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Evaluation of wood-polyethylene composites biodegradability caused by filamentous fungi

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A B S T R A C T

This study describes the impact of filamentous fungi on wood-polymer composites (WPCs) containing various types of fillers (coniferous, deciduous, cellulose) in the amount of 30 wt.% to 50 wt.%. The selection of fungal strain of filamentous fungi was performed prior to the study on the impact of the wood type on the progress of WPCs biodegradability. The changes associated with various water absorption of the examined WPCs, were observed using scanning electron microscopy (SEM). The impact of fungal mycelium, which had affected the changes in WPCs material, was examined using thermogravimetric analysis (TG). The results showed, that the growth of mycelium on WPCs, influenced mainly the temperature of decomposition and carbonization in wood fillers. Moreover, the measurements of analyzed fillers and composite materials, conducted by the use of FTIR/ATR technique (attenuated total reflectance Fourier transform infrared spectroscopy), have proved the existence of relevant structural differences, as well as qualitative and quantitative changes, which are depended on the amount and the type of the filler. Therefore, the rate of biodegradation of WPCs seems to be adequate to the processes of initial changes, caused in this material by the growth of filamentous fungi.

1. Introduction

In recent years, one of the directions of development of new materials are polymer composites with renewable plant fillers. This is due to the fact that natural fibres can give the characteristic of this reinforcement of composites, reduce production cost and usually increase the susceptibility of these materials to biodegradation and/or biodeterioration. One of the most popular composite used as a construction material is wood polymer composite (WPC). The constantly growing number of publications on such composites confirms the significant interest of the scientific community in the materials of this kind (Błędzki et al., 2012; Faruk et al., 2012).

Continuous exposure of materials to environmental factors, leads to such processes as disintegration and deterioration of the material, and degradation of its components (Gu, 2003). In the case of composites with plant fillers, such as WPCs, special attention should also be paid to the effects of water and microorganisms, mainly filamentous fungi. It is important to note that in WPCs, different structures of polymer matrices (i.e. functionality, stereochemistry, molecular weight, and crystallinity), type, size and share of wood, and the presence of other additives, as well as the method of preparation and processing, can influence the results of the fungal attack on the material. For example, a lower cohesion between the phases of individual components contributes to the formation of a higher number of voids in the composite, which act as channels for the fungal movement through the material (Catto et al., 2014).

During over 30 years numerous publications have appeared indicating that the biodegradation process of polyolefins (polymers with the world's largest consumption) is very slow under natural conditions. The utilization of those materials by microorganisms is physically limited by their hydrophobic character, lack of functional groups and high molecular weight (Restrepo-Flórez et al., 2014). There are many publications addressed to the mechanism of degradation of polyolefins, including particularly polyethylene.

In contrast, according to the latest literature data, biodegradation of polyolefin composites is not fully understood. Explanation of such kind of processes is quite difficult, due to the complexity of the phenomena occurring in multi-component systems with different structures and properties. Thus, the knowledge and understanding of the mechanisms involved in biodegradation of polyolefins (including polyethylene) (Gu, 2007; Eubeler et al., 2010; Miyazaki

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et al., 2012), which usually form the polymer-wood matrix of the composites, are not sufficient for the complete assessment of the biodegradation processes of WPCs. Even if the second basic ingredient of WPCs - the wood flour, belongs to the group of biopolymers that are totally biodegradable (Wang et al., 2011; Arantes and Goodell, 2014).

According to the study by Catto et al. (2014), the essential step in biodegradability tests of multi-component materials (which include composites), is the selection of a suitably active microorganisms that are able to biodegrade at least one of the components.

Special attention is paid to the assessment of resistance of WPCs to fungal decay. Fungi of the class Basidomycetes, which are usually used in the studies, cause white-rot decay (e.g. *Trametes versicolor*) and brown-rot decay (e.g. *Gloeophyllum trabeu*) (Schirp and Wolcott, 2005; Fabiyi et al., 2011; Mattos et al., 2015). On the other hand, there are known examples of studies on susceptibility of WPCs to filamentous fungi (generally Ascomycetes and Deuteromycetes) e.g. *Aspergillus* sp. (Kositchaiyong and Sombatsompop, 2012, 2013), *Penicillium* sp. (H'ng et al., 2011; Michalska-Pożoga and Czerwińska, 2015), *Trichoderma* sp. and many others e.g. *Chaetomium* sp., *Aureobasidium* sp., *Alternaria* sp. (Hosseinaei et al., 2012; Xu et al., 2015).

The HDPE-based WPCs consisting mainly coniferous wood, tested for the impact of white rot fungi (*Phlebia subserialis, Trametes versicolor, Xylobolus frustulatus*) and brown rot fungi (*Gloeophyllum trabeum, Postia placenta, Wolfiporia cocos*), showed increased susceptibility of materials containing greater shares of wood fillers. The increased water absorbability of the materials with higher amounts of wood particles was given as a factor contributing to this phenomenon (Mankowski and Morrell, 2000). Fabiyi et al. (2011) also analyzed durability of different WPCs - PEHD with five different wood species: black locust, hybrid poplar, penderosa pine, Douglas-fir and white oak, when infested by white and brown fungi. They proved that the greatest biological resistance was offered by black locust and white oak used as the fillers, what was associated with their low potential of water absorption. Moreover, it was described, what is commonly known (Boyle et al., 1992; Camarero et al., 2014), that the white rot fungi are responsible for degradation of lignin. In turn, the brown rot fungi are responsible for degradation of polysaccharides and lignin in woodextracell. Such kinds of fungal activity were explained by Filley et al. (2002), Yelle et al. (2008) or Kaffenberger and Schilling (2015) as demethylation of lignin and depolymerisation of cellulose. What is more, various types of bacteria and filamentous fungi were isolated from infected materials, depending on the type of environment and the type of material. Lugauskas et al. (2003) have presented the list of dominant strains from the genera *Aspergillus niger, Chaetomium globosum, Trichoderma koningii* as well as *Alternaria alternata, Peacilomyces variotii, Penicillum funiculosum* and many others on the surfaces of the polymeric materials exposed to different conditions, with the frequency of occurrence higher than 20%. In turn, the most frequently mentioned filamentous fungi infected the WPC-type materials include the species of *Aspergillus, Fusarium*, or *Penicillium*.

Summarizing, it should be emphasized that most examples of studies describe the impacts of white-rot fungi (Fabiyi et al., 2011; Hamdan et al., 2013; Catto et al., 2014) and brown-rot fungi (Fabiyi et al., 2011; Hamdan et al., 2013; Tazi et al., 2016) on WPCs. There are also known examples of research with the use of mold and soft-rot fungi (Dawson-Andoh et al., 2004; Kaczmarek and Bajer, 2007). However, according to our knowledge, there is the lack of studies showing differences in the impact of filamentous fungi on WPCs based on various types of wood flours, i.e. coniferous, deciduous or cellulose.

Therefore, the subject of our research was to assess whether different types of wood fillers (coniferous, deciduous, cellulose) influence the susceptibility of polyolefin-based WPCs to the processes of degradation caused by filamentous fungi. Moreover, monitoring of the growth of different species of filamentous fungi on tested wood-polymer composites was performed in order to find the species, which can be used to estimate biodegradation of polyethylene composites containing different wood fillers. Thermal and structural properties, as well as water absorption and surface changes of tested materials were analyzed before and after microbial activity. The evaluation of the quality changes caused by the processes of biodeterioration and/or biodegradation of tested WPCs depending on their composition, was the final stage of our study.

2. Materials and methods

2.1. Materials

The materials presented in this study were the composites with the HDPE matrix (Purell GA 7760, MFI = 18 g/10 min (190 °C, 2.16 kg), density 0.963 g/cm^3). The commercial wood flours Lignocel C120 (C120, 70–150 μm, mixture of coniferous wood materials) and Arbocel C320 (C320, 200–500 μm, cellulose flour) were obtained from Rettenmaier & Söhne GmbH CoKG. The natural, deciduous wood flour was prepared from beech (B) and it was sieved to the diameter < 500 μm. The wood flour was previously dried under temperature of 70 °C for 12 h to remove moisture. In addition, a compatibilizer was used in the composite, and it was polyethylene grafted with maleic anhydride. The composites were prepared on a laboratory (mini) twin screw extruder at the temperature profile of 155–170 °C and at the screw speed of 50 rpm, and then we obtained the specimens by injection molding.

The formulations and nomenclature for test samples were shown in Table 1.

2.2. Microorganisms and media used in biodegradation experiments

The studies were basically divided into two stages. During the first one, the strain was selected from among the six species of filamentous fungi, which, based on literature data (Lugauskas et al., 2003; Sánchez, 2009; Hatakka and Hammel, 2011; Guiamet et al., 2012), have been found as the most aggressive towards different materials. The fungi chosen for the experiments were the species: *Trichoderma koningii* (Tk), *Aspergillus niger* (As), *Fusarium solani* (Fs), *Alternaria alternata* (Aa), *Chaetomium globosum* (Cg), *Trichoderma reesei* (Tr) (obtained from CCM - Czech Collection of Microorganisms). Pure cultures of filamentous fungi were necessary to

Table 1
Nomenclature and formulation of materials samples.

Samples ID	Formulation [wt.%]		
	Matrix	Filler	Compatibilizer
PEHD	100	–	
PEHD_MAH/5	95	–	5
WPC with Lignocel C120			
PEHD_C120/30	70	30	–
PEHD_C120/40	60	40	–
PEHD_C120_MAH/40_5	55	40	5
PEHD_C120/50	50	50	–
WPC with Arbocel C320			
PEHD_C320/30	70	30	–
PEHD_C320/40	60	40	–
WPC with beech			
PEHD_B/30	70	30	–
PEHD_B/40	60	40	–
PEHD_B/50	50	50	–