Development and Application of an Exposure-based Framework for Assessing Nanomaterial Safety

C.M. Long

Gradient Corporation
20 University Road, Cambridge, MA 02138 USA, clong@gradientcorp.com

ABSTRACT

To address questions of nanomaterial product safety in this time of uncertain information, we have developed a risk assessment framework that can provide a tool for qualitatively assessing the exposure potential of commercial nanomaterials. Central to our framework is the assessment of potential exposures along each step of the product lifecycle (e.g., from manufacture to distribution to use to end-of-life disposal), and the use of both available nanomaterial-specific data as well as data for similar materials (i.e., "bridging" data) to fill in data gaps. We have applied our framework to the case of carbon nanotube (CNT) nanocomposites in sporting goods such as tennis rackets, skis, and baseball bats, finding that there is a low likelihood of release of free CNTs under typical use conditions but that available data suggests greater release and exposure potential for end-of-life processes such as landfilling.

Keywords: carbon nanotubes, nanocomposites, lifecycle, exposure assessment, product safety

1 INTRODUCTION

Although it is estimated that there are over 500 nanotechnology-based consumer products on the market [1], few published data are available to support thorough nanomaterial safety assessments. Given the present-day potential for general population exposures to nanoparticles, we have developed a risk assessment framework that can provide a tool for qualitatively assessing the exposure potential of commercial nanomaterials using available information. Since the health risk posed by a nanomaterial is a function of both toxicity and exposure and there remain large uncertainties regarding the toxicity of specific nanoparticle types, our framework focuses on exposure potential to assess product safety. In this paper, we apply our framework to the case of nanocomposite sporting goods consumer products.

2 FRAMEWORK DEVELOPMENT

As shown in Figure 1, our framework explicitly considers the several steps that typically connect nanoparticles within a product to a human exposure to free nanoparticles, including a product use or disposition that results in a release, environmental fate processes that can modify nanoparticle properties, and human exposure scenarios that bring people into contact with affected environmental media (e.g., air, water, food, soil). Following several recent studies where potential releases and adverse health effects of nanomaterials were approached from a lifecycle perspective [2, 3], the assessment of potential exposures along each step of the product lifecycle (e.g., from manufacture to distribution to use to end-of-life disposal) is central to our framework. In addition, key to our framework is the use of both available nanomaterial-specific data as well as data for similar materials (i.e., "bridging" data) to fill in data gaps. As shown in Figure 2, there may not be a large amount of exposure data for engineered nanoparticles, but there are ample data available for other nano-sized particles (*e.g.*, ambient ultrafines, manufactured carbon black, diesel exhaust particulate) and for other types of materials that may behave similarly to nanotechnology-based materials.

Exposure potential depends in large part on nanoparticle physical-chemical properties, and as shown in Figure 1, there may be changes in these properties not only along the various steps in the product lifecycle but also in the environment. Our framework thus highlights the relationship between nanoparticle physical-chemical properties and exposure potential, and the need for repeated characterization of nanoparticle properties given that they can change along each step of a product lifecycle and in the environment.

3 FRAMEWORK APPLICATION

We apply our framework to the case of carbon nanotube (CNT) nanocomposites in sporting goods such as tennis rackets, skis, and baseball bats. Figure 3 shows a typical product lifecycle for a sporting goods nanocomposite and the numerous potential exposure points that can occur along the entire product lifecycle. As shown in this figure, there are a variety of potentially exposed populations depending on the step in the product lifecycle, including workers in several industries, consumer user populations, and the general population. In this case study, we only consider a subset of this complete product lifecycle, namely the use phase and end-of-life, and the exposures that could potentially occur in these steps.

3.1 Typical Consumer Product Use

Available information on CNT nanocomposite characteristics indicates a low release potential of free NPs under typical consumer use conditions. This is supported by several key pieces of information, including the fact that CNTs are embedded within a solid, impermeable matrix in nanocomposite sporting goods. In addition, CNTs are typically minor constituents of nanocomposites, with common weight percentages of 1 to 5%. As extensively discussed [4], CNT surface treatment and dispersion techniques (*e.g.*, functionalization) promote a strong CNT-matrix interface, including covalent bonding.

3.2 Wear & Tear and Product Modification

Studies of carbon fiber and asbestos composites provide insight on the potential for free NP releases during wear and tear and product modification (*e.g.*, trimming bicycle handlebars and posts, sanding skis). Specifically, studies of potential fiber release during sawing and drilling of carbon fiber composites have reported that fibers remained bonded to matrix material [5]. In addition, studies of drilling, grinding, sawing, and sanding of asbestos-containing encapsulated products (e.g., brake pads, mastics, plastic resins) show little release of free asbestos fibers and provide evidence that asbestos fibers remain bound to the underlying matrix [6]. Although these findings need to be verified for CNT nanocomposites, they indicate a low likelihood of release of free CNTs from nanocomposites.

3.3 End-of-Life: Incineration

There is uncertain information available regarding the potential release of free CNTs during incineration of CNT nanocomposites. In particular, it is well-established that polymer matrices (e.g., epoxy resins) oxidize and burn away at temperatures well below those typical of municipal incinerators. Some studies [7] of CNT combustion indicate low thermal stability in oxidative atmospheres (e.g., findings of an onset temperature of 570 ^{o}C), while others [8] support very high thermal stability (e.g., findings of an onset temp. of 820 ^{o}C). Studies [5] have shown partial oxidation of carbon fibers for typical incinerator conditions but not complete burn-off. Additional study is needed.

3.4 End-of-Life: Landfilling

There is a general lack of data relevant to the stability of nanocomposites and the persistence of CNTs under typical environmental conditions. Research is needed in this area, especially given some studies [9] of the physical and chemical degradation of carbon fiber-reinforced epoxy composites that have reported severe erosion of epoxy matrix following exposure to UV radiation and moisture.

4 SUMMARY AND CONCLUSION

As summarized in Table 1, for our CNT nanocomposite case study, we found a low likelihood of release of free CNTs under typical use conditions but sparse data characterizing product degradation following typical end-of-life disposal scenarios such as landfilling, indicating that such scenarios should be a priority of future research. Our framework thus demonstrates the importance of full consideration of the entire product life-cycle for assessing the health and safety implications of a nanomaterial, and the utility of bridging data for providing insight on the release and exposure potential of particular product lifecycle steps or exposure pathways. Explicit consideration of exposure potential in the product design and development stages, and modification of nanoparticle properties (e.g., via functionalization) and/or product characteristics, offers a viable approach for proactive mitigation of possible product health and safety issues.

5 REFERENCES

[1] Nanotechnology Project. "Consumer Products: An inventory of nanotechnology-based consumer products currently on the market." www.nanotechproject.org, 2008.

[2] A. Kohler, C. Som, A. Helland and F. Gottschalk, "Studying the potential release of carbon nanotubes throughout the application life cycle." Journal of Cleaner Production, 1-11, 2007.

[3] A. Franco, S.F. Hansen, S.I. Olsen, and L. Butti, "Limits and prospects of the 'incremental approach' and the European legislation on the management of risks related to nanomaterials." Regul. Toxicol. Pharmacol., 48, 171-183, 2007.

[4] P. Eklund, P. Ajayan, R. Blackmon, A.J. Hart, J. Kong, B. Pradhan, A. Rao, and A. Rinzler. "International Assessment of Research and Development of Carbon Nanotube Manufacturing and Applications." World Technology Evaluation Center, Inc. 1-120, 2007.

[5] Bionetics Corp, "Carbon Fiber Data Base: Data Base Review and Assessment of Carbon Fiber Release into the Environment." 1982.

[6] F. Weir and L.B. Meraz. "Morphological Characteristics of Asbestos Fibers Released During Grinding and Drilling of Friction Products." Appl Occup Environ Hyg. 16:12, 1147-1149, 2001.

[7] Y.H. Wang, Y.N. Li, J. Lu, J.B. Zang and H. Huang, "Microstructure and thermal characteristic of SI-coated multi-walled carbon nanotubes." Nanotechnology, 17, 3817-3821, 2006.

[8] F. Cataldo, "A Study on the Thermal Stability to 1000ºC of Various Carbon Allotropes and Carbonaceous Matter both Under Nitrogen and in Air." Fullerenes, Nanotubes and Carbon Nanostructures, 10:4, 293-311, 2002.

[9] B.G. Kumar, R.P. Singh, T. Nakamura, "Degradation of Carbon Fiber-reinforced Epoxy Composites by Ultraviolet Radiation and Condensation." Journal of Composite Materials, 36:24, 2713-273. 2002.

Figure 1. Flow Chart of Potential Free Nanoparticle Exposures from Consumer Products

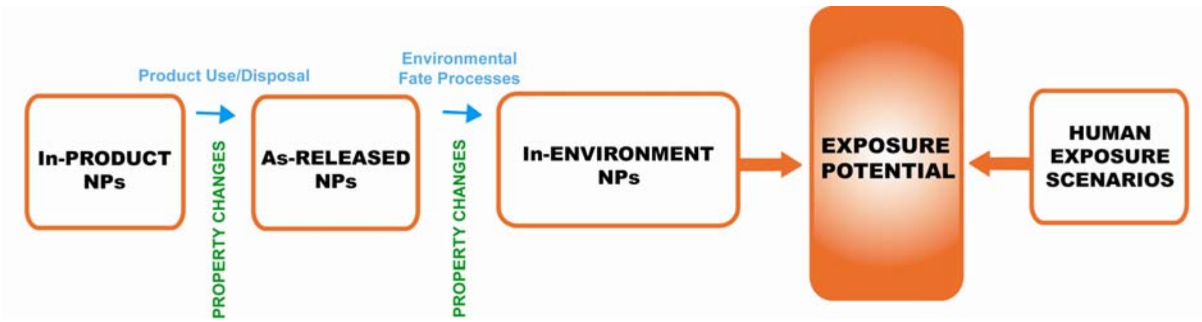
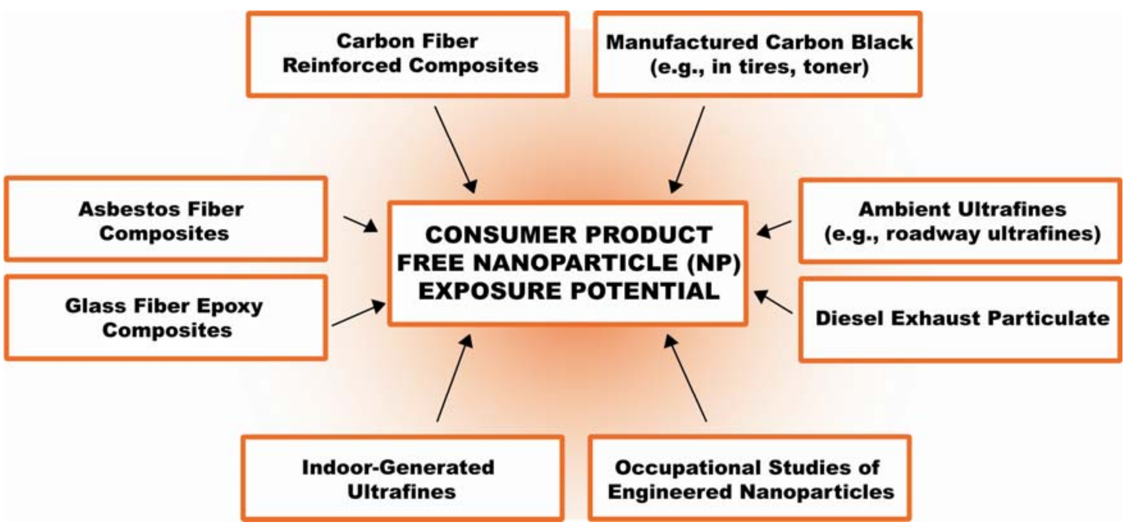


Figure 2. Utility of Bridging Information for Other Nano-sized Particles and for Similar Products



NSTI-Nanotech 2008, www.nsti.org, ISBN 978-1-4200-8504-4 Vol. 2

Figure 3. Sporting Good Nanocomposite Product Life-Cycle

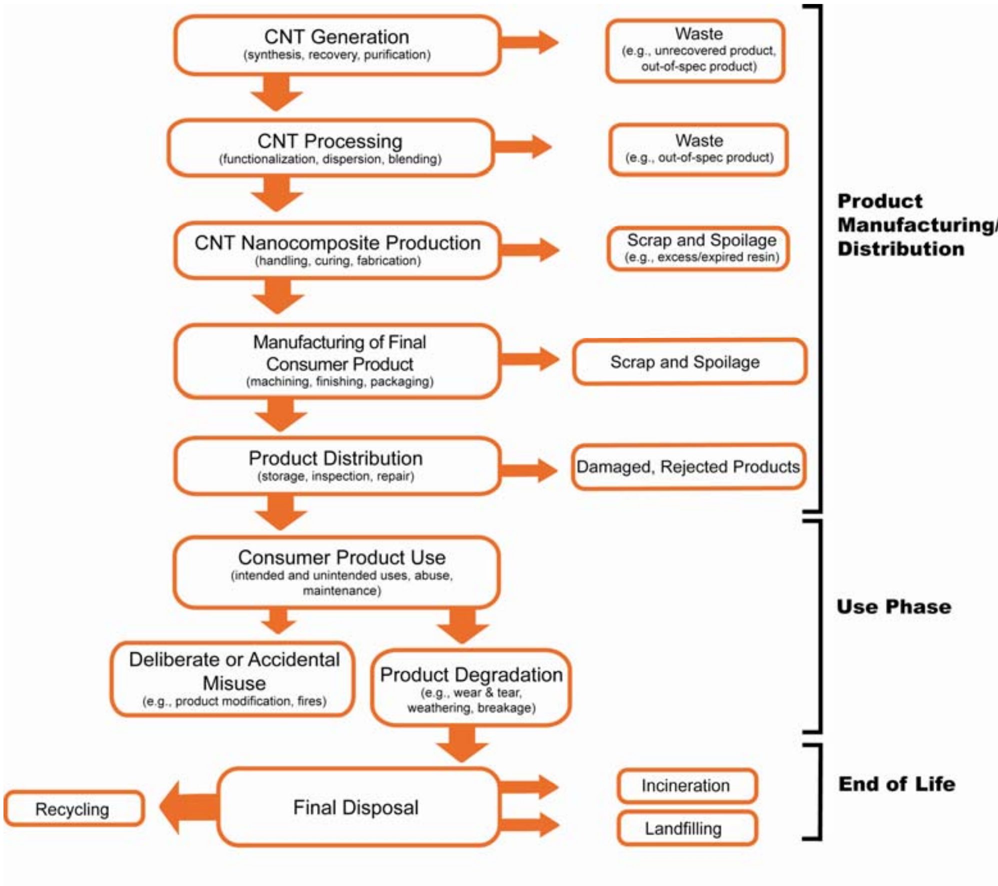


Table 1. Case Study Summary: Exposure Potential for Free CNTs Released from CNT Polymer Matrix Composite Consumer Sporting Goods

Life-Cycle Step	Qualitative Ranking of Exposure Potential	Basis
Typical Consumer Use	Low	CNTs in fixed form incorporated into solid product matrix; reportedly strong CNT-matrix interface
Deliberate or Accidental Consumer Misuse (*e.g.*, product modification, fire)	Uncertain	Potential for CNT release under some scenarios (e.g., fires), although lack of quantitative data
End-of-Life: Incineration	Uncertain	Uncertainty regarding extent of oxidation/combustion of CNTs under incinerator conditions; uncertain effects of particle controls
End-of-Life: Landfilling	Uncertain	Bridging data indicate breakdown of epoxy resin matrix; lack of CNT nanocomposite data and large uncertainty regarding environmental fate of released CNTs