

## **REVIEW OF RELEASE FROM SOLIDS EMBEDDED OR COATED WITH NANOMATERIALS**

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### **EXECUTIVE SUMMARY**

There is considerable interest in engineered nanomaterials. The novel physio-chemical properties of these materials can significantly improve a broad range of products, from targeted therapeutics to industrial materials. While several lines of research have improved our understanding of nanomaterial properties and their potential applications, other research efforts have focused on elucidating possible hazards and scenarios that could lead to harmful effects. However, major data gaps exist on the potential for nanoparticle release from products where nanomaterials have been embedded or coated onto a solid product. Such information is critical for conducting real-world assessments of risk.

At the time of writing, there were over 3,500 studies that investigated nanoparticle release. However, nearly all of these research efforts focused on release in a targeted drug therapy context and less than 20 focused on release from consumer products. Consumer products that contain or are coated with nanomaterials are referred to herein as carrier systems, which may contain any number of material combinations. The release studies found to date, investigated release from product coatings, fire retardants and fabrics, that contain a range of nanomaterials: carbon nanotubes, carbon black, graphite, carbon nanofibers, titania, zinc oxide, iron oxide, and silver. Based on the findings of these studies, a few common themes are beginning to emerge.

- Each of the release scenarios tested resulted in measurable particle emission, but release was not correlated to the presence or absence of nanoparticles in the carrier system.
- Under some circumstances the majority of released particles are nanoscale, while under others most release particles are greater than 100nm.
- The composition (e.g. polymers, textiles) of the carrier system and the nanoparticle used, and the methods employed to bind the nanoparticles to the carrier appear to significantly influence release rates and quantities.
- It appears rare to observe individual nanoparticles released from their carrier system under any of the release scenarios.

The dearth of rigorous study into release from consumer products made with nanomaterials represents a considerable data gap that warrants rigorous investigation. Filling this gap not only helps elucidate when and how release may occur, but it could bring critical insights to research on particle fate, transport, transformation, and effects. To move our understanding of release forward, three key recommendations are suggested.

1. Identify priority nanomaterials and carrier systems for further investigation.
2. Avoid the limitations illustrated by previous studies by:
  - Combining the strengths of multiple research centers.

- Developing “best practice” methods to induce, measure and characterize release.
  - Demonstrate the reproducibility of source terms, methodologies and results.
  - Build a depth of understanding by investigating nanomaterials that are representative of a class.
3. Build upon identified “best practices” by using these to develop international standards.

## **1. INTRODUCTION**

Engineered nanomaterials are typically defined as having at least one dimension less than approximately 100nm and exist in a wide range of forms: rods, spheres, sheets, wires and more elaborate structures like capsules (ISO/TS 80004-1:2010). An early overview report of the field by the Royal Society and Royal Academy of Engineering (2004) presents the broad scope of general interest in these structures. Commercial interest in nanomaterials is because the often novel physio-chemical properties can be used to improve a broad range of applications from targeted medicines to the construction materials (Maynard, 2007; Lee et al, 2010; van Broekhuizen et al, 2011). While several lines of research have improved our understanding of nanomaterial properties and their potential applications, other research efforts have focused on elucidating the possible harmful effects of nanomaterials. Indeed, over the past decade considerable attention has been directed toward clarifying the potential hazards that nanoparticles could pose given their roles in causing cellular damage in laboratory settings.

In terms of products where nanomaterials have been embedded or coated onto a solid, nanoparticle release would be an initial step in most exposure scenarios. A clear understanding of release, could be informative for both product development and risk assessment. The focus of this review is on the research efforts to understand, characterize and measure the release of nanomaterials from solid carrier systems.

Understanding the release from products is a standard component of regulatory review processes for product approval and safe handling practices. Investigating and developing methods to characterize the conditions of release has been an active field of research for decades. However, the unique nano-properties of many nanomaterials may require a re-examination of the methods used to assess hazards (Mittal, 2010). At present, only a few release studies specifically investigating carrier systems that are either doped with engineered nanoparticles or contain none have been performed. The authors report release of ultra-fine wear particles from all of these carrier systems in response to various release scenarios. The wear particles from carrier systems doped with engineered nanoparticles often contain those nanoparticles embedded within the released wear particle, but the release of wear particles is not correlated with the presence of engineered nanoparticles.

## **2. NANOMATERIALS AND ULTRA-FINES**

Engineered nanomaterials and many ultra-fine particles overlap in terms of size. In the context of this review, ultra-fine particles are considered non-engineered particles, while nanomaterials and nanoparticles are intentionally engineered (ISO/TS 27687:2008).

## **3. SCOPE**

This review discusses studies investigating release from solid consumer products containing nanomaterials. At the time of writing, there were over 3,500 studies that investigated nanoparticle release. However, nearly all of these research efforts focused on release in a targeted therapy context and fall outside the scope of this review. There are less than 20 studies within the scope of this paper (see Appendix A). These studies have investigated release from coatings, fire retardants and fabrics, containing a range of

nanomaterials: carbon nanotubes, carbon black, graphite, carbon nano-fibers, titania, zinc oxide, iron oxide, and silver. Additional relevant studies that have investigated changes in structural integrity from the addition of nano silica, alumina and silver have been included, although these studies do not directly examine release.

#### **4. CARBONACEOUS NANOMATERIALS**

The types of nanomaterials made from carbon atoms are numerous. The assembly, possible applications and potential hazards of carbonaceous nanomaterials have been the subject of numerous reviews (Aschberger et al, 2010). Although several reviews highlight the need to better understand release potential, there remains a dearth of information. At the time of writing, the four publicly available studies investigating release from carbonaceous materials were found and are discussed in the following sub-sections.

##### **4.1 CARBON NANOTUBES (CNTs)**

In a recent paper, Köhler et al (2008) considered two consumer products likely to contain CNTs, synthetic textiles and lithium-ion batteries. Based on their theoretical experiment, the authors draw the conclusion that CNT release should not only be considered in the context of workplace inhalation during product assembly, but also in relation to consumer product use and disposal. Despite the strength of the authors' argument, no consumer product release studies yet exist. Bello and colleagues (2009) were the first group to investigate release during abrasive processing of polymer composites that contain CNTs.

##### ***Release from Abrasion***

Both thermoset and thermoplastic polymers are the most common carrier matrices used to incorporate CNTs (Bello et al, 2009). Typical processing begins with curing the nanocomposite, followed by subsequent processing with abrasion (e.g. cutting, drilling and sanding), which places workers at a potential risk for inhalation of released nanoscale particles. Although several studies have examined the cytotoxic effects of CNTs (e.g. Donaldson et al, 1998, 2006; Lam et al, 2004, 2006; Poland et al, 2008), only a limited set of studies have explored the release of particles during CNT synthesis (Methner et al, 2007; Han et al, 2008), and only one study has examined release during abrasive processing of a solid matrix (Bello et al, 2009).

Bello et al (2009) used two carrier matrices in their study, an epoxy resin layer laminate with CNTs (CNT-carbon) and an alumina ( $\text{Al}_2\text{O}_3$ ) fiber cloth with CNTs impregnated with an epoxy (CNT-alumina). Multiple samples, with variable thicknesses (1-4 layers) were made and machine cut with either a band-saw or rotary cutting wheel in a research laboratory setting. Release measurements were taken over the course of 3 – 5 'cuts' per matrix, on three separate occasions over the course of a year.

The authors' report band-saw dry-cutting generated the greatest amount of ultra-fine particle release, regardless of composite type or the presence or absence of CNTs. In contrast, wet cutting generated a limited amount of aerosolized ultra-fine particle. Overall, dry cutting aerosolized particle fractions were found to be 71-89% in the 1-10 $\mu\text{m}$  range, 6-25% in the 0.1-1 $\mu\text{m}$  range with only 1-10% in the <100nm size range.

Subsequent transmission electron microscope (TEM) and scanning electron microscope (SEM) analysis revealed numerous submicron sized fibers, although no clearly identifiable CNT structures or bundles were observed. Although there was no correlation between the presence of CNTs and the generation of ultra-fine particles during cutting, the authors report a rough correlation between particle generation and the thickness of the test matrix. The four-ply (2.9mm thick) base-alumina composite generated the most, while the 1-ply (0.6mm thick) CNT-alumina composite generated the least. Without further elaboration, the authors do note that they often observed fibers with a diameter of 5-20nm under SEM, however they could not further quantify the structures.

The authors acknowledge several limitations of this study. First the fabrication of the test composites changed over the course of the study. Second, the experimental design changed from one visit to the next, and was modified based on the preliminary findings of the previous visit. Third, the study was focused on exposure to nanoscale particles, of which significant amounts were generated by cutting, but not on quantitative analysis of the nanoscale materials produced. This last limitation is important in the context of this review. As will be addressed more carefully in the summary of findings, several other studies have identified the generation of fine, ultra-fine and nanoscale particles in response to abrasion and weathering (Hsu and Chein, 2007; Kaegi et al, 2008; Koponen et al, 2009; Vorbau et al, 2009; Gohler et al, 2010).

#### **4.2 CARBON BLACK**

Koponen and colleagues (2009) were the first to specifically investigate release from paints containing nanoparticles in response to sanding. The authors obtained medium density fiberboard plates from the Danish paint industry and report their findings comparing test paints (containing engineered nanoparticles) and reference paints (control). A total of four plates were examined; two were coated with control paints, one was doped with 95nm carbon black and the other with 17nm TiO<sub>2</sub> nanoparticles. The results related to n-TiO<sub>2</sub> are discussed fully under section **5.1 Titania**. The authors did not provide additional details about the nanoparticles or the paints.

Previous studies showing that sanding generates large quantities of fine particle dust have focused on testing containment systems to reduce worker inhalation (e.g. Thorpe and Brown, 1994; Choe et al 2000; Scholz et al, 2002). In this study, the authors used an experimental design to allow measurement of wear particle size and concentration. A hand held orbital sander was used to abrade the surface of the paints and the exhaust from the sander was directed via tubing to a dust reservoir permitting aerosol particle sizer (APS) and fast mobility particle sizer (FMPS) measurement. The authors report that nanoscale and ultra-fine particles were emitted as a result of sanding, regardless of the paint sample (control or doped with carbon black).

The authors fitted the data to a five modal distribution curve based on released particle diameter. The smallest two peaks were <20nm, the middle peak was about 200nm and the largest two were 1 and 2µm. Because the experimental design used here did not separate emissions from the sander motor from the dust reservoir, the authors attribute aerosolized particles <50nm to the electrical motor itself. This assertion is based on running the

sander motor and measuring its emissions and from another study by Szymanczak et al (2007), which reported that electrical motors are a major source of particles smaller than 100nm. The authors attribute the 200nm mode to a combination of sander and paint dust, while the largest two modes are considered to contain mostly paint dust. The authors report that nanoparticles of carbon black were not released individually. In addition, the authors were able to conclude that there was no correlation found between the presence of carbon black nanoparticles and the release of nano-scale or ultra-fine particulates in response to sanding.

### **4.3 GRAPHITE**

Efforts to reduce the flammability of industrial and consumer products have resulted in investigations of the potential of flame resistant nano-composites. Researchers have shown nano-clays and nano-graphite / polymer composites to exhibit significant resistance to fire without compromising other physical attributes of the polymer used (Nyden and Gilman, 1997). However, the incineration of such composites presents a likely release scenario. Nyden and Gilman (1997) were the first to analyze mass-loss from polypropylene/graphite nano-composites resulting from “fire-like” heat fluxes. The authors report that the nano-composite undergoes a change from a delaminated structure to an intercalated structure in response to heat exposure. This change increases, rather than decreases, the nano-composites’ stability, reduces its flammability and dramatically reduces the mass-loss compared to other structures. Subsequent TEM examination of the remaining char reveals the structural change in the nano-composite. Although these results indicate a potential reduction in release, this was not specifically addressed for the smoke or the remaining char.

### **4.4 CARBON NANO-FIBERS (CNFs)**

Another nanomaterial with potential as an effective fire retardant are carbon nano-fibers. Nyden and Uddin presented findings from a study they conducted on the effects of adding nano-fibers to polyurethane foam. The authors report that no CNF were detected in the emitted smoke and suggest that any released CNFs were most likely destroyed during thermal decomposition, which was estimated to have a flame temperature in excess of 1200°C. The authors report previously observing CNF decomposition at 650°C. However, analysis of the remaining char revealed the presence of CNFs. Agitation of the char was reported to induce ultra-fine particle release in the range of  $6000\mu\text{m}^2/\text{cm}^3$  –  $14,000\mu\text{m}^2/\text{cm}^3$ , considerably higher than background levels  $\sim 3\mu\text{m}^2/\text{cm}^3$ . Nyden and Uddin conclude in their presentation that CNF release after incineration is most likely from the residual char, rather than from the smoke. However, the authors did not report further analysis of the char to indicate the presence or absence of dissociated or bundled CNFs.

### ***Summary of Carbonaceous Material Release Studies***

A few release studies have been found that investigate the potential for release from carbonaceous nanomaterials. In abrasion studies, authors reported particle release. In one study the bulk (70-90%) of the released particles were 1-10 $\mu\text{m}$  in size with less than 10% 100nm or smaller. In the other study, the authors reported particle emission to be multi-

modal, with considerable contribution to release from the sander's motor. In both studies, the authors reported individual nanoparticles were not released.

During the incineration studies, nanoparticles were not reported in the smoke. Instead, the authors report in both studies that the engineered nanomaterials were present in the remaining char. In the study one study, the authors report increased stability of the nanocomposite, while in the other, the authors report decreased stability after incineration. However, neither study further characterized the engineered nanomaterials remaining in the char. Despite the complexity and variability of carbonaceous nanomaterials, considerably more release research would need to be conducted to elucidate the differences found among these studies.

## **5. Metals and Metal Oxides**

In 2004, Warheit raised awareness that inhalation toxicity of nanoparticles was primarily based on fine particles of three types; diesel particulates, titania and carbon black (Warheit, 2004). More recently, some attention has been focused on resolving this data gap (Soto et al, 2005; Jeng and Swanson, 2006; Soto et al, 2007; Karlsson et al, 2008; Xia et al, 2008; Puzyn et al, 2011). However, the dearth of rigorous investigations into release indicates that there is an important data gap in understanding when products containing nanomaterials may present exposure hazards during the product life cycle. The following sections discuss in more detail the ten release studies that have been found that focus on nano-metals and nano-metal oxides: three studies are on titania (n-TiO<sub>2</sub>), two studies are on zinc oxide (n-ZnO), one study is on iron oxide (n-Fe<sub>2</sub>O<sub>3</sub>) and four studies are on silver (n-Ag). At the time of writing, there have been no studies identified that directly examine release from carrier systems containing silica (n-SiO<sub>2</sub>), alumina (n-Al<sub>2</sub>O<sub>3</sub>), cerium oxide (n-CeO<sub>2</sub>) or copper (n-Cu). Despite the lack of studies on a broad range of nano-metals and metal oxides, the studies conducted to date have typically focused on the nanomaterials in greatest production volume; nanoscale n-TiO<sub>2</sub>, n-Ag, n-ZnO, n-SiO<sub>2</sub> and n-Al<sub>2</sub>O<sub>3</sub> (Xia et al, 2008; Lee et al, 2010).

### **5.1 TITANIA (n-TiO<sub>2</sub>)**

Coatings on wood, glass, polymers and tile often contain n-TiO<sub>2</sub> particles as additives to improve scratch resistance and enhanced "self-cleaning" in response to ultraviolet (UV) light exposure (Bauer et al 2002; Reijnders, 2009). Although using n-TiO<sub>2</sub> as a filler improves durability, Bauer et al (2002) report that in a panel of nano-polyacrylate composites, the coating containing 27% n-titania was least resistant to abrasion caused by a standardized method using the Taber Abraser (ISO 5470-1:1999). Three other nanocomposites, containing 35% SiO<sub>2</sub>, 35% Al<sub>2</sub>O<sub>3</sub>, or 29% ZrO<sub>2</sub> were more durable.

#### ***Release from Abrasion***

As mentioned earlier in section **4.2 Carbon Black**, Koponen and colleagues (2009) were the first to specifically investigate release from paints containing nanoparticles in response to sanding. The authors obtained medium density fiberboard plates from the Danish paint industry and report their findings from sanding four plates; two coated with control paints, one doped with 17nm TiO<sub>2</sub> and the other doped with 95nm carbon black nanoparticles. The results related to n-TiO<sub>2</sub> are discussed here.

Briefly, the authors used an experimental design for this investigation to allow measurement of wear particle size and concentration resulting from sanding. A hand held orbital sander was used to abrade the surface of the paints and the exhaust from the sander was directed via tubing to a dust reservoir permitting aerosol particle sizer (APS) and fast mobility particle sizer (FMPS) measurement. The authors report that nanoscale and ultra-fine particles were emitted as a result of sanding, regardless of the paint sample (control or doped with n-TiO<sub>2</sub>).

As discussed earlier, the authors fitted the data to a five modal distribution curve based on released particle diameter. The smallest two peaks were <20nm, the middle peak was about 200nm and the largest two were 1 and 2µm. Because the experimental design used here did not separate emissions from the sander motor from the dust reservoir, the authors attribute aerosolized particles <50nm to the electrical motor itself. The authors attribute the 200nm mode to a combination of sander and paint dust, while the largest two modes are considered to contain mostly paint dust. The authors reported that nanoparticles of TiO<sub>2</sub> were not released individually. In addition, the authors concluded that there was no correlation between the presence of titania nanoparticles and the release of nano-scale or ultra-fine particulates in response to sanding.

### ***Release from Weathering***

To better understand the potential for human and environmental exposure to n-TiO<sub>2</sub> particle release, Hsu and Chein (2007) investigated coatings subjected to simulations of wind, sun and human contact. A laboratory-produced coating containing 5%, by weight, polycrystalline anatase n-TiO<sub>2</sub> was sprayed onto wood plate and polyethylene terephthalate (PET) polymer film samples. The second coating, a commercially available photo catalytic paint containing n-TiO<sub>2</sub> was applied to a ceramic tile sample. Additional details about the titania were not provided. Each sample was placed into a simulation box for a continuous two-hour exposure to UV or fluorescent light (sunlight) and fan (wind) with intermittent scraping by a rubber knife (1 minute of scraping every 10 minutes) to simulate human contact. The authors report nano-scale particle release from each of the samples during the course of the experiment, and note differences in response to both substrate and light source.

The wood samples were exposed to both the UV and fluorescent lamps, which revealed differences in the rate and concentration of released particles. The fluorescent light dramatically reduced both, without significantly affecting the median diameter (8.1 – 213.7nm) of the released nanoparticles. In addition, the authors highlight the apparently poor binding characteristics of the tile. However this is difficult to assess because the commercially available paint was not applied to the wood or PET film, and the lab-produced coating was not applied to the tile. Nonetheless, during the entire course of the 2-hour experiment, the rate of particle release from the tile continued to increase, which was not the case for any of the other samples.

Unfortunately, Hsu and Chein (2007) did not perform any analysis of the characteristics of the release particles through SEM or TEM. This could have been informative since

this study was the only to combine abrasion and weathering. In abrasion-only studies where such analysis was performed (Koponen et al, 2009; Vorbau et al, 2009; Göhler et al 2010), the released wear particles were always found to be a composite of coating with embedded nanoparticles. However, in the only other weathering release study conducted on n-TiO<sub>2</sub> paints, Kaegi et al (2008) report finding both individual n-TiO<sub>2</sub> particles and agglomerates of a few particles.

Kaegi and colleagues (2008) compared rainwater runoff from a model façade (new) and building façade (aged) painted with the same exterior paint containing 20-200nm n-TiO<sub>2</sub> particles. Prior to the experiment, the building's façade was exposed to natural weathering for two years. Water runoff samples were collected from below both the model and building façades, and further down stream as urban runoff, after complete rain events. Before analysis, the water samples were centrifuged to remove any particulates greater than ~300nm. Subsequent centrifugation was used to quantify the concentration of particles <300nm and follow up bulk chemical analysis was performed with inductive coupled plasma mass spectrometry (ICP-MS) and inductive coupled plasma optical transmission (ICP-OES). Examination of samples under TEM and SEM permitted further characterization of the released particles.

The authors reported identifying loosely bound n-TiO<sub>2</sub> in paint samples from both the new and aged façades, but suggest there were fewer nano-titania present in the aged paint. Analysis of the water runoff samples from both the new and aged façades revealed individual and clumped titania nanoparticles with diameters of roughly 150nm partially embedded in an organic matrix. In contrast, urban runoff samples obtained further away from the façades were shown to contain n-TiO<sub>2</sub> as single particles or in agglomerates of single particles. In addition to characterizing the released nanoparticles, the authors measured their concentration in the water samples. Mass concentrations of nano-titania in the water runoff were reported to be ~600 µg/L released from the model facade, ~350 µg/L released from the aged façade and ~16 µg/L in the urban runoff. Based on these measurements, and the fact that 85-90% of the n-TiO<sub>2</sub> particles were between 20-300nm, the authors estimate  $3.5 \times 10^8$  nano-scale particles/L in urban runoff.

### ***Summary of n-TiO<sub>2</sub> Release Studies***

Three studies were found each examining n-TiO<sub>2</sub> release from paints. One study investigated release from abrasion, while the other two explored release due to weathering/wear. Because of a confounded experimental design and lack of released particle characterization in the abrasion study, the results are difficult to interpret. Sufficient to say, ultra-fine particles were released during abrasion, but their source could have been the sander motor and/or the paints.

The weathering/wear studies were performed either in a laboratory simulation or outside in an urban setting. The authors of both studies report that detectable levels of nano-scale particles were released during their investigations. Characterization of the released particles in the outside study differed depending on how far away from the source (façade) samples were collected. Samples collected at the base of the façade contained nanoparticles of n-TiO<sub>2</sub> embedded in the released particles, very similar to the findings

reported by other studies. However, samples of urban runoff, collected further away from the source, appeared to contain dissociated and clumped nanoparticles of n-TiO<sub>2</sub>. The authors presume the observed n-TiO<sub>2</sub> was released from the source material, but this was not confirmed. Nonetheless, these studies provide useful insights and should prompt more rigorous follow up investigations.

## **5.2 SILICA DIOXIDE (n-SiO<sub>2</sub>)**

The benefits of silica nanoparticles as an additive to paint (Mizutani et al, 2006), dental polymers (Devaprakasam et al, 2008; Ahn et al, 2009) and polymeric coatings (Gläsel et al, 2000; Bauer et al, 2002) have been demonstrated by a number of studies testing composite structural integrity. However, none of these, nor any other studies have been found that directly examine release of n-SiO<sub>2</sub>. Given the wide spread use of silica nanoparticles as a filler, the dearth of studies examining release is alarming. Although none of the following studies should be considered rigorous release studies, they are informative in that they indicate a potential for release of n-SiO<sub>2</sub>.

### ***Emulsion Paints***

In a recent study by Mizutani et al (2006), the effectiveness of using nano-silica as an additive to interior paint was examined. The nano-composite emulsion (NCE) paint containing 1:1 silica and acrylic resin was prepared by the copolymerization of two acrylic monomers (methyl methacrylate and *n*-butyl acrylate) in the presence of silica sol. The resulting paint was spray applied to soft steel, glass and slate plates. The authors report improvements in terms of solvent, heat, water and pollution resistance, when compared to other standard wall paints. In terms of predicting the potential for release based on this study, the hardness, adhesion and gloss tests are helpful indicators. The authors report the NCE exhibited a mid-level of hardness when compared to the other paints and reduced gloss. The authors suggest the decreased gloss is a result of increased surface roughness due to the presence of the n-SiO<sub>2</sub>. Together, the decreased hardness and increased roughness of the NCE paint may result in an increased potential for release under suitable conditions.

### ***Coatings***

Two studies investigating the abrasion resistance of polymeric composites containing n-SiO<sub>2</sub> are discussed here (Gläsel et al, 2000; Baurer et al, 2002). While neither investigated release, both used standardized abrasion tests (Taber Abraser and micro-scratch test (MST)) that could be useful in subsequent release studies.

Gläsel et al (2000) prepared polymeric nano-composites with up to 35% (by weight) silica nano-powders (30-40nm) and applied a thin coating (10-100µm) on glass, paper, wood and polymer plates. The Taber Abraser test was used to induce haze, measured as a percent, on the polymer films coated on paper. The authors report the pure polymer film (without n-SiO<sub>2</sub> filler) had the highest percent haze (23) after the fewest abrasive rotations (2,700). Polymer films with 5, 10 and 35% n-SiO<sub>2</sub> as filler were reported to have less haze (19.6, 14.5, 5.9 respectively) after more rotations (3,900, 5,200, 8,300 respectively). These results indicate the presence of n-SiO<sub>2</sub> as a filler in the polymer composite improved resistance to abrasion, and that improvement was dose dependent.

Similar findings were reported in response to the micro-scratch hardness test. Despite the improvements attributed to the presence of n-silica, scratches and haze were induced in all the experiments, indicating that at least minor structural damage was caused.

In a more comprehensive study, Bauer et al (2002) prepared a panel of nanopowder-acrylate composites allowing comparison of four different nanoparticles as fillers ( $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{TiO}_2$ ). In this study, composite filling with pyrogenic (fumed) silica (12-40nm) was compared to colloidal (~50nm) silica. Based on results from the Taber Abraser (500 cycles) and micro-scratch hardness tests, the authors report considerable benefit from pyrogenic silica over colloidal silica as a filler. As in the Gläsel et al (2000) study, both tests did damage the composite surface, potentially resulting in release.

### ***Dental Materials***

Materials used to fill tooth cavities are typically subjected to long-term abrasion and pH fluctuations. As with the manufacture of many polymer composites, interest in additives of n- $\text{SiO}_2$  has been investigated. Devaprakasam et al (2008) recently compared the performance of two bio-compatible dental polymer composites. The micro- and nano-composites contained different reinforcing particulates. The nano-composite contained a mixture of zirconia and silica nanoparticles, while the micro-composite was a mixture of silica microparticles. By SEM, the authors report finding structural damage and associated debris after scratching the surface of the nano-composite with a rectangular stainless steel cantilever (PDNISP) of stiffness 240N/m with a diamond tip of radius ~40 nm. Although release was not measured, nor was the debris characterized in this study, the result is compelling in that structural micro-damage is observed.

### **5.3 ALUMINA (n- $\text{Al}_2\text{O}_3$ )**

For decades, polymers typically have been reinforced with micrometer-sized particles as fillers (Sepeur et al, 1999). More recently however, polymer composites are more often comprised of nanoparticles (e.g. alumina, silica) as fillers (Kojima et al, 1993; Tsai et al, 2008). The addition of nanoscale metal oxides has been shown to increase polymer hardness and improve scratch resistance. The following studies demonstrate these improvements but do not examine release. However, they are included here because they further demonstrate the utility of a set of standardized methods to test structural integrity.

### ***Coatings***

Sepeur et al (1999) examined the integrity of a polymer composite comprised of up to 43% (15nm) boehmite ( $\text{AlOOH}$ ) spin-coated onto polycarbonate (PC) plates to a thickness of 5 $\mu\text{m}$ . The coated plates were subjected to multiple test regimes designed to simulate weathering and abrasion. The authors report that resistance to abrasion during 1000 cycles of the Taber Abraser was dependent upon the concentration of  $\text{AlOOH}$  used as a filler in the composite coating. At the maximum concentration tested (~43%) the PC coated plates exhibited a haze of about 8%.

Unique to this study, Sepeur et al (1999) also exposed the coated PC plates to two 'weathering' simulations. To test the UV stability of the coated PC plates, the authors exposed the plates to a "Suntest" (Heraeus) with and without filters; in a separate test,

they placed the plates under a 765W sunlamp. Both exposure scenarios lasted for 14 days, but other experimental conditions (e.g. temperature, ventilation, angle, distance from ‘sun’ source) were not described. The authors report that after the two-week period, plates were visually inspected and no cracks or yellowing was observed. In addition to sun exposure, similarly coated PC plates were exposed to 65°C deionized water for 14 days, again without further description. Similar to the ‘sun’ exposure, the authors report no noticeable structural changes. Aside these limitations and lack detail in the Sepeur et al (1999) study, several possible methods are employed to approximate weathering. These methods, or modifications of them, could provide a starting point to more rigorously investigate release in response to weathering.

As mentioned in previous sections 5.1 and 5.2, Bauer et al (2002) compared abrasion resistance of a panel of nano-polyacrylate composite coatings using the Taber Abraser. The authors report that the nano-composite coating containing 35% n-alumina as a filler was the most resistant to abrasion compared to the other nano-composites tested.

#### **5.4 ZINC OXIDE (n-ZnO)**

As with other nanoscale metal oxides, zinc oxide is used as an additive because it is considered to enhance coating stability, thereby improving resistance to abrasion and UV exposure.

##### ***Release from Abrasion***

As highlighted in previous sections, the use of Taber Abraser in over a decade of studies has been highlighted because of its widespread use. However, not until Vorbau et al (2009) was this abrasion method used to induce abrasion in order to examine release. Although the study was primarily to demonstrate the utility of the modified experimental design for release studies, the authors measured release from three commercially available coatings. The test coatings were made as follows: (1) a two-pack polyurethane coating, with up to 6% n-ZnO applied three times to a steel plate and to an oak veneer fiberboard; (2) a UV curable clear coat with up to 3% n-ZnO, applied in two layers, with a third “top-coat” to oak veneer fiberboard; (3) white pigmented architectural coating with up to 5% n-ZnO, applied in two layers to fiber cement boards.

Based on previous tests, Vorbau et al (2009) report the optimal adjustment of the Taber Abraser was an applied force of 2.5N, using CS-17 abrasion rolls, run for 3 stressing cycles of 100 rotations. Of note, the CS-17 rolls are corundum ( $\text{Al}_2\text{O}_3$ ) particles (10-300 $\mu\text{m}$ ) embedded in a polymer matrix; thus, this experimental set up may not be suitable for nano-alumina release studies. In addition to the Taber instrument, the authors describe incorporating a scanning mobility particle sizer (SMPS) to measure particle size distribution and a condensation particle counter (CPC) to measure the released particle concentrations. Both of these instruments were connected to a low volume sampling hood, which encased the Taber Abraser. Four different samples of each coating (doped and non-doped) were run in triplicate, yielding 12 release measurements for each sample.

The authors report detectable, but insignificant, release resulting from abrasion. In addition, there was no correlation between released particle mass (<100nm or <625nm)

and nanoparticle content in the coatings. The authors also examined the release wear particles under TEM, and report finding n-ZnO embedded within the released particles.

### ***Release from Sanding***

Göhler et al (2010) were the first to develop a commercially relevant experimental design based on a survey of professional sanding process parameters (e.g. pressure, speed). The authors designed a laboratory-scale sanding simulation utilizing a Dremel tool (Model 400 series digital) that exhibited comparable forces to professional sanding. The entire setup was confined within a sterile environment (laminar flow box). In addition, the sander motor was exhausted outside the box. In this study, the authors examined release from two coatings (two-pack polyurethane and white-pigmented architectural coatings) either doped or not with n-ZnO, as prepared in the Vorbau et al (2009) study. These coatings were applied to either a steel plate or a fiber cement plate. In addition, one set of fiber cement plates were coated with white-pigmented architectural coating doped with n-Fe<sub>2</sub>O<sub>3</sub>, and this provides the only known analysis of nano-iron oxide release. The authors report that 75% of the n-ZnO additive particles were <100nm, while only 25% of the n-Fe<sub>2</sub>O<sub>3</sub> additive particles were less than <100nm. For each coating, five different samples were tested for a total of ten replicates.

To determine release particle size distribution, the authors used a FMPS along with a laser aerosol particle (LAP) size spectrometer. As in the previous study, a CPC was used to determine the number of particles released during sanding. The authors report sanding generated dust from all of the samples. Similar to the findings reported by Vorbau et al (2009), the number and size distribution of released particles did not correlate with the nanoparticle doped coatings. Most released particles were <100nm in size. A closer examination of the particle size released from the architectural coatings revealed bimodal distributions among from each of the samples. The un-doped architectural coating and the one doped with n-Fe<sub>2</sub>O<sub>3</sub> released particles around 25nm and 10nm, while the coating doped with n-ZnO released particles about 10nm and 100nm. This is an intriguing finding, as in general n-ZnO particles are smaller than n-Fe<sub>2</sub>O<sub>3</sub>. However, examination of the released coating particles under SEM revealed both n-Fe<sub>2</sub>O<sub>3</sub> and n-ZnO were embedded within the wear particles, and no free nanoparticles were observed.

Although considerably more small particles were released as a result of sanding, compared to the abrasion from the Taber Abraser, this is not surprising. It is worth noting that under both conditions, the presence of nanoparticles in the coatings did not alter the release. Furthermore, the released particles were not dissociated nano-metal oxides added to the coatings. Instead, the added nanoparticles remained embedded within the wear particles. These findings concur with other abrasion studies examining n-TiO<sub>2</sub> added to paint (Koponen et al, 2009) and CNTs in composites (Bello et al, 2009).

### ***Summary of n-ZnO Release Studies***

Two abrasion studies have been found, both examined release from coatings containing n-ZnO. In both studies, the authors' endeavored to control the experimental design. In one study mild abrasion, from the Taber Abraser, was used and in the other more robust sanding, with a Dremel tool, was used. Under both of these conditions, detectable levels

of ultra-fine particle release occurred. Close characterization of the wear particles revealed that the n-ZnO and n-Fe<sub>2</sub>O<sub>3</sub> nanoparticles were embedded in the released coating wear particles. These two studies provide perhaps the best examples of controlled release studies using abrasion. Since the same group performed both studies, it is likely that their future work will yield practical and robust findings.

### **5.5 SILVER (n-Ag)**

Of the nanoscale metals, nano-silver has the greatest production volume and has received the most research attention. Commercial interest in nano-silver is primarily driven by its antimicrobial properties and the benefits it may bring to a wide range of consumer products, from plastics to fabrics. Although there is general consensus that n-Ag (<30nm) is toxic to a broad range of microbes through the release of silver ions (Ag<sup>+</sup>), the specific mechanism of action remains to be elucidated (reviewed by; Wijnhoven et al, 2009; Johnson et al, 2010). Commercial interest in using n-Ag in a wide range of consumer products potentially increases the possibility of exposure. Thus, considerable attention has been directed to the estimating the possible affects n-Ag may have in the environment (Mueller and Nowack, 2008; Blaser et al, 2008) without first clearly establishing the potential for release (Benn and Westerhof, 2008; Geranio et al 2009; Benn et al, 2010; Kulthong et al, 2010).

#### ***Consumer Product Applications***

Several studies investigate the release of Ag<sup>+</sup> from n-Ag/polyamide composites (Kumar et al, 2005; Kumar and Münstedt, 2005), from n-Ag/polypropylene composites (Radheshkumer and Münstedt, 2006) and from oil-based paints (Kumar et al, 2008) under aqueous conditions. Their findings demonstrate that both the characteristics of the initial n-Ag filler powder and the composite manufacturing process affect ionic silver release rates. However, because only ion specific electrodes (ISE) were used to assess the presence of Ag<sup>+</sup>, these results speak to the release of non-ionic silver nanoparticles.

Another rough measure Ag<sup>+</sup> release is to assay the ability of the n-Ag/composites to kill bacteria in culture. Three notable studies assessed the antibacterial properties of n-Ag/polyethylene (n-Ag/PE) and n-Ag/polyvinyl chloride (n-Ag/PVC) composites (Marini et al 2007), of oil-based paint doped with n-Ag (Kumer et al, 2008) and of thin n-Ag/amino-hydrocarbon nano-composite coatings (Lischer et al, 2011). In all of these studies, the n-Ag/composite was shown to be an effective antimicrobial agent. These and similar results have encouraged manufactures to develop consumer products taking advantage of the biocidal properties of n-Ag. Although more release studies have been conducted on products containing n-Ag than any other nanomaterial, there are still only a limited number of studies publicly available.

#### ***Commercial Fabrics***

In addition to the use of n-Ag as an additive to plastic composites, a wide-range of fabrics contain n-Ag coatings. At the time of writing, three groups have published four investigations into the release of n-Ag from fabrics (Benn and Westerhoff, 2008; Geranio et al 2009; Kulthong et al, 2010; Benn et al, 2010). All of these studies used commercially available fabrics as carrier systems and either washing or exposure to sweat

as the release scenario. Although the fabrics were selected based on manufacture claims about the use of n-Ag, only Kulthong et al (2010) prepared a set of n-Ag/fabrics in the laboratory for comparison. In addition, Kulthong and colleagues (2010) were the only group to test the antibacterial effectiveness of the n-Ag/fabric samples. The results of these studies vary widely.

**Release from Washing**

Benn and Westerhoff (2008) were the first to examine release of n-Ag from fabrics during simulated washing. The authors report that, seven types of socks were selected from five different manufactures, but do not indicate the composition of any of the sock fabrics (e.g. cotton, synthetic, blend). One sock from each pair was fully digested in acid and ICP-OES was used to quantify the initial silver content. This process revealed that one of the socks had no detectable level of n-Ag, despite the manufacturing claim. The remaining socks had a wide range of silver content, from 0.9 – 1358.8 µg Ag / g sock. Once initial silver content was assayed, the remaining socks were subjected to a simulated washing scenario.

Each remaining sock pair was placed in an individual amber bottle with 500ml of ultra-pure water and agitated on an orbital shaker for at least 3 consecutive ‘washings’ of 1 or 24 hours in length. Benn and Westerhoff (2008) report variable release rates and amounts during the consecutive washings. The authors report a confusing set of findings, summarized in Table 1. The authors report more n-Ag released from socks 1a and 1b than initial n-Ag concentration measurements would have suggested, while socks 2 and 4 had no detectable release during the entire experiment.

Table 1: Summary of n-Ag release from socks after four 24 hr washing simulations (modified from Benn and Westerhoff, 2008)

Sample ID	Total sock n-Ag (µg)	Released n-Ag (µg)
1a	756	836
1b	1578	1845
2	60	<i>bdl</i>
3	31,241	165
4	2104	<i>bdl</i>
5	<i>bdl</i>	<i>bdl</i>
6	20	19

Sock 3 appeared to release only minor amounts of n-Ag compared to its initial concentration, while sock 6 released nearly all. Of these socks, the authors only analyzed the form of silver released from two socks, 1b and 3, and only after a series of three 1 hour washes. The authors used an ISE on unfiltered wash water and then centrifugation followed by filtration to identify the percent silver released that could be attributed to Ag<sup>+</sup> versus n-Ag. While the authors state that sock 3 released nearly all of its silver as n-Ag during wash cycles, their data indicate 5-70% was Ag<sup>+</sup>. Conversely, the authors report that sock 1b released 70-90% of its silver as Ag<sup>+</sup> meanwhile their data suggested at least 80% was n-Ag. These discrepancies are not explained. However, follow-up analysis of wash water using TEM to characterize the released silver was performed. Although the authors report that silver nanoparticles observed in the wash water were similar to those

observed by SEM after the acid digestion, this analysis was performed on sock 1a, which was not used in the filtration and ISE analysis.

The small sample size, lack of replicates and inability to compare data sets limit the usefulness of this study. Furthermore, the authors admit that using ultra-pure water likely confounded their results since it acted as an oxidizing agent during prolonged exposures. However, differences in release rates observed among the socks suggest variability in manufacturing practices and/or materials may affect the bond strength between n-Ag and fabrics.

Geranio and colleagues (2009) conducted a similar washing / n-Ag release study with textiles. However, several key differences in experimental design allowed Geranio et al (2009) to show for the first time the influence of pH on release as well as the form of silver released. The authors submersed nine different fabrics of known textile composition and method of n-Ag incorporation in a buffered solution of pH 10, with minor agitation (100-150 rpm) for 120 minutes and then added an oxidant to the solution. Under these conditions, all but one of the fabrics released nearly of their silver content as  $\text{Ag}^+$ , after the addition of the oxidant, or as particles  $<450\text{nm}$ . The authors suggest these findings are due to the fact that the fabrics contain zero-valent n-Ag, the oxidation of which was required before  $\text{Ag}^+$  could be detected. In contrast to these alkaline conditions, the silver released under standardized washing conditions (ISO 105-C06:1997, pH 7) was over 75% as particles  $>450\text{nm}$ , with minimal  $\text{Ag}^+$  release. The authors suggest this difference was in part due to the mechanical damage caused during the washing process. Geranio et al (2009) highlight a relationship between the amount of released silver with differences in incorporating the n-Ag in the fabrics. For example, the fabric sample with an electrolytically deposited layer of n-Ag released considerably more silver, while no Ag release was detected from the textiles with n-Ag incorporated as a salt (i.e.  $\text{AgCl}$ ). The authors did not perform further analysis of released particulate, which may be comprised of n-Ag on fiber fragments, n-Ag aggregates or  $\text{AgCl}$  precipitates.

Recently, Benn and colleagues (2010) published a second n-Ag release during washing study, this time from a range of commercial products: a shirt, medical cloth and mask, a towel and a toy teddy bear. Similar to their previous study, these products were selected based on advertising and required analysis to determine initial silver content. In contrast to their previous study, Benn et al (2010) performed the digestion assay on three replicates of each product and used tap water during washing instead of ultra-pure water. The washing simulation washing was only performed once on each product (i.e. no replicates) for one hour, without the addition of any detergents or modification of pH. The authors suggest this washing scenario was designed to provide estimates of release in more complex aqueous environments, including wastewater and saliva.

The authors report each product contained detectable levels of n-Ag, although the variance among the replicates was large, as much as 50%. The medical mask and cloth contained the most silver,  $590\mu\text{g}$  and  $810\mu\text{g}$  respectively. These figures would correspond to roughly 25% of the product weight. After the one hour washing protocol, n-Ag was released from all of the products tested. As in the previous study, the amount of

release differed among the products, but without replicates, the authors were unable to provide data about release rates. The medical mask, which contained the most silver, released less than 0.1%. In contrast, the shirt released the greatest amount, nearly 2% of its n-Ag content.

As in their previous study, Benn et al (2010) used filtration and SEM to measure and characterize the released n-Ag. Based on filtration, nearly all of the silver released from the child's toy, the towel and medical products was less than 20nm in size. In contrast, the results indicate about 2/3 of the silver released from the shirt was <100nm but greater than 20nm, the remaining 1/3 is less than 20nm. These findings are only partially supported by observations made under SEM, where agglomerates of 200-500nm are typically seen in addition to particles <20nm. The authors suggest that the agglomerates may be an artifact of sample preparation, or that the <20nm particles released during washing and not captured by filtration are actually Ag<sup>+</sup> and not n-Ag particles.

As Benn and colleagues (2010) point out, since several of the products tested did not release a considerable amount of their total silver during washing (<2%), the product should retain much of its n-Ag at the end of the product's lifecycle. To investigate the potential release of nano-silver from products in landfill conditions, the authors used the toxicity characterization leaching procedure (TCLP) developed by the U.S. Environmental Protection Agency (USEPA, 1992). A small portion of the medical cloth and mask were exposed to the TCLP and the results show an amount of released n-Ag similar to the washing protocol. As Benn et al (2010) discuss, the authors are focused on the potential environmental exposure of n-Ag released from a product's life cycle and not the potential for release during wearing or using these products.

### ***Release from Sweat***

Kulthong and colleagues (2010) provide the only study investigating n-Ag release as a result of exposure to sweat. The authors used a standardized artificial sweat applied to fabrics with known n-Ag loads and commercially available fabrics with unknown n-Ag loads. In addition, the authors tested the antibacterial activity of these fabrics on both Gram negative and Gram positive bacteria.

In this study, five cotton fabric samples were coated with known concentrations of n-Ag in the laboratory, and six commercially available fabrics were obtained from different manufactures in Thailand claiming to use nano-silver in their product. The initial silver content, in the laboratory prepared samples correlated closely with the known amount of silver coated onto the fabric (including the null). Half of the commercial fabrics had no detectable n-Ag, while the other half had what appeared to be low levels (<50%) when compared to the lab prepared samples. Interestingly, despite the low levels of detected n-Ag in the commercial fabrics, they were just as toxic as the lab prepared fabrics to Gram positive bacteria, and were more frequently toxic to the Gram negative bacteria.

To assess release in response to sweat, standardized artificial sweat formulations developed by the International Standards Organization (ISO), British Standards Institute (BSI) and American Association of Textile Chemists and Colorists (AATCC) were used

(ISO 105-EO4-2008E; BS EN1811-1999; AATCC test Method 15-2002, respectively). Two different ISO formulations were prepared at two different pH levels, 5.5 and 8.0. Because of the low concentration of silver in the commercial fabrics, these were soaked in artificial sweat at a ratio of 1:50 (w/v), while the lab prepared samples were soaked at a ratio of 1:100 (w/v). Samples were incubated in each of the four standardized artificial sweat formulations for 24 hours at 37°C and release was analyzed by graphite furnace atomic absorption spectroscopy. The laboratory prepared samples released n-Ag (except the negative control) in response to incubation in all of the sweat formulations. Comparisons between the two pH levels used in the ISO formulation indicate that a more alkaline pH results in greater release. In contrast to the lab prepared samples, there was variable release from the commercial fabrics that contained silver. One did not appear to release any under any conditions. Another released a minimal amount in the EN formulation only. The third released minor amounts of n-Ag in response to every sweat formulation.

### ***Release from Wound Dressings***

The use of n-Ag in hospital applications is attractive, especially in burn clinics, intensive care units and cancer care centers where patients are susceptible to nosocomial infection. The topical wound dressing, Anticoat™ uses a polyethylene mesh coated with n-Ag (~15nm) with the intent to minimize infections. Although there are a number of other manufactures marketing similar products, Arglaes™, Aquacel-Ag™, Silvasorb™, Actisorb™ -Silver-200 and Urgotul-SSD™, the Anticoat™ product appears to be the only one used to better understand n-Ag and Ag<sup>+</sup> release (Vlachou et al, 2007).

Trop et al (2006) reported that a burn patient suffered silver poisoning from Anticoat™ dressings beginning six days after injury. The patient's skin exhibited argyria-like symptoms, elevated Ag<sup>+</sup> levels were detected in the urine and blood, and liver tests indicated elevated levels of enzymes associated with hepatotoxicity (Trop et al, 2006). After removal of the Anticoat™ dressings, detectable silver levels in blood serum continued for seven weeks, but none were detected when tested again after 10 months (Trop et al, 2006).

Following up on the clinical observations of Trop et al (2006), Vlachou and colleagues (2007) conducted the first prospective study with 30 severe burn patients. The authors report the presence of Ag<sup>+</sup> in patient's serum, but were unable to assess whether nano-silver particles were also released from the wound dressings. Over the course of the study, the authors report similar findings as those observed by Trop et al (2006). There was a dose dependant relationship between increased exposure to Anticoat™ dressings and elevated levels of Ag<sup>+</sup> in blood, which decreased over time after dressing removal. In addition, Vlachou et al (2007) report that the Anticoat™ dressings appeared to delay the wound healing process, a point of contention among studies (Innes et al, 2001; Honari et al, 2001; Tian et al, 2007).

### ***Release from Catheters***

In addition to designing a catheter with an adequate balance of structural integrity and flexibility, manufactures have begun incorporating n-Ag particles in the catheter polymer

to minimize infections. Although these state-of-the-art antimicrobial polymer catheters were presumed to continuously release silver ions (Bechert et al, 1999; Böswald et al, 1999; Carbon et al, 1999), Joyce-Wöhrmann et al (2000) were the first to directly investigate release. In a brief communication, the authors report that  $\text{Ag}^+$  were released from thermoplastic polyurethane catheters doped with varying amounts of n-Ag after a 24 hour incubation in physiological saline held at 37°C. While the group reports dose dependant release of  $\text{Ag}^+$  from the catheters, they are unable to comment on the release of n-Ag from the polymer matrix.

### ***Summary of n-Ag Release Studies***

These studies highlight the need to conduct further investigation. Their differences in experimental design and limited detail make comparison difficult. However a few general themes can be mentioned. First, the data indicate that both n-Ag and  $\text{Ag}^+$  can release from fabrics under certain conditions. Second, the composition of the carrier system (in these instances, fabrics), the manner that n-Ag is bound to the carrier system and the conditions of the release scenario (e.g. pH, temperature, agitation) all affect release.

## **6. QUANTUM DOTS**

The unique electrical and optical properties, especially the fluorescence spectrum of quantum dots, make these an attractive tool for biomedical imaging (Chan et al, 2002; Alivisatos, 2004). Although several investigators are exploring the possible target specific imaging and drug delivery capabilities of quantum dots, almost no research is being conducted to understand the potential toxicological effects. Indeed, stability, aerosolization, half-life and potential routes of exposure are only beginning to be understood (Hardman, 2006; Rzigalinski and Strobl, 2009). While no quantum dot release studies were identified, there are studies investigating the potential release of elements (i.e. cadmium) commonly used in the particle core of quantum dots. However, the applications are in liquid form and beyond the scope of this review. Interested readers are directed to the follow reports for more information (Samia et al, 2003; Derfus et al, 2004; Kirchner et al, 2005).

## **7. CLAYS & ORGANO-CLAY HYBRIDS**

Nanoclays have been shown to improve barrier properties to moisture, solvents, UV and gases of several polymers (e.g. PET, PE, epoxy) while enhancing clarity, stiffness, thermal stability and scratch resistance (Bhat et al, 2008). Nanoclays are typically made from montmorillonite mineral deposits with platelet structures thickness of 1nm and widths of 70-150nm. Nanomer<sup>®</sup>, Nanofil<sup>®</sup> and Cloisite<sup>®</sup> appear to be commercially available nanoclays that are commonly used as fillers to reinforce plastic molded products (Bhat et al, 2008; Nanoclay.com, 2011). In addition to reinforcing plastics, investigators have explored the potential uses of nanoclays as additives to enhance fire retardant coatings (Nyden and Gilman, 1998; Zanetti et al, 2001; Hull et al, 2003). Although there have been no targeted release studies, both Zanetti et al (2001) and Hull et al (2003) reported improved thermal stability in polymer nanocomposites containing nanoclays. Further, there appears to be only one review the includes nanoclays, and interested readers are referred to Pandey et al (2005) which discusses the degradation of polymer nanocomposites generally.

## 8. SUMMARY OF FINDINGS

A total of four release studies have been found in the public literature on carbonaceous nanomaterials; two abrasion (Koponen et al, 2009; Bello et al, 2009) and two incineration studies (Nyden and Gilman, 1998; Nyden and Uddin, undated presentation). A total of five release studies have been identified on nano-metal oxides in coatings. Three of these studies examined n-TiO<sub>2</sub> (Hsu and Chein, 2007; Kaegi et al, 2008; Koponen et al, 2009) and two focused on n-ZnO (Vorbau et al, 2009; Göhler et al, 2010). In each of these studies, the nanoparticles were embedded in coatings and applied to various substrates, wood, medium density fiberboard, steel plate, cement fiberboard and ceramic tile. Abrasion was used in three studies to investigate release either during sanding (Koponen et al, 2009; Vorbau et al, 2009) or mild wear (Göhler et al, 2010). There are four studies in the literature directly investigating release of n-Ag from textiles either in response to washing (Benn and Westerhoff, 2008; Geranio et al, 2009; Benn et al, 2010) or simulated sweat (Kulthong et al 2010).

The limited number of studies investigating release from solid matrices containing or coated with nanomaterials highlights the need for rigorous investigation. Although differences among the experimental design makes comparison difficult, a few common themes are beginning to emerge.

- During all release scenarios particles are emitted from the carrier system.
- Under some circumstances the majority of released particles are nanoscale, while under others most release particles are fine scale.
- The composition of the carrier matrix, the form of nanoparticle used and the methods employed to bind the nanoparticles to the carrier appear to significantly influence release rates and quantities.
- It appears rare that individual nanoparticles are released from their carrier system under any of the release scenarios.

### *Release from Abrasion*

Bello and colleagues (2009) observed a laboratory setting over the course of a year that perform both wet and dry cutting of epoxy resin panels that contained carbon nanotubes. Of the two cutting methods, the authors report that dry cutting released considerably more particles. Unlike the Koponen et al (2009) study, Bello et al (2009) report the majority of the released particles (70-90%) were 1-10µm in size and less than 10% were 100nm or smaller. Despite these differences, neither SEM nor TEM observations revealed individual or bundled CNTs among the released particles.

Koponen et al (2009) used a hand held sander to abrade coatings containing either n-TiO<sub>2</sub> or carbon black and produced large quantities of fine and ultra-fine wear particles. The authors concluded that the majority of nanoscale particles were generated by the electrical motor of the sander and were not released from the paint. The authors go on to

suggest that the larger particles (>200nm) were combination of sander emitted particles and paint dust. Further analysis of the paint dust was not performed, but it is likely that the wear paint particles contained embedded n-TiO<sub>2</sub> nanoparticles.

In both the Vorbau et al (2009) and Göhler et al (2010) studies, the authors' endeavored to control the experimental design. One study examined release under relatively mild, longer-term abrasion stress by utilizing the Taber Abraser. Under these conditions, minimal levels of ultra-fine particle release occurred. Close characterization of the wear particles revealed that the n-ZnO nanoparticles were embedded in the released coating wear particles. In contrast, the second study used powerful but short abrasion with a Dremel tool to induce release. Under these conditions, considerably more nanoscale particles were released, the majority of them <100nm. Despite the increase in nano-scale particle release in this study, the authors reported finding both the n-ZnO and n-Fe<sub>2</sub>O<sub>3</sub> nanoparticles embedded within the released coating particles.

### ***Release from Incineration***

The authors of both incineration studies report nanoparticles were not likely released in the smoke (Nyden and Gilman, 1998; Nyden and Uddin, undated presentation). Instead, the authors report in both studies that the engineered nanomaterials were present in the remaining char. In the study investigating the graphite sheet nano-composite, the authors report that the high temperature of the incineration process caused a structural change that increased material stability. In the polyurethane foam / CNFs composite incineration study, the authors report significant release of ultra-fine particles from the char when mechanically disturbed. However, in neither study do the authors further characterize the remaining char in terms of the engineered nanomaterials.

### ***Release from Weathering***

In two studies, authors investigated the effects of weathering, either in simulation (Hsu and Chein, 2007) or outside in an urban environment (Kaegi et al, 2008). Not surprisingly, there is little similarity between these two studies. Hsu and Chein (2007) simulated weather and human contact for two hours in a simulation box and induced a detectable release of nano-scale particles. The amount of release appeared correlated to both the substrate and the light source (UV vs. fluorescent), but further characterization of the released particles was not reported. In contrast, Kaegi and colleagues (2008) compared an aged building façade and a new model façade coated with the same paint doped with n-TiO<sub>2</sub>. Both released detectable levels of nano-scale particles during a rain event. The authors report that the composition of the released particles differed depending on how far away from the source (façade) samples were collected. Samples collected at the base of the façade contained individual and aggregated nanoparticles of n-TiO<sub>2</sub> embedded in the released particles. Further away from the source, the authors collected urban runoff and reported finding dissociated and clumped nanoparticles of n-TiO<sub>2</sub>. It is presumed the observed n-TiO<sub>2</sub> was released from the source material, but this was not confirmed. These studies provide useful insights and should prompt more rigorous follow up investigations.

### ***Release from Washing***

Considerable attention has been given to understanding the release of silver, especially from textiles. The utility of adding nanoparticles of silver (n-Ag) to a product are in its ability to sustainably release silver ions ( $\text{Ag}^+$ ), making this a unique nanomaterial. A number of studies have shown that embedded n-Ag particles release  $\text{Ag}^+$  in aqueous environments, and that the rate and amount of release is dependent upon the carrier system/n-Ag composite. The studies that have been found investigating release of n-Ag have used various washing methods (Benn and Westerhoff, 2008; Geranio et al, 2009; Benn et al, 2010), and in one study soaking in standardized artificial sweat solutions (Kulthong et al 2010). Only Geranio and colleagues (2009) reported details on the composition of the fabrics and the methods used to incorporate n-Ag into the fabrics. In the other studies, the authors selected commercially available fabrics solely based on manufacturer's claims, which then needed to be tested to verify and quantify their initial n-Ag content. In all studies, the commercially available fabrics were reported to contain a wide range of quantities of silver, and in some instances, none was detected. Kulthong and colleagues (2010) provide the only investigation on the antimicrobial properties of the fabrics being tested. Their results indicate antibacterial potency does not appear directly related to the concentration of n-Ag incorporated in the fabric.

During washing and as a result of soaking in artificial sweat, most (but not all) fabric samples that contained n-Ag initially, released detectable amounts. However, due to limitations in experimental designs used by some authors, only Geranio and colleagues (2009) could quantify the release of n-Ag and  $\text{Ag}^+$ . Their findings illustrate what other studies suggest, that fabric composition, pH, and the method of n-Ag incorporation dramatically influence release of silver particles  $>450\text{nm}$ ,  $<450\text{nm}$  and of ionic silver. In addition to these parameters, several of the authors state that agitation and the presence of an oxidizing agent also affect release. Despite the intriguing results, these studies have limited sample sizes, a wide range of experimental designs and most often haven't been replicated. Thus as tempting as it may be to draw conclusions about the release of n-Ag or  $\text{Ag}^+$  during these scenarios, it is simply too early. Further, more rigorous experimentation needs to be performed.

### ***Limitations***

Although some studies highlight the experimental limitations faced by researchers investigating release better than others, measure release from products containing engineered nanomaterials is clearly a nascent field. Aside variations in the level of detail reported by the authors, many investigators performed experiments once, on a single sample and lacked proper controls. As a result, many of these studies need to be viewed more as initial observations rather than rigorous experiments. However, these limitations point more to a critical lack of standardized methodology, rather than poor experimentation. In a few studies, the authors have made noticeable efforts to bring existing, standardized, methods and measurement tools and applied them to study release from carrier systems containing nanomaterials. In every study this has been done, it has been highlighted in this review. Some of these methods may prove unhelpful in nanomaterial release studies, but they serve as a solid starting point for subsequent studies.

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