Health and Safety Screening of Advanced Materials: A User Interface for Test Design Selection and Documentation

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1 ABSTRACT

The novel properties of Advanced Materials (AdMs), including engineered nanomaterials (ENMs), offer new opportunities but uncertainty may place them into a higher Environmental Health and Safety (EHS) risk prioritization category, consequently delaying liability decisions and commercialization. To address this potential delay, we developed a tiered testing framework focused on release and exposure, since few comprehensive strategies were previously available. In this proceeding, the tiered testing and documentation process was demonstrated using a self-cleaning cement, a combustible casing material and temperature and moisture sensors. The process of evaluating these materials prompted a transition from a primary focus on "nano-scale" size to AdMs, which directs the question on whether unique properties cause uncertainty regarding EHS impact. The process and an associated tool were effective at prioritizing a large number of testing possibilities to a more feasible number of relevant tests, based upon predefined parameters.

Keywords: Nanomaterials, release testing, environmental health and safety, testing strategy, framework

2 INTRODUCTION

The novel properties of Advanced Materials (AdMs), including engineered nanomaterials (ENMs), offer opportunities to improve conventional products and create new material applications. However, these same properties may place AdMs into a higher risk prioritization category within the reformed Toxic Substances Control Act, now called the Lautenberg Chemical Safety Act (CSA). As with ENMs, the lack of specific Environmental Health and Safety (EHS) methods for characterizing the risk profile of emerging materials or new uses of conventional materials may delay regulatory and liability decisions and thus commercialization of AdMs. However, the CSA now seeks streamlining timely decisions by using tiered testing strategies, in addition to the risk prioritization process. To address this need prompted by the CSA, we published a tiered testing strategy [1] (Figure 1) for ENM-enabled products. The tiered strategy was previously employed using a nano-silver enabled, printed electrical circuit [2] that illuminated the ambiguity of definitions based exclusively on size, since in this case the hazard profile of the circuit was related to the released dissolved silver fraction, rather than a size-specific phenomenon. In this proceeding, three different case studies were executed to demonstrate the process and its application to AdMs. In each of the case studies, different release tests [3] were considered based on relevant use scenarios for the product. We previously demonstrated that the intended use of a ENM-enabled product is critical for determining what may be released into the environment using nanothermites [4,5]; in those studies, the ingredient ENM constituents sintered together outside the nano-scale range after combustion. These results inspired a transition of scope from a primary focus on "nano" size (1-100 nm definition [6]) to AdMs, which we define as "*materials that are intentionally engineered to exhibit novel or enhanced properties that confer superior performance relative to conventional materials*"; as a result of their unique characteristics and properties, AdMs have an uncertain EHS risk profile with the greatest need to focus on materials that have inherent hazard, secondarily produce something hazardous or have a unique property or exposure profile not previously characterized.

3 MATERIALS AND METHODS

3.1 Tiered testing framework

Decisions on the most relevant testing strategies and methods were made using the 5-tiered testing framework we previously published [1]. Briefly, the first tier involves defining if the material is nano-scale and if it has unique properties, then categorizing the nano-enabled product by its structure (e.g., free particles vs. composites). Tier 2 involves determining the relevant use of the enabled product and establishing the most relevant release tests to determine exposure pathways. Tier 3 assesses the fate and persistence of the material in relevant media. Tiers 4 and 5 determine the hazard of the material. To navigate the tiers, a visual basic tool was coded in Microsoft Excel, refered to as Nano Guidance for Risk-Informed Deployment (NanoGRID).

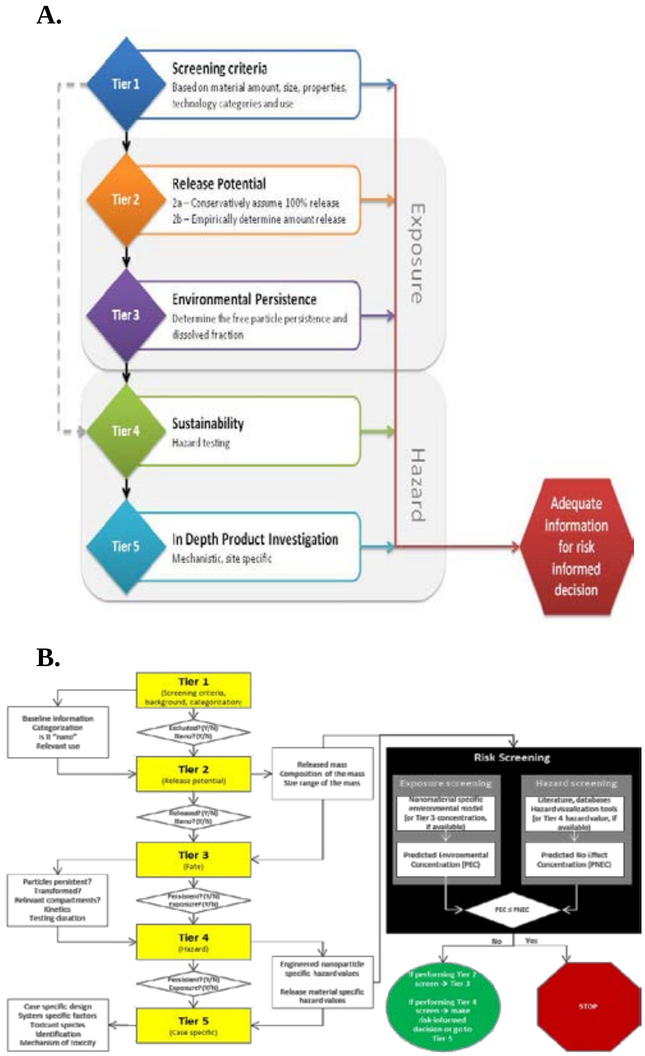

Figure 1. Summary of the tiered testing process modified from Collier et al. [1] (A) and a comprehensive screening approach being developed into standard guidance (B).

3.2 Case study materials

Three different ENM-enabled technologies were tested to demonstrate the framework. The first was a self-cleaning cement that relies on the photocatalytic properties of nano-TiO_2 to keep a pristine appearance. The second was a foamed nitrocellulose-based combustible casing material that also includes camphor and akardite-II to provide a hydrophobic property to protect munitions from moisture. The third considered temperature and humidity sensors containing carbon nanotubes (CNTs) that can monitor conditions in potentially harsh environments (e.g., water, soils) in near-real time.

3.3 Tier 1: Material categorization

Test materials were categorized by their structure, based on previous work [7]. Further, their potential for unique (previously undescribed) properties was considered using a dichotomous key (ERDC, unpublished) to identify each enabled product as a ENM, AdM or conventional material, thus facilitating the prioritization process.

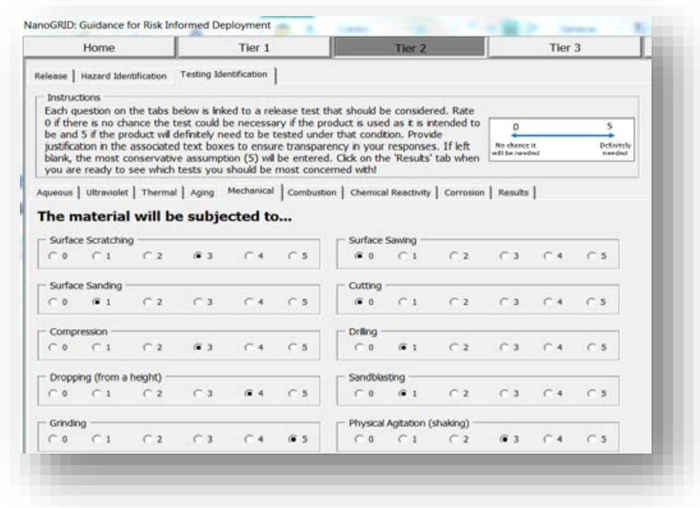

Figure 2. Example of relevant ranking of different environmental release scenarios using the NanoGRID tool.

3.4 Tier 2: Release relevance and ranking

NanoGRID was employed to design a relevant test strategy based on a use scenario for each of the case study materials. The TiO_2-cement in-use application involved coating a seawall that was exposed to periodic sunlight, water submersion and abrasion via boat rubrails. The energetic casing in-use application involved incremental exposure to water, humidity, and partial burning upon ignition. The CNT sensor hypothetical in-use application was outside deployment to measure temperature and moisture in air and in soil, subjecting it to temperature flux, periodic UV exposure, and abrasion from soil particles.

Environmental release scenarios including exposure to aqueous media, ultraviolent (UV) light, thermal and mechanical stress, aging, combustion, chemical reactivity, and corrosion were ranked 1 (least relevant) to 5 (most relevant) using NanoGRID (Figure 2). Analysis time, cost, complexity, and the need to test worst case scenarios were also weighted by importance for the TiO_2-cement (0.2, 0.15, 0.15, 0.5, respectively), energetic casing (0.125, 0.25, 0.125, 0.5, respectively) and CNT-sensors (0.0625, 0.125, 0.0625 and 0.75, respectively) using Multi-Criteria Decision Analysis (MCDA). The result was graphically visualized to select the most impactful, and practical release testing strategy, including combinational testing (e.g., UV-light exposure then abrasion).

4 RESULTS AND DISCUSSION

4.1 TiO_2-cement

The cement material was categorized as a 3-dimensional suspended solid object that has potential to release ENMs under certain environmental triggers. The TiO_2 used in the cement was nano-scale, as determined by scanning electron microscopy (SEM) and volume specific surface area [8]. Based on the in-use scenario described above, a release testing strategy was established to investigate the most relevant release triggers: combinations of (1) UV-exposure then aqueous exposure and (2) UV-exposure then abrasion (Figure 3). Pristine TiO_2 (P25, Evonik Industries AG, Essen Germany), used as a positive control, and the matrix bound TiO_2 were anatase and had photocatalytic properties. Tier 3 testing indicated rapid agglomeration and settling for pristine TiO_2 and the released cementatious material. The hazard of pristine TiO_2 to *Ceriodaphnia dubia* increased almost 100-fold from 2.5 to 0.03 mg/L in presence of continuous UV-light, likely due to short lived free radicals. Provided only acute data for one species were available in this study, a conservative safety factor of 1000 was used to generate PNEC values [9] of 0.0025 and 0.0003 mg/L for non-photo-oxidized and photo-oxidized TiO_2, respectively. Considering the rapid settling of this material, its persistence in waters with sufficient UV penetration may be short lived. A pronounced increase in photo-induced toxicity was not observed for the weathered, abraded and released material from the actual cement, for which the initial alkaline conditions associated with cement itself were of greatest acute consequence.

4.2 Energetic casing

The energetic casing was defined as an AdM due to its improved hydrophobic property over conventional casing. Although it had no intentional nano-dimensionality and the parent material itself was comprised predominantly of cellulose, which has low hazard/risk [10,11], the unique combination of three conventional materials to achieve hydrophobicity, in addition to the high-energy release via burning could constitute novel release potential. The relevance of different release tests were ranked via NanoGRID and the four highest ranked tests were selected (UV/abrasion, UV/water submersion, water/abrasion and burning), graphically represented in Figure 4. Abrasion testing indicated effectively no release of nano-scale aerosol particles. While the material released from abrasion resulted in little exposure or hazard in water up to the OECD limit test concentration of 100 mg/L [12], a statistically significant reproductive effect on *C. dubia* was observed for the spent (burnt) material at a relatively high concentration (23 mg/L). Using a modeled 10% inhibition concentration for survival of 15.2 mg/L and a conservative safety factor of 100 [9], any environmental concentration below of probable no effect concentration (PNEC) of 0.15 mg/L is unlikely to cause environmental risk.

4.3 Sensor

The ink used to print the CNT sensor was categorized as a fluid suspended nano-object, making it applicable to nano-specific testing. The printed sensor was categorized as a surface-bound nano object for which a potential exists for particles to break off or become released with certain triggers. However, it should be recognized that the CNTs are encased in multiple layers of filter and encapsulant materials within the actual sensor product, limiting direct exposure to environmental conditions. A worst-case release testing strategy was developed (Figure 5), and the selected release tests were UV/corrosion, UV/rainfall, thermal/rainfall, and grinding/abrasion. Preliminary testing is underway.

A.

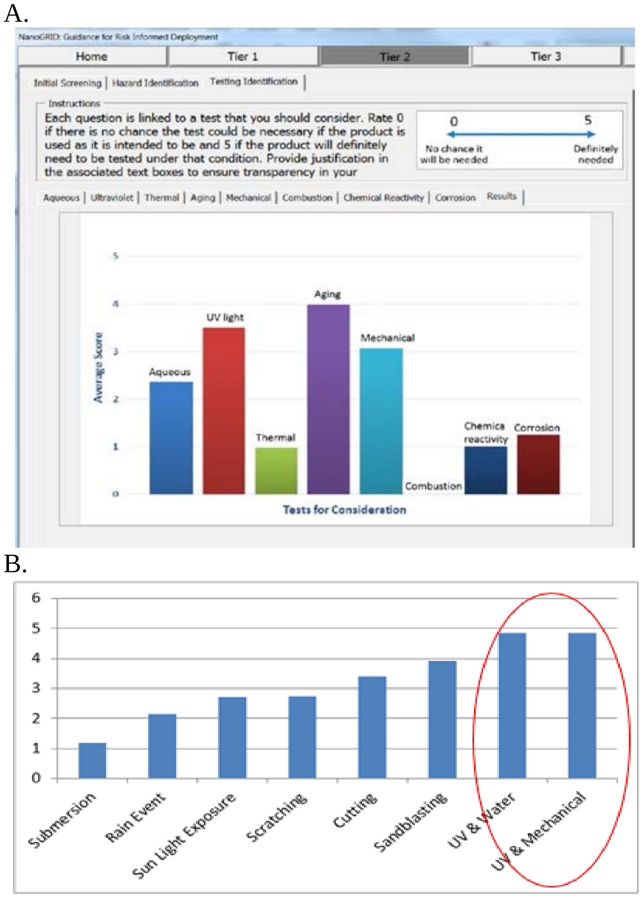

Figure 3. Testing prioritization for the TiO_2 concrete by relevance alone (A) and MCDA considering combinational testing (B).

A.

B.

Figure 4. Testing prioritization for the combustible casing by relevance alone (A) and MCDA considering combinational testing (B).

A.

B.

Figure 5. Testing prioritization for the temperature and moisture sensor by relevance alone (A) and MCDA considering combinational testing (B).

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TechConnect Briefs 2017, TechConnect.org, ISBN 978-0-9975117-8-9