and environmental sustainability.

WOOD PRESERVATIVES

Structure of cell membranes and deoxyribonucleic acid (DNA) have specific and crucial metal ions; half of that known proteins are predicted to be dependent on metal atoms for their structure and participation in key cellular processes (Waldron and Robinson, 2009; Andreini et al., 2004). In spite of that, these essential metals are lethal to all cells when present in excess, and certain non-essential metal such as silver (Ag), mercury (Hg) and tellurium (Te) are extremely poisonous even at exceptionally low concentrations. Consequently, metals have been used for their antimicrobial properties for thousands of years; they inhibit microbial growth, and kill microorganisms, and their application have also been prized in agriculture, as well as enjoyed a rich history in medicine (Lemire et al., 2013).

In regard to wood protection, several chemicals called preservatives are traditionally used as biocides. Preservatives have fungicide and insecticide action, and can be applied separated or together, according to the service requirements. Preservatives can also be incorporated to coatings to protect against others kinds of deterioration, as ultraviolet (UV) degradation, for example.

Wood preservatives can be classified according to the solvent, such as oil-borne solvent-borne and water-borne preservatives. The main oil-borne preservative is creosote, a derived from the distillation of coal tar, with fungicide and insecticide action, that consists of hundreds of compounds and has a variable composition. Solvent-borne preservatives include naphthenates (Cu and Zn), fire-retardants (borates), copper-8-quinolinolate (oxine copper), tributyltin oxide (TBTO), 3-Iodo-2-propynyl N-butylcarbamate (IPBC), and isothiazolones (Ash and Ash, 2004; Lepage et al., 2017). Pentachlorophenol is a solvent-borne preservative widely used as a pressure-treatment to wood in the USA (United States Department of Agriculture – USDA, 2018), even if it is prohibited in Brazil.

Water-borne preservatives include CCA and CCB, alkaline borates, copper azoles B (CA-B), micronized copper azoles (MCA-B and MCA-Q), and copper HDO (CXA). (Lepage et al., 2017). Ammoniacal copper zinc arsenate (ACZA), alkaline copper quaternary compounds (ACQ), and copper azoles are also water-borne preservatives (CBA-A). Some preservatives are no longer available commercially, as acid copper chromate (ACC), ammoniacal copper arsenate (ACA), ammoniacal copper citrate (CC), and copper dimethyldithiocarbamate (CDDC) (USDA, 2018). Besides these, chromated zinc chloride (CZC), ammoniacal copper zinc arsenate (ACZA), and other chemicals have been developed to control internal decay, and protect wood against surface degradation (Zabel and Morrel, 2012).

Insecticides for curative treatments, as pyrethrins and pyrethroids, neonicotinoids, fipronil, and fungicides as carbendazim; products for pretreatment based on carbendazim and cupper oxine; insecticides for plywood glue line, as cypermethrin and IPBC; and fumigant as bromomethane (methyl bromide) and phosphine, as well as, biological products, are used as preservatives (Lepage et al., 2017).

The evaluation of preservatives performance on wood protection is a slow and expensive process. Field-testing experiments of treated wood is the most reliable to evaluate performance with respect to durability and expected service life (Lepage et al., 2017). Unfortunately, the lack of data, the number of involved factors, and how deterioration affects treated wood performance, make service life prediction very hard and hypothetical (Van de Kuilen, 2007; Brischke et al. 2011; Lepage et al., 2017).

POTENTIAL OF NANOTECHNOLOGY ON WOOD PROTECTION

Nanotechnology has been described as the design, characterization, development and application of materials, devices and systems, by controlling shape and size at the nanoscale, with multiple applications in medicine, industry and commercial products. (Weir et al., 2008).

Nowadays, an increasing amount of consumer goods contains engineered NPs (Massari et al., 2014). Engineered NPs hold great promise for a variety of industrial and consumer applications, due to their properties (Kaiser et al., 2013a; Resch and Farina, 2015). The paint industry expects that nanomaterials improve ink properties such as water repellence, scratch resistance, durability and antimicrobial properties (Kaiser et al., 2013a). Preparation of self-cleaning surfaces and improvements of properties such as scratch and weathering resistance, have been achieved using NPs, which is also associated with antimicrobial properties of materials (Kandelbauer and Widsten, 2009).

Generally, in the form of nanoscale flakes, NPs are obtained from a wide variety of materials. The most common of the new generation of NPs are ceramics. They are divided into: (1) metal oxide ceramics, such as titanium (Ti), zinc (Zn), aluminum (Al), and iron (Fe) oxides; and (2) silicate nanoparticles (silicates, or silicon oxides, are also ceramic) (Holister et al., 2003).

Manipulation at the nanometric level can modify properties for new applications in physics, chemistry, biology, and materials science (Resch and Farina, 2015). The transition from microparticles to NPs can change a number of physical properties, because of the increase in the ratio of surface area to volume, and the quantum effects of the size particle (Holister et al., 2003). According to Liu et al. (2002), biocides can be incorporated into several different polymers, copolymers, and polymer blends. Metallic NPs, as photoactive nanoTiO_2 or nanosilica dioxide (nanoSiO_2), may improve paint properties, such as water repellence, scratch resistance, durability and antimicrobial properties (Kaiser, 2013a). Due to the innovation potential, market growth, and the benefits related to NPs, nanotechnologies are considered a strategic area (Resch and Farina, 2015).

Fungicides (tebuconazole, chlorothalonil, and kathon 930) and one insecticide (chlorpyrifos) incorporated into NPs were reported on wood protection with high biological efficacy for all of them (Liu et al., 2002). Nano wires of vanadium pentoxide were identified as having a potential to be an alternative approach to conventional anti biofouling agents (Natalio et al., 2012). Results of combination of cooper oxide NPs (nanoCuO) and fluconazole were reported as a potential treatment against fungi on humans (Weitz et al., 2015).

Performance of wood treated with metallic NPs, based on termite bioassays, was previously reported (Clausen et al., 2009; Kartal et al., 2009; and Mantanis et al., 2014). Treatments performed in southern yellow pine (SYP) with nanoZnO of 30 and 70 nm diluted in water (1.0, 2.5 and 5.0%) presented less than 4% of wood consumption, and caused 94 to 99% of termite mortality after 25 to 27 days incubation. In contrast, termites consumed 10 to 12% of the blocks treated with zinc sulfate ($ZnSO_4$), and termite mortality was considerably lower for all three $ZnSO_4$ treatment concentrations, 1.0, 2.5 and 5.0% (Clausen et al., 2009). Lower termite mortality in ZnSO4 treated wood compared to nanoZnO may be due to differences in bioactivity that results from changes in the chemical structures (Serine et al., 2009). Particles of boron (nanoB) of 30 nm (1%) and boric acid (H_3BO_3) control at 1% caused 100% of termite mortality in SYP, while NanoZn (30 nm) with surfactant (1%) caused moderate termite mortality (31%), and $ZnSO_4$ at 1% resulted in low mortality rates of 1-7% (Kartal et al., 2009). Treatments with particles of 80 nm (2%) of nanozinc borate ($B_2O_6Zn_3$) and nanozinc borate plus water-borne acrylic polymer emulsion caused 100% termite mortality in black pine treated wood (*Pinus nigra* L.), with a considerably low mass losses, i.e. 3.3% and 2.3%, respectively. NanoZnO (80nm, at 2%) formulations caused low mortalities at 9-10%, while suffered significantly low mass losses at 4-7% (Mantanis et al., 2014). NanoCuO provides no protection to termites (Kartal et al., 2009; Mantanis et al., 2014).

Attempts of mold growth control using metal NPs were reported in literature by several authors (Kartal et al., 2009; Clausen et al., 2009; Mantanis et al., 2014). Against mould growth, nanometals preparations of 30 nm (Cu, Zn or B at 1%) and respective controls (cooper sulfate (CuSO4), $ZnSO_4$, H_3BO_3 at (1%), and untreated) failed to provide adequate protection to wood (Kartal et al., 2009). However, results of Mantanis et al. (2014) demonstrate a slightly inhibition of mold fungi by nanozinc borate of 80nm (2%). At high concentration, NanoZnO treatments (30 and 70 nm, at 5%) resulted in moderate inhibition (20 – 32%) of mold and sapstain growth (Clausen et al., 2009). Concerning to nanosilver (nanoAg), it was reported the protective effect against mold, blue stain fungi and algae was insufficient for coatings (Künniger et al., 2013).

NPs (30 nm) of Cu, Zn and B at 1% inhibited the white-rot test fungus *Trametes versicolor* (Kartal et al., 2009). The same white-rot fungus (*Trametes versicolor)* was significantly inhibited by nanoZn-based preparations in different treatments and concentrations (Clausen et al., 2009; Kartal et al., 2009; Mantanis et al., 2014). Nanozinc borate (80 nm, at 2%) plus acrylic emulsion imparted very high resistance in pine wood to the white-rot fungus (Mantanis et al., 2014).

Prevention of decay caused by *Hypocrea lixii* (white-rot) and *Mucor circinelloides* (brown-rot) were reported in *Pinus Sylvestris* L., *Abies alba* M., *Junglas regia* L., *Castanea sativa* M., *Prunus avium* L., *Quercus petrea* L., *Fagus sylvatica* L., and *Fraxinus excelsior* L., independently of wood species and fungus type, through photo-catalytic activity of NanoTiO_2. In that work, TiO_2 impregnation was performed by immersion of untreated samples for seven days in a solution of TiO_2 NPs (0.25 mg/mL) and 0.01 mL of surfactant (De Filpo et al., 2013).

NanoZnO (30 and 70 nm) did not significantly inhibit brown-rot fungi *Postia placenta* (2.5 or 5.0%) or *Antrodia* sp. (1.0%). At 5.0%, nanoZnO caused 74% lower mass losses than in the untreated control in *Gloeophyllum trabeum* attack (Clausen et al., 2009). Copper-treated (30 nm, at 1%) specimens exposed to *Antrodia* sp. showed high mass losses (19 - 33%). However, mass loss of treated wood exposed to *G. trabeum* was greatly reduced (65%) with nanoCu (1%) or $CuSO_4$ (3–15%), compared with untreated controls (Kartal et al., 2009). SYP treated with kathon 930 in polyvinylpyridine, at levels of 0.1 Kg of biocide.m^{-3}, presented weight loss of only 5% after 50 days of exposure to *G. trabeum* (Liu et al., 2002). NanoZnO (80 nm, at 2%) and nanozinc borate treatments (80 nm, at 2%) did not inhibited the brown-rot fungus *Tyromyces palustris (*Mantanis et al., 2014). Treatments results of basic copper carbonate NPs ($CuCO_3 \cdot Cu(OH)_2$) against the brown rot fungus *Rhodonia placenta* also do not support increasing antifungal efficacy due to nanosizing effects (Civardi et al., 2015a).

NanoZnO particles (30 nm) were reported on wood weatherability control. Graying was significantly reduced by nanoZnO treatments at high concentration (5%), but it was not completely eliminated (Clausen et al., 2010). It happens because ZnO is a highly effective UV protector, due its strong UV absorption (Yu et al., 2010). Water repellency on wood surfaces persisted for 8 weeks. After 12 months of weathering, specimens treated with 1% nanoZn presented approximately 10% of reduction in 24 h water absorption, while specimens treated with 2.5 and 5.0% nanoZn showed 32% reduction in 24 h water absorption, when compared to untreated samples (Clausen et al., 2010). The water absorption changes founded are an important result, because imply in a decreasing of equilibrium moisture content of the wood; It is known that in moisture contents below the fiber saturation point natural resistance of wood to insects and fungi increase (Lepage et al., 2017).

Authors concluded that nanoZnO has desirable wood protection properties, such as leach resistance, UV protection, and termite resistance, even it would provide no adequate protection against decay or mold (Clausen et al., 2009).

In general, nanotechnologies have the potential to affect all wood preservation field through the development of new preservatives with low toxicity and high effectiveness. Nanotechnologies also can affect wood protection on several parameters as penetration, retention, and leaching. The next sections will discuss it.

PENETRATION INTO WOOD

According to Freeman and McIntyre (2008), the size of metal particles may affect penetration into wood cell walls and reactions with wood molecular constituents. The degree of penetration and uniformity of distribution of particles into wood cellular structure is inversely related to the prevalence of large size particles.

Large particles may obstruct tracheids and inhibit the preservative penetration. On the other hand, complete penetration and uniform distribution of preservative in wood is expected if the particle size of the preservative is smaller than the diameter of the window pit (10nm) or membrane openings in a bordered pit (400 – 600 nm). In concern to hardwoods, wood pore diameters are measured in micrometers. A diameter of 50 µm is considered a relatively small pore size (Maier, 2018), however it is greater than bordered pit of softwoods.

NPs are created with controlled particle size and some of them demonstrated high dispersion stability (Freeman and McIntyre, 2008), being this an important feature, since particles-size in the range of 1-100 nm may improve penetrability of chemical reagents into the wood (Freeman and McIntyre, 2008; Kartal et al., 2009). Nano metal preparations have low viscosity and a surfactant addition can further increase dispersion stability by enabling liquid dispersion of higher concentrations of nanometal particles (Kartal et al., 2009; Lykidis et al., 2013). Information about nanoTiO_2 penetration into the microscopic pores of wood are poorly reported. The depth of nanoparticles penetration can be estimate by SEM analysis. It was described as a thin homogeneous layer of TiO_2 NPs, with an average size of 50 nm covering wood internal structures, without changing natural appearance (De Filpo et al., 2013).

Regarding to wood protection requirements, nanometals show potential for great penetration and protection, with a more uniform particulate distribution over a wood surface.

CHEMICAL RETENTION IN THE WOOD

Retention is the amount of preservative that is retained in the wood after a treatment cycle. It is one measurement of the degree of protection provided by a treatment, been usually expressed as kilograms of preservative per cubic meter of wood (Canadian Wood Council, 2018). Specimen size and configuration cause differences in chemical retention (Kartal et al., 2009; Mantanis et al., 2014). Thin specimens had higher retention than large ones (Kartal et al., 2009).

Comparing NPs with microparticles, there was no difference between nanoB and H_3BO_3 chemical retentions, however, chemical retention of NanoCu was 30% less than $CuSO_4$. For nanoZn preparations (30 nm, without surfactant) and $ZnSO_4$, retentions were similar (Kartal et al., 2009). Otherwise, nanoZnO as aqueous dispersions (with 30 nm and 70 nm average diameters) presented higher chemical retentions than $ZnSO_4$ treated wood, for the same concentration (Clausen et al., 2011).

Surfactants affect chemical retention (Kartal et al., 2009; Mantanis et al., 2014). With surfactant, retentions were 30% and 16% lower than $ZnSO_4$, for nanoZn and nanoZn with Ag, respectively (Kartal et al., 2009), and the highest retention levels in treatments with nanoZnO were obtained without acrylic emulsion (Mantanis et al., 2014).

Due to differences that specimen sizes, emulsions and emulsifying agents cause to chemical retention of wood preservatives, it is hard to compare reported results. However, great development can be achieved by exploring these features.

CHEMICAL LEACHING OF THE NPS

Wood preservatives have to present ability to fixate inside wood. This parameter is usually expressed through leaching rates. Leaching is greatest in treatments with high retention levels and high exposed surface area. The highest rates of leaching occurs in the first months of service, and it is increased by exposing the wood to water flow, low pH, and water-soluble organic acids (Lebow, 1996).

Information provided over depletion of chemical retention of nanoZnO (30 nm) on wood weathered specimens (12 months of outdoor exposure) suggested specimens vacuum treated with 1% of nanoZnO were leach resistant, while $ZnSO_4$ readily leached (Clausen et al., 2010). It happens because $ZnSO_4$ leached faster than nanoZn (Kartal et al., 2009). NanoZnO retention in specimens treated with 1% nanoZnO presented no changes, but specimens treated with 2.5 and 5.0% nanoZnO showed 65 and 58% of nanoZnO loss, respectively (Clausen et al., 2010).

Leaching from wood treated with nanoCu (30 nm particle diameter) was barely detectable, but the rate of leaching for $CuSO_4$ was faster. On the same way, nano preparations of Zn and Zn with Ag showed lower leaching than $ZnSO_4$ (Kartal et al., 2009). NanoB presented very low leaching resistance (Mantanis et al., 2014; Lykidis et al., 2013; Kartal et al., 2009). Van der Waals forces and changes in charge can explain the low leaching of nanometals (Kartal et al., 2009; Clausen et al., 2009; Clausen et al. 2010).

NanoCuO treated specimens with and without emulsion showed low percentage of leaching (Mantanis et al., 2014; Clausen et al., 2009). Specimens treated with nanoCu, with and without surfactant, had high leaching resistance compared to the control $CuSO_4$. NanoZn and nanoZn plus Ag, both with surfactant, had low percentage of leaching (9% and 8%, respectively), when compared to Zn preparations without surfactant (31% and 33%), and $ZnSO_4$ (84%) (Kartal et al., 2009). Preparations of nanoZnO and zinc borate plus acrylic emulsion had a lower percentage of leaching than the same zinc preparations without emulsion. However, nanoCuO treated specimens without emulsion had the lowest percentage of leaching (7.5%), while nanCuO with emulsions had high percentage of leaching, 13% and 29%, respectively (Mantanis et al., 2014). It happens because addition of a water-borne acrylic emulsion binder in the compound may increase its affinity to wood polymers and subsequently decrease leaching (Lykidis et al., 2013).

It is possible to affirm that leaching can be controlled by using emulsions and surfactants (Kartal et al., 2009; Lykidis et al., 2013; Mantanis et al., 2014), but this affirmation has to be more explored in future researches, looking for improved results.

CONTROL OF RELEASING OF BIOCIDES

In order to control releasing, extend wood preservatives activity, and reduce their toxic effects, biocides NPs could be encapsulated. Encapsulation provides controlled means of prolonging biocidal activity, protecting against biocide leaching, UV-induced degradation, and consequently increasing lifetime effects (Sørensen et al., 2010). Besides, external conditions such as the pH, can be used for a controlled releasing when they reach specific required conditions (Pérez-de-Luque and Rubiales, 2009).

Controlled release of chemical substances can be evaluated by using different approaches. The surface assembly of polyelectrolyte multilayers on the microcapsule surface is a very promising tool for controlling the release of hydrophobic actives (Trojer et al., 2015).

Studies demonstrated the effectiveness of an environmentally friendly sustained releasing system of fipronil insecticide into silica nanocapsules against subterranean termites in laboratory tests (Wibowo et al., 2014). Polymeric capsules containing biocides improved the resistance of birch wood to white-rot attack, with a very low biocide loading required (0.1 to 0.8 $Kg.m^{-3}$). In general, nature-derived material, as carbon nanotubes, polymers, mesoporous alumina and mesoporous/hollow silica present high potential for controlled release systems, according to several authors cited by Mattos et al., 2017.

Even if studies about NPs control of releasing are still incipient, they are very promisors because they could increase effectiveness of wood preservatives, and consequently decrease costs of maintenance and replacement of wood products.

HUMAN AND ENVIRONMENTAL RISKS OF NPS

The increasing usage of engineered NPs intensify the probability of consumer and workers to get into contact with materials that might cause adverse health effects (Oberdorster et al., 2005; Silva et al., 2010). Despite this, there are few information about NPs safety.

The exponential developments of nanotechnologies contrast to concerns of public health, due to the insufficient risk assessment to environment and human health (Louro et al., 2013). Both beneficial (e.g. photocatalytic activity and water repellence) or harmful effects (e.g. induction of oxidative stress and cellular dysfunction) can be exerted by the desired properties of engineered NPs (Stoeger et al., 2009).

Künniger et al. (2013), studying functionality and environmental impacts of metallic NPs of Ag, found the total Ag released from products with nanoAg was proportional to the overall erosion of the coating, and there was indication that metallic nanoAg are transformed to Ag complexes less toxic than ionic Ag. NanoCu-based wood treatments may end up dispersed into the environment being inhaled, causing harm, and become a human health potential risk (Civardi et al., 2015b). It is advocated to intensify studies focused at a complete characterization of its toxicity and behavior in environmentally exposure (Anjum et al., 2015).

NPs of TiO_2 may undergo to physicochemical transformation during incineration, requiring further research to identify what NPs will be emitted to the environment from incinerated material (Massari et al., 2014). Engineered NPs from Ag had higher ecotoxic impact than those from TiO_2, with a linear regression between Ag content in products and the potential ecotoxicity impacts to environment (Miseljic and Olsen, 2014). Kaiser et al. (2013b), working about engineered NPs used at paint industry, showed that neither the gastrointestinal cells nor immune system cells were significantly affected when exposed to nanoTiO_2 and nanoSiO_2, while several cell parameters were affected when exposed to nanoAg. Future research aiming at unveiling the destination of nanoAg particles, its transformation, accumulation, and toxicity potential, as well as their impact on environmental and human health are recommended (Anjum et al., 2013).

NanoZnO has been indicated as a promising antibacterial, antifungal, and antiviral agent (Beegam et al., 2016) with promising results in the control of several kinds of cancer cells (Rasmussen et al., 2010; Wahab et al., 2013a; Wahab et al., 2013b; Selvakumari et al., 2015; Vinardell and Mitjans, 2015; Namvar et al., 2015; Bisht and Rayamajhi, 2016). Studies have also shown potential beneficial environment effects of nanoZnO (Beegam et al., 2016), but in order to understand their potential risk, a comprehensive material life cycle analysis is necessary (Bystrzejewska-Piotrowska et al., 2009; Oliveira et al., 2012; Silva et al., 2012a; Silva et al., 2012b).

Due to the increasing concern of NPs security, there is a deceleration in nanotechnology research, in the field of medical and food industries, because of the fact that researchers have found that NPs could diffuse into the human body and cause adverse effects. Considering the increasing of production and application of nanomaterials, as well as the related consumer products, it was suggested that a testing strategy for different kinds of NPs has to be established (Hougaard et al., 2015). Society might overestimate the short-term effects of nanotechnologies, while underestimating the long-term effects (Bystrzejewska-Piotrowska et al., 2009). Despite this, many authors regard nanotechnology as the base for the next industrial revolution (Resch and Farina, 2015).

PROSPECTS AND CONSIDERATIONS ON WOOD PROTECTION

There are many possibilities of nanotechnologies applications on wood protection. Nanometals-based treatments present good perspective to control water repellence, scratch resistance, durability, self-cleaning surfaces, wood biodeterioration, and also can improve weathering resistance.

White-rot fungus inhibition and termites control by using NPs were reported; but no nanometal preparation was effective against brown-rot fungi (*Meruliporia incrassate, Gloeophyllum trabeum* and *Tyromyces palustris*). However, control over decay caused by *Mucor circinelloides* was reported.

Authors reported information about chemical retention and leaching of NPs and weathering protection through NPs, with good results. No significant differences between different NPs sizes were reported for leach resistance and termites. However, some NPs can be considered as friendly biocides with potential application on wood protection industrial process in the future, as nanoZnO and nanoTiO_2.

NPs-based wood preservatives have to be properly explored in future researches, focusing on the most promising results reported, as well as other chemical substances with biocides activity, exploring the nanotechnology open issues. It is necessary to keep in mind that there are not sufficient risk assessment for human health and the environment impacts of NPs yet. However, although there is no answer to all questions, based on this review, it can be considered that NPs-based treatments may perform an important role on the next generation of wood protection.

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PAPER 2 – PERFORMANCE OF ZINC OXIDE AND TITANIUM DIOXIDE NANOPARTICLES ON WOOD PROTECTION

Abstract

The main objective of this study was to evaluate zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles-based treatments performance on wood protection. The experiment was designed with six treatments of ZnO and TiO_2 nanoparticles in water dispersion, i.e., a) 1 (2% ZnO); b) 2 (1.5% ZnO, 0.5% TiO_2); c) 3 (1% ZnO; 1% TiO_2); d) 4 (0.5% ZnO; 1.5% TiO_2); e) 5 (2% TiO_2); f) 6 (untreated). Wood samples were vacuum-treated (45 min vacuum at 550 mmHg). Chemical retentions were analyzed by inductively coupled plasma emission spectroscopy (ICP-AES). Penetration was visualized by scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). Treatments performance was evaluated by accelerated fungal decay resistance, a no-choice termite bioassay, and natural weathering. Results of chemical retention showed that ZnO retention decreased according to the decreasing of the oxide concentration of each treatment, while TiO_2 retentions were low detectable. Results of mass loss of accelerated decay test demonstrated variation according to the fungus and chemical treatment. Treatment 2 showed the best result in termite bioassay. Treatments 1 and 3 also presented low average of loss mass, with 2.4 and 4.1% of wood consumption, respectively. Average termite mortality rated three treatments at 100% of mortality: 1, 2, and 3. Regarding weathering tests, treatment 5 presented itself brighter than all other treatments in the exposed face. In the unexposed face, treatment 1 was less gray and brighter than all treatments. Based on the results, we can conclude that both zinc oxide and titanium dioxide could be included as multi-components of a new generation of wood preservatives.

Keywords: Treated wood, nanotechnology, fungal decay, termites, weatherability resistance.

INTRODUCTION

Wood is a primarily cellulose material with natural and renewable credentials, available to several applications due to its great diversity of color, texture, anatomic, mechanical, chemical, and physical properties, as well as natural resistance and beauty, among different species. Some species of wood have natural resistance to microorganisms and insects, however, they are scarce or do not grow fast enough to attend the demand of the market. Wood protection is a solution to this impasse.

Preservative treatments can increase the wood service life. Through them wood products can be protected, reducing replacement costs and allowing more efficient use of forest resources (Lebow, 2010). Besides, wood treatments have a positive environmental contribution increasing time of storage of carbon in each wood product, and avoid replacements, as well as new environmental impact (Alfredsen et al., 2017).

In Brazil, chromated copper arsenate (CCA-C) and chromated copper borate (CCB) based treatments are the most utilized in order to increase wood service life (Vidal et al., 2015). However, all chromated arsenical products have been re-evaluated to ensure chemicals preservatives can perform their function without adverse effects on human health or environment (EPA, 2015). Thus, the searching for new treatments with efficiency, low toxicity, no danger to human health, and viability of costs production has been a challenge for researchers on wood protection.

Nanotechnology holds great promise for a variety of industrial and consumer applications, been considered a strategic area due to the innovation potential, market growth, and the benefits related to nanoparticles; manipulation at the nanometric level can modify material properties for new applications in physics, chemistry, biology, and materials science (Resch and Farina, 2015). It happens because the transition from microparticles to nanoparticles can change a number of physical properties, due to the increasing in the ratio of surface area to volume, and the quantum effects of the size particle (Holister et al., 2003).

Until recently, there was no much information about nanoparticles efficiency on wood protection. However, studies in this field have been developed in order to improve durability and extend wood service life (Kartal et al. 2009; Clausen et al. 2010; 2011; De Filpo et al., 2013; Lykidis et al. 2013; Afrouzi et al., 2013; Mantanis et al. 2014; Lykidis et al., 2016).

Previous results reported that zinc oxide nanoparticles preparations inhibited significantly the white-rot fungus *Trametes versicolor* in different treatments and concentrations (Clausen et al., 2009; Kartal et al., 2009; Mantanis et al., 2014; Marzbani et al., 2015). The brown-rot fungi *Postia placenta*, and *Antrodia* sp. were also significantly inhibit by zinc oxide nanoparticles, while *Gloeophyllum trabeum* attack was reduced in 74% (Clausen et al., 2009). *Tyromyces palustris* was reported as not inhibit by zinc oxide nanoparticles *(*Mantanis et al., 2014). Prevention of fungal decay due to the brown-rot fungus *Coniophora puteana.*was also reported (Marzbani et al., 2015). Prevention of decay caused by *Hypocrea lixii* (white-rot) and *Mucor circinelloides* (brown-rot) was reported, independently of wood species and fungus type, through photo-catalytic activity of titanium dioxide nanoparticles (De Filpo et al., 2013).

Performance of wood treated with zinc oxide nanoparticles, based on termite bioassays was also reported with promising results (Clausen et al., 2009; Kartal et al., 2009; Mantanis et al., 2014; Lykidis et al., 2016). Studies about zinc oxide performance on wood decay due weathering exposition demonstrated that graying was significantly reduced, even if it was not completely eliminated (Clausen et al., 2010; Afrouzi et al., 2013; Weththimuni et al., 2019).

In line with the results previously reported, the main objective of this work was to evaluate the performance of zinc oxide and titanium dioxide nanoparticles-based treatments on wood protection against fungal decay, termite damage, and weathering exposition.

MATERIAL AND METHODS

Wood samples

V&M Florestal, a company located in Paraopeba, MG, Brazil (19°14' S and 44°27' W) provided *Eucalyptus urophylla* S.T. Blake wood, 6.7 years old, for test sample manufacturing. The trees were from clonal tests managed for charcoal production, planted on 3 x 3 m, with a diameter at breast height of around 16 cm. The selected trees had representative average development for the stand, with linear stem and good phytosanitary conditions.

Due to standard methods orientations, the size of the test samples varied according to the test. For health protection of operators, samples dimensioning was always performed before the chemical treatments. After dimensioning, all samples were weighed for moisture variation control and conditioned at 20°C and 65% of RH, before chemical treatment.

Nanoparticles and wood treatment

Zinc oxide (ZnO) and titanium dioxide (TiO_2) nanoparticles were provided by US Research Nanomaterials, Inc. (Houston, TX, USA). Both nanoparticles were as an aqueous dispersion: ZnO (20.6 wt%) size 30-40 nm, and TiO_2, rutile (20 wt%), size 30-50 nm.

The experiment was set in a completely randomized design, with six nanoparticles-based treatments, with different concentrations of zinc oxide and titanium dioxide nanoparticles, as designed on the Table 1. Test samples, previously conditioned at 20^{o}C and 65% of relative humidity (RH), were vacuum-treated (45 min vacuum at 550 mmHg). Treatments were monitored and all data recorded with a pressure sensor coupled to an Arduino controller system.

Table 1 – Treatments design with ZnO and TiO_2 nanoparticles

Treatment	ZnO concentration (%)	TiO_2 concentration (%)	Initial volume (ml)	Final volume (ml)	Consumed volume ($l.kg^{-1}$)	Consumed volume ($l.m^{-3}$)
1	2.0	0.0	1700.0	1590.0	0.3	210.2
2	1.5	0.5	1700.0	1580.0	0.4	229.3
3	1.0	1.0	1700.0	1560.0	0.4	267.5
4	0.5	1.5	1700.0	1557.0	0.5	273.3
5	0.0	2.0	1700.0	1550.0	0.5	286.6
6	0.0	0.0	-	-	-	-

The total wood volume of each treatment was 5.23 x 10^{-4} m^3 (specific gravity at equilibrium moisture content (EMC) = 601.43 $kg.m^{-3}$). Untreated samples were the controls. After chemical treatment, treated samples were reconditioned at 20°C and 65% of RH.

Chemical retention and penetration of nanoparticles into the wood

Three samples (19 x 19 x 19 mm) of each different treatment performed were ground to pass a 30-mesh screen, and analyzed by inductively coupled plasma optical emission spectroscopy (ICP-AES) for determination of zinc oxide and titanium dioxide retentions, according to the American Wood Protection Association AWPA - A21 (2014). The equipment utilized was a SPECTRO spectrometer, model Blue, and the digestion was made by per chloric acid method, AWPA - A7 (2014) and wood specific gravity of reference was 740 $kg.m^{-3}$, obtained at 0% of moisture content (MC).

Penetration of zinc oxide and titanium dioxide into wood was evaluated by scanning electron microscopy with dispersive spectroscopy (SEM/EDS). Analyses were performed in order to locate zinc and titanium atoms on the surface of thin wood samples (~2.5 x 2.5 x 0.5 mm). The outermost part of the wood was eliminated, and test samples were made from internal material, around 3 mm depth. Samples were previously prepared, polished, dried at 0% of moisture content, and recovered with a very thin layer of carbon, before analysis. SEM Images were systematically obtained from the transverse face of the wood; The SEM/EDS spectra were obtained on a ZEISS microscopy, model EVO 40 LEO, and analyzed with Quantax software. Values were adjusted to express zinc oxide and titanium dioxide.

Fungal decay tests

The treatments performance on wood durability was evaluated through the test method of accelerated decay resistance, according to American Society for Testing and Materials ASTM D1413 - 07 (2007). Five samples (nominal dimensions of 19 x 19 x 19 mm) per treatment group were exposed to white-rot fungi *Pycnoporus sanguineus* (L.: Fr.) Murr. (PD1), *Schizophyllum commune* Fr. (PD21), *Trametes elegans* (Spreng.) Fr. (PD68), and brown-rot fungus *Gloeophyllum abietinum* (Bull.) P. Karst (PD63) in a soil-block test and incubated at 27^oC and 80% RH, during 12 weeks. After this time, fungal mycelium were brushed from the samples, and they were over dried, reconditioned, and reweighed for mass loss percentage calculation. Fungi are catalogued in the Forest Phytopathology Laboratory of the Federal University of Lavras.

Mass loss was evaluated in completely randomized design, in a factorial design 6x4 (6 treatments x 4 fungi). Data were transformed using Box-Cox (Box and Cox, 1964) and the sum of 0.5 for all data (Yamamura, 1999). The analysis of variance was doubled within each type of fungus to evaluate the effect of the chemical treatments; when this was significant, the Tukey averages test was performed ($\rho \leq 0.05$).

Termite bioassays

No-choice termite resistance tests with the subterranean termites *Nasutitermes aquilinus* (Isoptera, Termitidae, Nasutitermitinae) were performed using ten test samples (with nominal dimensions of 25 x 25 x 6.4 mm), previously oven dried and weighted, for each treatment group. Termites were collected in Lavras, MG, Brazil (21°13' S and 44°58' W). The termite bioassays were conducted at 27^{o}C and 85% RH, during 4 weeks, based on ASTM D3345 - 17 (2017). Each wood sample was placed in the bottom of an acrylic cylindrical container (100 mm diameter and 60 mm height) with 200 g of moist sand. 1.00 ± 0.01 g of *N. aquilinus* subterranean termite (about 120 termites, at least 90% workers) was added to each of the previously prepared containers. Tests were periodically observed for moisture and mortality. In the end of the first and fourth weeks, tunneling presence, termite position, and mortality were evaluated. After the bioassay, wood samples were oven dried and reweighed to calculate mass loss. Termite bioassays mass loss was evaluated through Variance Analysis and Tukey mean test ($\rho \leq 0.05$). Termite mortality rate was estimated by weighing the remaining live termites. Wood samples were also visually rated (0 to 10), being 10 = sound, surface nibbles permitted; 9 = light attack; 7 = moderate attack, penetration; 4 = heavy; 0 = failure (ASTM D3345, 2017). The *N. aquilinus* specie was chosen due it be one of the most common wood feeder termite, in the Lavras region. Dr. Reginaldo Constantino, Associate Professor at the University of Brasília, identified the *N. aquilinus* termite.

Weatherability

Samples of all six treatments (25 x 25 x 100 mm) were weathered outdoor in Lavras, MG, during 12 months. Three samples per treatment plus untreated controls were placed horizontally on a screened tray in direct sunlight. After that, samples were visually evaluated for ultraviolet (UV) damage (splitting, checking, brightness, and graying), being rated from zero (without) to 100 (all surface recovered) for splitting and checking, and ordered according to brightness and graying presence. The exposed surface was the specimen surface in direct light, and the unexposed was the underside of each specimen surface.

RESULTS AND DISCUSSION

Chemical retention and penetration of nanoparticles into the wood

Results of chemical retention of treated wood are in Table 2, where it can be observed that zinc oxide retentions decreased according to the chemical concentration of each treatment. However, titanium dioxide retentions of the same treatments were low detectable.

Clausen et al. (2009; 2010) have reported retention values of 3.78 kg.m^{-3} and 1.61 kg.m^{-3}, for solutions of concentration 2.5% and 1%, respectively, in their study about zinc oxide nanoparticles in southern yellow pine. These values are similar to the findings presented in Table 2.

Table 2 – Average retention values of the ZnO and TiO_2 nanoparticles

Treatment	ZnO concentration (%)	TiO_2 concentration (%)	ZnO retention (kg.m^{-3})	TiO_2 retention (kg.m^{-3})
1	2.0	0.0	2.70	0.00
2	1.5	0.5	1.06	0.00
3	1.0	1.0	0.45	0.01
4	0.5	1.5	0.33	0.03
5	0.0	2.0	0.05	0.25
6	0.0	0.0	0.01	0.00

Mantanis et al. (2014) working with three different zinc oxide nanoparticles-based treatments (without acrylic solution, and two different acrylic solution, all at 2% of concentration) reported higher retentions values than ours. Differences among zinc oxide nanoparticles retentions can be explained by the wood species, since they were working with *Pinus nigra* L.; usually *Eucalyptus* shows low permeability, as well as more heartwood, even in young wood material. Besides, samples size, and emulsions, also cause differences in chemical retention of wood preservatives (Kartal et al., 2009; Mantanis et al., 2014). Due to differences caused by sample sizes, emulsifying agents and wood species, it is hard to compare results of chemical retention of wood preservatives (Borges et al., 2018).

Figure 1 shows the presence of nanoparticles according to the color, where green is related to zinc atoms (1A, 1B, 1C, and 1D), while blue color corresponds to titanium (1B, 1C, 1D, and 1E). Figure 1F corresponds to untreated samples.

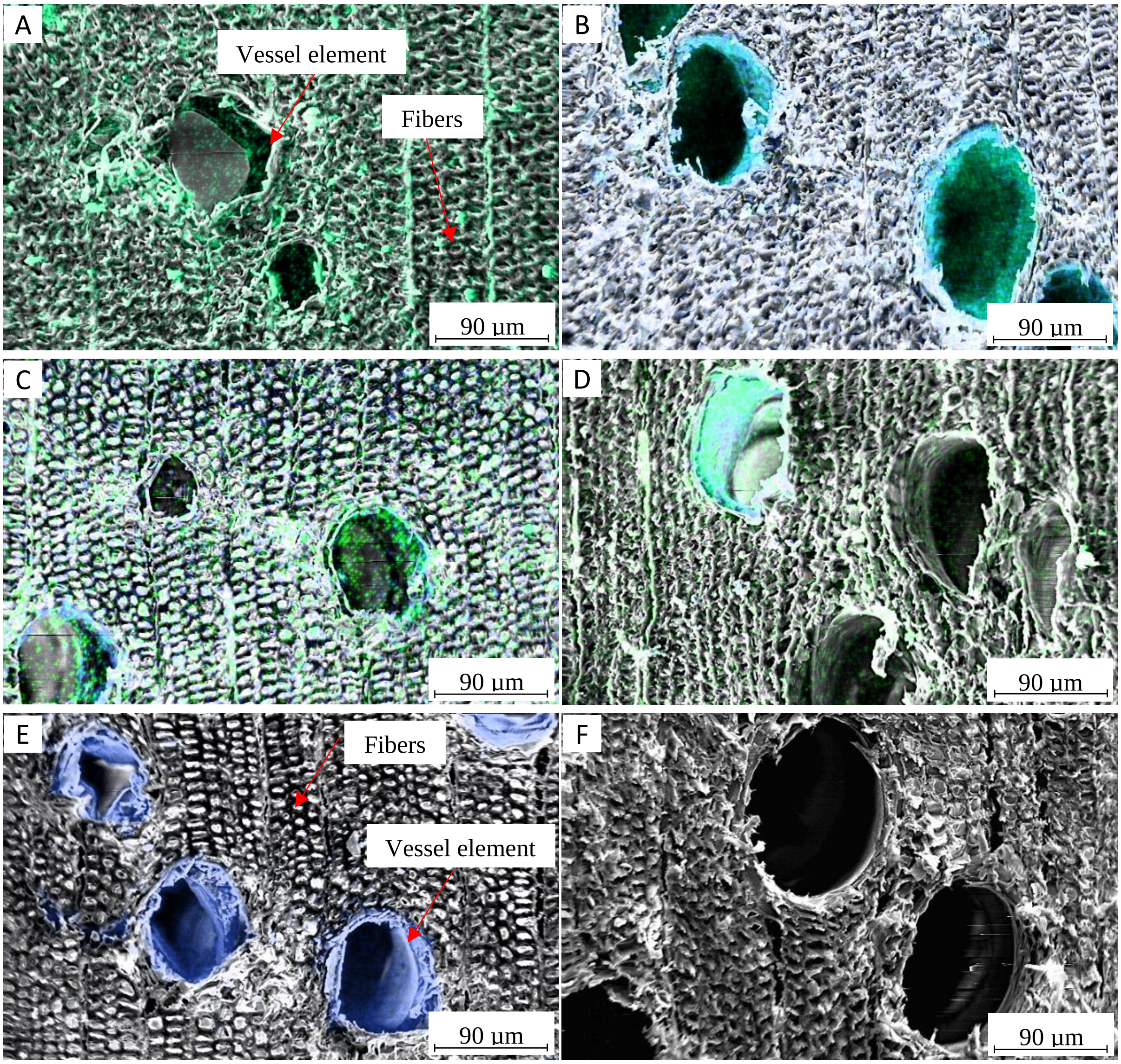

Figure 1 – SEM/EDS micrographs of treated *E. urophylla* wood samples: A) Treatment 1 (2% ZnO); B) Treatment 2 (1.5% ZnO, 0.5% TiO_2); C) Treatment 3 (1% ZnO; 1% TiO_2); D) Treatment 4 (0.5% ZnO; 1.5% TiO_2); E) Treatment 5 (2% TiO_2); F) Treatment 6 (untreated).

Comparing treatment 1 (Figure 1A), performed with zinc oxide nanoparticles at 2% concentration, without titanium dioxide (2% ZnO), and treatment 5 with 2% of titanium dioxide (Figure 1E), without zinc oxide, it was possible to observe that zinc oxide are homogenously distributed on fibers and vessel elements, while titanium dioxide seems more concentrate on internal wall of vessel elements.

Information about nanoparticles penetration into wood are poorly reported, it could even be estimate by SEM analysis. De Filpo et al. (2013) have described that titanium dioxide nanoparticles deeply penetrate in the microscopic porous of wood, covering wood internal structures with a thin homogeneous layer of an average size of 50 nm, without changing natural appearance. In their research, titanium dioxide impregnation was performed by immersing untreated samples for seven days, while in the present work the impregnations were made through application of vacuum (45 min vacuum at 550 mmHg), what may have caused differences of penetration depth. However, their description about titanium nanoparticles behavior, as a thin homogeneous layer covering wood internal structures, may explain why penetration could be observed, even if a low retention was found, since we also observed nanoparticles in thin layers covering internal structures of wood.

Fungal decay tests

Results of mass loss of nanoparticles-based treated wood exposed to white-rot fungi *Pycnoporus sanguineus*, *Schizophyllum commune*, *Trametes elegans*, and brown-rot fungus *Gloeophyllum abietinum* in a soil-block test reported differences, according to the fungus and treatment performed (Figures 2A, 2B, 2C, and 2D).

On *Pycnoporus sanguineus* fungus control (white-rot) (Figure 2A), treatment 1 (2% ZnO) showed the more effective results. In this treatment, mass loss was lower than in other treatments, and untreated wood. Treatment 4 (0.5% ZnO; 1.5% TiO_2) did not present statistical difference of the treatment 1. However, specifically on that treatment, a phase separation occurred during the impregnation process, consequently affecting results. Treatments 2 (1.5% ZnO, 0.5% TiO_2), 3 (1% ZnO; 1% TiO_2), 5 (2% TiO_2) and 6 (untreated) did present statistical differences among them.

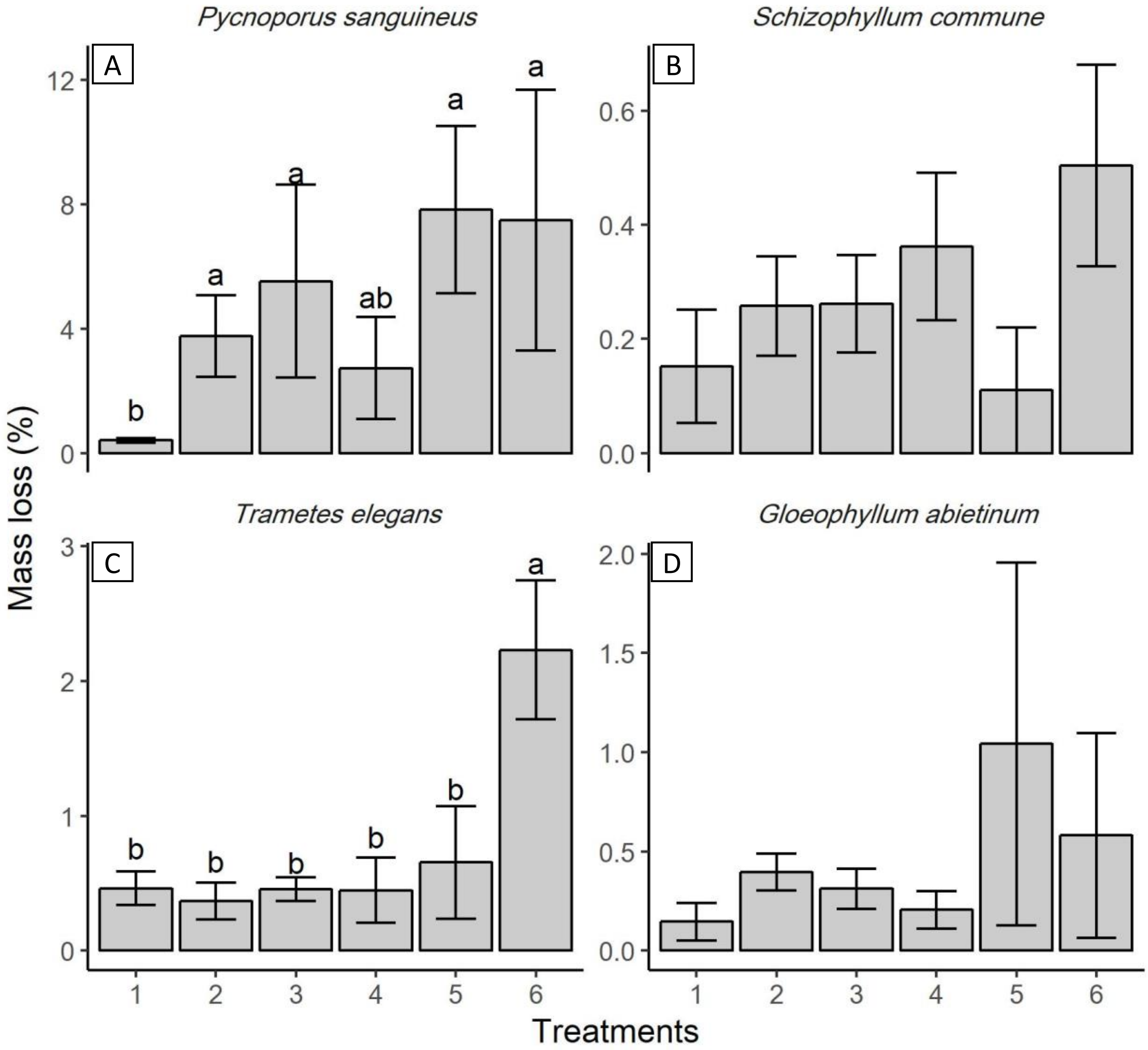

Figure 2 – Average and standard deviation values of the mass loss (%) caused by fungal decay on *E. urophylla* treated samples. A) *Pycnoporus sanguineus*; B) *Schizophyllum*; C) *Trametes elegans*; D) *Gloeophyllum abietinum*. Groups sharing the same letter are not significantly different (ρ≤ = 0.05). Treatment 1 (2% ZnO); treatment 2 (1.5% ZnO, 0.5% TiO_2); treatment 3 (1% ZnO; 1% TiO_2); treatment 4 (0.5% ZnO; 1.5% TiO_2); treatment 5 (2% TiO_2); and treatment 6 (untreated).

On white-rot fungus *Trametes elegans* test (Figure 1C), all treatments (1 to 5) can be considered effective to control wood damage, since they did not present any statistical difference among them, with a low mass loss (< 1%) when compared to the untreated wood (treatment 6).

Damage caused by attack of the white-rot fungus *Schizophyllum commune* (Figure 1B), and the brown-rot fungus *Gloeophyllum abietinum* (Figure 1D) was considered not significant due to the low attack degree, even on untreated wood (Treatment 6). Nevertheless, the graphs are indicative of tendency. Interaction between fungi and wood was also evaluated, and differences were found in *Pycnoporus sanguineus* when compared to the others, being the mass loss caused by its attack higher than other due interaction.

White-rot fungal decay control with treatments based on zinc oxide nanoparticles in different concentrations and nanoparticles size were previously related by several authors with *Trametes versicolor* (Clausen et al., 2009; Kartal et al., 2009; Mantanis et al., 2014). However, zinc oxide nanoparticles treatments did not inhibited neither the brown-rot fungi *Tyromyces palustris* in black pine wood *(Pinus nigra L.)* (Mantanis et al., 2014), *Postia placenta,* nor *Antrodia* sp. in southern yellow pine, but caused 74% lower mass losses than in the untreated control in *Gloeophyllum trabeum* attack in the same wood species (Clausen et al., 2009). Results of zinc oxide nanoparticles into urea-formaldehyde glue in cottonwood (*Populus deltoides*) particleboards also demonstrated that it had good effects on preventing fungal decay and weight loss due to the white-rot fungus *Trametes versicolor* and the brown-rot fungus *Coniophora puteana* (Marzbani et al., 2015).

Antifungal and biocidal properties of titanium dioxide nanoparticles treated wood over white-rot fungus, *Hypocrea lixii,* and brown-rot fungus, *Mucor circinelloides* were reported by De Filpo et al. (2013), for several wood species. In their research, titanium dioxide nanoparticles prevented the growth of white and brown-rot fungi through photo-catalytic action, while untreated samples colonization was dependent on wood and fungus type.

Termite bioassays

Resistance to the subterranean termite *N. aquilinus* attack are summarized in Figure 3A. Termite consumption of each treatment samples was based on mass loss and visual rating.

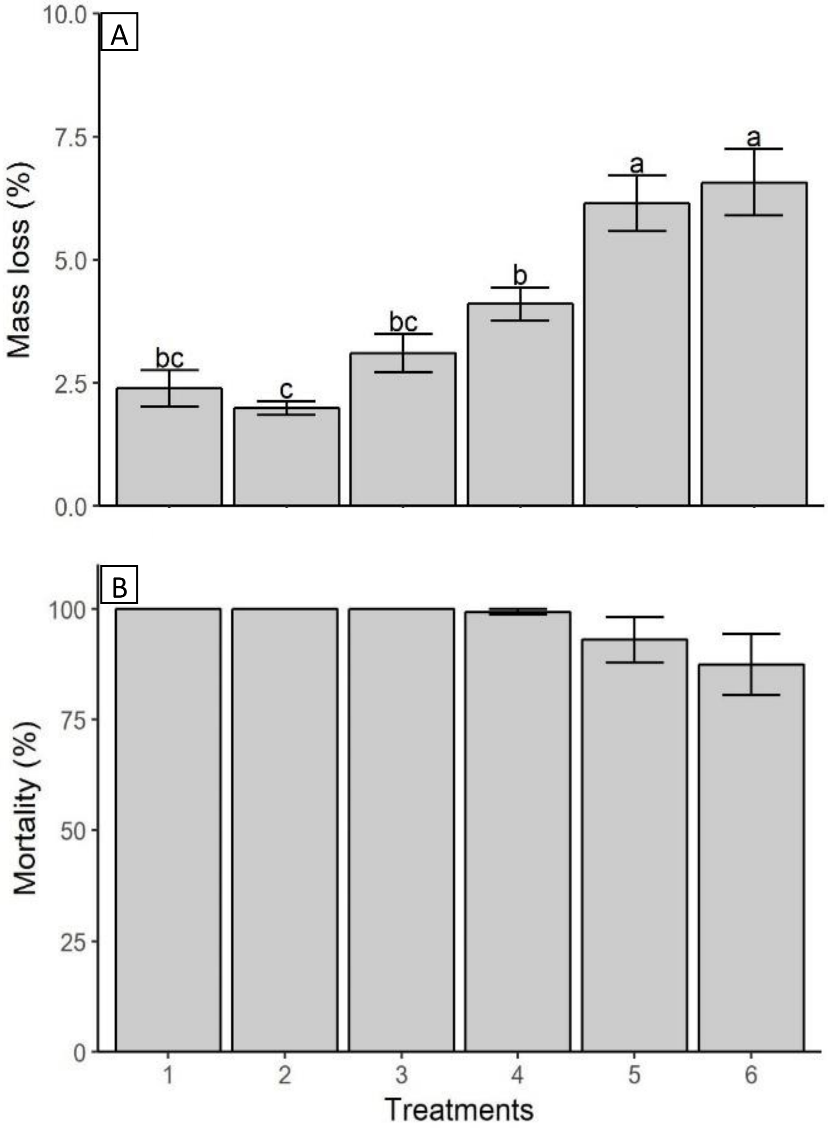

Figure 3: A) Average damage (mass loss) caused by subterranean termites on *E. urophylla* wood samples (treated and untreated). B) Average rating mortality of *N. aquilinus* subterranean termites. Groups sharing the same letter are not significantly different (ρ≤ = 0.05). Treatment 1 (2% ZnO); treatment 2 (1.5% ZnO, 0.5% TiO_2); treatment 3 (1% ZnO; 1% TiO_2); treatment 4

(0.5% ZnO; 1.5% TiO_2); treatment 5 (2% TiO_2); and treatment 6 (untreated).

Based on average visual rating and mass loss (Figure 3A), a synergy result between zinc oxide and titanium dioxide nanoparticles was observed in treatment 2 (1.5% ZnO, 0.5% TiO_2), which had the lowest mass loss due to termite damage. However, statistically, treatments 1 to 3 were considered equivalents. Wood consumption for treatments 1 (2% ZnO), 2 (1.5% ZnO, 0.5% TiO_2) and 3 (1% ZnO; 1% TiO_2) was less than 4% (2.4%, 2.0% and 3.1%, respectively), which is indicative of treatment non-palatability or repellency attack (Clausen et al., 2011). Treatment 5 (2% TiO_2) did not differ of untreated samples (treatment 6), showing titanium dioxide nanoparticles, without zinc oxide nanoparticles, was not efficient to prevent damage by subterranean termite, in the concentration of the test.

Treatments performed with zinc oxide nanoparticles were previously reported with low wood consumption (Clausen et al. 2009; Kartal et al., 2009; Mantanis et al., 2014; Lykidis et al., 2016). Regarding the inhibition of termite feeding, weight loss was strongly ($R^2 > 0.85$) correlated to the nominal concentration (Lykidis et al., 2016).

The termite bioassay also permitted comparison of natural resistance of pine wood (*Pinus sp.*) and *E. urophylla*, whose mass loss were 2.6% (Group a) and 6.6% (group bc), respectively. The low consumption of pine wood by *N. aquilinus* can be an evidence of feeding preference, since both were untreated and *E. urophylla* consumption by the termites was almost 3 times greater.

Average mortality of subterranean termites was summarized in Figure 3B. Termite mortality was made through visual inspection, according to the termite bioassay (ASTM D 3345, 2017). In the first analysis, after one week of the test installation, tunneling presence was observed for all treatments. After 4 weeks, almost all termites were dead, except for treatments 5 (2% TiO_2) and 6 (untreated). Termite mortality for treatments 1 (2% ZnO), 2 (1.5% ZnO, 0.5% TiO_2) and 3 (1% ZnO; 1% TiO_2) was 100%.

Termite mortality caused by zinc oxide nanoparticles-based treatments were previously reported by other authors (Clausen et al., 2009; 2011; Mantanis et al., 2014; Lykidis et al., 2016). In a research performed with *Reticulitermes flavipes* in southern yellow pine (SYP), with six zinc oxide nanoparticles preparations (1%, 2.5%, and 5%, 30 nm and 70 nm), it was reported that zinc oxide nanoparticles caused 94% to 99% of termite mortality after 25 to 27 days of incubation (Clausen et al. 2011), results similar to ours. In another termite bioassay performed with the subterranean termites, *Coptotermes formosanus* (Shiraki) in pine wood (*Pinus nigra* L.), with three zinc oxide nanoparticles formulations (2% ZnO without emulsion; 2% ZnO with emulsion SurfaPore W emulsion formulation, and 2% ZnO with linerar acrylic emulsion with TiO_2) caused low mortalities at 10%, 9% and 9%, respectively. However, samples still suffered significantly low mass losses, i.e., 4%, 7% and 5% for the three treatments above, respectively (Mantanis et al., 2014). Zinc oxide nanoparticles dispersions at three concentrations (0.5%, 1.0% and 2.0%) were also reported in a treatment of European beech (*Fagus sylvatica* L.) performed against the *Reticulitermes grassei* with a termite workers survival rate of 0% for all tested treatments (Lykidis et al., 2016). Differences among results could be explained by termite specie, wood specie, emulsions, and different concentration utilized on each bioassay.

The average visual rating of damage caused by the subterranean termite *N. aquilinus* on *E. urophylla* treated wood blocks resulted in two groups of classification. Treatments 1 (2% ZnO), 2 (1.5% ZnO, 0.5% TiO_2) and 3 (1% ZnO; 1% TiO_2) were rated as 9, i.e. light attack, while treatments 4 (0.5% ZnO; 1.5% TiO_2), 5 (2% TiO_2) and 6 (untreated) were rated as 7, considered a moderate attack. A previous research reported that tests performed with *Reticulitermes flavipes* in southern yellow pine and six zinc oxide nanoparticles preparations (1%, 2.5%, and 5%, 30 nm and 70 nm) were all rated as 9 (Clausen et al. 2011). It is possible to suppose that they are related to zinc oxide nanoparticles concentration, comparing results.

Weatherability

After 12 months of exposition, at the exposed face, all five treatments 1 to 5 were less gray than untreated. There was few difference of bright among treatments, however treatment 5 (2% TiO_2) presented brighter than other four treatments, as well as the control untreated. Visually, it was not possible to observe differences among treatments 2 (1.5% ZnO, 0.5% TiO_2), 3 (1% ZnO; 1% TiO_2), and 4 (1% ZnO; 1% TiO_2), but untreated samples were less bright and grayer than all treatments.

The unexposed faces were less gray than exposed faces. Treatment 1(2% ZnO) was less gray and brighter than all treatments, including untreated samples, followed by treatment 2 (1.5% ZnO, 0.5% TiO_2). Treatment 5 (2% TiO_2) presented grayer stains than others did in this face. Treatments 3 (1% ZnO; 1% TiO_2), and 4 (1% ZnO; 1% TiO_2) did not showed visual differences among treatment 6 (untreated) at the unexposed face.

Weathering results, previously reported, showed graying was diminished by zinc oxide nanoparticles treatments, at concentrations of 2.5 and 5% of zinc oxide, but not eliminated (Clausen et al., 2010). Results of artificial weathering damage control with zinc oxide nanoparticles treatments (20 nm, concentrations of 0.5%, 1%, 1.5%) in poplar wood samples (*Populus deltoides*) also support that graying was significantly diminished by the zinc oxide nanoparticles-based treatments, at higher treatment concentrations, although it was not completely eliminated (Afrouzi et al., 2013). Maple wood surface coated with nanostructured zinc oxide exposed to artificial weathering also showed that changes observed on samples containing ZnO were significantly lower than on untreated wood, suggesting that the presence of nanostructured ZnO on the surface of maple reduces (if not prevents) the effects of the UV-induced decay on the wood (Weththimuni et al., 2019). It happens because of ZnO ultraviolet absorption, zinc oxide works as UV blocker (Yu et al., 2010; Clausen et al., 2010). This behavior can be assigned to the efficiency of ZnO nanoparticles as UV absorber (Cristea, et al, 2011; Salla et al. 2012).

Results of assessment of defects caused by weathering showed that there was checking damages at the ending and surface of samples, for all treatments samples, due weathering exposition. Splitting was absent. Among the treatments performed, treatment 1 (2% ZnO), without titanium dioxide, presented less checking than others; however its checking was higher than observed in untreated samples. Checking happens because of mechanical surface changes (i.e. fuzzing) caused by zinc oxide nanoparticles, being more remarkable in higher concentrations treatments (Clausen et al. 2010; Afrouzi et al., 2013).

Due to the variation of the results found, it was not possible to conclude that titanium dioxide nanoparticles can improve resistance to checking, but there were indicatives for end checking. Related to zinc oxide nanoparticles, differences between samples of treatment 1 (2% ZnO) and untreated were not so remarkable, indicating that 2% of zinc oxide concentration can be considered a low concentration, for this concern.

CONCLUSIONS

Based on results, it was possible to conclude that zinc oxide retentions decreased according to the decreasing of the oxide concentration of each treatment, while for titanium dioxide retentions, most part of the treatments were low detectable. On fungal decay tests, for *Pycnoporus sanguineus* fungus (white-rot) attack, treatment 1 (2% ZnO) was more effective to prevent this kind of fungus damage. All treatments based on different concentrations of zinc oxide and titanium dioxide nanoparticles were effective to control wood damage caused by the white-rot fungus *Trametes elegans*. Treatment 2 (1.5% ZnO, 0.5% TiO_2) performed the best synergy to control damage on termite bioassay. Treatments 1 (2% ZnO), 2 (1.5% ZnO, 0.5% TiO_2), and 3 (1% ZnO; 1% TiO_2) showed less than 4% of wood consumption on the termite bioassay, what is an indicative of non-palatability or repellency attack of treatments. Termite mortality for treatments 1, 2, and 3 was 100%. Regarding weathering, all treatments 1 to 5 were brighter and less gray than untreated wood. Samples of the treatment 5 (2% TiO_2) presented brighter than other treatments in the exposed face, performing best weatherability protection to that situation. In the unexposed face of samples, treatment 1 (2% ZnO) was less gray and brighter than all treatments. Results suggest that both zinc oxide and titanium dioxide should be considered as components of a generation of multi-compounds wood preservatives, based on nanotechnology.

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