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Development of a conceptual framework for evaluation of nanomaterials release from nanocomposites: Environmental and toxicological implications

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HIGHLIGHTS

- The UV-induced degradation of multiple carbon nanotube-epoxy composites is studied.
- The toxicology of these materials is explored with a Drosophila model.
- A life cycle analysis of carbon nanotube release from composites is proposed.

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ABSTRACT

Despite the fact that nanomaterials are considered potentially hazardous in a freely dispersed form, they are often considered safe when encapsulated into a polymer matrix. However, systematic research to confirm the abovementioned paradigm is lacking. Our data indicates that there are possible mechanisms of nanomaterial release from nanocomposites due to exposure to environmental conditions, especially UV radiation. The degradation of the polymer matrix and potential release of nanomaterials depend on the nature of the nanofillers and the polymer matrix, as well as on the nature of environmental exposure, such as the combination of UV, moisture, mechanical stress and other factors. To the best of our knowledge there is no systematic study that addresses all these effects. We present here an initial study of the stability of nanocomposites exposed to environmental conditions, where carbon nanotube (CNT) containing polymer composites were evaluated with various spectroscopic and microscopic techniques. This work discusses various degradation mechanisms of CNT polymer nanocomposites, including such factors as UV, moisture and mechanical damage. An *in vivo* ingestion study with Drosophila showed reduced survivorship at each dose tested with free amine-functionalized CNTs, while there was no toxicity when these CNTs were embedded in epoxy. In addition to developing new paradigms in terms of safety of nanocomposites, the outcomes of this research can lead to recommendations on safer design strategies for the next generation of CNT-containing products.

1. Introduction

There is growing interest in the development of new organic polymer composites. Traditional composites have been used extensively in civil infrastructure applications; their use continues to grow in new and existing structures *via* retrofits, rehabilitations, and repairs. They are also used in consumer products, and in the automotive and aerospace industries. One of the most promising trends in composites is the use of nanomaterials to revolutionize properties of existing composites. Polymer nanocomposites are multicomponent systems where polymers are combined with nanomaterials, often called nanofillers. Nanofillers, even at small concentrations, can dramatically enhance material properties, such as scratch resistance, elasticity, conductivity, etc. These new materials are already being used in the place of conventional composite materials.

Among many different types of polymers used in nanocomposites, epoxy polymers are standard materials used for aerospace, infrastructure, and consumer products owing to their excellent mechanical properties (specific strength, stiffness), good chemical resistance, and resistance to hydrolytic degradation (Spitalsky et al., 2010). These

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properties can be increased even further through the addition of nanofillers such as carbon nanotubes (CNTs). Given the CNTs' high tensile modulus, strengths, low mass density, and large aspect ratio, their addition to polymers can improve the tensile stress, Young modulus, fracture toughness and storage modulus of the polymer matrix. Among other industrially relevant properties of nanocomposites attributed to CNTs are reduced gas and liquid permeability, increased thermal stability, lower flammability, low percolation threshold for electrical conductivity and higher wear resistance (Schlagenhauf et al., 2012) (Wohlleben et al., 2013a,b). CNT composites have already been used in products including sports bicycles, ship hull antifouling treatment, transistors, and even on the Juno spacecraft (De Volder et al., 2013).

The chemical, physical, and structural properties of the polymer/nanofiller–interface all play a vital role in nanocomposite degradation. Interfacial adhesion of CNTs to the polymer can be enhanced by chemical modification of the CNTs (*i.e.*, functionalization), or by using surfactants to moderate the physical interactions between the carbon nanofillers and matrix. There are certain advantages of this latter method, given its simplicity and lower cost compared to chemical functionalization (Fiedler et al., 2006).

Despite promising developments in nanocomposites, several important questions related to their safety for humans and the environment have not been properly addressed. For example, it is known that CNTs provide vehicles for drug delivery, as they are able to cross cell membranes carrying a variety of biologically functionalized amendments (Kostarelos et al., 2007). *In vitro* studies give mixed results, some find no toxicity (Cherukuri et al., 2004), or toxicity only in modified CNTs (Kam et al., 2004), possibly because they more readily cross cell membranes. *In vivo* toxicological studies under various delivery methods revealed that longer CNTs are more toxic (Poland et al., 2008); their needle-like fiber shape has similarities to that of asbestos. Inhalation studies in mice showed the lung has difficulty clearing CNTs. Longer multi-walled CNTs (MWCNTs) (higher aspect ratio) induced inflammation, nodular lesions (granulomas) and scarring in the mesothelial lining, symptoms which mirror asbestos inhalation phenotypes (Nagai et al., 2011; Ryman-Rasmussen et al., 2009). Shorter or tangled nanotubes, and carbon black controls, had much less of an effect. Inhalation studies in mouse mesothelial lining also resulted in granuloma formation (Poland et al., 2008). These CNTs were found three months following intravenous injection, and resulted in low levels of oxidative stress (Yang et al., 2008). Minimal bioaccumulation and toxicity were generally reported for unmodified MWCNTs in environmental studies (Li et al., 2013; Shrestha et al., 2013). Research still needs to be done to verify if this finding for a broader range of CNT functionalizations and types (*i.e.* single-walled and double-walled).

Encapsulation into a polymer matrix is thought to negate these aspects of CNTs' toxicity, but with little experimental support. The most probable source of CNT nanocomposite toxicity is in their potential to generate degradation products in an environmental setting *via* weathering. Polymer photodegradation by UV light can expose CNT ends at the nanocomposite surface, or potentially release free CNTs. Epoxy-CNT composites showed significantly less photodegradation than equivalent SiO_2 nanocomposite (Nguyen et al., 2011). *In vivo* toxicity studies have not yet been performed on nanocomposites or nanocomposite byproducts during manufacturing or environmental weathering. These are needed, as *in vitro* nanoparticle toxicology does not necessarily predict *in vivo* toxicology (Posgai et al., 2011).

An important question to address is whether there are realistic scenarios of CNT release from the polymer nanocomposites which could cause unwanted human and/or environmental toxicity. It is conceivable that such release can be caused by mechanical damage, chemical degradation under UV light and moisture, and biodegradation. This paper addresses some of the gaps in current knowledge in terms of clarifying the release pathways and the most likely release scenarios.

Current research on the environmental stability of nanocomposites has focused primarily on short-term stability and performance, whereas the longer-term issues have not been properly addressed. This knowledge gap has the potential to hinder both applications and acceptance of these advanced composites in various industries. It is known that polymer matrices can undergo degradation when exposed to various environmental conditions during production, use and disposal. Therefore, it is critical to scrutinize the behavior of nanocomposites under relevant environmental conditions at all stages of the material's life cycle. Ideally, this approach should be applied to all manufacturing processes that use nanomaterials. Undertaking a comprehensive risk analysis of the environmental and health impacts of nanocomposites is still a considerable challenge (Petersen et al., 2011a). Moreover, it is also important to consider other mechanisms related to end-of-life stage of these materials, including incineration. (Petersen et al., 2011b). Fig. 1 shows a conceptual scheme of Life Cycle (LC) and potential mechanisms of release of nanomaterials from the composites. More specifically, it considers several stages of the LC, including the following:

1.1. Manufacturing stage

This stage includes handling of nanomaterials, which are present either in dry or already liquid-dispersed form. Due to the fact that this step involves raw nanofiller is conceivable that the highest risk of freely dispersed CNT release would occur during this stage. There are several other manufacturing steps beyond raw nanomaterial handling which could lead to exposure. These include nanofiller encapsulation into composites, machining (such as cutting, drilling and sanding), and assembly of nanomaterials into the final products. There are, however, several methods of nanomaterials containment, which, coupled with personal protection, can mitigate the exposure risks, especially those resulting from inhalation exposure (Kohler et al., 2008; Schlagenhauf et al., 2012; Bello et al., 2009).

Depending on the type of CNT (SWCNT or MWCNT), surface functionality, and presence or absence of catalyst residue, unencapsulated CNTs pose different toxicity. There are already numerous studies of this scenario (Ahamed et al., 2010; Fenoglio et al., 2012; Sharifi et al., 2012), although reproducibility and consistency of this data is an issue. Although chronic respiratory exposure to catalyst metals such as cobalt, a common nanotube contaminant, can cause bronchial asthma(Swenn et al., 1993), the extremely small percent composition of catalyst impurities after processing (generally <0.2 at.%), would most likely cause their health effects to be greatly outweighed by those of the CNTs.

1.2. Use

This stage poses the most significant risk to consumers. Repairs and certain patterns of use might lead to mechanical abrasion and to various types of materials failure originating from mechanical stress (Bello et al., 2009). Given that consumers do not usually practice nanomaterials containment procedures available at the manufacturing stage, there is a vital need to ensure that normal use of nanocomposites does not pose any risk greater than those inherent with the polymer substrate.

Normal use of nanocomposites might entail mechanical, physical and chemical factors leading to composite degradation. For example, environmental conditions might result in combined or individual exposure to UV light, humidity, temperature, chemical and biological factors. Linking nanomaterials release to physicochemical properties of nanocomposites and the environment has only been addressed sparsely in the current literature (Wohlleben et al., 2013a,b). Wohlleben *et al.* examined the combined effects of mechanical stress *via* shaking and ultrasonication with UV light exposure, but the particulate detection methodology could not discern between exposed CNTs and other particulates smaller than 150 nm.