

Article

Termite Resistance of a Fast-Growing Pine Wood Treated by In Situ Polymerization of Three Different Precursors

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Abstract: This study aims to compare the resistance against subterranean termites of wood–polymer composites produced by in situ polymerization. The biological tests were carried out by choice and no-choice feeding tests. Poly (furfuryl alcohol), poly(styrene) and poly (methyl methacrylate) were studied here. They were impregnated into a Brazilian fast-growing pine wood using a vacuum:pressure method and then cured under simple heating. These treatments were evaluated using chemical (by infrared spectroscopy) and morphological (by scanning electron microscopy) analyses. The termite attack was evaluated by mass loss determination and photography. In general, all the treatments were effective in protecting the fast-growing pine wood. Results obtained by no-choice tests indicated that the treatment solution with 75% of furfuryl alcohol was less effective than the others, which indicates that both choice and no-choice tests may be important in a comprehensive study on the termites resistance of solid woods.

Keywords: termites; wood biodeterioration; wood treatment; furfuryl alcohol; styrene; methyl methacrylate

1. Introduction

Brazil and other tropical countries have a high availability of several native kinds of wood with high technological performance. However, these woods are unsustainably consumed, which has resulted in large areas of deforestation [1]. Since the 1960s, tax incentives have been implemented in some of these countries, and exotic fast-growing species were promptly planted, to create new alternative raw materials to meet certain demands for wood products [1,2]. Nevertheless, these woods became economically attractive for some other applications, and progressively dominated several markets, although timbers from these species frequently have inadequate properties for many traditional applications, especially for structural purposes [2].

Among Brazilian fast-growing species, pine wood (PW) is one of the main genres [3]. The planted pine forests currently cover about 2 million hectares in Brazil, especially in the south and southeast regions, wherein these trees are processed to access both their wood and resin [4]. In general, these PW present some good features, including low cost, good strength/weight ratio and easy processing [5].

Nevertheless, Hadi and co-workers affirmed that PW and other fast-growing woods may present a high formation of juvenile wood, which has inferior physico–mechanical properties and durability

compared to those of mature wood grown in adult trees [6]. In general, a Brazilian PW only starts to produce mature wood after 10–15 years of life [7], which explains why most of the available PW-based lumber was cut from juvenile trees, and consequently may be susceptible to be biodegraded by fungi and insects.

Among these xylophages, Gascón-Garrido and co-workers confirmed that subterranean termites are one of the most important wood-destroying agents, since they cause extensive damage to wooden structures, leading to billions per year in worldwide costs [8]. They also mentioned that these insects are able to promote impairments in both constructions and indoor elements (doors, windows, wood flooring, furniture, etc.) [8]. Indeed, most subterranean termites live in soil, but they can build mud tubes to move from the soil towards wood-based parts, which can be in contact with or above the ground [9]. Moreover, for Forschler and Henderson, these insects play a remarkable role in forests, digesting lignocellulosic materials and excreting some nutrients previously locked in recalcitrant coarse woody debris, which contributes to the long-term soil nutrient cycle [10].

According to Afzal and co-workers, subterranean termites are considered the major economic pest in some rural regions, since they cause tremendous injures to crops and tree plantations, especially in tropical and subtropical climates [9]. Further, wooden buildings located in tropical countries are especially prone to be colonized by subterranean termites, due to their warm and humid climate conditions [11]. In this sense, Shelton and Grace mentioned that subterranean termites of the genus *Coptotermes* are the greatest pests for wooden structures in tropical countries, like Brazil [12].

A culture of wood preservation needs to be encouraged to minimize future resource losses. Chemical treatments have received much attention since the middle of the 20th century [13], and many of these preservation methods can extend the service lives of wooden products. However, most of the currently used methods consist of impregnating or applying toxic chemicals to solid woods [14]. Some of these extensively applied treated woods may have toxic volatiles and leachates, which may contaminate the environment. For instance, several copper-based preservatives were recently addressed [8,15]. Among them, chromated copper arsenate (CCA) and chromated copper borate (CCB) have been widely used for more than a century, since they provide broad protection against fungi and termites. However, some countries, like Brazil and the United States, have implemented legislative restrictions against these chemicals, due to environmental concerns.

Additionally, there are other commonly used compounds which are poisonous to humans and other living organisms, like chlorine-based products. Indeed, certain chemicals, such as organochlorine, phosphorus, carbamates and synthetic pyrethroids, are no longer acceptable for wood protection due to health concerns [9,16]. Some of their known negative effects against human health include metabolic and central nervous system disorders, hyperglycaemia, and oxidative stress [16]. Furthermore, Afzal and co-workers reported that some well-known organochlorines are progressively losing their effectiveness since certain insets have evolved and acquired resistance to these insecticides [9].

These concerns have been emboldening scientific efforts on the improvement of the performance of PW, especially utilizing environmentally benign treatments [2]. Among these procedures, the production of wood–polymer composites (WPC) by the in situ polymerization of monomers into wooden parts stands out. This product consists of a microstructurally organized wood applied as a matrix for an in situ synthesized polymer derived from unsaturated monomers, which acts as a reinforcement [17]. Magalhães and co-workers highlighted that the PW are proper to the manufacture of this type of WPC, since this softwood presents a simple anatomical structure, which may be easily penetrated by chemicals, especially if compared to that of hardwoods [18]. In general, the decay-resistance of neat lumbers is dependent on some endogenous factors (including specific gravity, moisture content, chemical composition and anatomical structure) [19], as well as environmental features like temperature, relative humidity and oxygen content [19]. In inducing a significant improvement to biological performance, the wood treatments normally lead to other positive effects, such as hydrophobization of the wood cell wall, cell wall bulking, and changes in the wood surface

energy [20]. Therefore, impregnated polymers may cover the wood cell wall, hindering the access of termites and fungi [21,22].

Furfuryl Alcohol–C₅H₆O₂ (FA) is a bio-based monomer derived from furfural, which can be produced from lignocellulosic agricultural residues, such as corn-cobs, woody products, cottonseed hulls, oats husks, rice husks and sugarcane bagasse [23]. The furfurylated PW presents some excellent mechanical, hygroscopic, aesthetic and durability characteristics [18]. Gascón-Garrido and co-workers exposed a composite made of PW impregnated with poly (furfuryl alcohol) (PF) to subterranean termites using a no-choice test [8]. They classified that product as durable since it presented an excellent termite resistance, indicated by a low mass loss of only 6.7% after 56 days (eight weeks) of exposure.

Styrene is another highly valuable precursor, and has been traditionally used to synthesize different kinds of styrofoams. Some authors recently reported increased technical properties for WPC produced by in situ polymerization and in situ copolymerization, compared to their respective pristine woods [24,25]. Hadi and co-workers affirmed that the impregnation of wood parts with poly (styrene) (PS) may extend their service life, and the produced WPCs are safe to any living organism [26]. In another study, Hadi and co-workers treated an Indonesian PW (*Pinus merkusii*) with in situ polymerization of PS, and reported an increased resistance to subterranean termite attack compared to the pristine PW [27].

Methyl methacrylate (MMA) is also an important vinyl monomer, and has shown great performance when applied to modifying PW, including increases in mechanical, hygroscopic, thermal and biological properties [17,28]. According to Mattos and co-workers, the in situ polymerization and copolymerization of the poly(methyl methacrylate) (PMMA) into PW converts a low-quality wood product into a high-performance material, and then diverse applications become possible [28]. This WPC allies an ease of processing (associated with the low time for wood production since the PW presents a fast growth) with the low cost of the involved chemicals. The PMMA is a durable and recyclable material, and is also known as one of the main translucent polymers [29].

Therefore, PW plays a crucial role in the timber trade (especially in tropical countries) and has been used for several structural purposes, although its service life is low without a protective treatment, which must be developed taking into account a series of environmental concerns. Some previous studies focused on the decay-resistance of certain woods treated by impregnation with polymeric substances against both fungi and termites, using no-choice feeding tests [21,30,31]. However, following this methodology, it is hard for the wood specimens to achieve good performances, since they are exposed to an aggressive environment, in which the termites are forced to feed on whatever resource is available for survival. Hence, the decay-resistance of different treated woods can only be fully elucidated and reliably compared using choice tests, which allow the termites to preferentially attack the more susceptible substrates, like untreated PW [32].

The existing literature lacks results obtained by choice-tests for PW treated via in situ polymerization with different traditional monomers. This study aims to use choice and no-choice feeding tests to compare the biological resistances (against subterranean termites) of Brazilian fast-growing PW treated by in situ polymerization with PF, PS or PMMA.

2. Materials and Methods

2.1. WPC Production

25-year-old trees were selected in a homogeneous pine (*Pinus elliottii* Engelm.) forest located in Piratini/Brasil. The species was determined based on the growth characteristics of the trees (e.g., shape of both their bark and leaves) and the age was determined by counting their growth rings. Prismatic samples were cut according to the requirements of each characterization technique and then conditioned in a climatic chamber (under 20 ± 2 °C temperature and 65% ± 3% RH) until reaching equilibrium moisture content. To facilitate the impregnation of the monomers, the pristine samples were oven-dried at 70 °C until reaching a constant mass.

High purity solutions of FA (98%), styrene (99%) and MMA (99%) were acquired from Sigma Aldrich and used as received. Each precursor was manually homogenized with its respective additives for 15 min before the impregnation process. Three FA-based solutions were prepared with variable FA concentrations (c.a. 25 wt. %, 50 wt. % and 75 wt. %), in which distilled water (c.a. 5 wt. % in all cases), citric acid (c.a. 5 wt. % in all cases) and ethyl alcohol (c.a. 65 wt. %, 40 wt. % and 15 wt. %) were used as an emulsifier, anti-volatilizing agent and catalyst, respectively. The styrene- and MMA-based solutions were prepared using 1.5 wt. % of benzoyl peroxide as a catalyst.

Regarding the impregnation procedure, 1180 cm³ (about 35 wood samples) was placed in a 2300 cm³ horizontal autoclave, wherein an initial vacuum (close to 0 Pa) was applied for 40 min using a vacuum pump (Marconi brand) to fully remove any trapped air. Then, a valve was opened to pour in 1.3 L of the treatment solution, taking advantage of the pressure difference caused by the vacuum, and a positive pressure of 0.8 MPa was applied for 180 min. The impregnated PW was cured at 50 °C for 24 h and an extra 70 °C for 72 h. The wood treatments presented the following weight percentage gain (WPG) means: 8.55%, 26.51%, 93.66%, 113.35% and 70% for PF25%, PF50%, PF75%, PS and PMMA, respectively. These data were determined with the aid of an analytical balance (0.0001 g resolution).

2.2. Termite Tests

Termite tests were carried out following two different methodologies, known as choice and no-choice feeding tests. For the first one, a termite mound (colonized by several termite species) with a volume of about 1 m³ was collected in a wood forest located at Canguçu/Brazil. This mound was placed inside a plastic tank. The bottom of this recipient was filled with a 5 cm thick layer of white sand moistened at about 65%. Afterwards, 10 prismatic samples (15 × 15 × 125 mm³, with the larger dimension in the longitudinal direction) from each group were randomly inserted in the sand around the mound and this bioassay was kept for 45 days in complete darkness.

For the no-choice tests, five cubic samples (side equal to 15 mm) from each group were evaluated, following ASTM D3345 [33] with some adaptations (c.a. samples with different dimensions and half of the amount of sand). A glass container capped by a perforated lid was filled with 200 g of white sand moistened with 10 mL of distilled water. Then, five PW samples from the same group and 100 termites (workers from *Coptotermes curvignathus* Holmgren species) were placed into the recipient, in which they were kept for 10 days, at a temperature of 20 ± 2 °C, an RH of 65 ± 3% and complete darkness. The termites were identified according to the methodology described by Lepage [34], and especially based on their head morphology, as indicated by previous studies [35]. The mass loss was used to evaluate their effectiveness against termite attack, whereby a lower mass loss indicates a higher resistance to termite attack.

2.3. WPC Characterization

2.3.1. ATR-FTIR

Chemical groups were evaluated by attenuated total reflectance–Fourier transform infrared spectroscopy (ATR-FTIR) in a Jasco 4100. A total of 32 scans (600–1800 cm⁻¹ range) were performed at 4 cm⁻¹ resolution and 2 mm·sec⁻¹ scanner velocity.

2.3.2. Scanning Electron Microscopy (SEM)

The transverse views (concerning the orientation of the fibers) of the treated specimens were analyzed in a Phenon World Pro-X scanning electron microscope.

2.4. Statistical Analyses

A completely randomized design (CRD) was applied to analyze all the data. Homogeneity of variances and data normality were ascertained using Levene and Shapiro-Wilk tests, respectively.

Whenever the null hypothesis was rejected, Fisher's tests were performed to compare the means. All statistical analyses were conducted at a significance level of 1%.

3. Results

3.1. ATR-FTIR Spectra

All the studied WPC presented particularly prominent peaks, which indicate the presence of each polymer inside the wood tracheids and/or inside the wood cell wall (Figure 1).

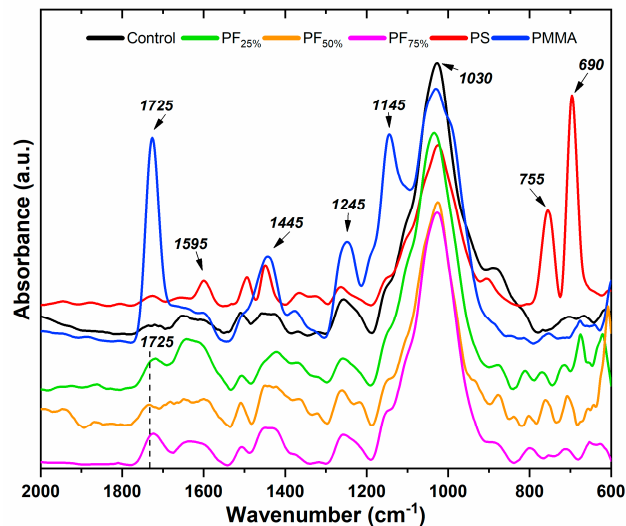


Figure 1. FTIR spectra for control and treated pine woods. Where PF_{25%} is 25% of poly (furfuryl alcohol), PF_{50%} is 50% of poly (furfuryl alcohol), PF_{75%} is 75% of poly (furfuryl alcohol), PS is poly (styrene) and PMMA is poly(methyl methacrylate).

3.2. SEM Images

Figure 2 shows SEM images for the studied WPC. Different from the other treated PW, the PF-based WPC did not show tracheids mostly filled by its polymeric substance (Figure 2A).

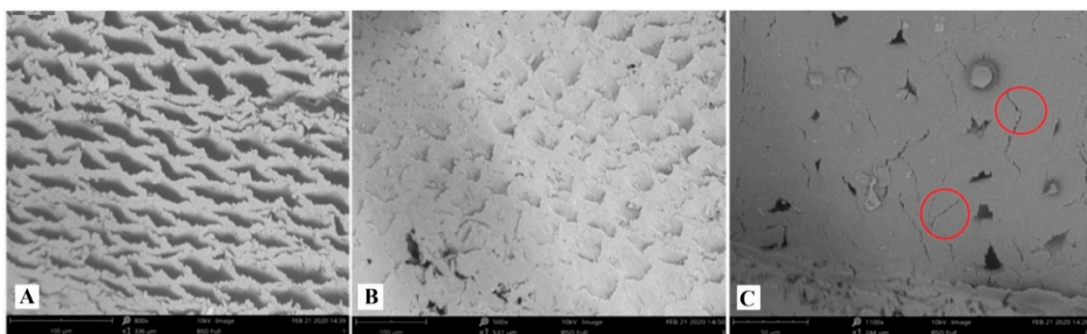


Figure 2. SEM images for the pine woods treated with 75% poly (furfuryl alcohol) (A), poly (styrene) (B) and poly (methyl methacrylate) (C).

3.3. Termite Tests

Figure 3 shows the mass loss data obtained using both choice and no-choice feeding tests. All the treatments were effective in the protection of PW against termite attack in both tests, and yielded mass loss means below 10%.

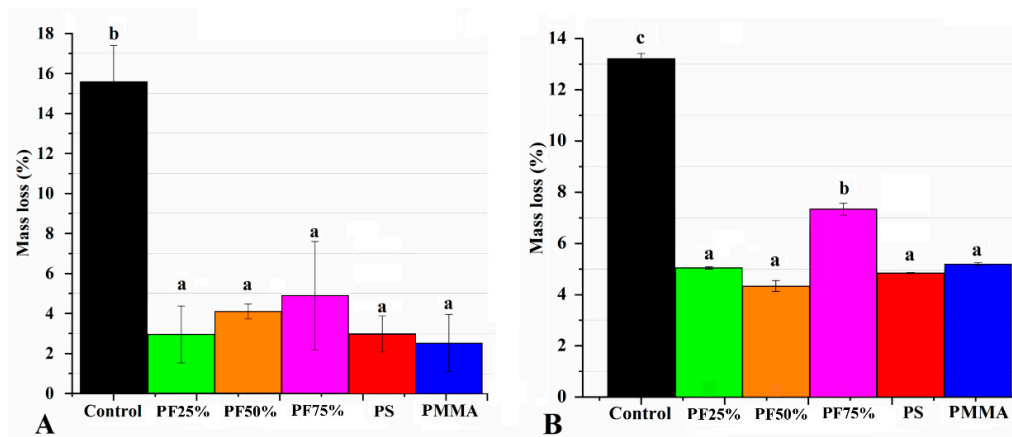


Figure 3. Mass losses for control and treated pine woods exposed to termite attack using choice (A) and no-choice (B) feeding tests. Where PF25% is 25% of poly (furfuryl alcohol), PF50% is 50% of poly (furfuryl alcohol), PF75% is 75% of poly (furfuryl alcohol), PS is poly (styrene) and PMMA is poly (methyl methacrylate). Different letters above the bars indicate statistically different averages.

The treated PW did not show traces of termite attack, unlike the control group, which was severely destroyed, as shown in Figure 4. Moreover, the control PW was also colonized by some white-rot fungus, which was identified according to apparent characteristics, namely an almost uniform bleached appearance, and a spongy or stringy mass, which was visually assessed as a pocket rot [36].

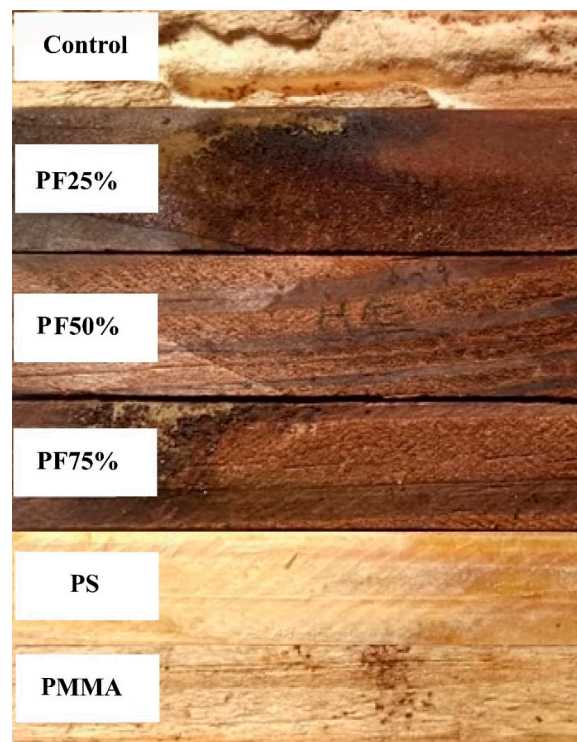


Figure 4. Photos for the control and treated pine woods subjected to termite attack. Where PF25% is 25% of poly (furfuryl alcohol), PF50% is 50% of poly (furfuryl alcohol), PF75% is 75% of poly (furfuryl alcohol), PS is poly (styrene) and PMMA is poly (methyl methacrylate).

4. Discussion

4.1. ATR-FTIR Spectra

The PF-treated PW presented some minor peaks in the 700 to 850 cm^{-1} range, which are related to the toluene and cymene groups belonging to the PF [37]. Further, major peaks at 1725 cm^{-1} , 1595 cm^{-1} , 1470 cm^{-1} , 1245 cm^{-1} and 1030 cm^{-1} are associated with typical chemical groups from the PW, the PF, and some derivatives (like methyl furans and methanol) from carbonyl ester and ether bonds between the FA and chemical compounds from PW, like lignin and hemicelluloses [37]. The comparison between the PF-based WPCs revealed that the PW treated with 75 wt. % of FA presented the highest peak at 1725 cm^{-1} , which is strongly related to carbonyl bonds, which have a higher presence the more efficient the catalyst action is [37]. Therefore, it seems that the formulation with the highest FA concentration (PF75%) yielded the most completed polymer formation, which also explains the highest WPG in this case. Even with the formation of these chemical groups during the polymerization of the PF, this WPC is free of toxic constituents, it does not release any polyaromatic hydrocarbon above the normal levels for wood combustion, and its leachates do not present a significant ecotoxicity [38].

The PW treated by PS presented major peaks at 1595 cm^{-1} , 1445 cm^{-1} , 755 cm^{-1} and 690 cm^{-1} , which are related to the bending deformations and stretching vibrations in the aromatic rings belonging to the impregnated PS [22,39]. Benzoyl free-radicals and other toxic chemical groups are generated during the PS formation, and compose the gaseous styrene, which is naturally scattered in the air. If inhaled by humans or animals, it is partly retained in their lungs and may lead to several diseases [40]. Nevertheless, the final PS-based WPC is safe for humans and other living beings [26].

Regarding the PW treated with PMMA, there were prominent peaks at 1725 cm^{-1} (C=O bonds in carboxylic groups from lignin), 1445 cm^{-1} (stretching vibrations and deformation of C–O bonds), 1245 cm^{-1} , 1145 cm^{-1} and 1030 cm^{-1} (C–O bonds and deformation of the C–H bonds in guaiacyl units from lignin), which are associated with the presence of the PMMA in the inter- and/or intra-cellular spaces of the PW, and certain reactions with its lignin [41,42]. According to Zeng and co-workers, this polymer does not present high toxicity, since the combustion products generated by PMMA burning are carbon monoxide and carbon dioxide [29]. That said, these authors reported that these compounds are narcosis-producing toxicants, and can cause central nervous system depression, loss of consciousness, and ultimately death.

4.2. SEM Images

According to Mantanis and co-workers, the furfural resin polymerizes in the cell lumen or attaches itself to the wood cell wall, forming an inside coating, which seals the lumen surface and can also lead to an increase in cell wall thickness (Figure 2A) [23]. From a chemical standpoint, this mechanism is attributed to interactions between the FA and the lignin located at the middle lamella and the corners of the wood tracheids [43].

As shown in Figure 2B,C, the wood tracheids were mostly filled by the solid polymers. When impregnated into wood parts, vinyl monomers (like styrene and MMA) normally fill the capillaries, vessels and other void spaces in the wood structure [44]. Figure 2B,C also suggests that the wood cell wall was penetrated by the polymers, which was reported in some previous studies [17,45]. Additionally, Figure 2C shows dark lines (highlighted in red color), which probably represent micro-cracks in the PW–PMMA interface, which suggests a weak chemical interaction in this case, probably due to the non-polar structure of the PMMA [46].

4.3. Termite Tests

According to Venäläinen and co-workers, a mass loss above 10% (such as was obtained in the present study) indicates structural impairments in wood specimens exposed to accelerated decay tests with soil contact [46]. It probably means that after this damage level, structural polysaccharides from wood (namely cellulose and hemicellulose) may be decomposed [2]. The treated PW presented mass

loss means of less than 50% of those of the control group. This high degradation of the pristine PW also strengthens the validity of the present study.

Regarding the no-choice tests (results shown in Figure 3B), the PW furfurylated at 75% showed a greater mass loss than the other PF-treated PW. In this case, the FA probably grafted to some wood components, as suggested by previous NMR (nuclear magnetic resonance) studies [13], which may generate certain chemical groups susceptible to being consumed by termites. Myer and co-workers reported that formaldehyde, levulic acid, some weak organic bases and terminal methylol groups are some of the derivatives from the reactions of FA with lignin and hemicelluloses from wood [47].

Termites have an efficient digestive system able to consume over 90% of the cellulose molecule [48], which requires the synergistic action of many different enzymes that live inside these insects [49]. In general, higher termites, like those used in the present study, have a complex digestion mechanism, which begins with the action of their mandibles and proventriculus, which grind the wood particles down to microscopic size, creating an enormous surface area [49]. Then, symbiotic agents (like protists, bacteria and archaea) convert the lignocellulose into smaller molecules able to be absorbed as nutrients [49]. The role of each involved microorganism has not yet been fully understood, and there are many controversial hypotheses.

The mass losses obtained in the present study are comparable with similar studies, which were conducted using choice tests [8,11]. For instance, Hadi and co-workers studied a PW (*Pinus merkusii*) treated by in situ polymerization of styrene, and exposed it to subterranean termites for 90 days in a field test located in Indonesia [11]. Their obtained mass loss means ranged from 5% to 66%, and they concluded that their treated PW achieved increased biological resistance compared to their respective pristine PW. Sivrikaya [50] thermally treated a PW (*Pinus sylvestris*) for different times and at different temperatures. They used no-choice tests to expose their PW to *Reticulitermes grassei* termites for 56 days (eight weeks), and obtained mass losses of 6%–12%. Regarding the standardized no-choice test, the studied PW samples also reached similar mass loss means if compared to some PW treated via traditional methods. For instance, Mantanis and co-workers treated a PW (*Pinus nigra*) using different solutions of zinc- and copper-based compounds [23]. Their mass loss means ranged from 3% to 17%.

5. Conclusions

All the treatments were effective in protecting the PW against the subterranean termites, which was probably due to the induced decrease in hydrophilicity and hindered access to wood cell walls caused by the impregnated polymers. It seems that the subterranean termites were able to consume certain furfurylation products, although this was not fully clear. Because of that, the PF75-treated PW presented a performance inferior to that of the other treated PW in the no-choice feeding tests. This finding also indicates that both choice and no-choice tests should be performed in an elucidative study on the termite resistance of wood products. Further studies may address a similar scope using wood-rot fungi.

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