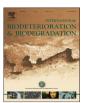
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Wood plastic composites weathering: Effects of compatibilization on biodegradation in soil and fungal decay



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ABSTRACT

Material performance testing of wood plastic composites (WPC) requires an efficient evaluation of the resistance against biodegradation. This study investigates the effects of natural weathering on WPC and subsequent material degradation in soil and by fungi. Besides, the effectiveness of using coupling agent (CA) on adhesion of WPC and its influence in degradation was investigated. The WPC composition used was recycled polypropylene – ethylene vinyl acetate/wood flour (70/30 w/w). Four white rot fungi, Trametes villosa, Trametes versicolor, Pycnoporus sanguineus and Fuscoporia ferrea were used in a fungal decay test. For the biodegradation in simulated soil was used respirometric test. Weight loss of all materials, without and with previous natural weathering, was evaluated and surface morphology was examined by scanning electron microscopy (SEM). The results showed that natural weathering accelerated degradation process, influencing the respirometric test and fungal growth. By SEM, it was observed agglomerates of microorganisms, indicating the possible formation of biofilms. The F. ferrea fungus was more effective in surface colonization, with higher weight loss and even the emergence of reproductive structures after the incubation time.

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1. Introduction

The wood plastic composites (WPCs) are mainly proposed as an alternative for reuse of solid residues (sawing wood and plastics) and to be used mainly for outdoor applications (Butylina et al., 2011). Wood plastic composites (WPC) are increasingly employed as interior and exterior building materials such as e.g. deckings or door and windows frames (Klyosov, 2007). Their composition varies generally between 30 and 70% wood particles, 30–55% polyolefin polymer and 0.5–15% additives (Taylor et al., 2009). Soft and hard wood such as spruce, pine, eucalyptus, maple, beech and oak are commonly used as wood flour or shavings embedded in a polymeric matrix such as polypropylene, polyethylene and polyvinylchloride (Clemons and Ibach, 2004). WPC materials were developed to combine the advantages of wood and polyolefin polymers, especially long-term performance, cost-effectiveness,

shape flexibility and "carbon footprint" (Manning et al., 2006; Naumann et al., 2012a).

The addition of wood significantly improves thermal stability, mechanical (stiffness) and working properties of the WPC. The disadvantages of using wood fibers are their low bulk density, low thermal stability, high tendency to absorb moisture and susceptibility to fungal attack (Clemons, 2002). Plastic coating of wood particles in a WPC can reduce the moisture uptake while enhancing dimensional stability and protection against fungal attack. Furthermore, wood particles also reduce the need to use more costly thermoplastics (Carll and Highley, 1999).

The properties of WPCs are determined by a great number of factors, such as wood types, particle size, polymer type, additives, and manufacturing process used. The use of coupling agents in composites will serve as important factor to determine the properties that are wished (John and Thomas, 2008). Such coupling agents may influence structure, properties and the behavior of the composites considerably (Staiger and Tucker, 2008). Copolymers containing maleic anhydride, such as maleated polypropylene (MAPP) or maleated polyethylene (MAPE) are the most commonly reported coupling agents used in WPC. The

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presence of polar groups for the surface oxidation process of nonpolar polymers changes in the characteristics of hydrophobicity (Nourbakhsh and Ashori, 2009).

In WPC, plastics are generally resistant to fungal attack; however a major concern with these materials is that wood in the composite remains susceptible to biological degradation. Many manufacturers avoid this risk by producing products for interior uses where little or no water is present, thereby minimizing the risk of fungal attack (Bourmaud and Baley, 2009). Initially, it was presumed that plastic encapsulate the wood fibers, protecting them from wetting and further decay, but a number of tests suggest that wood encapsulation by plastic is incomplete. As a result, the wood component in these materials reaches moisture levels suitable for fungal attack (Shah et al., 2008; Sivan et al., 2006; Soni et al., 2009; Zahra et al., 2010; Chiellini et al., 2007). The expanding commercial production and marketing of WPC for use in exterior applications has encouraged research on the durability and service life of WPC.

Biodegradation is the mineralization of materials as a result of the action of naturally-occurring microorganisms such as bacteria and fungi (Bonhomme et al., 2003). The biodegradation of polymers is caused by microorganisms that colonize its surface forming biofilms. These biofilms consist of cells embedded in a polymeric matrix of their own origin, containing polysaccharides and proteins (Mankowski and Morrel, 2000). Biodegradation of plastics is limited by their molecular weight, chemical structure (Gómez et al., 2011), water solubility and the fact that most plastics are xenobiotic. Composting of these materials also reduces their environmental impact in that they will largely be converted to CO2 and not to CH4 as they would be in a landfill (Narayan, 2006). As this CO₂ was originally fixed from the atmosphere into renewable biomass, on balance it will not increase atmospheric CO₂, provided that new biomass keeps on growing and with that capturing CO₂ (Vroman and Tighzert, 2009). In the present paper, the biotic test used was the technique of biodegradation in simulated soil, wherein during the experiment the CO₂ generated by degradation of the WPC samples is quantified.

The most serious kind of microbiological decay of wood is caused by fungi because they can cause rapid structural failure (Blanchette, 2000). Fungal colonization and decay of WPC can be occasionally observed after outdoor exposure of WPCs, especially under favorable conditions of warm temperatures and high moisture conditions (Mateo et al., 2007; Stephan et al., 2000). White rots are the most frequently found wood rotting organisms (Morris, 1997). They are characterized by their ability to completely degrade lignin, hemicelluloses and cellulose, thereby often giving rise to a cellulose enriched white wood material (Lucas et al., 2008). The degradation of wood by white rot fungi can occur in two ways: the most common involves the simultaneous removal of all components; where the cell wall is attacked progressively from the cell lumen towards the middle lamella. Degradation is associated with the fungal hyphae and substantial amounts of undecayed wood remains (Ferraz, 2004; Harju et al., 2003). Other less common, involves the selective removal of lignin and polyoses while maintaining substantially intact cellulose (Monrroy et al., 2011).

The aim of this study was to investigate how the previous natural weathering affects the biodegradation in soil and fungal decay of WPCs, evaluating the durability of these composites prepared from waste, in order to develop new materials, more sustainable and environmentally friendly.

2. Materials and methods

2.1. Materials and preparation of wood plastic composites

The materials used were post-consumer waste from bottle caps of polypropylene (PP) and ethylene vinyl acetate copolymer (EVA), latter present in the internal "liner" of covers, provided in the "flakes form", and two types of wood flour; eucalyptus (Eu) and pine (Pi), from species Eucalyptus grandis and Pinus elliottii respectively, from state of Rio Grande do Sul, Brazil. This wood flour was obtained from lumber industries which work only with these wood species, in the form of sawdust. Various tests were performed to determine the characteristics of sawdust as TGA, DSC analysis and particles size by laser diffraction. These analyzes assist in the characterization of the raw material for the subsequent production of composites and evaluating their final properties (Nourbakhsh and Ashori, 2009: Naumann et al., 2012a, 2012b). Bottle caps for mineral water and soft drinks as polymeric matrix were chosen because they are materials with great consumption and large amounts generated for disposal after use (Cempre - Corporate Commitment to Recycling, 2014). The PP-EVA sample was already ground, obtained from a recycling company (Prisma Montelur S.A). Thermal analyzes and FTIR were also performed to determine the characteristics of the polymers (Naumann et al., 2012a, 2012b). A bottle cap was weighed with and without the internal "liner" to verify the EVA present proportion in the total mass, and it was found 9% w/w of EVA in bottle cap. The coupling agent (CA) used was grafted copolymer of polypropylene with maleic anhydride (PP-g-MA), commercially known as Fusabond MZ-109D (Dupont S.A.), with 0.57% maleic anhydride, melt flow index of 3.4 g/10 min and density of 0.91 g/cm³; (Chanprapanon et al., 2009). The wood flour was submitted size separation in a sieves system with series of 32 and 60 Tyler mesh, and selected particle size of >250 and $< 500 \mu m$, due to the larger amount retained between these particle sizes. The blends were processed on a single screw extruder (L/D: 22), with temperature profile of 170°–190 °C and screw speed of 65 rpm, and perforated in the "pellets form". Flakes of PP-EVA with the coupling agent (CA) was first processed in the extruder in order to functionalizing the polyolefin, and after it was added sieved wood flour (30% w/w). After mixing by extrusion, samples were cropped in a shredder. The test specimens were prepared by injection molding (Mini Thermo Scientific Haake MiniJet II) at temperature of 180 °C and pressure of 600 bar for fungal decay tests and by thermal compression in a hydraulic press (Marconi MA 098/ A3030) at temperature of 180 °C and pressure of 2 ton for respirometric test. The formulation of the substrates was performed as shown in Table 1.

2.2. Natural weathering

The tests were carried out according to Chiellini et al. (2003) and Montagna et al. (2013). Tests conducted in accordance with this practice are used to evaluate the stability of plastic materials when

Table 1Nomenclature and formulation of samples.

| Samples | WPC formulation | | |
|--------------|-----------------|-------------------|--------------|
| | Matrix (PP-EVA) | Filler (Eu or Pi) | CA (PP-g-MA) |
| PP-EVA-Eu | 70% w/w | 30% w/w | _ |
| PP-EVA-Pi | 70% w/w | 30% w/w | _ |
| PP-EVA-Eu-CA | 67% w/w | 30% w/w | 3% w/w |
| PP-EVA-Pi-CA | 67% w/w | 30% w/w | 3% w/w |

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