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Biodegradability of carbon nanotube/polymer nanocomposites under aerobic mixed culture conditions

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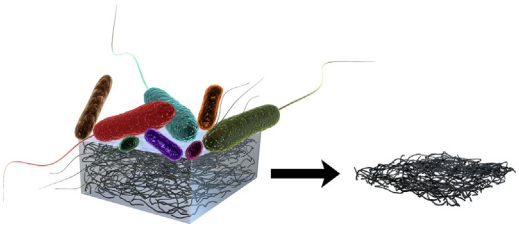
HIGHLIGHTS

- Polymer matrices of MWCNT/polyhydroxyalkanoate (PHA) nanocomposites were biodegraded using an aerobic mixed culture.
- The extent and rate of PHA matrix biodegradation was not affected by the presence of (0-10% w/w) MWCNTs.
- MWCNTs formed a compressed, interconnected mat with a thickness decrease of >70% after PHA biodegradation.
- The MWCNT mat formed contained the same MWCNT masspresent in the initial nanocomposite, indicating a lack of MWCNT release.

GRAPHICAL ABSTRACT



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ABSTRACT

The properties and commercial viability of biodegradable polymers can be significantly enhanced by the incorporation of carbon nanotubes (CNTs). The environmental impact and persistence of these carbon nanotube/polymer nanocomposites (CNT/PNCs) after disposal will be strongly influenced by their microbial interactions, including their biodegradation rates. At the end of consumer use, CNT/PNCs will encounter diverse communities of microorganisms in landfills, surface waters, and wastewater treatment plants. To explore CNT/PNC biodegradation under realistic environmental conditions, the effect of multi-wall CNT (MWCNT) incorporation on the biodegradation of polyhydroxyalkanoates (PHA) was investigated using a mixed culture of microorganisms from wastewater. Relative to unfilled PHA (0% w/w), the MWCNT loading (0.5–10% w/w) had no statistically significant effect on the rate of PHA matrix biodegradation. Independent of the MWCNT loading, the extent of CNT/PNC mass remaining closely corresponded to the initial mass of CNTs in the matrix suggesting a lack of CNT release. CNT/PNC biodegradation was complete in approximately 20 days and resulted in the formation of a compressed CNT mat that retained the shape of the initial CNT/PNC. This study suggests that although CNTs have been shown to be cytotoxic towards a range of different microorganisms, this does not necessarily impact the biodegradation of the surrounding polymer matrix in mixed culture, particularly in situations where the polymer type and/or microbial population favor rapid polymer biodegradation.

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1. Introduction

Nanomaterial fillers can improve numerous polymer properties, which has led to the increasing production of polymer nanocomposites (PNCs). Tensile strength, modulus, light absorption, thermal resistance, and electrical conductivity are just a few of the properties that can be modified by the incorporation of nanomaterials into polymers (Zaman et al., 2014; Kumar et al., 2009). In particular, the high aspect ratio, durability, flame resistance, electrochemical properties, and mechanical strength of carbon nanotubes (CNTs) can markedly improve the properties of a polymer at a relatively low loading, typically between 0.1 and 5% w/w (Moniruzzaman & Winey, 2006; Sahoo et al., 2010; Du et al., 2007; Harrison & Atala, 2007; De et al., 2013). An additional benefit of CNTs is that they allow polymers to remain lightweight upon CNT incorporation as opposed to metallic additives, which can significantly increase polymer weight (De et al., 2013; Coleman et al., 2006; Sarkar et al., 2018).

The beneficial effect of CNTs on polymer properties are particularly important when the nascent properties of a polymer are improved by CNT inclusion to the extent that they become useful for certain applications (Mittal, 2011). For example, the petroleum-based polymer, poly-ε-caprolactone (PCL) is ideal for use in the body but requires the inclusion of CNTs to improve its mechanical strength and temporal stability in tissue scaffolding applications (Gupta et al., 2013; Pan et al., 2012; Mattioli-Belmonte et al., 2012). Another class of polymers, bio-derived polymers, often have poor physico-chemical properties including low melting points, low tensile strength, and minimal conductivity, which prevent or limit their use in a wide range of applications (Mittal, 2011; Posen et al., 2016). There is, however, considerable interest in the manufacture and use of bio-derived polymers due to low production costs, which are a result of simple synthetic routes that make use of renewable precursors derived from microorganisms, plants, and fungi (Mittal, 2011; Posen et al., 2016). For these polymers, the inclusion of CNTs can produce a dramatic improvement in their properties, facilitating their use in commercial products (Mittal, 2011). For example, <1% w/w multi-wall CNTs (MWCNTs) increases the stiffness of starch by 70% (Fama et al., 2011). Furthermore, the addition of only 0.8% w/w oxidized multi-wall CNTs (O-MWCNTs) to chitosan, a bio-derived polymer used in food packaging and filtration, improves the tensile modulus and strength by 93% and 99%, respectively (Aider, 2010; Wan Ngah et al., 2011; Miretzky & Cirelli, 2011; Wang et al., 2005).

Many of these bio-derived polymers and even some petroleum-based polymers are biodegradable. For example, PCL, poly(vinyl alcohol), poly(butylene succinate), poly(ethylene succinate), starch, cellulose, and polyhydroxyalkanoates (PHA) typically biodegrade on the order of days to months (Mittal, 2011; Tokiwa et al., 2009a; Luckachan & Pillai, 2011; Premraj & Doble, 2005). Other polymers such as chitosan and polylactides (PLA) are also biodegradable, albeit over longer time scales, and are often blended with more biodegradable polymers (Tokiwa et al., 2009a; Wu, 2005; Wu & Liao, 2007). While CNTs can enhance a range of materials properties, the inclusion of CNTs may, however, affect the biodegradation of the polymer matrix. Moreover, there is the potential for CNT exposure and release into the environment as a result of microbial degradation of PNCs post-consumer use (Mittal, 2011; Luckachan & Pillai, 2011; Stuart, 2008; Deshmukh & Mhadeshwar, 2011; Ging et al., 2014). Other types of nanomaterials, such as nanoclay and graphene oxide, have been incorporated into biodegradable polymers to assess changes in biodegradation rates. For example, nanoclay incorporation into PHB or poly (hydroxybutyrate-*co*-valerate) (PHB/V) led to an increased biodegradation rate of the copolymer during composting (Maiti & Prakash Yadav, 2008; Singh et al., 2011). The authors suggested that the smaller polymer spherulites formed as a result of the nanoclay incorporation increased the interfacial area available to extracellular enzymes, thereby enhancing the biodegradation rate (Maiti & Prakash Yadav, 2008; Singh et al., 2011). In contrast to nanoclay, graphene oxide (GO) was shown to reduce polymer biodegradation due to GO cytotoxicity, but the presence of carbon-based nanofillers did not prevent the polymer from biodegrading (Peña-Bahamonde et al., 2018). CNTs are also known to be cytotoxic to a wide variety of microorganisms, (Goodwin et al., 2015; Santos et al., 2012; Lanone et al., 2013; Yang et al., 2017) and therefore have the potential to inhibit rather than accelerate biodegradation rates in the absence of structural changes to the polymer, as we have seen in our previous study using a monoculture (Goodwin et al., 2018). Several other studies have shown the accumulation of CNTs and other carbon-based nanomaterials occurs at the surface of polymer nanocomposites during aerobic mixed culture biodegradation or other environmental processes (e.g. ultraviolet weathering) (Peña-Bahamonde et al., 2018; Fan et al., 2017; Goodwin et al., 2016; Petersen et al., 2014; Nguyen et al., 2009; Kim et al., 2009). Moreover, only a select few isolated microorganisms have been shown to biodegrade CNTs and even then at extremely slow rates under optimized laboratory conditions (Parks et al., 2015; Zhang et al., 2013; Chen et al., 2017). Consequently, CNTs are expected to persist much longer in the environment than biodegradable polymers. Since their ecotoxicity is of concern, the benefits of using CNT additives during consumer use may therefore be compromised by the ultimate fate of PNCs when they enter landfills, surface waters, and/or wastewater treatment plants (De et al., 2013; Mittal, 2011; Goodwin et al., 2015; Gottschalk & Nowack, 2011; Petersen et al., 2011; Hossain et al., 2014; Freixa et al., 2018).

To date, the biodegradation behavior of CNT/PNCs containing a biodegradable polymer matrix has received little attention. In a single culture of *Pseudomonas aeruginosa*, we have previously shown that CNT fillers can impact the biodegradation kinetics and persistence of a polymer (Goodwin et al., 2018); however, it is unclear whether this behavior will persist under more environmentally relevant conditions (i.e. in the presence of an aerobic mixed culture). In one of the few studies on aerobic mixed culture biodegradation of CNT/PNCs containing biodegradable polymers, Wu et al. investigated the biodegradation of CNT/PLA nanocomposites buried in soil for five months (Wu et al., 2010). Their results showed that the presence of CNTs reduced the degradation rate, driven by both microbial and chemical processes, of PLA (Wu et al., 2010). Unlike an enzymatic study by Tsuji et al. reported that the incorporation of single-wall CNTs (SWCNTs) into PLA accelerated the enzymatic degradation of CNT/PLA nanocomposites. The authors explained that the poor interfacial interaction between the CNTs and the PLA matrix may have accelerated the degradation process by creating more PLA surface area exposed to enzymes (Tsuji et al., 2007). In contrast to the results reported by Wu and Tsuji, Zeng et al. reported that PCL grafted onto CNTs biodegraded at the same rate as pure PCL in the presence of *Pseudomonas* lipase, a bioactive enzymatic catalyst (Zeng et al., 2006).

In the present study, we have conducted a systematic investigation on the biodegradability of CNT/PNCs containing a biodegradable, bio-derived polymer (PHA) matrix exposed to an aerobic mixed culture. Primary effluent from a domestic wastewater treatment plant was used as the source of the mixed culture since it contains a wide range of microorganisms prevalent in the environment (EPA, 2001; Gilmore et al., 1993; Leja and Lewandowicz, 2010; Massardier-Nageotte et al., 2006). PHA was selected as the polymer matrix because it can be rapidly biodegraded in the environment, on the order of weeks, it is sustainably produced, (Lee et al., 1999). PHA is also being increasingly used as a substitute for traditional plastics in commercial products that include films, pins, and screws due to its low cost (Volova, 2004; Sudesh, 2012; Misra et al., 2006). Furthermore, it has been shown that CNTs can improve PHA properties for broader use in many applications (Bhatt et al., 2008; Jendrossek & Handrick, 2002; Jendrossek et al., 1993; Madbouly et al., 2014; Mas-Castellà et al., 1995; Numata et al., 2009; Ohura et al., 1999; Shah et al., 2010; Shah et al., 2008; Volova et al., 2011; Volova et al., 2010; Volova et al., 2007; Weng et al., 2011; Mergaert et al.,