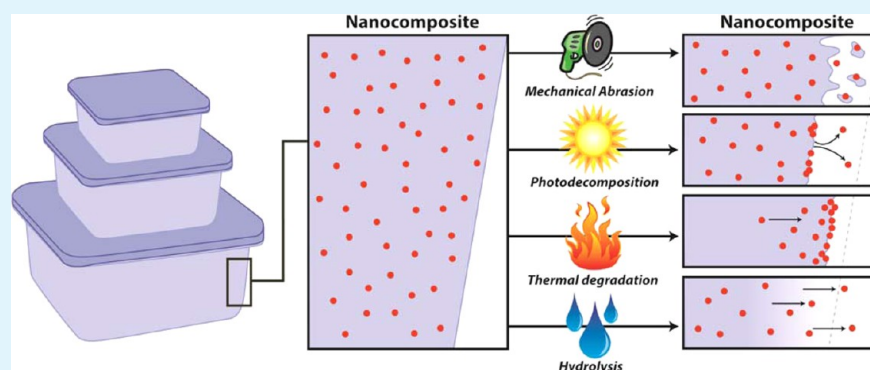# Release of Engineered Nanomaterials from Polymer Nanocomposites: the Effect of Matrix Degradation

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ABSTRACT: Polymer nanocomposites—polymer-based materials that incorporate filler elements possessing at least one dimension in the nanometer range—are increasingly being developed for commercial applications ranging from building infrastructure to food packaging to biomedical devices and implants. Despite a wide range of intended applications, it is also important to understand the potential for exposure to these nanofillers, which could be released during routine use or abuse of these materials so that it can be determined whether they pose a risk to human health or the environment. This article is the second of a pair that review what is known about the release of engineered nanomaterials (ENMs) from polymer nanocomposites. Two roughly separate ENM release paradigms are considered in this series: the release of ENMs via passive diffusion, desorption, and dissolution into external liquid media and the release of ENMs assisted by matrix degradation. The present article is focused primarily on the second paradigm and includes a thorough, critical review of the associated body of peer-reviewed literature on ENM release by matrix degradation mechanisms, including photodegradation, thermal decomposition, mechanical wear, and hydrolysis. These release mechanisms may be especially relevant to nanocomposites that are likely to be subjected to weathering, including construction and infrastructural materials, sporting equipment, and materials that might potentially end up in landfills. This review pays particular attention to studies that shed light on specific release mechanisms and synergistic mechanistic relationships. The review concludes with a short section on knowledge gaps and future research needs.

KEYWORDS: nanocomposites, release, environmental health and safety, nanoparticles, exposure, mechanical abrasion, photodegradation, thermal degradation, hydrolysis

1. INTRODUCTION

This article is the second in a series of two that provide a critical review of what is currently known about the potential release of engineered nanomaterials (ENMs) from polymer nanocomposite (PNC) materials, focusing on potential release mechanisms. Polymer nanocomposites are polymer-based materials that incorporate filler elements possessing at least one dimension in the nanometer range, and because nanoscale matter can exhibit different chemical or physical properties, these nanocomposites can display superior or unusual properties compared with similar materials fabricated from polymers alone. Some of the potential applications of PNCs are briefly described in the Introduction of the previous article in this series and include infrastructural or construction materials, aerospace and automotive components, packaging, textiles, and bioactive materials and medical devices.[1] Measuring exposure of the external environment to the nanofiller is one of the necessary components required for assessing the safety of a PNC for a specific use. Therefore, it is important to understand the potential for ENMs either embedded in the interior of a polymer, or bound to its surface, to become released into the external environment during routine use or abuse of these materials. Understanding the exposure scenarios will aid in determining whether these materials or consumer products fabricated from them pose a potential risk to either human health or the environment.

The previous article focused on release of ENMs from PNCs, primarily into liquid media, by mechanisms or combinations of mechanisms that to a first approximation do not entail alterations to the integrity of the host matrix. These mechanisms include *diffusion* of ENMs from the interior of the polymer matrix to the external environment, *desorption* of ENMs bound at the polymer-environment interface, and *dissolution* of ENMs and subsequent diffusion of the ionic residuals to the external environment. These release scenarios, which are discussed in more detail in the earlier paper, may be the most relevant to direct human exposure from PNC-enabled consumer products, such as food packaging and medical devices, in which nanocomposites will be in contact with liquid environments for long periods of time. However, even if theoretical and experimental work on ENM release into liquid media were to show unequivocally that whole ENMs do not become passively released into the environment over relevant time scales, diffusion, dissolution, and desorption are not the only mechanisms by which ENMs may be released from PNCs. Regardless of how fast or feasible diffusion of ENMs through a polymer matrix may be, if the polymer matrix is degraded, ENMs would become released into the surrounding medium by default. This is not only a consideration for PNCs likely to be exposed to liquid media but also a consideration for other PNC applications in which mechanical or chemical degradation of the host matrix could lead to direct release of embedded ENMs to the environment.

The present article is concerned with release mechanisms involving destruction or other chemical or physical alteration of the host matrix, including mechanical abrasion and several forms of chemical decomposition (including UV-assisted, thermal, and hydrolytic degradation). In the former case, ENMs may become released by aerosolization of degradation products, which could represent a route of occupational exposure via inhalation or could represent a route of ENM release into the general environment (e.g., sedimentation of abraded dust particles). On the other hand, chemical decomposition of the host material could lead to direct release of ENMs either by exposing embedded particles to the material surface or by indirect release via attenuated diffusion properties. Photo-degradation in particular might be especially relevant to PNCs intended for construction materials or other materials likely to be exposed to extensive outdoor weathering, whereas thermal and hydrolytic degradation may be relevant to materials likely to be subjected to frictional heating or long-term storage in liquid media. UV-mediated ENM release and hydrolysis may also be important when considering the fate of PNC-based products that may end up in land-fills. A schematic diagram depicting some potential release mechanisms is provided in Figure 1.

II. RELEASE OF ENMS DUE TO MECHANICAL DEGRADATION OF THE HOST

Distributing ENMs throughout a polymer matrix improves strength and other critical mechanical properties of the host material. The production of stronger-yet-lighter materials is anticipated to be a major benefit of PNC technology. These strength gains appear to be maximized when the distributed particle has a high aspect ratio, and thus, reports of nanocomposites intended for structural materials applications often involve host matrixes containing anisotropic, fibrous nanofillers, such as carbon nanofibers (CNFs) and nanotubes (CNTs) or platelet-like nanofillers such as layered aluminosilicate clays.

Because of the likelihood of this class of nanocomposites being machined (e.g., cut, grinded, drilled, and sanded) during manufacture or recycling, abrasion and other forms of mechanical wear are envisioned as possible ENM release mechanisms.

Studies that assess the release of ENMs from nanocomposites as a result of mechanical destruction of the matrix have tended to focus on nanocomposites filled with high-aspect-ratio particles. This is reflected in Table 1, which presents a brief summary of the abrasion-assisted ENM release literature. (Here, a broad definition of "abrasion" is considered to include any kind of machining or processing that uses mechanical force to destroy or physically alter the nanocomposite material.) A little over half of the studies we identified in this area focus on CNT- or CNF-based nanocomposites, with a smaller number of studies investigating materials embedded with clays, silicates, or (mostly in paints and coatings) more isotropic particles such as titanium and zinc oxides. Focus on these types of materials is reflective of their corresponding likelihood to be used in construction, infrastructural, and automotive applications, in which mechanical wear will be an important aspect of the material's lifecycle. In a typical release experiment, test materials are subjected to some form of mechanical sanding intended to either simulate a sanding manufacturing process or to simulate the long-term wear of a material during "everyday use" (e.g., a floor tile that might be subjected to daily scuffing and scratching from shoes). For the latter scenario, an instrument called a Taber abraser is often employed (Figure 2), which fixes the specimen on a rotary turntable and subjects it to wear from an abrasion wheel and allows ejected materials to be analyzed; factors such as rotary speed, the wheel grit level (coarseness and hardness), and applied downward force can be varied to simulate different wear conditions. Studies intended to simulate active sanding processes tend to use motorized industrial or laboratory scale sanding equipment, and a few studies of manual sanding with commercial sandpaper have even been published.[2,3] Release during and after other manufacturing processes such as drilling,[4,5] grinding,[2] cutting/sawing,[2,6,7] and shredding[8] has also been explored.

Most research efforts that study the effects of abrasion on release of ENMs from nanocomposites are concerned with potential inhalation exposures, and therefore, they have tended to focus exclusively on aerosol and airborne particle analysis. Typical experiments enclose the test material and abrasion equipment in a chamber with controlled air flow (sometimes an entire room if commercial equipment or manual abrasion is being assessed[7]), and then analytical equipment capable of measuring airborne particle properties is placed at strategic locations around the chamber; for example, it may be placed where the nose and mouth of an equipment user might be during operation. Usually a combination of instruments capable of measuring particle number concentration and size (from several nanometers through several micrometers) is used along with particle capturing strategies that permit electron microscopic analysis of released particles to provide information on particle morphology and composition. A few studies also use advanced surface analytical techniques such as X-ray photoelectron spectroscopy (XPS) or secondary ion mass spectroscopy (SIMS) to provide information on whether free ENM fillers are adsorbed onto or protrude from the surfaces of released airborne particles.
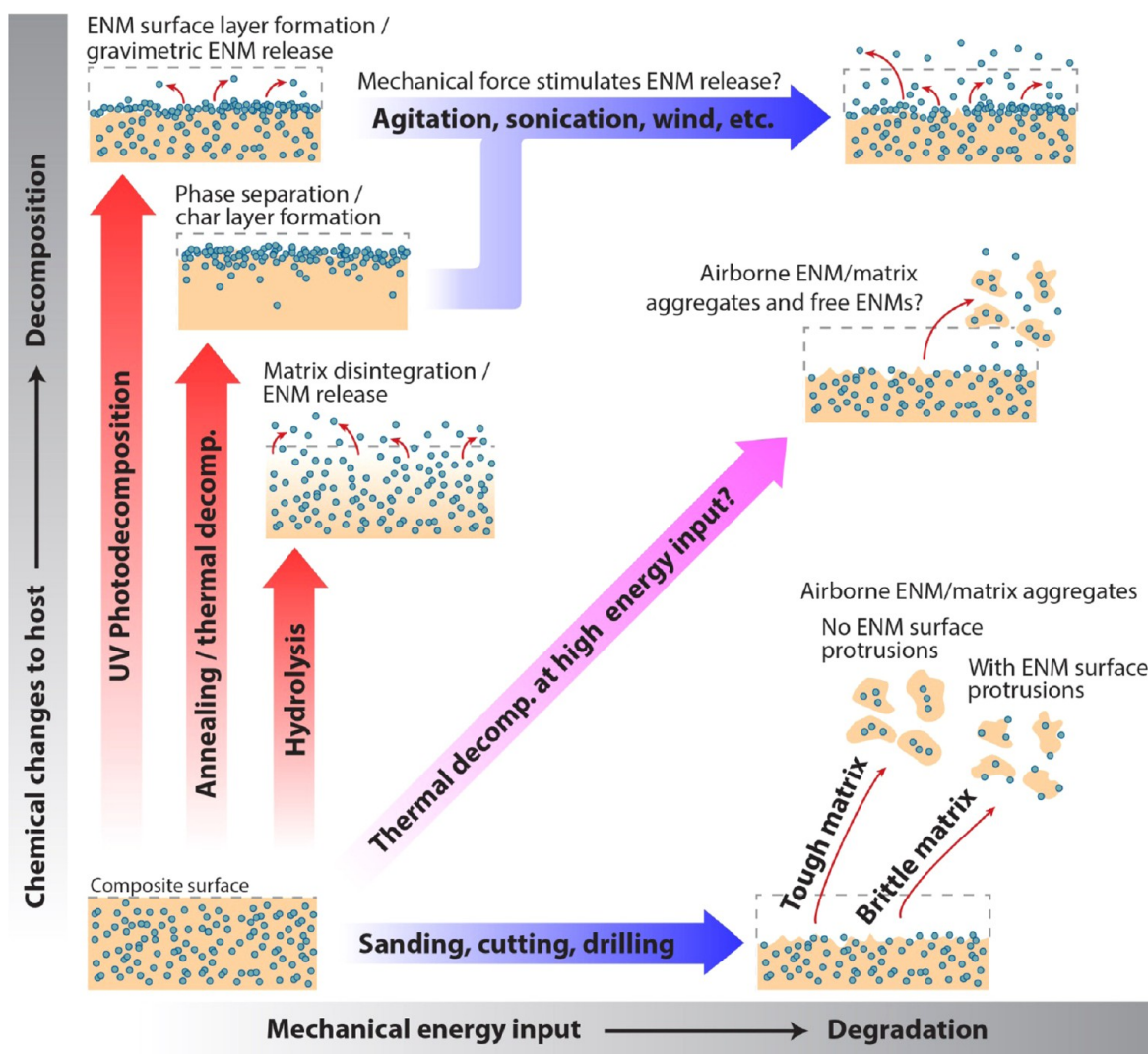
Figure 1. Schematic showing some potential ENM release pathways from polymer nanocomposite materials due to mechanical degradation or chemical decomposition of the host material. Nanofillers are represented as spherical particles, but the schematic also applies to fibrous and platelike nanoparticles. Different release pathways may be more or less relevant, depending on particle morphology and host material composition, as discussed in the text.

Every study summarized in Table 1 reported the release of micrometric or submicrometric (or both) particles when either nanocomposite or control materials were abraded, even during low-energy inputs like manual sanding. In most studies that analyzed the composition of particles released during abrasion, released particles were agglomerates of the related host material and the ENM filler, and the size distributions of released particles were multimodal and identical or very similar to those released from the respective control materials under the same conditions. (To avoid confusion, "particles" in the context of abrasion-assisted release may refer to any material released during abrasion, which may or may not include embedded nanofillers, as described below. When the nanofillers themselves are released during abrasion, either embedded in released particles or individually, this will be explicitly stated.) Typically, the number concentration of submicrometric particles exceeds that of supramicrometric particles, but the supramicrometric particles usually account for most of the released mass. Among studies that employed an imaging technique, the morphologies of released particles were highly variable, but particles typically

were irregularly shaped and sometimes featured protrusions of the nanofiller elements from the released particle surfaces.

Given the large variety of materials and abrasion methods applied in these studies, it is difficult at this time to formulate a comprehensive predictive model for release characteristics across the full spectrum of nanocomposites and abrasion conditions likely to be encountered. Nevertheless, some general conclusions can be drawn with respect to the nanofiller, host material, process type, and the composition and morphology of the released particles, as discussed below.

Effect of the Nanofiller. Although variations in the size distribution of released particles between the nanocomposite and control materials are generally modest, the number concentration of released particles tends to be more variable. In particular, the addition of nanofillers has been found to increase the number of released particles in some studies and decrease it in others, sometimes even for the same filler/host combinations. For example, mechanical sanding of fiberboard coated with a kaolinite-dispersed wall paint (kaolinite is a type of layered clay similar to montmorillonite) was found to result in more than double the total released particle number concentration

Table 1. Summary of Studies Related to the Release of ENMs from Composite Materials Due to Mechanical Abrasion[a,b]

nanomaterial	host material(s)	sheer application	nanofiller release?[c]	release characteristics	ref
calcium carbonate (with perlite)	fine-grained filler for wall finishing	mechanical sanding	N/A	material with nanofiller has ~18% higher TNC of released particles than the reference material; size distributions of released particles were multimodal, spanning submicrometer through micrometer ranges; no morphological analysis of released particles was performed	9
CSH	cement	manual sanding, Taber abraser	no	micrometer-scale CSH/cement particles liberated, but no release of free CSH was detected in either simulated wear scenario	10
carbonaceous? (unspecified)	PVC-based fabric (unspecified)	Taber abrader with steel rake, vibrating engraver, rotating metallic brush	possibly	substantially more nanometric particles released from ENP-fabrics than controls; steel rake attachment dislodged ENPs more efficiently than the engraver tool, possibly due to micro shocks induced by teeth passing over the roughened surface; released particles were carbonaceous	11
carbon black	acrylic paint on wood	mechanical sanding	N/A	paints containing nanofiller released slightly more particle TNC than the reference, but particle size distributions were similar and multimodal; no morphological analysis of released particles was performed	9
CNFs	epoxy	wet saw cutting, dry surface grinding, manual and table belt sanding	yes	particle TNCs for <300 nm size ranged from 2600 (wet saw cutting) to 490 000 particles/cm^3 (surface grinding); during most tasks, CNFs were observed, either free or in clusters/bundles	2
kaolinite clay	wall paint on fiberboard	mechanical sanding	N/A	kaolin-containing paints released >2× higher particle TNC than the reference; size distributions of released particles were similar and multimodal, spanning submicrometer through micrometer ranges; no morphological analysis of released particles was performed	9
iron oxide	acrylic paint on substrate	mechanical sanding	no	released particles <100 nm were agglomerates of polymer and iron oxide ENMs; no free ENMs detected; presence of ENMs did not significantly impact the number concentration of released <100 nm particles.	12
MMT clay	PA-6 and PP	drilling	N/A	released particles were agglomerates with geometric mean sizes <100 nm, irrespective of presence of nanofiller; TNC of particles was greater for PA6 than PP, both with and without clay; clay suppressed particle release in PA6, but the opposite was observed in PP; did not report whether released particles were free clay fragments or polymer/clay aggregates.	5
	PP	shredding	no	MMT suppressed ultrafine particle release; for both control and PNC, the median released particle diameter was ~10 nm, and no differences in morphology observed; released particles appear to be composed of host polymer only	8
MWCNTs	epoxy	manual sanding	no	CNT/epoxy agglomerates released; released particles were >300 nm in size, irregularly shaped, and had frequent CNT protrusions	3
	epoxy, PC, PA	Taber abrader with steel rake, vibrating engraver, rotating metallic brush	yes	in most cases, size distributions of released particles were similar between nanocomposites and reference; increasing abrasion speed, hardness of abrading surface, and normal force increased quantity of released particles; more homogeneous CNT/polymer dispersion resulted in less free CNT release	11
	epoxy, Cement, TPU, POM	sanding simulation (epoxy) or mechanical sanding (others)	no	agglomerates of CNTs and host matrix were released into air during sanding; released particles were 1–20 μm in size and irregularly shaped; particles from CNT/epoxy and CNT/cement had frequent CNT protrusions, but those from CNT/TPU and CNT/POM had no CNT protrusions	13
	epoxy	mechanical sanding	yes	bimodal size distribution for released particles, <100 nm and 0.5 to 5 μm; released particles were epoxy/CNT aggregates with CNT protrusions; TNC was positively correlated to filler concentration in the host matrix; free CNTs were released in CNT/epoxy materials with 4 wt % CNT, but not with 1–3 wt % CNT	14
	epoxy	Taber abraser	yes	CNT/polymer aggregates and free CNTs released; the mean aggregate size in the nanometric range was larger for the CNT/epoxy composites than for neat epoxy	15
	cement and POM	mechanical sanding, Taber abraser	no	micrometer-scale CNT/cement and CNT/POM agglomerate particles liberated, but no release of free CNTs was detected in either simulated wear scenario; released CNT/cement particles had exposed CNTs on their surfaces.	10
	TPU	mechanical sanding, Taber abraser	no	released CNT/polymer aggregates mostly in micrometer range. CNT presence resulted in slightly larger released particles' size but did not impact airborne particle TNC; released particles were smooth and had no protruding or exposed CNTs; normal wear simulation (Taber abraser) resulted in lower released particle TNC.	16
	epoxy, codistributed with carbon or alumina fibers	dry and wet saw cutting, wet and dry drilling	yes	all materials released fibers and particles during dry machining, but TNCs and size distribution depended on machining type; alumina-based materials generated more particles than carbon-based materials; no individual CNT structures or bundles were observed in fibers or particle agglomerates during cutting, but were observed during drilling; wet-machining significantly reduced airborne exposures.	4, 7
silica	PA-6 and PP	drilling	N/A	released particles were agglomerates with geometric mean sizes <100 nm, irrespective of presence of nanofiller; TNC of particles was greater for PA6 than PP, both with and without SiO$_2$ particles; presence of SiO$_2$ increased concentration of released particles compared with neat polymers; not reported whether released particles were free SiO$_2$ particles or polymer/SiO$_2$ aggregates	5
	PA	manual sanding, Taber abraser	no	for manual sanding, released SiO$_2$/PA agglomerate particles had sizes predominantly in the several-micrometers-diameter range; no exposure of SiO$_2$ fillers on the surface of the released particles was observed; simulated long-term wear (Taber	10

Table 1. continued

nanomaterial	host material(s)	sheer application	nanofiller release?[c]	release characteristics	ref
	acrylic paint on wood, lacquer on particle board	mechanical sanding	N/A	abraser) showed small amount of particle release and no significant difference between the nanocomposite and reference material	9
	paint	Taber abrader	yes	released particle TNC depended highly on the host material type; the harder material (lacquer) generally resulted in more released particles; no morphological analysis of released particles was performed	11
talc	PP	shredding	no	particles released from the ENP paints were of a concentration and size similar that of those released from control materials; no. of particles released during simulations of "normal wear" were less than more aggressive abrasion methods; same observations as above for shredding of MMT clay/PP nanocomposites; talc (20 wt % loading) suppressed particle release at all particle sizes compared with MMT clay (5 wt %)	8
titania	paint on glass substrate	Taber abraser	no	Micrometric and submicrometric TiO$_2$/paint composite particles were observed; the TNC of released particles increased when the abrasive material was harder	17
	paint on PVC substrate	Elcometer 1720 abraser	no	TiO$_2$/paint composite particles observed in liquid medium after abrasion; particle size distribution ranged from 0.3 to 700 μm and was similar for control and NP-containing samples	17
	spray coating on wood, PET, and tile	simulated wind and cutting with a rubber knife	N/A	cutting increases the TNC of released particles, but size distribution remains similar; most released particles were in 50–150 nm range; no morphological analysis of released particles was performed	8
	acrylic paint on wood	mechanical sanding	N/A	size distributions of released particles from paints filled with 17 nm anatase TiO$_2$ particles and control paints were similar, but a lower TNC in the size range of 130 to 180 nm was observed for the nanocomposite; no morphological analysis of released particles was performed	9
	wall paint on fiberboard	mechanical sanding	N/A	composites with both rutile (220 nm) and anatase (<100 nm) forms of TiO$_2$ were investigated; little difference in the size distributions of released particles between these samples and the reference material observed, although the anatase composite had a higher TNC of released particles between 130 and 180 nm; no morphological analysis of released particles was performed	9
zinc oxide	poly(urethane) coatings and acrylic paint on substrate	Taber abraser	no	ZnO/polymer aggregate particles observed; no free ENPs detected; quantity of mass loss depends on host polymer type and substrate type, less so on the presence of ENPs	18
	poly(urethane) coatings and acrylic paint on substrate	mechanical sanding machine	no	materials released significant quantities of particles <100 nm that were agglomerates of polymer and ENPs; no free ENPs detected; presence of ENPs did not significantly impact the number concentration of released <100 nm particles	12

[a] In all cases save one (Göhler et al.[12]), mechanical abrasion studies surveyed particles released into the air (aerosols). [b] Abbreviations in this table: CNFs = carbon nanofibers; CSH = calcium silicate hydrate; MMT = montmorillonite; MWCNTs = multiwalled carbon nanotubes; PA = poly(amide); PC = poly(carbonate); PET = poly(ethylene terephthalate); POM = poly(oxymethylene); PP = poly(propylene); PVC = poly(vinyl chloride); TNC = total number concentration; TPU = thermoplastic poly(urethane). [c] This column specifies whether the authors of the respective study observed any of the filler particles released whole and free (i.e., not agglomerated to host material). In most cases, an "N/A" means that the study did not employ a measurement technique capable of making a positive determination about freely released nanofiller, whereas a "no" indicates that the authors employed experimental techniques capable of identifying freely released nanofillers but were unable to observe any.
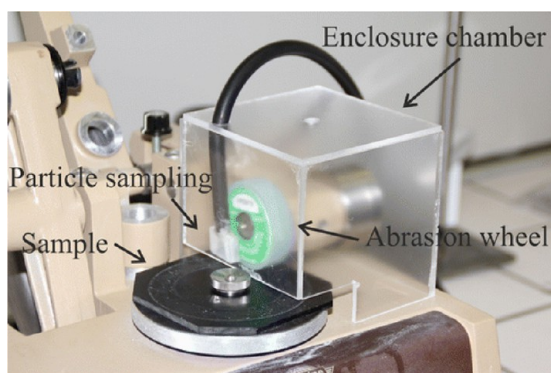
Figure 2. Photograph of a Taber abraser to assess effect of "normal use" wear on a PNC and subsequent airborne release of distributed ENM fillers. Reprinted with permission from Schlagenhauf et al. Release of Carbon Nanotubes from an Epoxy-Based Nanocomposite during an Abrasion Process. *Environ. Sci. Technol.* **2012**, 46, 7366−72. Copyright 2012 American Chemical Society.

of the reference material.[9] Conversely, the addition of 5 wt % montmorillonite (MMT) clay to polypropylene has been reported to suppress the release of ultrafine particles during shredding, even though the median particle diameter remained the same;[8] this same study also performed identical experiments on a material embedded with 20 wt % talc (also a layered silicate material) and found an even higher degree of suppression of particle release, though whether this enhancement of the suppression effect was due to the material's composition, physical dimension, dispersion characteristics, or higher weight loading is unclear. Another study directly compared the release of particles from MMT/polymer composites with different host materials during drilling and reported a similar suppression of particle release when MMT was dispersed in polyamide (Nylon), but the opposite effect (enhancement of the total number concentration of released particle concentration compared to the reference) was observed when identical clays were deposited in polypropylene instead.[5]

Apart from clays, a few other studies have investigated abrasion of materials that differ only in the type of nanofiller additive. Göhler et al. dispersed iron oxide nanoparticles in white pigmented architectural coatings (on fiber cement) and contrasted their particle release properties during mechanical sanding with an identical material containing zinc oxide nanoparticles as well as a control coating with no nanoparticle filler.[12] The authors found no significant difference in particle release properties among the three test materials, despite the differing composition and size distribution of the nanofillers and the fact that one of the test materials contained no nanofillers at all.

Koponen et al. investigated the effect of sanding on a variety of related materials and observed various trends.[9] For example, indoor wall paint containing 220 nm rutile titanium dioxide particles exhibited almost no increase in the total number of released particles compared with the reference material, but when the same paint was loaded with <100 nm anatase titanium dioxide particles, a greater than 4-fold increase in the concentration of aerosolized particles over all measured size regimes was observed. Among the eight different nanocomposite materials investigated in this study, the authors found wide variations in the number concentrations of released particles compared with those of reference materials, including both suppression and enhancement effects, but they observed much smaller variations in mean particle sizes across the board.

The authors cite the sheer number of variables involved as a confounding factor toward making meaningful conclusions about whether ENMs generally increase the risk of exposure to airborne particles from mechanical abrasion of materials.

Although the impact of nanofiller presence on the particle release properties of solid materials during abrasion is not easily generalized in terms of magnitude or direction, the nanofiller concentration has been documented to have an effect on the released particle concentration and size distribution. Mechanical sanding of CNT/epoxy nanocomposites exhibits a clear positive correlation between the wt % of dispersed CNT (ranging from 1 to 4 wt %) and both total number concentration and respirable mass concentration of released particles, although the total number concentration of released particles from the reference material (no nanofiller) lay near the middle of the range exhibited by the nanocomposites.[14] Released particles in the 0.5−500 μm range, which account for most of the released mass, were smallest for the 4 wt % CNT/epoxy material and largest for the neat material. The tendency of nancomposites loaded with more nanofillers to release a higher quantity of smaller particles was attributed to an increase in the brittleness of the material as a function of filler loading percentage, consistent with similar correlations made between released particle characteristics and mechanical properties of the host material (see below). Interestingly, a separate study[15] on CNT/epoxy composites found an opposite effect: although particle size distributions were still multimodal, particles in most size ranges released from neat materials were found to have slightly smaller median diameters than those of the composites, although in this case, smaller filler concentrations were explored (0.1 and 1 wt %) and the abrasion mechanism was different (low-energy Taber abraser at 60 rpm vs high-energy mechanical sanding at 1425 rpm), which might account for this difference. More studies that probe the effect of filler concentration and other characteristics on the particle release properties are needed, especially for fillers other than CNTs. In addition, there have been few studies that have investigated the impact of compatibilizers or other nanofiller surface modifications on the vulnerability of such materials to become released from polymers or other host materials due to mechanical wear.

Effect of the Host Material. There are data to suggest that the nature of the host material has a greater influence on the characteristics of particle release from nanocomposites during mechanical abrasion than the characteristics of the nanofillers. For instance, when zinc oxide nanoparticles were dispersed in either polyurethane, UV-curable clear coat, or white-pigmented architectural surface coatings and subjected to a Taber abraser,[18] both the host material and the sample carrier (coated substrate) were found to exert a far greater influence on the total mass loss during abrasion than the presence or absence of zinc oxide nanoparticles, although statistical error in aerosolized particle concentrations made it impossible to define a clear correlation between mass loss and number of released particles. In a different study, when nanoclay platelets or silica nanoparticles were dispersed in polyamide 6 and subjected to drilling, the total number concentration of aerosolized particles was significantly greater (usually more than 10×) than when the same particles were dispersed in polypropylene.[5] This same effect was observed when comparing drilling of the two host materials without nanofillers, suggesting the nanofiller characteristics play only a minor role in the release properties compared to the host material.

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Taken as a whole, the available evidence indicates that effects such as those described in the preceding paragraph can be related to the mechanical properties, including strength, hardness, and fracture toughness, of the composite material, which are in large part driven by the mechanical properties of the host material. For instance, it has been speculated[15] that some of the observed differences in the diameters of abraded particles released from CNT/epoxy and CNT/polyoxymethylene in two different studies[10,15] are possibly attributed to the ~10-fold difference in fracture toughness values of epoxy and polyoxymethylene. The fracture toughness values for these materials directly impact the lateral crack length and, hence, the mean size of particles resulting when sheer forces applied during abrasion cause brittle fracture of the material. The authors noted that local inhomogeneities created by ENM dispersion may introduce more complicated behavior in certain circumstances, which may explain some of the complex trends in released particle size and number concentration observed when comparing nanocomposites of different compositions.

Another possibility related to number concentration of released particles is that tougher host materials may simply be able to absorb more sheer energy before fracture and thus exhibit less mass loss overall than composites formed from more brittle matrices. This may explain, for instance, the observation that abrasion (sanding) of nanocomposite coatings consisting of hard but brittle lacquer released a higher number of emitted particles compared with those manufactured with softer, more elastic materials such as acrylic paints, which can transfer some sheer energy into deformations.[9] Ultimately, however, the macroscopic properties of a material are dependent on a variety of interrelated factors, including humidity level, molecular weight, and the presence of additives and plasticizers. ENMs also alter the bulk mechanical properties of the host material in complex ways, so predicting the effect of the host material on the release behavior during abrasion will likely continue to be challenging.

Effect of Process Type. Regardless of the type of host material or nanofiller utilized, the type of machining process directly impacts the number concentration and size of released particles during abrasion of nanocomposites. For instance, Wohlleben and co-workers demonstrated that simulated long-term wear using a Taber abraser resulted in fewer released particles from CNT-based composites than more aggressive sanding processes applied to identical materials.[10,16] Bello and co-workers assessed release of airborne particles from CNT/epoxy-based materials after either sawing or drilling and found that drilling resulted in significantly higher peak exposures than sawing (3.9×10^6 to 1×10^7 vs 2×10^4 to 6×10^6 particles/cm^3), whereas sawing resulted in more complex particle morphologies;[4,7] drilling was also found to be more likely than sawing to generate free filler particles (vide infra) and resulted in a larger dependence of particle size distribution on the host material composition. In a similar study on airborne release of particles from CNF/epoxy composites as a result of hand sanding, belt sanding, surface grinding, and wet sawing, surface grinding was found to result in substantially more released particles in the 20−300 nm range at both the breathing zone and the immediate process area, although other methods released a more substantial quantity of larger particles.[2]

Although it is not always explicitly stated, it appears that a large factor in the number concentration, and perhaps size distribution, of particles released during the machining of nanocomposite materials is the amount of sheer energy applied.

This observation seems to be conserved regardless of the host material or nanoscale filler composition. For example, in the aforementioned study by Bello et al. on the effect of solid core drilling CNT/epoxy composites, the number concentration of released particles was positively correlated to the drilling speed (rpm) and bit diameter.[4] At the highest drilling speeds, smoke was liberated along with CNTs in a free state (not bound to polymer), suggesting enough sheer energy is applied under these conditions to thermally degrade the host matrix. In a different study on similar materials, Huang et al. observed an increase in number concentration of released particles from 2 wt % CNT/epoxy as a function of sanding speed and sandpaper coarseness, although finer sandpapers produced the highest respirable mass concentrations of aerosolized particles.[14] These findings are consistent with the work on nanotitanium paints coated onto glass substrates conducted by Golanski et al.,[17] who reported a positive correlation between released submicrometric particle number concentration and the hardness of the abrasion material; these authors reported similar results for nanosilica paints as well.[11]

Most likely, the differences in released particle characteristics observed in the few studies in which multiple abrasion methods (e.g., drilling versus sawing) or abrasion materials (e.g., grit level or hardness of sandpaper) are directly compared are related in some way to either the magnitude or directionality of sheer forces applied during the respective machining process, such as downward force during sawing or rotary force during drilling. One study on the release behavior of ENM-loaded PVC-based fabrics, for instance, observed a large quantity of nanometric particles released when the standard abrasion wheel of a Taber abraser was swapped for a custom-made stainless steel rake.[11] The authors concluded that the enhancement in ENM release was due to "microscopic scale instantaneous shocks" created when the teeth were dragged over the irregular woven fabric surface, which supplied enough energy to overcome van der Waals forces between the imbedded particles and the substrate. Conversely, a custom-made engraver tool, the action of which did not transmit such shocks through the material surface, was found to not be an efficient tool for detaching ENMs, presumably because the nature of the contact forces between the abrading and material surfaces were not conducive to this. Beyond this work, however, few studies on nanocomposites have investigated specific relationships between the abrading forces and the material surface in enough quantitative detail to draw broader conclusions about these effects. Moreover, the extent to which embedded ENMs can attenuate or enhance the effect of these sheer forces on the degradability of the host material has yet to be systematically explored.

Composition and Morphology of Released Particles. A majority of the articles summarized in Table 1 include use of imaging or surface analysis techniques to reveal details about the composition and morphology of airborne particles released during abrasion. In almost all cases, at least a portion of the released particles were found to be composed of nanofillers partially or fully embedded in aerosolized fragments of the host material. These composite particles are typically irregular in shape, although roughly spherical, and may or may not be aggregates of smaller particles of identical composition. Two related studies[4,7] found sharp, needlelike fibers among the released particles, although the test composite in this case was a laminate material with an internal architecture involving CNTs and either macroscale carbon or aluminum fibers deposited in
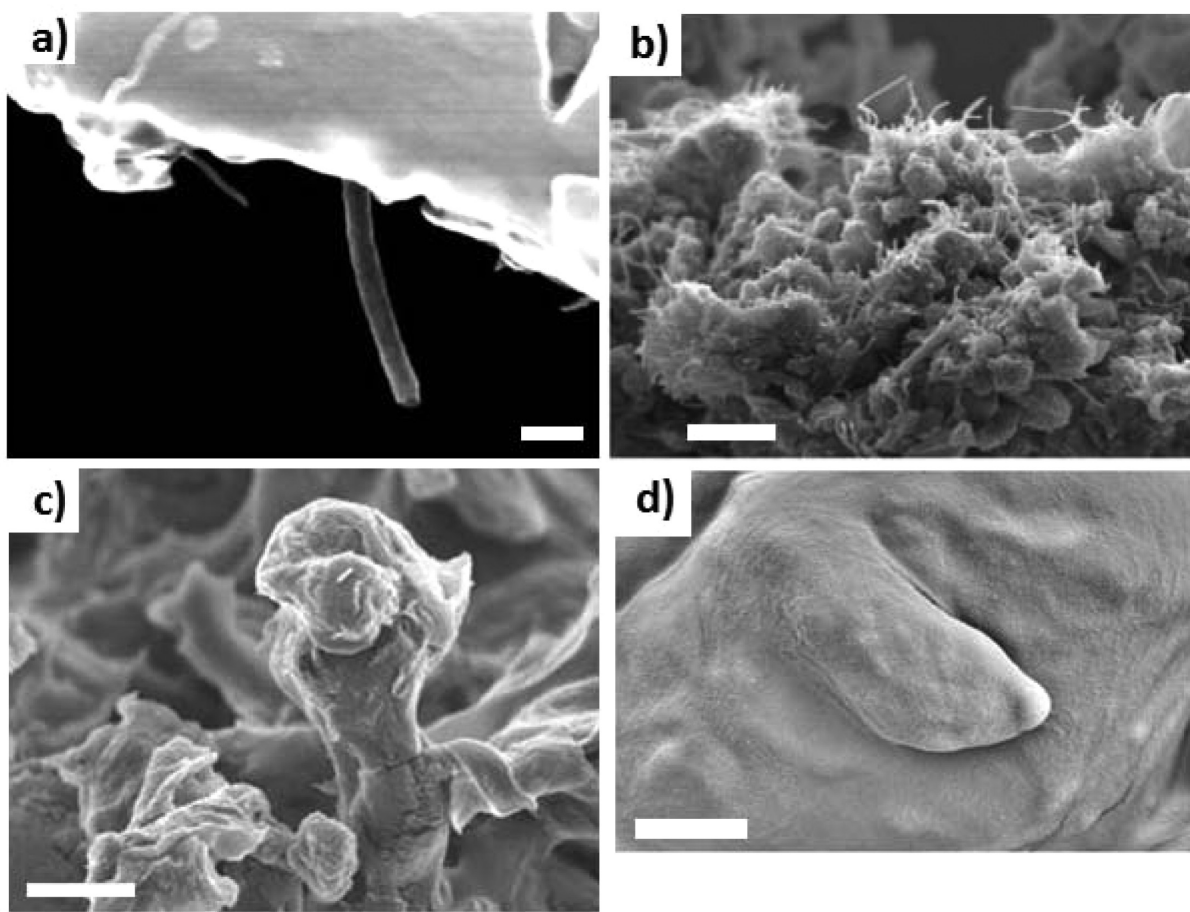
Figure 3. Electron microscope images of sanding fragments from nanocomposites of CNTs in (a) epoxy, (b) cement, (c) poly(oxymethylene), and (d) thermoplastic poly(urethane). Note the protrusions of CNTs in sanding fragments from the epoxy and cementitious materials (panels a and b) and lack of protrusions from the poly(oxymethylene) and poly(urethane) materials (panels c and d). Scale bars in panels a, b, c, and d are 100 nm, 500 nm, 1 μm, and 1 μm, respectively. Reproduced from Hirth et al., Scenarios and methods that induce protruding or released CNTs after degradation of nanocomposite materials. *J. Nanopart. Res.* **2013**, 15, 1504.

epoxy, which may have facilitated precise fracturing of the material along the fiber axes or at the interfacial boundaries between layers during machining.

In several materials, particularly those in which the nanocomposite being abraded includes a fibrous nanofiller such as CNTs, particles aerosolized during abrasion exhibit protrusions of the nanofiller from the particle surface.[3,10,13,14] Examples of this are shown in Figure 3, which is reproduced from a study by Hirth et al.[13] on the effect of mechanical sanding of nanocomposites composed of CNT fillers deposited in a variety of host matrixes, including epoxy, cement, TPU, and POM. It is readily apparent from the electron microscopy images (and confirmed from XPS-based surface analysis,) that fragments abraded from CNT/epoxy and CNT/cement exhibit protruding CNTs, whereas those abraded from CNT/POM or CNT/TPU retain smooth surfaces with no protrusions. The particles liberated from the cementitious material, in particular, are rife with CNT protrusions, forming a "hairy layer" with length around 300 nm in which all visible CNTs emerge from cement grain surfaces, with one end of each CNT free and the other end deeply embedded in the inorganic matrix.[10,13]

Hirth et al. concluded from their work that CNT protrusions are a material-dependent phenomenon related to the toughness of the host matrix and are likely to occur only in particles released from host materials with elongation-at-break values greater than ~10%.[13] In materials with large elongation-at-break values (e.g., thermoplastic polymers such as Nylon, PE, PET, etc.), necking of the host matrix is expected to inhibit the formation of CNT protrusions; that is, the host material will "stretch" around nanofillers rather than simply break off to leave nanofillers exposed. The authors also concluded that the formation of protrusions is not directly related to the sheer energy applied, which is consistent with another study[3] that found evidence of CNT protrusions in particles abraded from CNT/epoxy nanocomposites during sanding by hand with sandpaper. Importantly, the nanofillers themselves have high tensile strengths and do not break or become released without further chemical degradation of the host matrix (see below), which is why they are left protruding from released matrix particles even after the host matrix has mechanically degraded around them. A macroscale analogy is the exposure of embedded steel rods (rebar) out of weathered reinforced concrete.

A critical question that many release studies seek to answer is whether nanofillers are released in a "free" state—that is, not embedded in fragments of abraded host material. This question cannot be easily answered simply by analyzing the size distribution of aerosolized particles because composite particles or incidental particles (e.g., released from the abrasion equipment) may also be in the nanoscale regime or because freely released nanofillers may constitute too small a portion of

the total released mass that instruments are not sensitive enough to detect them.[15] In addition, free nanofillers could adhere to the surfaces of larger abraded particles and thus remain hidden from conventional particle sizing experiments. Therefore, studies that do not employ some kind of compositional analysis, surface analysis, or imaging technique are not appropriate for drawing conclusions about the presence of free nanofillers in the aerosol resulting from mechanical abrasion.

Only in a few cases have free nanofillers been observed after mechanical abrasion of nanocomposites. Carbon nanofibers were released in either a free state or in bundles when CNF/ epoxy materials were subjected to wet saw cutting, dry surface grinding, and both manual and table belt sanding.[2] Free, aerosolized CNTs were observed when CNT/epoxy nanocomposites were mechanically degraded, but usually only at either the highest loading percentages (4 wt %, but not 1−3 wt %)[14] or during specific types or magnitudes of sheer forces (observed during drilling but not during cutting).[4,7] One study observed free CNTs released from a different CNT/epoxy material (in addition to composite particles with CNT protrusions), but the released CNTs appeared to be fragmented and could not be easily quantified.[15] No studies have observed free particles released from nancomposites with small, spherical nanofillers (such as silica particles), but it is possible that such small nanoparticles could be missed if they are adsorbed onto the surfaces of micrometric particles composed of abraded host material. This stresses the utility of surface analytical techniques such as SIMS and XPS, which can unequivocally reveal whether nanofillers are present on abraded particle surfaces. For example, Wohlleben et al. used XPS and SIMS to show that silica nanoparticles were exposed on the surfaces of composite particles released from silica/polyamide PNCs, but only in concentrations similar to what is found in the bulk composition of the PNCs;[10] if silica nanofillers were released in a free state and then adsorbed onto the surface of particles composed of the host material after aerosolization, XPS and SIMS would reveal disparate concentrations of silicon between the postabrasion released particles and the preabrasion bulk material. A wider application of surface analytical techniques could reveal more about the conditions under which free nanofiller release is likely.

Beyond Airborne Release. An overwhelming majority of nanocomposite abrasion studies are focused on analysis of airborne particles. Although this is certainly important from an occupational safety standpoint, it is not a complete picture of how ENMs may be released into the environment during abrasion of nanocomposite-based materials. For example, ENMs contained in micrometer-scale composite sanding fragments could be more easily released via diffusion or dissolution due to the larger exposed surface areas of these particulates compared with that of the unabraded bulk material, particularly if the nanofillers are protruding from the host material after abrasion. The abraded surface of the bulk material may also be more susceptible to weathering effects, a possibility that has only briefly been explored (see below).

Another area that has received only a small amount of attention is the potential release of nanofillers directly into liquids when abrasion occurs while the nanocomposite is wet or submerged. A few studies have assessed airborne release of nanofillers during wet machining.[46a,47b] Not surprisingly, abrasion during wet conditions often results in a significant reduction in the number of aerosolized particles, although perhaps not in the total amount of material released (in the cited literature studies, the liquid was not assessed for particle

content). Methner et al. observed free CNFs in aerosolized water droplets during wet saw cutting, although given that free CNTs were also observed during dry machining, the nanofillers may have become incorporated in the liquid before or after the droplets were aerosolized.[2] Only one study was found that assessed release of particles directly into liquids rather than into air. In this report,[17] titanium dioxide nanoparticles were dispersed in paint, coated onto a polyvinylcarbonate (PVC) substrate, and then agitated with a Elcometer 1720 abrader, which pumps a surfactant solution onto the coating and then linearly rubs it to create friction. Using laser granulometry and SEM, the authors found released particles with sizes in both the submicrometric and supramicrometric size regimes, but no particles with diameters less than 300 nm. No free nanofillers were observed; rather, released particles were agglomerates of the nanofillers and the host matrix, similar to what is typically observed in the air-release studies discussed above. Unfortunately, because only a single condition was tested in this study, it is difficult to make any broad conclusions at this time about the propensity of nanofillers to become released into liquids during abrasion. Furthermore, no studies were found that have assessed the potential for passive ENM release into liquid medium after abrasion (e.g., rain weathering of mechanically abraded surfaces).

In summary, the available literature on release of ENMs from nanocomposites as a result of mechanical degradation suggests that the physical properties of the host material (and the types of forces applied) are integral to determining the number and size of particles released. To the extent that ENMs impact the release properties, it appears that their influence on the bulk mechanical properties of the material may be more important than the intrinsic properties of the ENMs themselves, although more work needs to be done to show this explicitly. It is noteworthy that the effect of the nanofiller on the bulk physical properties of the host depends a lot on the dispersion characteristics (nanoclay exfoliation, for example)[19] and because these properties have not often been controlled, this may explain some of the inconsistencies among the studies presented above. An intriguing work published by French researchers[11] has, for example, shown that when the CNTs are well distributed through a polymer matrix, they are less likely to become released in a free state (i.e., not bound to host material) during abrasion by a rotating steel brush, possibly because well-dispersed ENMs have more attractive forces than poorly dispersed ENMs between the host material and the ENM surfaces (Figure 4). Despite this singular example, differences observed in released particle concentration, size, and even morphology of released ENMs may be more often due to mundane factors, such as the grit level of the sand paper used or the instrumentation used to capture and analyze particle characteristics. Unfortunately, the degree of variation in the experimental methods and also the test material characteristics from one study to the next precludes any kind of rigorous meta-analysis of the available studies on mechanical degradation of nanocomposites. All of this highlights the need for more detailed and systematic investigations that probe the relationships between nanofiller charcteristics and bulk release properties.

III. RELEASE OF ENMs DUE TO PHOTOCHEMICAL DEGRADATION OF THE HOST

Ultraviolet radiation is an efficient catalyst of organic polymer decomposition.[20] The photoinitiated chemical reactions occurring in polymeric materials are complex and polymer-specific.

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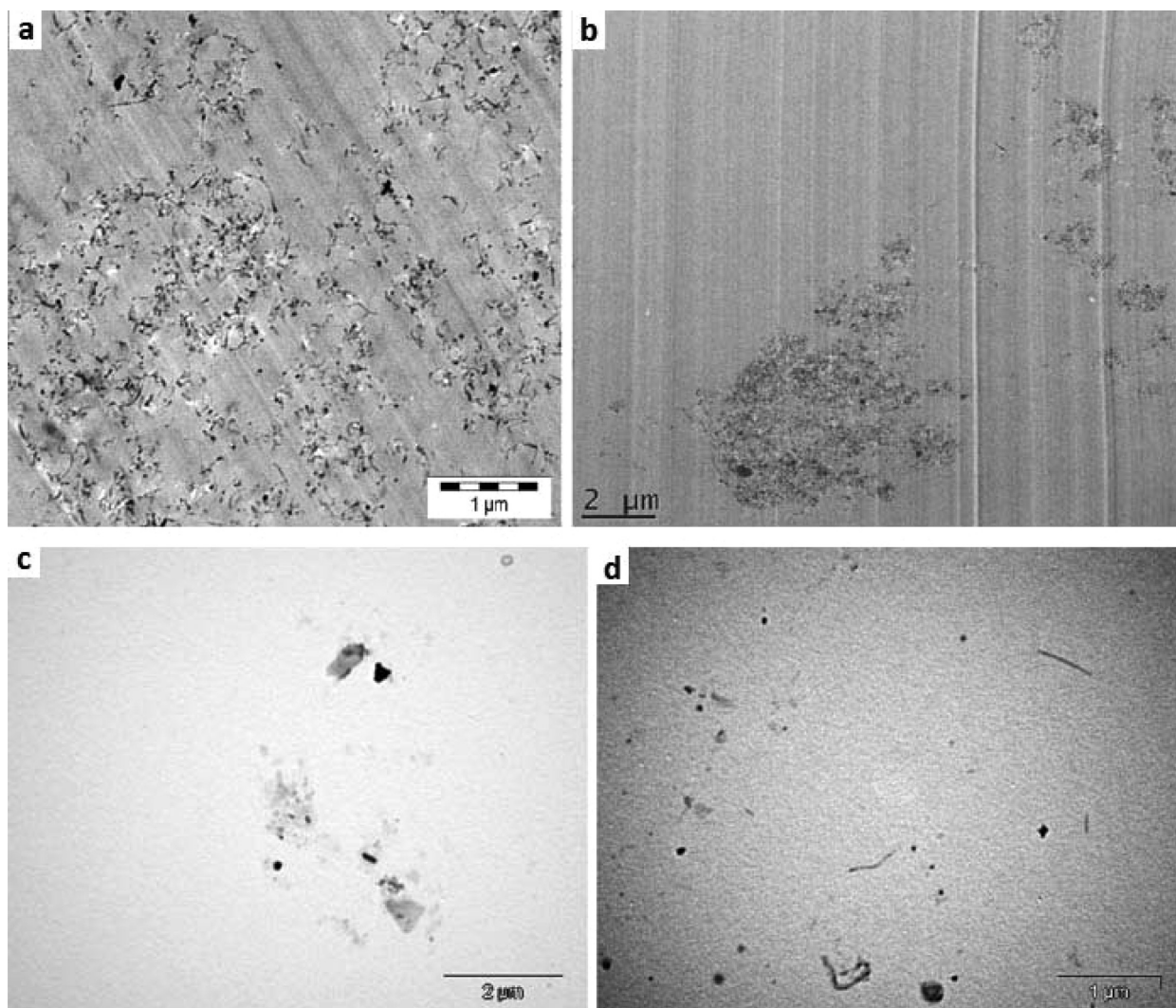
Figure 4. Electron microscope images of 0.8 wt % CNT/epoxy PNCs with (a) good dispersion and (b) bad dispersion. Images c and d show particles released from these respective materials during abrasion with a Taber abraser adapted with a steel-brush. Note that a larger quantity of fragments are released from the poorly dispersed material, as well as what appears to be free CNTs. Reproduced with kind permission from Golanski et al., Release-ability of nano fillers from different nanomaterials (toward the acceptability of nanoproduct). *J. Nanopart. Res.* **2012**, 14, 962. Copyright 2012 Springer Science and Business Media.

These reactions generally involve the formation of free radicals along the polymer backbone, which react with oxygen to result in chain scission, carbonyl formation, and other end points. Polymers featuring aromatic functional groups that efficiently absorb UV radiation and can photosensitize free radical or singlet oxygen production, such as aromatic polyamides and polyethylene terephthalate, may be most susceptible to such UV aging processes. Macroscale properties affected by UV aging may range from purely cosmetic (yellowing) to the catastrophic (complete disintegration), depending in large part upon the extent of exposure.

Nanofillers may attenuate the photodegradability of the host polymer in often unexpected ways.[21] A full assessment is beyond the scope of this article, but studies and reviews that explore the effect of UV radiation on PNCs filled with CNTs,[22,23] nanoclays,[24−28] and metal oxide[29−33] nanoparticles are available. Studies on whether nanofillers accelerate or inhibit the rate of polymer photodegradation are often contradictory, suggesting a complex relationship exists between photodegradability and the nanofiller composition, size, crystal phase, and dispersion characteristics. For example, one study found that LDPE composites containing nanoclays and silica nanoparticles had accelerated photodecomposition, whereas those containing multiwalled carbon nanotubes (MWCNTs) were UV-stabilized.[34] Another study reported that the photodegradability of nanoparticulate-TiO_2-filled poly(lactic acid) was markedly different depending on whether the embedded nanoparticles were rutile or anatase phase.[33] Pigment surface treatment and particle dispersion also impacts degradability of filled coatings.[35] In some cases, UV-absorbing ENMs, such as those composed of TiO_2 and ZnO, have been specifically added to polymers to increase their photodegradability,[29,30,32] leading to putatively more ecofriendly materials (i.e., they would degrade faster in landfills). Of course, although the host material may certainly decompose faster with these nanofillers present, the claim of an environmentally friendlier material disregards the ultimate fate of the ENMs that were integrated into the matrix. Table 2 summarizes research reports that have explored the fates of ENMs after host matrix photodegradation.

Some of the most active researchers in understanding the relationship between UV exposure and ENM release from

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Table 2. Summary of Studies Related to the Release of ENMs from Composite Materials Due to Photochemical Decomposition[a]

ENM	host material	exposure type	air or liquid?[b]	nanofiller release?[c]	release characteristics	ref
CSH	cement	UV weathering only	air	no	no degradation of the cement observed, CSH nanopartides remain dispersed in cement	10
GO	WBPU	UV weathering only	N/A	N/A	GO accumulated on the material surface as host matrix degraded; release of GO into the external medium not assessed.	39
MWCNTs	cement, TPU and POM	shaking or ultrasonic sheer after UV weathering	liquid	yes	fraction of particles <150 nm depends on sheer energy used; fraction of particles in micrometer range independent of agitation method; no. of released micrometer-scale particles was the same for the composite and control materials; free MWCNTs detected after highest levels of sheer (ultrasonic)	13
	epoxy coating on substrate	UV weathering only	air	no	progressive UV exposure destroys the epoxy matrix, leading to accumulation of MWCNTs on the material surface; accumulated MWCNTs form a dense, tangled network that protects against further degradation of the matrix and against release of free MWCNTs	37
	cement and POM	UV weathering only	air	no	no degradation of the cement matrix observed, and MWCNTs remain dispersed; POM degraded substantially, particularly with MWCNTs present; MWCNT network exposed but not easily liberated by sonication.	10
	TPU	UV weathering, with simulated rain cycles	air and liquid	no	UV weathering degraded the polymer surface, leaving MWCNTs exposed; effect was worse with simulated rain; immersion of weathered samples in surfactant solution resulted in no observation of released MWCNTs	16
	epoxy	UV weathering with scratching	N/A	N/A	gross findings similar to Nguyen at al.;[37] scratch lithography showed that the surface-bound MWCNTs were more resistant to scratching than epoxy-rich regions, which might indicate MWCNTs are not readily able to be released from UV-damaged MWCNT/polymer composites	38
silica	PA	UV weathering only	air	no	no degradation of the cement matrix observed, silica nanoparticles remain dispersed in polymer	10
	epoxy coating on substrate	UV weathering only	air	yes	progressive UV exposure destroys the epoxy matrix, leading to accumulation of silica particles on the material surface; free silica particles passively fell off the exposed surface	36,37
titania	direct coating on wood, PET, and tile	UV weathering with agitation	air	N/A	UV light increased the number of released particles due to weakening of the particle-substrate interactions; visible light showed no effect.	6

[a] Abbreviations in this table: CSH = calcium silicate hydrate; GO = graphene oxide; MWCNTs = multiwalled carbon nanotubes; PA = poly(amide); PET = poly(ethylene terephthalate); POM = poly(oxymethylene); TPU = thermoplastic poly(urethane); WBPU = water-borne poly(urethane). [b] This column specifies whether the release of particles was assessed in air (aerosol) or liquid media. N/A indicates that particle release was not assessed in this study. [c] This column specifies whether the authors of the respective study observed any of the filler particles released whole (i.e., not agglomerated to host material). In most cases, an "N/A" means that the study did not employ a measurement technique (compositional or imaging analysis of released particles) capable of making a positive determination about freely released nanofiller, or the study was not focused on identifying released particles, whereas a "no" indicates that the authors employed experimental techniques capable of identifying freely released nanofillers but were unable to observe any.
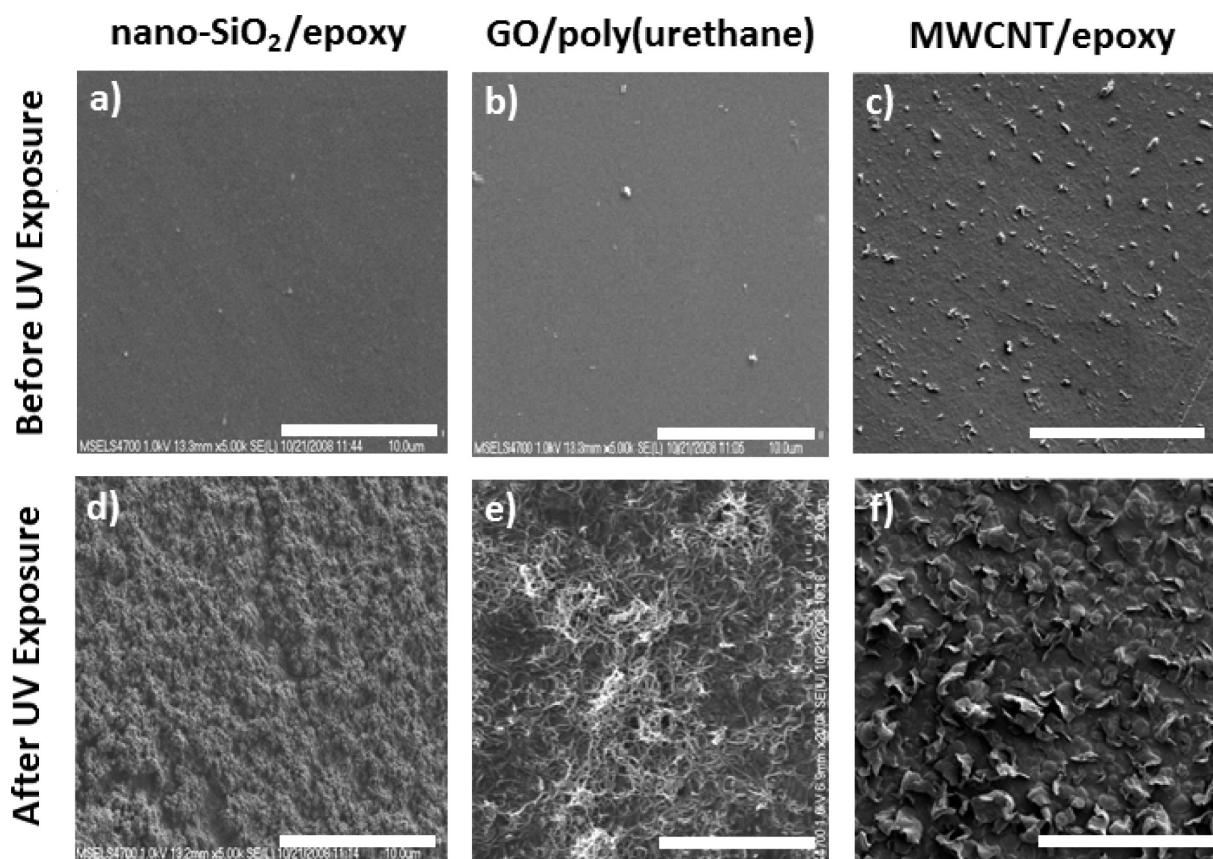
nano-SiO₂/epoxy GO/poly(urethane) MWCNT/epoxy

Figure 5. Electron microscope images of the surfaces of silica nanoparticle/epoxy, GO/polyurethane, and MWCNT/epoxy PNCs before (a, b, and c, respectively) and after (d, e, f) UV irradiation. The irradiation duration was 43 days for panels d and f and 60 days for panel e. In all cases, UV-assisted decomposition of the host matrix resulted in progressive coating of the PNC surface with the free or entangled nanofillers. The scale bars are 10 μm for panels a, b, and d; 2 μm for panel e; and 20 μm for panels c and f. Panels a and d are reprinted with permission from Nguyen et al., *J. Nanosci. Nanotechnol.* **2012**, 12(8), 6202−6215,[36] Copyright 2012 American Scientific Publishers. Panels b, c, e, and f are reproduced from Bernard et al.[39] and Nguyen et al.,[37] with permission from the authors.

PNCs have been from the US National Institute for Standards and Technology (NIST), where a specialized weathering chamber called SPHERE (Simulated Photodegradation via High Energy Radiant Exposure) is available to facilitate well-controlled photodegradation studies. In a series of studies, Nguyen and co-workers fabricated polymer nanocomposites containing silica nanoparticles,[36,37] MWCNTs,[37,38] and exfoliated graphene oxide platelets[39] and observed changes to the surfaces of these materials after prolonged UV exposure. All of these materials were found to gradually lose mass as a function of UV exposure time, and FTIR spectroscopy revealed the appearance of carbonyl peaks, signaling photo-oxidative chemistry and chain scission. The MWCNT-based composites exhibited the smallest rate of mass loss after 43 days exposure, and the silica nanoparticles exhibited the largest rate of loss, with the neat epoxy material being intermediate.[37] The authors suggested that the inhibitory role of MWCNTs on photo-degradation may have been due to the MWCNTs' ability to filter incoming radiation and also interact strongly with any photogenerated free radicals. Several other studies have also identified CNTs as possibly able to make materials more resistant to UV damage.[23,34,38,40]

Microscope imaging of the nanocomposite surfaces by Nguyen and co-workers in the above-mentioned studies provide a glimpse of what happens to embedded nanoparticles as the host matrix falls apart. Representative SEM images of the MWCNT/epoxy, silica nanoparticle/epoxy, and GO/polyurethane PNCs as a

function of UV irradiation time are shown in Figure 5. In all three cases, the surfaces of the PNC material are fairly smooth prior to the UV exposure with good surface coverage of the host matrix, but after several weeks, the respective ENM has been exposed on the surface as a result of destruction of the surrounding material. At the longest exposure times, the surface is almost completely covered by a dense network of exposed ENMs that accumulate gradually as the host matrix disintegrates. In the case of MWCNTs, the increasing surface coverage by exposed nano-fillers has also been recently demonstrated using X-ray photo-electron spectroscopy (XPS), which reveals a steady growth of a MWCNT-associated peak at ∼284.5 eV as the cumulative radiation dose increases, as well as energy-filtered TEM (EFTEM), which can be used to distinguish between crystalline (MWCNT) and amorphous (polymer matrix) carbonaceous regions.[38]

Because ENMs accumulated on the PNC surface during UV exposure are no longer surrounded by the host matrix, Nguyen and co-workers suspected that these ENMs may be prone to release with very little force applied (Figure 1). To ascertain whether this was the case, they analyzed particles collected at the bottom of the sample holder and found evidence of free silica nanoparticles in the case of the silica/epoxy material but no evidence of free MWCNTs in the case of MWCNT/epoxy.[36,37] The authors suggested that MWCNTs, being long, fibrous materials, form entangled networks on the PNC surface as the host matrix photodecomposes, which precludes their
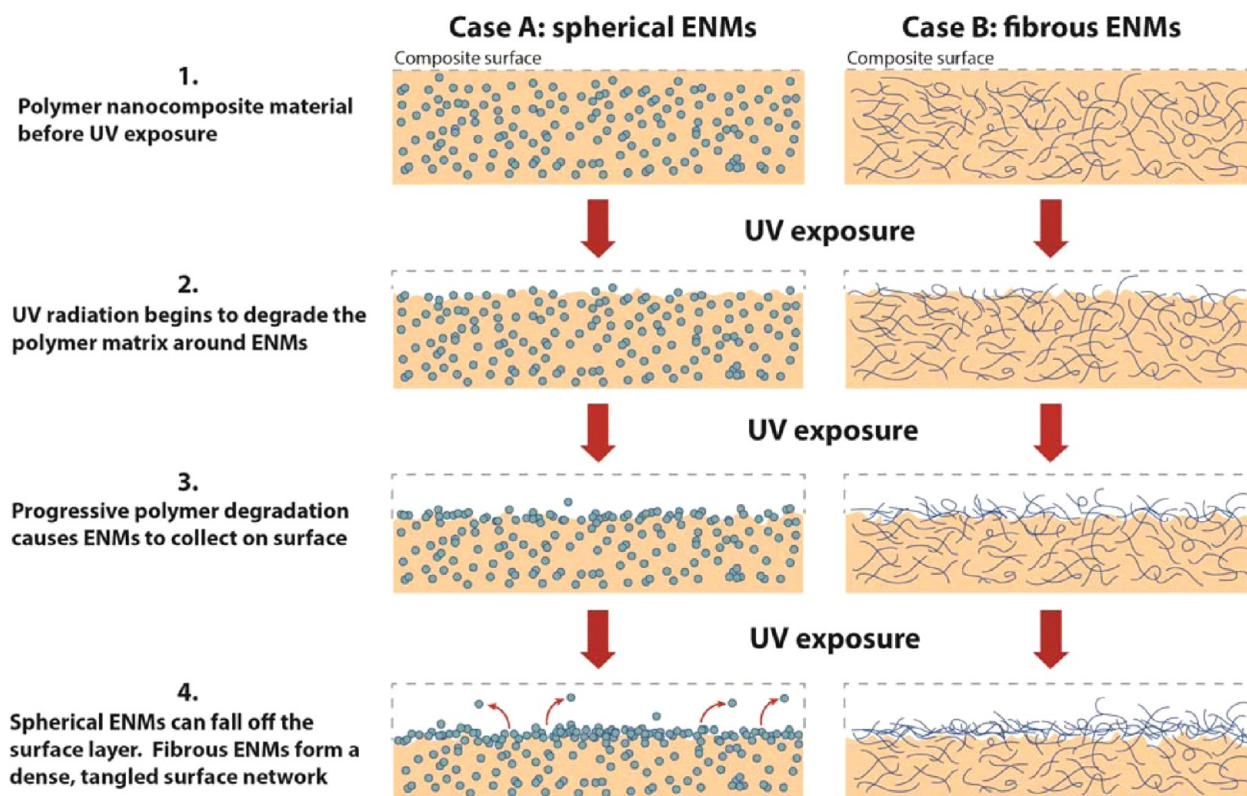
Figure 6. Conceptual model of ENM release from UV-degraded polymer composites for (A) spherical ENMs (e.g., silica nanoparticles) and (B) fibrous ENMs (e.g., CNTs). Platelet shaped ENMs may behave like spherical ENMs, but this has not been experimentally verified. Adapted from Nguyen, et al., Fate of nanoparticles during life cycle of polymer nanocomposites. *J. Phys. Conf. Ser.* **2011**, 304, 012060(1−12).

easy gravitational dropping off the vertically aligned PNC. Spherical silica particles cannot entangle and easily fall off the surface as they become exposed, although the researchers did not determine whether the free nanofillers were aggregated with remnants of the host materials. This allowed the researchers to formulate a conceptual model of ENM release from UV-damaged nanocomposites, shown in Figure 6. The researchers did not do a similar assessment of the release potential of UV-damaged graphene-based materials,[39] but nevertheless, it seems clear that the ENM morphology impacts how easily the ENM can become released from UV-damaged PNCs. Filler morphology also impacts the release rate indirectly by attenuating the rate of decomposition, since fibrous ENMs that remain entangled on the surface may filter UV radiation incident on the surface and protect the remaining host material underneath the entangled layer.

If photodecomposition of PNCs enables ENMs in some cases to simply fall off a damaged PNC surface, researchers speculate that UV weathering combined with mechanical agitation could give rise to enhanced ENM release, and this supposition is borne out in the literature. Direct coatings of TiO_2 nanoparticles on wood, polymer, and tile substrates have been shown to liberate more particles in the nanoscale size regime when scraping with a rubber knife after simulated UV and wind weathering than with UV and wind weathering alone,[6] although the liberated particles were not characterized for composition, morphology, or surface characteristics. Interestingly, the underlying substrate was found to affect the concentration of released particles, suggesting that desorption of nanofillers from a PNC surface to the external environment

may be enhanced or inhibited by some types of substrate materials, even under moderate sheer stresses.

The effect of mechanical sheer forces and additional forms of weathering on UV-exposed PNCs was assessed in more rigorous detail by Wohlleben and co-workers,[10,13,16] who studied the release of MWCNTs, silica nanoparticles, and calcium silicate hydrate nanoparticles from several types of host materials, including cement, POM, TPU, and polyamide. MWCNTs were found to enhance the rate of photodecomposition of POM (as opposed to the inhibitory effect observed in many other studies discussed above), leaving an entangled network of MWCNTs on the polymer surface, but these CNTs were not easily liberated, even with ultrasonic treatment.[10] MWCNTs distributed in TPU and subjected to UV weathering were also found to form a collective network on the PNC surface as the TPU degraded, and this effect was enhanced when the UV weathering was supplemented with simulated rain cycles and humidity.[16] No UV damage was observed for any of the cement-based composites or for silica nanoparticles dispersed in polyamide, showing that the susceptibility of the host material to UV damage will play a dominant role in the likelihood of ENM release from PNCs due to weathering.[10] Finally, these authors are the only ones to date who have explored the ability of UV-damaged PNCs to give rise to nanofiller release when submerged into liquid media and exposed to mechanical sheer forces. Although UV-damaged MWCNT/TPU composites did not release CNTs without agitation after being submerged in aqueous SDS solutions,[16] application of mechanical energy in the form of a shaker, ultrasonic bath, or ultrasonic probe led to progressively larger quantities of released particles in the <150 nm range;[13] at the

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highest input energy, individual CNTs were observed suspended in the liquid.

These last studies offer an intriguing view of the important relationship between applied mechanical energy, UV weathering, and the potential for ENM release; however, with only a few available pieces of data, it is hard generalize what types of materials constitute the greatest likelihood for ENM release under these combinations of input conditions. More studies that assess the impact of sheer forces, and particularly mechanical abrasion, on nanofiller release after prolonged UV exposure of nanocomposites would be very useful. In addition, the application of new analytical techniques to better understand release behavior at a microscopic level (to shed light on release mechanisms) is needed. As an example of the utility of novel experimental approaches, consider the recent work of Petersen et al., who utilized AFM scratch lithography to quantify how easy it is to mechanically deform the entangled MWCNT surface layer from UV-damaged MWCNT/epoxy composite materials, compared to epoxy-rich surface regions.[38] Interestingly, while epoxy-rich regions could be scratched with a normal load of 0.5 μN, visible scratches were only observed in MWCNT-rich regions where loads were greater than 5 μN, with some evidence of discontinuities indicative of possible breaks apparent at 1 μN. The authors concluded that MWCNT-covered regions may be more resistant to mechanical degradation than epoxy-rich regions, suggesting that MWCNTs in UV-damaged MWCNT-based composites may be "unlikely to be readily released", although they are careful to point out that these results may not be relevant to macroscopic abrading tools. It would be particularly interesting to see this kind of technique applied to composite materials with nonfibrous nanofillers, such as spherical particles or nanoclay platelets, which likewise are known to accumulate on the PNC surface during UV-exposure. More generally, there have been few studies that have directly investigated whether the specific resistance of the host matrix to UV damage impacts the potential for nanofillers to be released, and there have been few studies that evaluate the role that UV-stabilizers or other polymer additives play in such processes. Such studies would provide a more robust understanding of the link between UV exposure and potential nanofiller exposure scenarios.

IV. RELEASE OF ENMS DUE TO THERMOCHEMICAL DEGRADATION OF THE HOST

Like any organic material, polymers are susceptible to combustion, pyrolysis, and other chemical degradation processes as they are heated. The introduction of a nanoscale filler can impact the thermal stability of an organic polymer,[41,42] and indeed, there have been numerous reports in the literature of nanoparticles added to polymers for the specific purpose of increasing their flame retardancy.[43−45] It stands to reason that if a polymer is heated such that it begins to decompose, any nanoscale fillers contained within the material may become released into the external environment, although to our knowledge, there have been no studies published that explore the dynamics of such a possibility in any rigorous detail. Although not explicitly related to "degradation", it would also be useful to have data on the propensity for a PNC to release nanofillers at intermediate, subdecomposition temperatures, where the bulk properties of the host material may be affected by changes in polymer viscosity, density, and crystal structure.

Although release of ENMs due to thermal degradation of PNCs has not been explicitly evaluated, there are data to suggest that nanofillers may be easier to liberate from the host matrix under such circumstances. A substantial body of work by Lewin and co-workers,[46−54] as well as some other independent researchers,[55−57] has established that nanofillers (particularly exfoliated clays) tend to gravitate toward the air–polymer interface when the material is substantially heated (Figure 1). The mechanisms giving rise to this mass movement are complex, but essentially boil down to a combination of temperature and viscosity gradients established within the material during unidirectional heating; gas bubbling occurring during host matrix degradation; and the interfacial tension between the nanofiller and the host matrix, which is less than the molten polymer's surface free energy.[47] This last factor, especially, appears to play a dominant role during nondirectional heating. The presence or absence of oxygen[49,51,54] and of compatibilizers[50] also impacts the extent of nanofiller relocation to the surface due to mediation of the host matrix polarity, which can in turn create a driving force for exfoliation. Importantly, this relocation of ENMs to the material's surface occurs at temperatures below which the matrix undergoes complete decomposition. As an example, when a 5 wt % organically modified MMT, 0.5 wt % maleated anhydride polypropylene PNC was annealed at 225 °C,[50] the ratio of nanoclay at the material surface compared with the reference value of unannealed PNC was nearly 7; since the reference value was related to a 5 wt % clay, this means that the surface of the material has a clay content after subcombustion annealing of almost 35 wt %, indicating that ENM relocation can occur prior to complete decomposition.

The movement of nanoclays to the polymer–air interface during annealing is thought to be one of the primary reasons why clay/polymer nanocomposites can behave as flame retardant materials. The presence of a clay-rich layer at the surface of the material slows down the rate of heat transfer between the external environment and the interior of the material, effectively forming a heat shield (Figure 7). Studies concerning nanoclay behavior during annealing have not addressed whether the clay-enriched surface may make clay nanofillers easier to become released either during or after the heating process. If nothing else, a higher concentration of nanoparticles near the material surface might give rise to a higher concentration of released particles by other potential mechanisms (e.g., diffusion, desorption, dissolution). At high enough temperatures, where the polymer combusts, an inorganic-rich char layer may form,[51] which could be an avenue for release of nanoparticles (or degradation products thereof) as a result of flaking under the application of even very low sheer forces (Figure 1). However, all of this is conjecture at this point, and these possibilities need to be explored rigorously. The potential for surface relocation of nanofillers during thermal treatment has been investigated almost exclusively for nanoclays. Despite the focus on nanoclays, there is also evidence that other types of particles may exhibit similar behavior,[52] but this remains an area for further exploration. Acquiring a mechanistic understanding of how other types of nanofillers behave during application of heat to PNCs would be a good use of resources.

The potential for ENM release in a thermochemical degradation context has also appeared in the mechanical abrasion literature discussed earlier. Almost any mechanical force applied to a polymer will generate frictional heating, and if the amount of heating is large enough, release of nanofillers may be
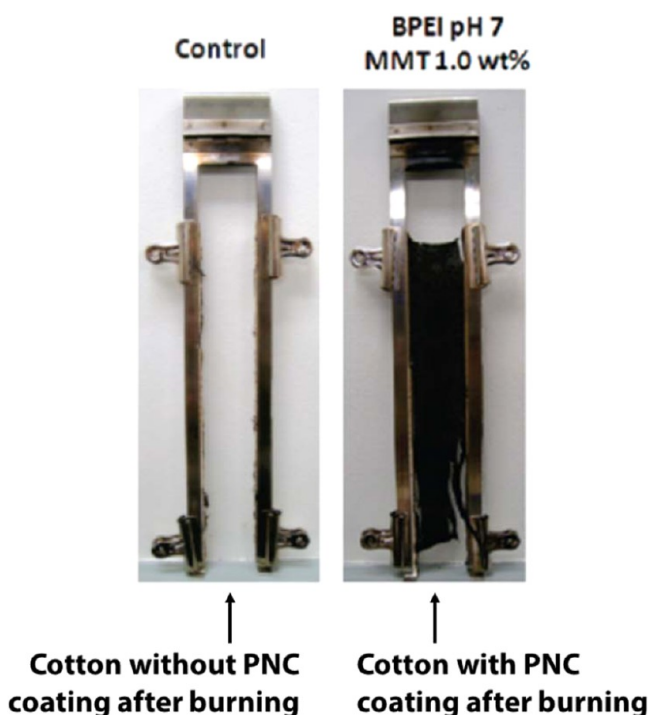
Figure 7. Comparison of (left) uncoated cotton and (right) cotton coated at pH 7 with a 20 bilayer layer-by-layer assembled PNC composed of 1.0 wt % MMT in branched polyethylenimine (BPEI) after subjecting the materials to a vertical flame test. The clay/polymer PNC coating protects the fabric from burning, possibly as a result of the formation of a protective ceramic char layer during heating. Adapted with permission from Li et al., Flame Retardant Behavior of Polyelectrolyte−Clay Thin Film Assemblies on Cotton Fabric, *ACS Nano* **2010**, 4, 3325−3337. Copyright 2010 American Chemical Society.

accelerated compared with what might otherwise be released from abrasion alone. For example, in studies that explored the effects of drilling of aluminum- and carbon-fiber reinforced CNT/epoxy nanocomposites, Bello et al. observed white plumes of smoke at the highest drilling speeds.[4] This smoke was attributed to thermal degradation of the host material and was usually coincident with the highest observed aerosolized particle concentrations in the nanoscale size regime. No similar thermal degradation was observed during analogous studies on dry saw cutting,[7] and so, although it deserves further investigation, the fact that free (i.e., not aggregated with chunks of polymer) CNTs were observed only during drilling may be related to the propensity of drilling to give rise to thermo-chemical destruction of the host material. As depicted in Figure 1, destructive heating of the polymer may unavoidably accompany any high-energy machining, and the impact such heating plays in the potential for nanofillers to become released into the environment during the lifecycle of PNCs needs to be looked at more closely.

V. RELEASE OF ENMS DUE TO HYDROLYSIS OR ENZYMATIC DEGRADATION OF THE HOST

Transfer of mass between a polymer and the external environment does not only proceed from the inside outward: gases, liquids, and other small molecules can transfer from the external medium into polymers as well. If the polymer is a thin film, absorbed substances can transit through to the interfacial

boundary on the opposite side. In the case of a reasonably inert gas, absorbed molecules may not impact the chemical integrity of the polymer, but when a polymer is submerged in a liquid, there is a potential for additional chemical changes to occur. Such changes can range from the fairly benign (absorption of water, leading to swelling of the polymer) to the more serious (oxidation, chain scission, or complete degradation), depending on the nature of the polymer and the liquid being absorbed. Polymer swelling due to water absorption can lead to considerable attenuation of mass transport properties (diffusivity of internal components), particularly in hydro-philic polymers such as Nylon[58] and ethylene vinyl alcohol (EVOH),[59] and bioderived polymers such as thermoplastic starch.[60] When more extensive hydrolytic damage to the matrix occurs, release rates of matrix additives and contaminants might be expected to alter even more dramatically, although it could be hard to directly establish causal relationships. In the extreme case, such as during biodegradation in a landfill, the polymer can fall apart completely. In such a scenario, potentially harmful additives in the polymer would be de facto released to the environment. During postconsumer-use stages of product lifecycles, biological (enzymatic) degradation of the matrix (e.g., from microbes in soils) is also likely to be an important process, especially for polymers that are designed to degrade quickly during composting. In addition, enzymatic degradation of polymers may be an important consideration in the release behavior of materials intended for biomedical applications, such as in artificial tissues, implants, and so forth.

The effect of nanofillers on the hydrolytic or enzymatic degradation behavior of polymers has been extensively evaluated, particularly for synthetic and bioderived polyesters. The various studies that have investigated these phenomena will be not discussed here, but a recent review that offers some coverage is available.[61] In some cases, nanofillers have been observed to accelerate the rate of enzymatic or hydrolytic degradation of polymers during composting or simulated hydrolysis experiments;[62−65] in other cases, the opposite effect or no effect occurs.[66−68] Figure 8 shows photographs depicting how the presence of nanoclays in polylactide greatly accelerates the rate of biodegradation.[62] At such point that the polymer has completely disintegrated, any nanofillers contained within the polymer would be completely transferred to the surrounding environment. More work needs to be done to understand the morphology and (eco)toxicological impact of nanofillers released in this manner, but other questions to address include (1) Under what conditions are PNCs more or less likely to degrade by hydrolytic and enzymatic mechanisms? (2) How do water absorption and hydrolysis affect the diffusivity of nano-fillers within polymers? and (3) What is the release behavior of nanofillers at intermediate stages of hydrolytic and enzymatic degradation of PNCs?

The first question has received some attention in the literature (see example references above), although primarily from the perspective of the material's integrity rather than the whereabouts of the embedded nanoparticles. The second question may be difficult to answer experimentally, has not been looked at theoretically, and in any case may be moot if the third question can be answered satisfactorily. But it has been difficult to find dedicated studies focused on the question of how and under what circumstances moderate hydrolytic degradation causes release of embedded nanofillers. One of the only examples identified was a study published by van der Zande et al. in 2011,[69] in which gadolinium-tagged CNTs were

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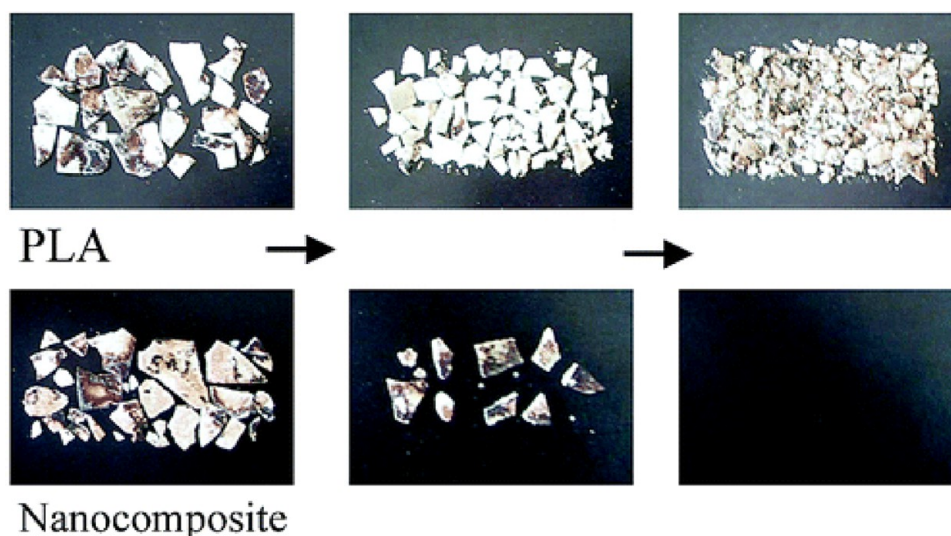dx.doi.org/10.1021/am5062757 | *ACS Appl. Mater. Interfaces* 2015, 7, 20−39

Figure 8. Series of photographs comparing biodegradation of neat polylactide (top row) and a nanocomposite of organically modified MMT in polylactide (bottom row) after 32 days (left column), 50 days (middle column), and 60 days (right column) recovered from composting. Reprinted with permission from Ray et al., Polylactide-layered silicate nanocomposite: A novel biodegradable material. *Nano Lett.* **2002**, 2, 1093−1096. Copyright 2002 American Chemical Society.

incorporated into discs composed of poly(lactic-*co*-glycolic acid) (PLGA), after which the discs were subcutaneously inserted into rats and MRI was used to image where the Gd-labeled CNTs went over the course of 5 weeks. PLGA is a copolymer polyester utilized ubiquitously in the biomedical arena (e.g., for sutures) because it rapid hydrolyzes in the presence of water into nontoxic byproducts. These desirable degradation properties allow for PLGA to be an excellent material for studying the impact of hydrolysis on nanofiller release. MRI studies showed heightened Gd-derived contrast in the area surrounding the implanted Gd-CNT-PLGA discs at around the 3 week mark, followed by gradual weakening of the signal, which they interpreted as evidence of Gd-CNT release from the hydrolyzing composite material (Figure 9).

Van der Zande et al. did not quantify the extent of nanofiller release, and neither did they explore release mechanisms. Nevertheless, their study is a unique view into the effect of hydrolysis on nanofiller release from PNCs. Importantly, it suggests that hydrolytic degradation can be a vehicle for nanofiller release, especially for highly anisotropic nanofillers such as CNTs that are too big to become released via simple diffusion, and therefore deserves far more attention than it has heretofore received. This is especially true given the expanding interest in the use of PNCs in applications that require long-term exposure of these materials to biological matrixes.

VI. CONCLUSIONS AND KNOWLEDGE GAPS

In the past decade, there has been a growing interest in the safety of ENMs, including those embedded in polymer nanocomposites. The majority of work in this area has been focused on the toxicological and ecological impact of free ENMs, with a comparatively small amount of attention being paid to exposure to ENMs from PNCs. Understanding the exposure to ENMs that are embedded in otherwise inert materials is one component in determining the safety of consumer products made from such materials (i.e., whether the ENMs pose a risk to human health or the environment). If the embedded ENMs are not released during the product lifecycle, then the exposure to the ENMs is minimized. However, in the event that whole

ENMs are able to relocate to the external environment during either routine use or abuse of nanocomposite-enabled consumer products, then consumer exposure is increased and must be considered during safety assessments.

There are now a few dozen published reports that use varied methodologies to assess ENM release from polymers into liquid media,[1] and an equal number dedicated to understanding how various types of matrix degradation can impact the fates of ENMs in nanocomposites. Despite this progress, an evaluation of existing literature on this topic has revealed several areas of deficiency. The first is a tendency, especially among immersion-style release tests, for researchers to use poorly characterized or uncharacterized test materials. In certain instances, this is unavoidable because manufacturers of commercial PNCs may be unwilling or unable to provide specific details to researchers about ENM characteristics. Even in cases that the characteristics of the test materials are known, commercial materials may incorporate ENMs that have poorly controlled structural features (e.g., broad size polydispersity). The primary limitation of studies that utilize poorly characterized materials is that without a keen understanding of specific structure−function relationships (e.g., the effect of particle size or shape on release rate), it may be difficult to clarify release mechanisms, which in turn limits our ability to formulate predictive frameworks for ENM release phenomena. Therefore, it would be useful to have more studies that report ENM release data from thoroughly characterized materials, preferably those that are manufactured in-house from ENMs and polymers with well-controlled structural parameters. Additional studies that probe potential release mechanisms that have not yet received much attention, such as enzymatic hydrolysis, are also needed, as are studies on classes of nanocomposite materials that have heretofore been neglected, such as those using biopolymers and other biodegradable host matrixes. More studies that involve nanocomposites incorporating nanofillers with a broader range of morphologies (i.e., aspect ratios) and chemical profiles would also be beneficial because the available literature on mechanical degradation currently has an arguably unbalanced focus on CNTs.
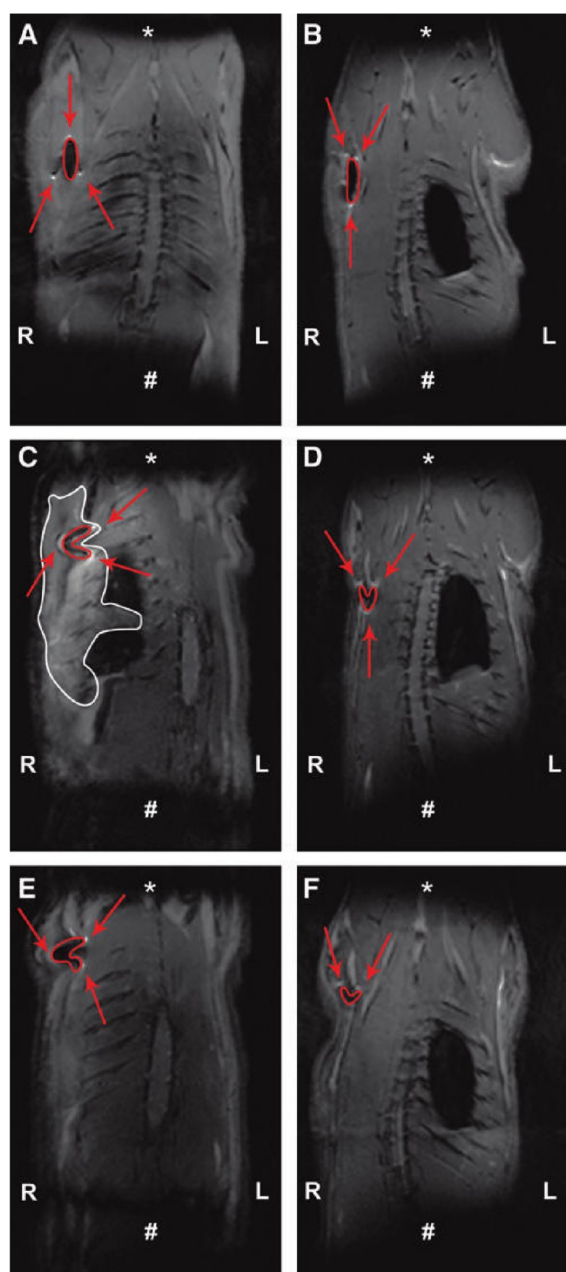
Figure 9. Magnetic resonance images of rats implanted with gadolinium-tagged CNT/PLGA nanocomposite (A, C, E) and control PLGA materials (B, D, F). Panels (A, B), (C, D), and (E, F) were acquired at the start of the experiment, after 3 weeks, and at the end of experiment, respectively. The *, #, R, and L, mark the head, tail, right side, and left side of the rats, respectively. The implanted material is marked by a red outline. Susceptibility artifacts are indicated with red arrows. An area with increased contrast due to the release of gadolinium-tagged CNTs from the degrading PLGA material at 3 weeks is indicated by a white outline in panel C. Reproduced with permission from van der Zande et al., In Vivo Magnetic Resonance Imaging of the Distribution Pattern of Gadonanotubes Released from a Degrading Poly(lactic-*co*-glycolic acid) Scaffold. *Tissue Eng. C* **2011**, *17*, 19−26. The publisher for this copyrighted material is Mary Ann Liebert, Inc., publishers.

The second factor currently hindering scientific evaluations of ENM release from PNCs is the lack of standardized analytical methods for measuring ENM properties, especially in complex environments. With respect to release into liquid environments, the difficulty in distinguishing whole particles from dissolved particles is a significant challenge; given the concern that ENMs may have different toxicological profiles from macroscale matter is an especially important problem to solve. More broadly, early studies on ENM release relied heavily on ICP-MS or similar techniques to detect ENM residuals in solution or basic particle counting to assess aerosol content after abrasion studies. Recognizing the limitations of these techniques in providing detailed information about ENM presence and characteristics, recent experimental efforts have employed more advanced measurement techniques, including electron microscopy, surface analysis methods, and single-particle ICP-MS. This has provided a better appreciation for the morphology and composition of particles released from PNCs under varying conditions, yet more work needs to be done to standardize the available toolset for assessing ENM release and to understand what techniques are best suited for specific materials and release scenarios. Insofar as characteristics of released ENMs may be closely tied to sample handling methods (including before, during, and after the release experiments), detailed studies are needed on how experimental procedures, sample preparation techniques, and data reporting methods impact exposure assessments. This is no truer than in the case of CNTs: accurately measuring release rates of such materials requires distinguishing background carbon from carbon in CNTs in a time-resolved manner. Although several approaches have been utilized in the literature to accomplish this,[70] standardization and validation of these techniques remains a challenge that needs to be addressed.

From a broader standpoint, degradation-assisted nanocomposite release studies could be made more impactful by expanding them to encompass the potential toxicological end point of either released particles or the (degraded) nanocomposites. For instance, although conventional toxicological or ecotoxicological studies on CNTs may offer insight into the general potential health consequences of exposure to CNTs in an idealized laboratory setting, these conclusions may not be relevant to a real-life scenario in which consumers utilize CNT/polymer composites as floor tiles or components of automotive braking systems. Put another way, if a research study finds that degradation a CNT/polymer composite releases CNTs, CNT fragments, or CNT/matrix aggregates, an immediate question that arises is whether the released particles pose a real risk to human health or the environment. Such a question can be answered only by assessing the toxicological or ecological impact of CNTs with the exact form and concentration of the CNTs found to be released during the exposure assessment. Only one study, published by Ging et al., was identified that takes this expansive approach to the problem of degradation-assisted nanocomposite release.[71] These authors exposed CNT/epoxy materials to UV light at NIST's SPHERE facility and observed the degradation of the polymeric host material and condensation of embedded CNTs at the material surface, as described above in other UV exposure studies; the researchers then ground the degraded nanocomposite and measured the toxicological effects of feeding this powder to fruit flies as a model organism, finding that even when photodegraded and then mechanically damaged, the polymer matrix inhibited any measurable toxicological response of the embedded CNTs. Although it is hard to make any sweeping conclusions from this single study, it is a unique example of how cross-fertilization between the exposure assessment and toxicological sciences communities may give rise to more realistic portrayals of

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nanocomposite safety. More studies like this one would certainly be a great asset to the field.

In conclusion, although much work still needs to be done, the nanotechnology research community seems to appreciate the need for continued study on the safety of polymer nanocomposites, and activity in this area of ENM release is accelerating. Of the ENM release studies cited here and in the previous article in this series, a large majority of them have been published since 2010. The fact that so much has been learned about ENM release in only a few years is certainly impressive, and bodes well for the future of nanocomposite applications.

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Notes

This article has been reviewed in accordance with the US FDA's peer and administrative review policies and approved for publication. The statements made in this report do not necessarily represent the official position of the US FDA or affiliated organizations. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use by the US FDA.

The authors declare no competing financial interest.

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