Degradation of Highly Filled Biocomposites Based on Synthetic Polymers and Natural Polysaccharides Under the Action of Climatic Weathering and Biodegradation (Review)

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Abstract. The abiotic and biological weathering of highly filled composites based on polyolefins and natural fillers was considered. It was found that majority of studies were devoted to artificial weathering of wood polymer composites (WPC) and its effect on composites properties. The biodegradability investigations of such materials were limited by outdoor weathering and model studies under laboratory conditions. The fungal decay was the main topical issue. In the case of natural filler composites (NFC) the biodegradation studies under the natural and laboratory conditions were discussed wider.

1. Introduction
Development of new reinforced composite materials for various applications (furniture, architectural, automotive industries and etc.) has been an actual problem due to deteriorating factor. From the one hand, these materials should be mechanically and chemically stable for a certain period of time. From the other hand, it should be capable of decomposition in the environmental conditions. The optimized solution of this dilemma is to develop highly filled composites based on commercial synthetic polyolefins (polyethylene (LDPE [1] and HDPE), polypropylene (PP), ethylene-octene copolymer (EOC)) and natural fillers (NF). These composites combine the advantages of synthetic matrices [2–4], such as stability and durability, and of NF, such as biodegradability and wide availability as natural wastes from agriculture and wood-making industry [5]. The biodegradation and weathering processes of highly filler composites based on synthetic polyolefins and natural fillers (highly filled NFC) has been under the discussion nowadays [6–8]. It is known that composites biodegradation is the complicated process, which consists of several steps [9]. To sum up, filler chemical composition and bonding of components have an influence on biodegradation rate of composite materials, but at the same time environmental conditions (e.g., temperature, moisture and pH of soil, microbial population, and nutrient supply) effect significantly.

In general, the biodegradation of polymers may contain a number of different steps. A first stage, deterioration of the polymer is caused by decomposing organisms and/or abiotic factors, such as degradation through mechanical, thermal, chemical effects and electromagnetic radiation. At second stage, the depolymerization occur via secreted enzymes and free radicals leading to reduction in
molecular weight. Finally, the assimilation of polymer residues takes place, which caused by microorganisms [10]. In other words, the degradation process can be presented through three basic phases, such as lag phase, degradation phase and plateau phase. The lag phase is the time measured from the start of the test until the degree of biodegradation has reached about 10% of the maximum level of biodegradation. The degradation phase is the time from the end of the lag phase of the test until about 90% of the maximum level of biodegradation. Finally, the plateau phase is the time from the end of the biodegradation phase until the end of the test [11].

The aim of this brief review is to highlight the main regularities of degradation of highly filled composites based on polyolefins and natural fillers in natural and artificial conditions.

2. Wood plastic composites (WPC)

WPC are materials, which contain 30-55% of polymer matrix and 30-70% of wood derivatives (fibers, flour, pulp, softwood/hardwood, etc.). WPC are developed for long-term performance and durability. The Table 1 presents the several studies on highly filled composites including WPC in 2000-2020.

Most scientists [3,6,12] who examined the artificial weathering of WPC with filler content more than 50% wt. found that fading color and loss of mechanical properties of composites has become a great problem. As wood content increased, the weathering performance of WPCs decreased. It was explained by the hydrophilic nature of the wood fiber. The components of wood, cellulose, hemicellulose, lignin, and extractives are variously susceptible to photodegradation. At very first stage the transformation of lignin into water-soluble products occurred. The amount of lignin decreased; the cellulose content increased, which resulted in general wettability of composites [3]. The degradation of wood substances effected on increased lightness that reflected yellowish and reddish light, resulting in a bleaching effect of the composite samples. In addition, it was revealed that the presence of lignin influenced on decreased degree of crystallinity of HDPE [13]. Mechanical properties of WPC (fracture strain, impact strength, flexural strength and flexural modulus) changed insignificantly in dependence to filler content [13]. However, other investigators found that average decline of modulus of rupture of WPC with 30-50% filler was 20% [14]. It can be attributed to low bonding between matrix and fiber.

| Thermoplastic matrices | Vegetal filler |
|------------------------|----------------|
| Low density polyethylene (LDPE) | wood flour [15], kenaf cellulose [16] |
| Polypropylene (PP) | wood flour [7,6,13], hemp shives [17], olive stone flour [7], rice cellulose [18], bamboo fiber [11] |
| High density polyethylene (HDPE) | wood flour [3,6,12,15,19–21], kenaf [22] |
| Ethylene-octene copolymer | wood flour [24-25] |

Microbiological attack is an urgent problem for WPC in general and with outdoor uses in particular. Fungi, especially white rots, can rapidly colonize and decay WPC, enhanced by warm temperatures and high moisture environments [11]. Several studies are devoted to model tests of HDPE/ wood flour samples in laboratory conditions [19]. Composites were covered by fungal isolates in order to establish the impact of white rot fungi (Trametes versicolor) and brown rot fungi (Gloeophyllum trabeum). It showed increased susceptibility of materials containing greater percentages of wood fillers. It was revealed that increased water absorption of the materials is correlated with higher share of wood particles. In another study [21] the filamentous fungi were chosen for the microbiological testing of the 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). Cultures were grown for 14 days and after that the dried mycelium was weighted. Analyzing the results, it was found that the highest growth rate in the carbon-deficient conditions was found for T. reesei, C. globosum and A. niger. The other
tested fungi grew much more slowly in all tested materials. It can be explained by the ability of these cultures to produce intensively extracellular cellulolytic enzymes. Moreover, the dynamics of mycelium growth on the surface of samples is attributed to filler type (coniferous, deciduous). The composites containing deciduous flour showed higher water absorption in comparison to those with the addition of coniferous flour, which is explained by higher content of hydrophobic substances, such as resins of coniferous trees.

3. **Natural filler composites (NFC)**

Natural fibers may reinforce the material significantly because of its ability to absorb the energy stress without deterioration of the material. Fibers can be of an animal (e.g., hair, wool, feather, silk) or vegetal (e.g., flax, hemp, sisal, jute, kenaf, coir) origin. The vegetal fibers can be contained in stems, leaves, or seeds of plants. It is known that lignin-rich fibers (e.g., coir: 40–45%) have more flexibility, which results in higher maximum deformation (ε), while cellulose-rich fibers (e.g., cotton: 90%, pineapple leaves: 70–85%) have more hardness [25].

The most important weathering factors are fungal resistance, ultraviolet (UV) resistance, moisture resistance, and dimensional stability [26]. Popa et al [17] examined the artificial weathering of composites with hemp shives (HS). It was found that the loss of mechanical properties was caused by the degradation of all main polymeric components of the composites, such as cellulose, hemicelluloses, and lignin. The elongation at break of samples with highest HS content decreased rapidly after 200 hours of UV exposure due to both lignin degradation and subsequent PP chain scission. It led to the remarkable reduction in the molecular weight.

The impact of polyethylene glycol (PEG) on biodegradability of LDPE/kenaf cellulose composites was evaluated. The biodegradation test under laboratory conditions was conducted for 4 months at temperature of 26 °C using topsoil from Seri Serdang, Selangor, Malaysia [16]. It was concluded that biodegradability of composites enhanced as kenaf cellulose content increased. Moreover, as PEG content increased, the weight loss decreased due to encapsulation of filler particles.

Chattopadhyay et al. assessed the degree and rate of aerobic biodegradation of high strength PP composites reinforced with biofibers such as pineapple leaf fiber, banana, and bamboo fiber, in contact with soil under laboratory conditions. In terms of this article, the composites based on bamboo fibers (50% wt.) were considered. The degree of biodegradation of composites (15%) was higher in the case of highest fiber content (bamboo fiber) in comparison with other samples. It was concluded that degradation occurred only in those areas of the fibers that did not link chemically with compatibilizer (maleic anhydride PP) [11].

4. **Conclusion**

The brief overview of highly filled composites based on NF and commonly used polyolefins was made. It was shown that majority of previous tests to determine the degree of polymer material degradation were carried out under controlled conditions and that the information relating to natural conditions is very limited. The main disadvantage of such articles is the difficulty to determine the impact of individual environmental factors (moisture, temperature, microbial biomass, etc.) on the rate of polymer material degradation. Authors emphasized that natural fibers can be applied more extensively in order to reduce the amount of polymer content, which will reduce the generation of waste of the nonbiodegradable polymers.

5. **References**

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