Environment International 59 (2013) 1–11

Contents lists available at ScienceDirect

Environment International

journal homepage: www.elsevier.com/locate/envint

Review

Potential release scenarios for carbon nanotubes used in composites ☆

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ARTICLE INFO

Article history:
Received 12 December 2012
Accepted 16 April 2013
Available online 23 May 2013

Keywords:
Carbon nanotubes
Exposure
Release
Scenarios

ABSTRACT

The expected widespread use of carbon nanotube (CNT)-composites in consumer products calls for an assessment of the possible release and exposure to workers, consumers and the environment. Release of CNTs may occur at all steps in the life cycle of products, but to date only limited information is available about release of CNTs from actual products and articles. As a starting point for exposure assessment, exploring sources and pathways of release helps to identify relevant applications and situations where the environment and especially humans may encounter releases of CNTs. It is the aim of this review to identify various potential release scenarios for CNTs used in polymers and identify the greatest likelihood of release at the various stages throughout the life-cycle of the product. The available information on release of CNTs from products and articles is reviewed in a first part. In a second part nine relevant release scenarios are described in detail: injection molding, manufacturing, sports equipment, electronics, windmill blades, fuel system components, tires, textiles, incineration, and landfills. Release from products can potentially occur by two pathways; (a) where free CNTs are released directly, or more frequently (b) where the initial release is a particle with CNTs embedded in the matrix, potentially followed by the subsequent release of CNTs from the matrix.

The potential for release during manufacturing exists for all scenarios, however, this is also the situation when exposure can be best controlled. For most of the other life cycle stages and their corresponding release scenarios, potential release of CNTs can be considered to be low, but it cannot be excluded totally. Direct release to the environment is also considered to be very low for most scenarios except for the use of CNTs in tires where significant abrasion during use and release into the environment would occur. Also the possible future use of CNTs in textiles could result in consumer exposure. A possibility for significant release also exists during recycling operations when the polymers containing CNTs are handled together with other polymers and mainly occupational users would be exposed.

It can be concluded that in general, significant release of CNTs from products and articles is unlikely except in manufacturing and subsequent processing, tires, recycling, and potentially in textiles. However except for high energy machining processes, most likely the resulting exposure for these scenarios will be low and to a non-pristine form of CNTs. Actual exposure studies, which quantify the amount of material released should be conducted to provide further evidence for this conclusion.

Contents

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http://dx.doi.org/10.1016/j.envint.2013.04.003

1. Introduction

The prospective widespread usage of carbon nanotubes (CNTs) in industrial applications and consumer products and articles creates the potential for release of CNTs that could result in a possible increase of human and environmental exposure to CNTs (Gottschalk and Nowack, 2011; Koehler et al., 2008). As a starting point to exposure assessment, exploring sources and pathways of release helps to identify relevant applications and situations where humans or the environment may encounter releases of CNTs. By tracking the life cycle of products, it is possible to explore whether and in which situations a release of CNTs from applications may occur (Upadhyayula et al., 2012).

The focus of this review is on release as a prerequisite for exposure. Exposure scenarios are used to describe the conditions that may result in exposure, see for example the REACH definition of an exposure scenario: "Set of conditions, including operational conditions and risk management measures, that describe how the substance is manufactured or used during its life-cycle and how the manufacturer or importer controls, or recommends downstream users to control, exposures of humans and the environment" (ECHA, 2008).

A catalogue of generic and specific exposure scenarios (ESs) has been developed for engineered nanomaterials (ENM), taking into account the release scenarios over the entire life-cycle of these materials (Brouwer et al., 2010; Clark et al., 2012). For occupational exposure scenarios, published measurement data and contextual information were collected. These were reviewed to describe and characterize occupational exposure and the available tools and models to predict occupational exposure to the ENMs. For the development of generic exposure scenario descriptions, a library for the collection of exposure scenarios according to REACH Guidance was developed. From the 57 occupational exposure scenarios (Brouwer et al., 2010), 14 are related to carbon-based nanomaterials, generating 35 contributing exposure scenarios describing some facet of occupational exposure. Most of the ESs were from the production/synthesis of carbon-based nanomaterials or from handling materials (weighting, removing, sonication, etc.); two scenarios addressed tasks related to the machining of composites containing CNT.

Based on the process of developing these ESs, several main conclusions could be drawn (Clark et al., 2012): Most studies reported had an explorative character and were focused on concentration/emission analysis. Therefore, the reports from these studies did not include most of the information necessary to build ESs, e.g. amount used and frequency of activities. Basic characterization of the products used was often not available and operational conditions were often not described. Most concentration/emission-related measurement results were task-based. An important observation was the lack of harmonization of either the measurement strategy including distinction between manufactured nanoaerosols and 'background' aerosols, or the analysis and reporting of measurement data.

ENM-release during synthesis is best described by an emission factor (EF), which is defined as number, surface area and/or mass (volume) per unit of time released to the environment (Fissan and Horn, 2013). The ENM-release per unit of mass of produced material is best described by a release factor (RF), defined as number, surface area and/or mass (volume) per unit of mass of nanostructured material (Fissan and Horn, 2013). This depends on nanostructured material properties and the amount and kind of energy input during the different kinds of treatments of the material. The ENM emission and release factors can be considered to be important process and material properties, since without emission and release there is no exposure and therefore no risk.

An international Technical Specification has been developed in ISO/TC 229 "Nanotechnologies" and published by ISO, ISO/TS 12025:2012 "Nanomaterials — Quantification of nano-object release from powders by generation of aerosols". CNTs are included in the term nano-object, together with nanoparticles and nanoplatelets. This Technical Specification provides a methodology for the quantification of nano-object release from powders as a result of treatment, ranging from handling to high-energy dispersion, by measuring aerosols liberated after a defined aerosolization procedure. In addition to information in terms of mass, the aerosol is characterized for particle concentrations and size distributions. This Technical Specification provides information on factors to be considered when selecting from the available methods for powder sampling and treatment procedures and specifies minimum requirements for test sample preparation, test protocol development, measuring particle release and reporting data. In order to characterize the full size range of particles generated, the measurement of nano-objects as well as agglomerates and aggregates is recommended in this Technical Specification.

In the context of this review, we describe release scenarios as opposed to exposure scenarios. The definition of a release scenario is not unambiguous; however, for the purpose of this review a release scenario is defined as *the operational and or environmental conditions of any treatment or stress of CNTs or CNT composite material during all life-cycle phases that results into the release of CNTs/composite material into indoor environments, e.g. workplace, dwellings, and/or environmental compartments (air, water, soil and sediments), and the set of parameters to describe the type, form and magnitude of release*.

The aim of this review is to build release scenarios for CNTs in polymer composites. It focuses on multi-wall CNTs, which is the form of CNTs normally used in polymer composites. The general term "CNT" is used throughout the manuscript as a synonym for multi-wall CNTs. In a first part the available literature on release of CNTs is reviewed, in a second part nine relevant release scenarios are described in detail: Injection