Analysis of Factors Associated with the Releasability of Carbon Nanotubes (CNTs) from Materials Containing Nanocomposites

M. Kovochich*, R. Avanasi, and A.K. Madl** ChemRisk, LLC

ChemRisk, LLC, 130 Vantis, Suite 170, Aliso Viejo, CA 92656
*mkovochich@chemrisk.com, **amadl@chemrisk.com

ABSTRACT

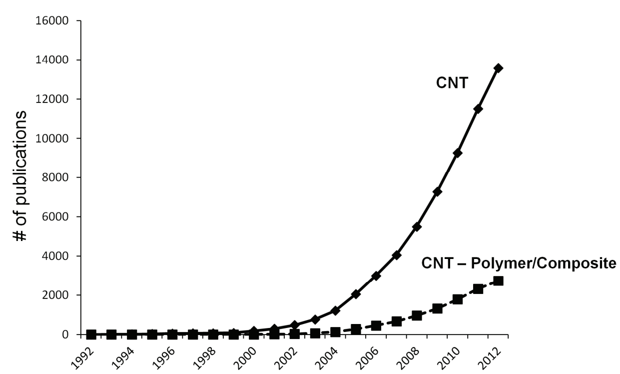
The development and use of engineered nanomaterials offer innovative advancements for a wide range of industrial and consumer product technologies which promise to have global economic impact. Composites made with engineered nanomaterials (nanocomposites) are currently being used in applications ranging from basic consumer goods to critical national defense technologies, with carbon nanotubes (CNTs) being popular due to their enhanced mechanical, thermal, and electrical properties. Some concerns have been raised regarding the potential for exposure and health risk of nanocomposites containing CNTs due to comparisons to other high aspect ratio fibers. For these reasons, assessing the release of CNTs from composites is paramount in understanding the potential exposure scenarios that may occur during handling and manipulation of the product. We analyzed available data on the release of CNTs from nanocomposites as a result of various stressors.

Keywords: carbon nanotubes, nanocomposites, releasability, risk assessment

1 INTRODUCTION

Nanomaterials contain at least one dimension in the nanoscale range (1-100 nm) and utilize novel properties to enhance various applications. Nanomaterials are currently being developed by most major industries (including energy, chemical, mechanics, electronics, consumer goods, and medicine) and markets incorporating nanotechnology are expected to grow to hundreds of billions of dollars by 2015. However, concerns have been raised over introducing nanomaterials into the environment and their effects on human health. In particular, carbon nanotubes (CNTs) have received attention due to comparisons made with the toxicology of high aspect ratio fibers. CNTs are found in a variety of materials including composites (nanocomposites) used for numerous consumer and industrial applications. After the first publication on the use of CNTs in composites in 1994, industrial process advancements in the early 21st century spurred greater interest in CNTs and their use in composite materials (Figure 1). However, as research and use of CNTs in nanocomposites increase, the likelihood for human contact and potential exposure increases, which will be largely driven by the releasability of CNTs from the matrix. Therefore, we aimed to understand the factors that affect the releasability of CNTs from nanocomposites. To this end, we analyzed data related to the release of CNT from various nanocomposites. We hypothesized that various features of the nanocomposite material would influence release of CNTs including: 1) location of the CNTs within the matrix, 2) CNT-matrix interactions influenced by dispersion and functionalization techniques, and 3) energy input, or stressors tested.

Figure 1: Number of publications related to CNTs and their use with polymer or composite materials



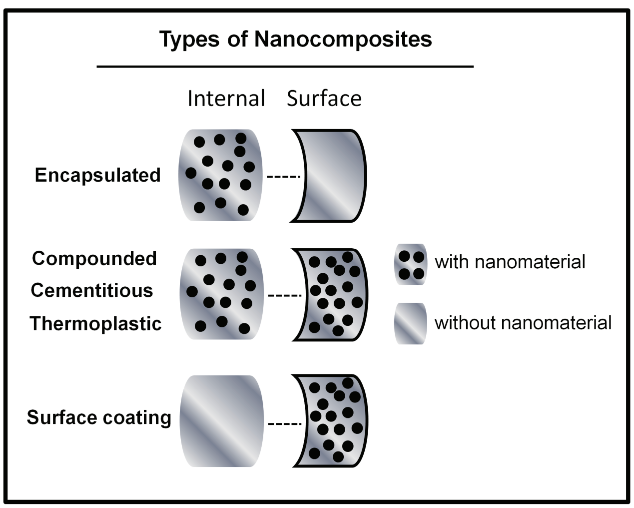
2 RESULTS

Our data search generated eleven published studies that evaluated the release of CNTs from various nanocomposites that may be potentially used for consumer or industrial applications (Bello et al. 2009; Bello et al. 2010; Cena and Peters 2011; Golanski et al. 2012; Halada 2012; Methner et al. 2012; Nguyen et al. 2011; Schlagenhauf et al. 2012; Uddin 2011; Wohlleben et al. 2011; Wohlleben et al. 2013). Data was analyzed for matrix type, dispersion techniques, functionalization, release process, detection of release, and associated methods. Discussion of potential for CNT release was documented as an indication of the direction of future research. It is important to note that standard methods for detection of CNT release have not been developed and each study used a different combination of parameters for release assessment. Techniques including elemental carbon detection by NMAM 5040, TEM image analysis, and real-time particle counts all represent various strategies for assessing CNT release (Golanski et al. 2012; Methner et al. 2012; Schlagenhauf et al. 2012). However, limitations in each method represent the difficulty of properly characterizing release in a quantitative manner than can be related to toxicological data. For example, if aspect ratio is a critical factor for toxicological responses, then elemental carbon analysis may not represent a relevant benchmark. Further, although TEM images can help determine fiber morphology, quantification of CNTs is difficult. Therefore, although multiple methods for release were used by different researchers, our analysis relied on the author's interpretation of their data as an indication for results. It will be critical for future research to develop standard methods for characterizing and quantifying CNT release in order to properly assess potential human health risk.

2.1 Matrix Type

We hypothesized that matrix type or location of CNTs within the matrix could influence potential for release (Figure 2). Encapsulated products contain at least one layer that is free of nanomaterials and enclose a portion of the nanocomposite. Thermoplastic, compounded, or cementitious products contain nanomaterials both internally and on the surface while coatings only contain nanomaterial on the surface. Release of CNTs have been studied in several matrix types including epoxy based composites, woven alumina fiber cloth, cement, polyoxymethylene thermoplastics, polyurethane thermoplastics, polyurethane foam, and polycarbonate and polyamide polymer coatings.

Figure 2: Location of nanomaterials within various types of nanocomposites



Seven of the eleven studies used epoxy composites to test CNT release under various conditions (Bello et al. 2009; Bello et al. 2009; Cena and Peters 2011; Nguyen et al. 2011; Golanski et al. 2012; Methner et al. 2012; Schlagenhauf et al. 2012). Three of the seven studies using epoxy-based composites observed release (Golanski et al. 2012; Methner et al. 2012; Schlagenhauf et al. 2012); additionally one study observed release of CNT aggregates in epoxy and alumina fiber composites (Bello et al. 2010). CNT content in the original matrix material for each study varied from 0.03%wt - 4%wt, and one study with no information. Other matrix types including woven alumina fiber cloth, cement, polyoxymethylene thermoplastics, polyurethane thermoplastics, polyurethane foam, and polycarbonate and polyamide polymer coatings did not display release of CNTs under various conditions.

2.2 Dispersion and Functionalization

Dispersion of CNTs within the matrix of a nanocomposite will influence the performance capabilities of the material. However, fabricating a nanocomposite with proper CNT dispersion has presented several challenges. Individual CNTs that are manufactured for nanocomposite integration remain entangled in bundles due to van der Waals forces between the individual tubes. As a result, it is difficult to disperse the individual CNTs in the matrix during polymer processing. In addition, the highly hydrophobic nature of CNTs results in poor interfacial interaction with the polymer matrix. Therefore, with the goal of producing properly dispersed CNT-nanocomposites, researchers have utilized several mechanical dispersion techniques such as ultrasonication, calendering, ball milling, stirring, and extrusion (Table 1).

Manufacturers generally use different dispersion techniques based on their specific needs and applications. Ma et al., 2010 compared these techniques with respect to factors such as suitability with different polymer matrices, availability, damage to CNTs and others (Ma et al. 2010).

Table 1: CNT dispersion techniques for nanocomposites and effects on CNT damage and aggregation

Dispersion Technique	Matrix/polymer state	Common CNT damage	Common CNT re-agglomeration
Ultrasonication	soluble/low viscous	+	-
Calendering	liquid	-	+
Ball milling	powder	+	-
Stir and shear mixing	soluble/low viscous	-	+
Extrusion	thermoplastic	-	-

Adapted from Ma et al. 2010

Ultrasonication utilizes the application of ultrasound energy to disperse CNTs in low viscosity liquids. Since polymers are usually in a solid/viscous state, they are first dissolved in a solvent and then CNTs are dispersed by ultrasound waves. Calendering or three roll milling utilizes shear forces by rollers to disperse and mix CNTs into the polymer matrix. It has been shown to produce a relatively good dispersion. Ball milling utilizes grinding to disperse CNTs in the matrix, and in the presence of chemicals, CNTs can be chemically functionalized, thereby improving the interaction with the matrix. Stirring is another common mechanical technique used to disperse CNTs in the polymer matrix. Extrusion utilizes rotating twin screws to create high shear forces to disperse CNTs in the polymer matrix. Thermoplastics with CNTs are generally produced using this technique. These techniques are important to keep in mind when assessing the potential release of CNTs from nanocomposites as each process will affect the physical and chemical properties of the CNTs as they are processed into the end product.

Almost all the mechanical dispersion techniques (except for ball milling in the presence of a chemical molecule) result in the interaction of CNTs with the matrix through van der Waals interactions only. This is because of the inability of the chemically inert carbon atoms on the CNT walls to interact with the matrix. Functionalization is a technique, where the surface properties of CNTs are modified in order to improve the interaction with the polymer matrix, as was reviewed by Ma et al. 2010. Functionalization can either be performed chemically or physically with varying effects on CNT-matrix interactions and CNT properties (Table 2). In chemical functionalization, the covalently added functional groups can form stronger interactions with the matrix in comparison to physical functionalization which utilizes non-covalent interactions. Chemical functionalization can also form defects or CNT fragmentation while physical functionalization usually avoids these effects. It is important to keep in mind that the method of dispersion and functionalization plays a major role in the resulting interactions between the CNTs and the polymer matrix, and in turn, may play a role in the releasability from the finished product.

Table 2: CNT functionalization in nanocomposites and effects on CNT binding, damage, and aggregation

Functionalization method	Strong interaction with matrix	Common CNT damage	Common CNT re-agglomeration
Chemical - side wall	+	+	+
Chemical - defect	+	+	+
Physical - polymer wrapping	+/-	-	-
Physical - surfactant adsorption	-	-	-
Physical - endohedral	-	-	+

Adapted from Ma et al. 2010

Interestingly, detailed information regarding dispersion and functionalization was not provided for the majority of release studies. Of the three studies that observed release (Golanski et al. 2012; Methner et al. 2012; Schlagenhauf et al. 2012), only Schlagenhauf et al. (2012) provided dispersion techniques and involved calendering to produce a good dispersion of CNTs. Although Golanski et al. (2012) observed release of CNTs from epoxy-based composites under "poor dispersion" compared with "good dispersion", detailed information on how the materials were formulated, including functionalization, were not provided. No information regarding dispersion or functionalization was provided in Methner et al. (2012); CNT release was observed from epoxy based composites. Release of CNT aggregates from epoxy or alumina fiber composites did not provide detailed information regarding dispersion techniques; however, previous studies indicated that functionalization may have been performed using capillarity driven wetting techniques (Bello et al. 2009; Bello et al. 2009). Taken together, there is limited data regarding the effect of dispersion and functionalization on the influence of CNT release from nanocomposites.

2.3 Release Process

It is important to understand the effects of various stressors on nanocomposites as each material may be handled differently depending on the consumer or industrial application. Energy input can range from environmental factors such as weathering, to mechanical input, and finally end of product life scenarios including incineration. Four studies examined the effects of UV weathering on CNT release from various nanocomposites including epoxy, thermoplastic, and cement-based materials (Wohlleben et al. 2011; Nguyen et al. 2011; Halada and Orlov 2012; Wohlleben et al. 2013). No CNT release was detected in any of the studies; however, CNT surface aggregation was detected in all four studies using either epoxy or thermoplastic composites (Wohlleben et al. 2011; Nguyen et al. 2011; Halada and Orlov 2012; Wohlleben et al. 2013). No CNT surface aggregation was observed using a cement-based nanocomposite (Wohlleben et al. 2011).

Mechanical processes including sanding, grinding, saw cutting, and instantaneous stress using a steel brush and engraver caused CNT release from epoxy-based composites (Golanski et al. 2012; Methner et al. 2012; Schlagenhauf et al. 2012). However, in other studies, sanding, rotary cutting, band saw cutting, normal-use abrasion, and soft to hard abrasion did not induce release of CNTs from various composite materials including epoxy, cement, and thermoplastic nanocomposites (Bello et al. 2009; Wohlleben et al. 2011; Wohlleben et al. 2013). Release of CNT aggregates was observed after drilling compared with no release from cutting the same epoxy or alumina fiber composite materials (Bello et al. 2009; Bello et al. 2010). Finally incineration of polyurethane foam did not release individual fibers; however, CNTs were detected after mechanical disturbance of the char residue (Uddin et al. 2011). These studies demonstrate a wide variability in results when comparing different stressors with different composite materials. Future studies will need to use standardized testing for comparable results across materials and actions tested.

3 DISCUSSION

Few studies have been conducted characterizing the release of CNTs from nanocomposites; therefore, interpretation of the results is preliminary. However, certain trends can be observed and used to direct future research efforts. Three of the eleven studies observed release of CNTs and all nanocomposites were epoxy-based (Golanski et al. 2012; Methner et al. 2012; Schlagenhauf et al. 2012). One study observed release of CNT aggregates from epoxy or alumina fiber composites (Bello et al. 2010). However, several variables limit the interpretation of these data. Detection methods and quantification of released fibers varied between studies. The relationship between released fibers and corresponding toxicology was not demonstrated in any of the studies that detected release. Physical and chemical characterization of the released material, as well as dose and respirability will influence toxicology and potential human health of released CNTs; however, many of the studies do not take all of these parameters into account.

CNT dispersion was determined to be important in one study that compared "poor" vs. "good" dispersion (Golanski et al. 2012). CNT release, although determined to be low, was detected in poorly dispersed composites; however, details regarding the dispersion techniques were not provided. In contrast, Schlagenhauf et al. (2012) observed release with good dispersion of CNTs. Therefore, future studies will need to determine the role of dispersion on release of CNTs from nanocomposites. To this end, various dispersion and functionalization techniques can be tested for their influence on CNT-matrix binding interactions and potential for CNT release.

Weathering processes did not induce release of CNTs from nanocomposites but generated aggregated bundles of CNTs on the material's surface. Future research will be necessary to determine if mechanical processes can influence release of aggregated CNTs after weathering effects. Multiple stressors can be tested to examine the effects of weathering and mechanical input that may be encountered in certain consumer or industrial scenarios.

Interestingly, the majority of the studies discussed the potential for CNT release under different testing conditions or the release of nano-sized dust emphasizing the need for further characterization. This demonstrates that these preliminary findings will necessitate further research into potential release mechanisms as well as standardizing techniques for quantification of release.

4 CONCLUSION

A better understanding of the factors that play a role in the release of CNTs from nanocomposite materials should improve technological development and safe handling of nanocomposites while minimizing any potential health risks. Preliminary results indicate that certain processes may influence release of CNTs; however, a couple recommendations can be made for future studies that aim to assess the health risk of CNT exposure associated with nanocomposites. First, standardization of quantification methods and thorough characterization of the released material will be necessary to relate data across various studies and assess potential human exposure and adverse health effects. For example, the agglomeration and physicochemical characteristics of the CNT with the associated matrix will likely influence respirability, biopersistence, and potential health effects. Understanding how the characteristics of free CNTs versus matrix-coated CNTs impact different biological responses will be important for human health risk assessments of nanocomposites in various consumer or industrial settings. Second, further research is needed to characterize the wide range of available composite materials with an emphasis on how CNT-matrix interactions may influence CNT release, including matrix type, dispersion/functionalization techniques, and physical or non-physical stressors. Understanding the primary internal and external factors which influence the nanocomposite physicochemistry and the potential release of nanomaterials in the environment will better inform risk assessment throughout the product life cycle and enlighten risk management decisions to minimize potential environmental and human health impacts.

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