Framework for Quantitative Exposure Assessment of Nanostructured Materials in Occupational Settings

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ABSTRACT

The first step in nanomaterial regulation is defining what constitutes a "nanomaterial". Most definitions focus on particle size; however, the applicability of these definitions is unclear for materials that aggregate/agglomerate to form larger particles in the ambient environment (e.g. nanostructured materials). This work proposes a framework understanding exposure to nanostructured materials, using carbon black and amorphous silica as examples. We review characteristics of these materials as used in the tire industry and the history of use with respect to health effects. Both carbon black and amorphous silica have a history of safe use and are used in a form (pellet) that should minimize exposure to nanoscale particles. While exposure to nanoscale particles of these materials is presumed to be negligible, there is no existing empirical evidence defining the distribution of particle size to which workers may be exposed. Thus, we reviewed available methods for nanomaterial sampling to identify the best suited equipment for exposure assessment and identified the low-pressure cascade impactor as the best method for understanding nanoscale exposure to specific particles in mixed-dust manufacturing environments. This approach may be applicable to industries looking to understand exposure to other nanostructured materials.

Keywords: carbon black, amorphous silica, exposure assessment, low pressure cascade impactor

1 INTRODUCTION

Nanomaterials are increasingly being incorporated into industrial processes and consumer products. The range of potential applications for nanomaterials spans from electronics to cosmetics and personal care products. In light of the science indicating the potential for nanomaterials to exhibit toxicity that is unique based on size, there is a growing need to regulate these materials to protect workers and consumers. However, in order to properly regulate these materials, a uniform definition of a "nanomaterial" must be established. The European Union was the first government body to establish a regulatory definition of a nanomaterial. According to their definition, any material that meets the following criteria will be considered a nanomaterial: "A natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm - 100 nm."

Though the European Union has established a definition for regulatory purposes, other proposed definitions are not as clear in distinguishing whether internal (primary particle) or external (aggregate or agglomerate) sizes should dictate whether the material is considered a nanomaterial. Nanostructured materials, or those materials that contain primary structures in the nanoscale (1-100 nm) but that aggregate and agglomerate to form larger structured particles, may require special consideration when determining how to regulate these materials, and whether they fall under certain definitions of a nanomaterial. In particular, one may consider whether the nanostructured material poses a unique risk based on structure or primary particle size, or whether there is a need for special regulation based on toxicological or exposure properties. In particular, tools used for exposure assessment of nanomaterials may not be ideal for evaluating potential exposure to nanostructured materials.

The purpose of the work presented here was to propose an approach for understanding the risks associated with nanostructured materials, with a particular focus on exposure assessment strategies. In developing a framework for evaluating nanostructured materials, we used as an example two nanostructured materials commonly used in the tire industry, carbon black and amorphous silica. In this report, we evaluate the known physical and toxicological properties of carbon black and amorphous silica and identify, given a range of possible options, the best suited exposure assessment methods for predicting exposure to these materials in an industrial setting, such as a tire manufacturing facility.

2 CARBON BLACK AND AMORPHOUS SILICA: REVIEW OF INFORMATION

2.1 Particle Size Characteristics

Characteristics such as particle size and shape are important considerations when deciding if a material will fall under the definition of a nanomaterial established by the European Union or other agencies. Furthermore, understanding the physical structure of a material will be critical to identifying the best methods for conducting exposure assessment on the material.

Amorphous precipitated silica, which is used as a filler for rubber in tires, is produced from vitreous silicate. The vitreous silicate is dissolved in water and transferred to a reactor out of which, through acidification and under agitation, amorphous silica is precipitated [1, 2]. During this precipitation there is an instantaneous formation of primary nanoscale particles (from approximately 2 to 40 nm) of a very short lifespan [1, 3]. These particles, however, immediately cluster to form non-dissociable aggregates (from approximately 100 to 500 nm in size) based on covalent bonds [3, 4]. Because of the nature of these bonds, these aggregates cannot deaggregate under normal manufacturing conditions [1]. The aggregates subsequently electrostatically bind together to form agglomerates from 1 to 40 μm [4]. Therefore, while amorphous silica has a primary structure that is based on nanoparticles, the aggregated and agglomerated particles are substantially larger.

Carbon black is similar to amorphous silica with respect to aggregation of primary particles and agglomeration of the aggregates during production processes. During the first split second of the combustion reaction, carbon nodules are formed with dimensions from approximately 5 to 100 nm, depending on the grade of carbon black to be produced [5]. However, the lifespan of these nodules is very short as they immediately cluster together to form aggregates of sizes between approximately 70 and 500 nm [5]. Because aggregation involves the formation of covalent bonds between primary particles, these bonds are not typically broken by physical means. In addition to aggregation, the aggregates are then subsequently combined together to form agglomerates after a few short seconds. The resulting agglomerates typically measure between 10 and 100 μm [6].

Based on this data, both carbon black and amorphous silica contain primary but not external structures in the nanoscale (Table 1). Thus, one would anticipate that worker exposure in a manufacturing setting such as a tire manufacturing plant would not result in nanoparticle exposures from carbon black or amorphous silica, and thus these materials would not require special regulation as nanomaterials.

Material	Primary Particle Size (nm)	Aggregate Size (nm)	Agglomerate Size (nm)
Amorphous Silica, precipitated	2 to 40	100 to 500	1,000-40,000
Carbon Black	5 to 100	70 to 500	10,000-100,000

Table 1: Summary of Physical Dimensions of Carbon Black and Amorphous Silica Structures

2.2 Toxicology

In addition to understanding physical characteristics of a given material, knowledge of the toxicological behavior of a material is important when predicting the potential for health risk and the likelihood of future regulation. Both amorphous silica and carbon black have a long history of safe use in the tire industry. Most forms of amorphous silica are considered to be of low toxicity by governmental agencies, including precipitated silica [7, 8]. In animal models, amorphous silica causes only a mild and transient inflammatory reaction that fully disappears upon cessation of exposure. There is no evidence of adverse response to amorphous silica exposure in exposed worker populations. In spite of the long history of safe use in industrial settings, emerging literature on "nano" amorphous silica suggests that nano-sized amorphous silicas may behave differently than bulk synthetic amorphous silica, such as that used in the tire industry [9-11].

The toxicology of carbon black has also been thoroughly reviewed by government agencies [12-14]. Carbon black causes a mild inflammatory response in the respiratory system of exposed animals following both short- and long-term exposures. However, in worker populations, carbon black has not been demonstrated to cause adverse health effects at exposure concentrations below 5 mg/m3. As with amorphous silica, literature on "nano" carbon black indicate a different toxicity profile associated with nanoscale particles of carbon black [15-17].

3 METHODS FOR EXPOSURE ASSESSMENT OF NANOPARTICLES

Though nanoscale particles of amorphous silica or carbon black are not expected to exist in manufacturing settings based on physical properties, to date, no empirical evidence is available to quantify exposure to nanoscale particles of carbon black or amorphous silica. Therefore, in determining the potential for risk associated with the use of these materials in the tire industry, a method must be developed for conducting exposure assessment for nanoscale particles of carbon black and amorphous silica.

Several challenges exist in conducting nanomaterial exposure assessment in environments where there are a variety of potential contributing materials. Traditional particle counting may not be sufficient, as it is not material-specific and cannot provide a quantitative estimate of exposure to single material entities. Therefore, we evaluated the literature to determine the best method for measuring exposure to nanoscale particles of carbon black and amorphous silica. The desired characteristics of a sampling methodology include: portability for sampling in manufacturing facilities; capability of distinguishing nanoscale particles from particles of larger sizes; ability to collect samples for chemical analysis by size fraction; and the ability to conduct microscopy.

Much of the available equipment with capability of detecting and quantifying exposure to nanoscale particles, such as particle counters (condensation and optical), or scanning mobility particle sizers (SMPS), do not allow for chemical speciation of the particulate and are thus not suitable for quantitative exposure assessment in mixed dust environments, such as a manufacturing facility (Table 2). Equipment such as the electrostatic precipitator, which allows for collection of samples for laboratory analysis, may not provide quantitative data for exposure assessment, such as particle number or mass of analyte. The best suited equipment for quantitative exposure assessment of nanoscale particles in a mixed dust environment are the low pressure impactors, such as the Electrical Low Pressure Impactor. (ELPI) manufactured by Dekati. This equipment provides both real-time particle

Method	Portable?	Measures particle #?	Differentiate by size and chemistry?	Measures real-time?	Types of post-sampling analysis	
					Microscopy	*Chemistry*
Particle Counters (CPC, OPC)	Yes	Yes	No	No	No	No
Scanning Mobility Particle Sizer (SMPS)	No	Yes	No	Yes	No	No
Electrostatic Precipitator	Not typically	Indirectly (microscopy)	Yes (via microscopy)	No	Yes	Yes, but not quantitative
Low pressure cascade impactor	Yes	Directly or indirectly (microscopy)	Yes	Yes for some models	Yes	Yes; qualitative and quantitative

Table 2: Summary of Selected Available Equipment for Nanomaterial Exposure Assessment

counting data and allows for subsequent off-line chemical analysis by size fraction of samples collected

4 CONCLUSIONS

In order to determine whether a nanomaterial or nanostructured material may represent a health risk, several pieces of information must be considered including physical characteristics, toxicity, and exposure. The methodology applied here represents a good framework for evaluating new or existing materials for potential risk and future regulation as nanomaterials. In this study, we reviewed the existing information on carbon black and amorphous silica using this framework. Based on existing information regarding toxicity and exposure potential, there appeared to be a low risk for adverse health outcomes from carbon black and amorphous silica exposure. However, given the emerging literature on toxicity of nanoscale particles and the absence of empirical data on exposure to nanoscale particles of these materials during tire manufacturing, additional exposure assessment may be warranted. In order to fill this data gap, we identified a strategy for quantitative nanomaterial exposure assessment using the low pressure cascade impactors. These impactors have great power to obtain critical information for quantitative nanomaterial exposure assessment, as they can provide data on chemistry, size, and particle number in a single sampling event. This framework and exposure assessment strategy can be applied to determine potential risks to both existing and new nanomaterials in industrial applications.

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