

Review

Release of Carbon Nanotubes from Polymer Nanocomposites

Lukas Schlagenhauf^{1,2,3,*}, Frank Nüesch¹ and Jing Wang^{2,3}

- ¹ Laboratory for Functional Polymers, Swiss Federal Institute for Materials Testing and Research, Dubendorf, Switzerland; E-Mail: frank.nueesch@empa.ch
- ² Laboratory for Analytical Chemistry, Swiss Federal Institute for Materials Testing and Research, Dubendorf, Switzerland; E-Mail: jing.wang@ifu.baug.ethz.ch

³ Institute of Environmental Engineering, ETH Zurich, Zurich, Switzerland

* Author to whom correspondence should be addressed; E-Mail: lukas.schlagenhauf@empa.ch; Tel.: +41-58-765-6122; Fax: +41-58-765-4614.

Received: 11 February 2014; in revised form: 21 March 2014 / Accepted: 21 March 2014 / Published: 28 March 2014

Abstract: Carbon nanotube (CNT)/polymer nanocomposites have superior properties compared to the neat polymer matrix. They now are widely used in industry, but questions have been raised about the risks of such materials since CNTs can be toxic when inhaled. For a risk assessment of CNT nanocomposites, it is crucial to know whether CNTs from nanocomposites can be released into the environment or if they remain embedded in the matrix. This review article summarizes the studies that investigated the release of CNTs from nanocomposites during the service life. Three scenarios are reviewed, the release of particles due to mechanical impact, the release due to weathering processes, and the release due to fire. A release during composite production and disposal is not incorporated.

Keywords: carbon nanotubes; nanocomposites; release; nanosafety

1. Introduction

Carbon nanotubes (CNTs) exhibit unique mechanical, electrical, and optical properties, therefore they have been considered as a nanofiller for composites. CNT nanocomposites have superior or additional properties compared to their neat matrix materials. These include mechanical properties such as tensile strength and Young's modulus [1,2], energy absorption [3], improved scratch and wear resistance [4], electrical and thermal conductivity [5,6], fire resistance [7], and optical properties [8]. Nowadays, CNT

nanocomposites are widely used for a variety of applications in different industries, e.g., for automotive, aerospace, defense, electronics, energy, and sporting goods [9].

Because of the extensive usage, the question has been raised whether these nanocomposites pose a threat to the human health and the environment since it is already known, that CNTs can cause health problems. They can cause oxidative stress, genotoxicity, inflammation, and also fibrosis [10–16].

During the life cycle of a CNT nanocomposite, different scenarios can be identified where CNTs might be released into the environment and pose a threat. Those scenarios have already been developed in several publications [9,17–23]. In general, the life cycle can be divided into three stages where exposure to humans can occur, production and processing, service life, and disposal. The purpose of this paper is to review the scientific work up to date that investigated the potential of release of CNTs into the environment. It concentrates on the possible release during the service life where untrained humans are in contact with nanocomposites. Three possible pathways are considered, particle release due to mechanical impact, degradation of the matrix due to weathering processes, and release due to fire incidents.

A summary of all used abbreviations in this review is presented in Table 1.

ABS	Acrylonitrile butadiene styrene
ATR-FTIR	Attenuated total reflectance—fourier transform infrared spectroscopy
AUC	Analytical ultracentrifugation
CNF	Carbon nanofiber
CNT	Carbon nanotube
CRP	Carbon fiber reinforced plastic
EVA	Ethylene-vinyl acetate
PA6	Polyamide 6, Nylon 6
PC	Polycarbonate
PE	Polyethylene
PEN	Polyethylene naphthalate
PMMA	Poly(methyl methacrylate)
POM	Polyoxymethylene
PP	Polypropylene
PS	Polystyrene
PU	Polyurethane
SEM	Scanning electron microscope
SMPS	Scanning mobility particle sizer
TEM	Transmission electron microscopy

Table 1. Abbreviations.

2. Results of Release Studies

2.1. Release of Particles Due to Mechanical Impact

From nanocomposites, particles can be released due to several mechanical actions. Those involve scratching, sanding, sawing, and drilling. So far, no standard method has been established to simulate these actions and also no model has been established to compare them. To measure the release of particles during the lifespan of a consumer product, the Taber Abraser can be used. It is a widely used device to simulate sanding processes and to study abrasion resistances of materials and coatings with its own international standards (e.g., ISO 7784-2:1997; ISO 9352:1995; ISO 5470-1:1999; ASTM G195-08). It provides a continuous abrasion process under defined conditions that can be repeated by any other laboratory. Several studies have already used the Taber Abraser to generate particles from nanocomposites, to measure the particle size distribution, and to search for released nanoparticles [24–28].

Other studies simulate sanding process directly with sanding machines and other workshop tools. Those measurements are closer to the reality for processes with high shear forces but it is more complicated to measure the particle size distributions because it can happen that the sanding device is producing nanoparticles itself [29,30], or that big differences in the particle concentrations can appear either because the particle concentration depends on the applied pressure, or due to burst events [28]. To achieve repeatable results for real sanding studies, self-made measurement devices have to be established as it has been done e.g., by Göhler *et al.* [31].

For the characterization of the released particles, several measurement devices are available. A review on that subject has been done already by Kuhlbusch *et al.* [32]. Generally, it is expected that an abrasion experiment releases particles in the size range from a few nanometers to several micrometers. A determination for the full size range has been done e.g., by Wohlleben *et al.* [28]. They used Fraunhofer diffraction and measured particles with diameters up to 200 μ m for a PU nanocomposite. To measure the release of individual free standing CNTs, measurement devices that can detect and collect particles in the nanosize are preferred.

The reviewed papers of this section are summarized in Table 2.

The first study that investigated the release of nanofibers from a nanocomposite was done by Mazzuckelli *et al.* [33]. They measured the release of particles and fibers from a carbon nanofiber (CNF) composite during different stages of the production process including wet sawing. Particle concentration measurements during weighing and mixing of CNFs in an unventilated area and also during wet-saw cutting of the composite revealed a release of airborne particles. Further, filter sampling according to NIOSH Manual of Analytical Methods (NMAM) method 5040 showed that also CNFs have been released during those treatments.

Bello *et al.* [34–36] have published several studies with applied wet and dry drilling, band-sawing under dry conditions, and sawing with a rotary cutting wheel under wet conditions on nanocomposites. The investigated samples consisted either of a carbon fiber/epoxy composite with aligned CNTs placed at the center ply interface or a woven alumina fiber cloth with aligned CNTs grown on the surface of the fibers, impregnated with an epoxy. During the processing of the composites, the aerosol particle

concentration and particle size distribution in the nano- and microrange was measured. Further, particles were collected with an asbestos sampling cassette for fiber analysis and also TEM samples have been produced.

 Table 2.
 Carbon Nanotube (CNT) release studies - Release of particles due to mechanical impact.

Study	Material	Particle generation method	Nanofiller release?
Mazzuckelli et al. [33]	CNF/polymer composite	Composite preparation and wet sawing	Free standing CNFs collected on filter after CNF weighing and wet sawing
Bello et al. [34–36]	Microfiber (carbon or alumina)/CNT/epoxy composite	Wet and dry drilling, band-sawing under dry conditions, and sawing with a rotary cutting wheel under wet conditions	Submicron and sharp fibers found for all samples, release of CNT agglomerates only for drilling
Cena and Peters [37]	CNT/epoxy composite	Sanding	Release of nanosized particles with irregular shapes and protruded CNTs, no free standing CNTs found
Wohlleben et al. [25,28]	CNT/POM and CNT/PU composites	Sanding and Taber Abraser	No nanofiller release
Methner et al. [38]	CNF/epoxy composite	Wet sawing, surface grinding, and belt sawing	Free standing CNFs found in the process area and at the personal breathing zone
Ogura et al. [39]	SWCNT/PP composite	Microgrinder	ParticleswithprotrudingSWCNTs,noreleaseofstanding SWCNTs
Golanski <i>et al</i> . [40]	CNT/PC and CNT/PA6 composites	Rake and metallic brush	No release for the rake, release of CNTs by metallic brush only when CNTs are poorly distributed in the polymer matrix
Schlagenhauf et al. [27]	CNT/epoxy composite	Taber Abraser	Release of CNTs (average length $\approx 304 \text{ nm}$)
Hellmann <i>et al</i> . [41]	CNT/epoxy composite	Sanding	Particles with protruding CNTs, no release of free standing CNTs
Huang <i>et al</i> . [42]	CNT/epoxy composite	Sanding	No release of CNTs except for a 4 wt% CNT sample

The aerosol measurements showed that drilling releases more particles with a broader particle size distribution than sawing, this is partially caused by smoke that is generated during drilling. TEM analysis of collected particles show that respirable fibers are released during all processes, but single CNTs have not been found. In contrast to sawing, drilling caused a release of CNT agglomerates [36].

Cena and Peters [37] investigated the particle release during weighing of CNTs and sanding of a 2 wt% CNT/epoxy composite. Only few airborne nanoparticles were measured during the two actions.

Images from TEM imaging show micrometer sized particles with protruding CNTs. The authors conclude that as long as the toxicity of such particles is unknown, precautions should be applied to avoid exposures to workmen. Further, they found out that a biological safety cabinet was more effective than a custom fume hood to avoid exposures.

A POM/CNT nanocomposite was investigated by Wohlleben *et al.* [25]. Abrasion was applied by the Taber Abraser or by a sanding machine. The particle size distribution of abraded particles was measured by AUC (sanding machine) and by SMPS (Taber Abraser, only for airborne particles). The AUC data shows that particles >2.7 μ m represent more than 99 wt% of the released particles. According to the SMPS data, 80% of the measured particles in the nanorange are smaller than 100 nm, but no influence of the nanofiller on the particle size distribution could be detected neither by AUC nor by SMPS. Further, no release of CNTs due to abrasion was measured. The authors also investigated the toxicology of abraded particles by *in-vivo* instillation in rats. No difference could be observed between powders from the neat matrix material and the nanocomposites.

With the same methods, Wohlleben *et al.* [28] also investigated a PU/CNT nanocomposite. Measurements by SMPS show that only few particles in the nanorange are generated and a release of CNTs was not detected. Most of the released particles were bigger than 10 µm and no protruding CNTs are visible on TEM images. The authors explain the missing protruding CNTs with the possibility that the elasticity of the PU allows the polymer to reflow around the CNTs during fragmentation. Cytotoxicity tests with abraded particles showed no difference between the PU and the CNT/PU samples, no acute toxicity was measured for both samples.

Methner *et al.* [38] investigated the release of CNFs from an epoxy composite during wet sawing, surface grinding, and belt sanding. Particles for TEM measurements were collected in the process area and at the personal breathing zone. Except a sample from belt sanding where the ventilation was turned on, all TEM samples contained free standing CNF fibers and sometimes also a larger amount of loosely agglomerated CNFs was found.

Ogura *et al.* [39] used a microgrinder to release particles from a 5 wt% of SWCNT/PP nanocomposite. The released particles were characterized by SMPS and SEM. By the usage of a thermodenuder with a working temperature of 190 °C, they were able to show that more than 99.9 % of the detected particles, in the range from 10 nm to 1000 nm, are volatile particles that have been released by the friction heat of the grinding process. The SEM images from collected particles show particles with protruding CNTs but no free standing CNTs.

Golanski *et al.* [40] researched the release of CNTs from CNT/PC and CNT/PA6 composites with up to 4 wt% of CNTs. They simulated low abrasion with a rake mounted on a Taber Linear Abraser and high abrasion with a metallic brush. With the rake, only few particles were emitted (< 100 p/cm³) and no release of CNTs was detected. With the metallic brush, two kinds of samples were investigated, one with well dispersed CNTs and one sample with poorly dispersed CNTs. No release of CNTs could be measured for the samples with well dispersed CNTs, however for the samples with poorly distributed CNTs, individual free standing CNTs were observed on TEM grids. The authors concluded that if there are CNT agglomerates present in the material due to a bad dispersion, these CNTs have a greater probability to be aerosolized.

Schlagenhauf *et al.* [27] investigated the release of CNTs from an epoxy/CNT nanocomposite with 0.1 wt% and 1 wt% CNTs. Particle generation was conducted with a Taber Abraser and all abraded particles were collected and characterized. The particle size distributions show for all samples four size modes, one in the nanorange at about 400 nm, and three in the microrange at about 0.7 μ m, 1.2 μ m, and 2.4 μ m while the sample with 1 wt% CNTs showed slightly larger particles for all modes. TEM sampling of released particles revealed that particles with protruding CNTs, agglomerates of CNTs, and also free standing CNTs were emitted during the abrasion process (see Figure 1). The free standing CNTs are clearly shorter than the incorporated CNTs (between 50 nm and 1 μ m) and thus have been chopped during the abrasion process. Despite that a release of the nanofiller was observed, it was not possible to detect it with aerosol instruments. The authors explain this with the fact that both the low filler content of the CNTs in the composite and the broad size distribution of the free standing CNTs does not allow a detection by SMPS. The size mode, generated by the CNTs seemed to be within the measurement error.

Figure 1. TEM images of abraded particles from an epoxy/CNT nanocomposite. (**a**) A free standing individual CNT; (**b**) an agglomerate of CNTs with a couple of individual CNTs scattered nearby; (**c**) protruding CNTs from an abraded particle [27].



Hellmann *et al.* [41] measured the particle release from a CNT/epoxy composite during sanding by a sanding machine. SEM measurements show particles with protruding CNTs, but no free standing CNTs have been found.

Huang *et al.* [42] investigated self-made and commercial available CNT/epoxy nanocomposites with up to 4 wt% CNTs. Abrasion was simulated with a sanding machine using different grit sizes and sanding speeds. The measured particle size distributions show two size modes, the first one with particles smaller than 100 nm contains the major amount of particles, the second mode contains particles from 500 nm to 5 μ m. The measured particle concentrations increased with higher CNT loads. No free CNTs were observed except for the sample with 4 wt% of CNTs.

2.2. Release Due to Weathering Processes

Weathering can cause a weakening or even a degradation of a nanocomposite matrix and thus expose the nanofiller to the environment. It can be categorized based of three sources of weathering, UV-light, elevated temperatures, water absorption, or a combination thereof. Degradation by UV-light causes mainly damage on the sample surface [43]. Combined with the presence of oxygen, UV-light can cause oxidation of the polymer and chain scission can form molecular products that are either volatile or lie at the surface. A common instrument to characterize the UV degradation process is the ATR-FTIR [44]. It allows to follow different degradation products and to define a polymer specific degradation index [43,45,46].

Elevated temperatures can cause thermooxidation with similar degradation products as UV degradation [44]. Thermooxidation first affects the surface layer, this is important for coatings and adhesives. Depending on the oxygen diffusion kinetics, also bulk properties of composites will be affected [47].

Degradation by water uptake can influence the bulk properties of polymers and their composites. The affected properties among others are the stiffness, the interfacial strength, the damping ratio, weakening of the fiber-matrix interface in composites, plasticization, swelling, and softening [48]. The maximum water uptake depends on the relative humidity but not on the temperature [49]. Further e.g., for epoxy, different species of water are observed in the polymer, it can be free or bound to the matrix [50]. Different models for the water uptake of nanocomposites have been developed and tested by Liu *et al.* [51,52].

The reviewed papers of this section are summarized in Table 3.

Nguyen et al. and Petersen et al. [53-55] investigated the degradation of a CNT/epoxy nanocomposite under intensive UV-light [63]. They measured the weight loss of the samples and the degradation of the matrix by ATR-FTIR. The results show that the composite degrades slower than the neat epoxy. In contrary to a SiO₂/epoxy that the same research group investigated [46], a release of the nanofiller could not be measured. Due to degradation of the matrix material, CNTs formed a network on the surface of the samples but an analysis of released particles did not show free standing CNTs. Further, the scratch resistance of the CNT layer was tested. It could be shown that CNT network on the weathered epoxy surface is more mechanically resistant to scratching than the neat epoxy. The authors conclude that this finding indicates that it is unlikely that the CNTs are readily released into the environment.

The degradation by UV-light of a CNT/PP and a CNT/PE composite has been investigated by Bocchini *et al.* [56]. The degradation of the matrix was measured by ATR-FTIR and the results show that the two matrix materials behave differently. The CNT/PP composite shows a similar behavior as the analyzed CNT/epoxy nanocomposite of Nguyen *et al.* [53,54], the CNTs are adsorbing the UV-light and thus, less degradation compared to the neat PP can be measured. For the CNT/PE composite, almost no difference between polymer and composite can be measured. The authors propose that besides the photooxidation by the UV light, also thermooxdiation plays a role during the degradation process. Since the CNTs are converting light into heat, they conclude that the composites have a higher temperature during the degradation experiment and thus have a higher thermooxidation. For the PE composite, the positive effect of the CNTs seems to be balanced by the negative effects of the higher temperature.

Besides the abrasion processes, Wohlleben *et al.* [25,28] and Hirth *et al.* [57] investigated the UV-degradation of CNT/POM, CNT/epoxy and CNT/PU nanocomposites. During the experiment, the samples were protected by covers to ensure that no loose particles are blown or washed away. Afterwards, either the loose particles on the sample surface, or particles that have been released into water during sonication have been analyzed by TEM. For the CNT/epoxy composite, the TEM images show

particles with embedded or protruding CNTs. By application of high shear forces, also free standing CNTs were observed.

Asmatulu *et al.* [58] investigated the resistance against weathering of neat epoxy and CNT/epoxy coatings. The coatings were exposed to UV-light only or to a combination of UV-light and salt fog (according to ASTM B117). The coatings with incorporated CNTs showed a slower weight loss and smaller cracks were generated on the surface compared to the neat epoxy.

Orlov *et al.* [59] degraded different nanocomposites with CNTs and amino functionalized CNTs with a combination of UV light and moisture. The authors observed degradation of the matrix by FTIR and the formation of cracks by microscope. SEM imaging of samples revealed that loose CNTs can be found on the samples surfaces as well as within the cracks. Even though the amino functionalized CNTs were better dispersed, the polymer matrix was much less homogeneous. This might be explained with a lower degree of polymer cross linking compared to the composite with neat CNTs.

Study	Material	Weathering process	Nanofiller release?
Nguyen <i>et al.</i> [53,54] and Petersen <i>et al.</i> [55]	CNT/epoxy composite	UV degradation	Formation of a CNT layer on the surface, no release of CNTs
Bocchini et al. [56]	CNT/PP and CNT/PE composites	UV degradation	Not measured
Wohlleben <i>et al.</i> [25,28] and Hirth <i>et al.</i> [57]	CNT/POM, CNT/epoxy, and CNT/PU composites	UV degradation with or without moisture	Release of CNTs only when high shear forces are applied on released particles
Asmatulu et al. [58]	CNT/epoxy composite	UV degradation only or with salt fog	Not measured
Orlov <i>et al</i> . [59]	Different CNT/polymer composites	UV degradation with moisture	Loose CNTs on surface and in cracks are observed by SEM, a release of CNTs was not measured
Vilar <i>et al.</i> [60]	CNT/PA6 composite	UV degradation with moisture	Exposed CNTs on the sample surface, weathered and calcinated samples showed a release of CNTs
Busquets-Fitè et al. [61]	CNT/PP, CNT/EVA, and CNT/PA6 composites	UV degradation with moisture	No release of CNTs
Ging <i>et al.</i> [62]	CNT/epoxy composite with neat and amino functionalized CNTs	UV degradation with high humidity	Formation of a CNT layer on the surface, release not measured
Barkoula <i>et al</i> . [48]	CNT/CRP/epoxy composite	Water bath	Not measured
Starkova <i>et al</i> . [49]	CNT/epoxy composite	Humidity	Not measured

Table 3. CNT release studies—Weathering.

Vilar *et al.* [60] investigated a CNT/PA6 composite. They weathered the samples under UV light in combination with moisture. After the weathering process, SEM images showed CNTs that are exposed to the environment on the sample surface. The authors also calcinated the samples in order to regain the

nanofillers. In contrary to the unexposed samples, the calcination of aged samples caused the release of free standing CNTs.

Busquets-Fitè *et al.* [61] weathered CNT/PP, CNT/EVA, and CNT/PA6 nanocomposites under UV light combined with moisture. They gathered the aging water and collected the released particles. No released CNTs have been found.

The degradation of a CNT/epoxy nanocomposite with neat and amino functionalized CNTs by UV light and elevated humidity has been investigated by Ging *et al.* [62]. Images by SEM revealed that several forms of CNTs can be found on the weathered surface, free standing agglomerates of CNTs, partially exposed CNTs due to crack formation, and encapsulated CNTs (see Figure 2). The authors conclude that there is a possibility that CNTs can be released into the environment after the matrix is degraded, but it has to be considered that this process takes time and thus the releasing rate would be rather low. Further, the authors milled the exposed nanocomposite films and tested the toxicity of the particles with Drosophila larvae. In contrary to the neat CNTs, the embedded CNTs were not toxic.

Figure 2. Impact of UV light on a CNT/epoxy nanocomposite: the initial flat surface (left) gets cracks and unprotected CNTs are forming a layer (right). Reprinted from Science of the Total Environment, 473474, J. Ging *et al.*, Development of a conceptual framework for evaluation of nanomaterials release from nanocomposites: Environmental and toxicological implications, p. 9–19, Copyright © 2014, with permission from Elsevier [62].



Changes in the electrical conductivity of a CNT nanocomposite can be used to monitor its degradation. Therefore Barkoula *et al.* [48] made an attempt to correlate the water uptake of a CNT/CRP/epoxy composite with the change of the electrical resistance. They also compared the water uptake of a CNT/epoxy composite with the neat epoxy. The neat epoxy system exhibited a slightly lower water uptake than the modified systems. These results are in good agreement with the results of Starkova *et al.* [49] where the water uptake of a CNT/epoxy composite was measured under different relative humidities and different temperatures. At lower temperatures, it could be shown that the water uptake rate for the neat epoxy is faster in comparison with the nanocomposites but the equilibrium weight gain was not influenced by the nanofiller. Further, the addition of CNTs to the epoxy also did not influence the swelling of the samples.

2.3. Release Due to Fire

Due to improper disposal by fire or by accidental burning of CNT nanocomposites, the nanofiller can be released into the environment since the decomposition temperature of CNTs is much higher than of the polymer matrix, they can be stable up to $600 \,^{\circ}$ C [64]. So far, no detailed study has been published that investigates the release of CNTs from nanocomposites due to an event of fire. However, in the field of fire inhibition, CNT/polymer nanocomposites have been already investigated and the analysis of the produced char can give an indication of the possible release of CNTs into the environment.

The reviewed papers of this section are summarized in Table 4.

Study	Material	Results
Kashiwagi <i>et al.</i> [7,65–67]	CNT/PP, CNT/PS, and CNT/PMMA composites	Partially oxidized CNTs found in char with oxidized CNT catalyst
Schartel et al. [68]	CNT/PA6 composite	Residuals consisted of a CNT network
Verdejo et al. [69]	CNT/silicone foam	Residuals consisted of a CNT network
Kim <i>et al</i> . [70]	CNT/PEN composite	Residuals consisted of a CNT network
Fu et al. [71]	CNT/wood/PE and CNT-OH/wood/PE composites	Free CNTs on char surface for CNT/wood/PE composite, no CNTs found on char for CNT-OH/wood/PE composite
Zammarano <i>et al.</i> [72], Nyden <i>et al.</i> [73], Uddin <i>et al.</i> [74]	CNF/PU foam	No CNFs in smoke, free CNFs found in char, aerosolization of CNFs from the char due to shaking
Dittrich et al. [75]	Different carbonaceous nanofillers in PP composites	Formation of residual protection layer, no further investigation of the char
Bouillard <i>et al</i> . [76]	CNT/ABS composite	Release of free CNTs and agglomerates of CNTs into air during burning in furnace

Table 4. CNT release	studies-	—Fire.
----------------------	----------	--------

Kashiwagi *et al.* [7] studied the mechanism of fire inhibition by CNTs with a PP nanocomposite. The experiments showed that the present CNTs modified the thermal and oxidation properties of the PP matrix. Cone calorimetry measurements showed that the heat release of the PP nanocomposite is significantly reduced compared to the neat PP. The analysis of the sample residues revealed that partially oxidized agglomerated CNTs are present in the char (see Figure 3). Further, the color of the char was red because the iron catalyst in the nanotubes was oxidized. The authors concluded that the formed CNT network increased the mechanical integrity of a protective layer which could act as a thermal insulation layer and also as a barrier for evolved degradation products to the gas phase.

Further experiments by the same group with PP, PS, and PMMA nanocomposites confirmed these results [65–67]. For all samples, a protection layer made of CNTs was formed during cone calorimeter experiments. The network layer showed physical integrity and had about the same mass as the initial mass of the CNTs in the nanocomposite.

Schartel *et al.* [68] investigated the fire resistance of a CNT/PA6 nanocomposite. They showed that the CNT network remained in the composite, influenced the melt viscosity, and thus prevented dripping

and flowing of the burning sample. The authors concluded that CNTs may be a highly interesting filling material for flame retardation, but only for distinct systems and scenarios. Since dripping is inhibited by the CNT network, the conversion of the material is increased, this might be negative for passing flammability tests.

Verdejo *et al.* [69] used CNTs to change the fire properties of silicone foams. Also for this study, a CNT network was observed in the residues of the burned foams.

Figure 3. SEM picture of the residues from a burned CNT/PP nanocomposite. Reprinted from Macromol. Rapid Commun., 23, T. Kashiwagi *et al.*, Thermal Degradation and Flammability Properties of Poly(propylene)/Carbon Nanotube Composites, p. 761–765, Copyright © 2002, with permission from Wiley-VCH [7].



Kim *et al.* [70] investigated a CNT/PEN nanocomposite. The thermal stability could be enhanced by adding CNTs to PEN, but the thermal decomposition kinetics depended strongly on the CNT content. SEM analysis of the residues showed also for this nanocomposite the formation of a CNT network during the decomposition process.

Fu *et al.* [71] created a CNT/wood/PE nanocomposite that contained either neat CNTs or hydroxylated CNTs (CNT-OH). The hydroxylated CNTs showed a slightly better flame retardancy due to their improved interfacial compatibilization between CNT-OH and wood flour as well as the polymer matrix. SEM images of the char residues of the composite with untreated CNTs showed free CNTs on the char surface. For the composite with functionalized CNTs, no free CNTs could be detected. Zammarano *et al.* [72] produced a PU foam with incorporated CNFs und tested the flammability of the composite by a cone calorimeter. Due to the incorporated CNFs, flame spread was reduced by preventing the heat transfer of burning material to adjacent surfaces. A thermal stable entangled fiber network was formed that also prevented the collapse of the foam. Smoke and char of this burned CNF/PU foam was then analyzed by Nyden *et al.* [73] and Uddin *et al.* [74]. They burned the composite and collected samples from the released smoke on filters. Further, they also suspended the char in water in order to collect particles for electron microscopy analysis. The analysis of the samples showed that free standing CNFs are present in the char but they were not airborne. The authors conclude that any airborne CNF has been destroyed in the flames. Further, collected char was shaked to see whether CNFs can be

released into air. The measurements showed that the particle concentration was increased by an order of magnitude. The released particles further were trapped in water and by measuring their concentration, the rate of aerosolization of the CNFs was approximately determined to 1.4 mg/hour.

Dittrich *et al.* [75] compared the flame retardance properties of different carbonaceous nanofillers. All filler materials enhanced the flame retardancy of the PP matrix by the formation of a protection layer. Functionalized graphene showed the highest potential as flame retardant material.

Bouillard *et al.* [76] was the first study to investigate the formation of airborne CNTs during the combustion of a CNT nanocomposite. They used a CNT/ABS composite with 3 wt% of CNTs, combusted the sample in a furnace and collected released particles on TEM grids. Analysis by TEM revealed that free standing CNTs and also agglomerates of CNTs were released into the air. The authors report that the numbers were quite significant posing a possible sanitary risk in the case of accidental scenarios.

3. Conclusions

A summary for all investigated release studies is given in Table 5, it shows that there are still some gaps that have to be filled. Further, the CNT release from other polymers that have been considered as matrix material for CNT nanocomposites have not been investigated at all, e.g., polyvinyl acetate (PVA) [77], polyimide (PI) [78], polytrimethylene terephthalate (PTT) [79], or vinylester/polyester [80].

Polymer	Abrasion	Weathering	Fire
ABS			[76]
Epoxy	[27,34–38,41,42]	[48,49,53–55,57,58,62]	
EVA		[61]	
PA6	[40]	[60,61]	[68]
PC	[40]		
PE		[56]	[71]
PEN			[70]
PMMA			[66,67]
POM	[25]	[25]	
PP	[39]	[56,61]	[7,65,75]
PS			[67]
PU	[28]	[28]	[72–74]
Silicone			[69]

Table 5. Release studies for all investigated polymers.

The studies that investigated the release due to mechanical impact do not give a coherent picture. It stands out that both studies that investigated the release of CNFs from composites find airborne CNFs

in the breathing area, not only under dry conditions but also for wet sawing. The number of studies however is limited and no universal conclusions can be drawn.

For CNT nanocomposites, it can be concluded that the expected release scenarios include free standing CNTs, agglomerated CNTs, and particles with- and without protruding CNTs. Depending on the applied shear force during the abrasion process, it is also expected that released CNTs will be shorter than the processed CNTs in the composite. Normally during abrasion processes, the particle concentration in air is too low for particle agglomeration. This means that the finding of agglomerates can indicate a poor distribution of the CNTs in the investigated nanocomposite.

As already discussed by Hirth *et al.* [57], the release abilities of CNT/polymer composites can be divided into two categories. The first category includes the ductile matrix materials. A release of CNTs has not been observed for those materials. It seems that the ductile matrix is able to reflow around the CNTs during fragmentation [28], for those composites, no or only few protruding CNTs from abraded particles are expected. The second category includes brittle materials, here protruding CNTs from abraded particles are observed for all tested composites. For this category, also a release of CNTs has been observed but only for few tested materials or under special circumstances as a high filler loading [42] or the presence of agglomerated CNTs in the material [40]. If other factors, such as the influence of the filler-matrix interface, play a role in the CNT release abilities of brittle composites still has to be evaluated. An approach to reduce or even to prevent the release of CNTs due to abrasion can be the functionalization of CNTs. E.g., for epoxy composites, functionalized CNTs can be better dispersed in the epoxy resin [81] and the interaction between CNT and matrix can be improved [82].

For the weathering studies, no differences among the investigated CNT/polymer composites can be found. All of them expose CNTs to the environment when the matrix is degraded by UV-light. The CNTs form a network and are not easily to detach from the samples. Even though already several studies have been published with confirming results, it is not possible to draw a conclusion for a risk assessment of the considered scenarios since only the worst case has been investigated where the composite has not been protected by additives. Further, the investigation of a CNT release due to a combination of weathering and abrasion processes would be interesting since it is closer to the real life (e.g., usage of outdoor materials or polishing of a dulled surface). Also toxicity studies on this subject are desired. The formed CNT layer on the surface of weathered composites could be a source of a high quantity of released free standing CNTs and thus maybe pose a health risk. For the weathering by elevated temperatures and water, no conclusions can be drawn since their effect on the CNT release has not been investigated yet.

In contrary to incineration where under high temperatures CNTs are destroyed [83], a fire does not degrade all CNTs in composites, they even can be used as flame retardants. All the fire release studies show that during a fire incident, a network of CNTs is formed in the char. It hinders a dripping of molten composite and influences the degradation properties. For future studies, despite the positive flame retardant properties, also exposure to CNTs has to be regarded. For CNFs, it has been already shown that they can be released from the char into the air. For CNTs, such measurements are still missing. Further, the toxicity of the inhalable fraction of the released particles would be important. As a fire is a single incident, only short term exposure would have to be considered.

Acknowledgments

This study was financed by the Swiss National Science Foundation (NFP 64), "Evaluation platform for safety and environment risks of carbon nanotube reinforced nanocomposites", 406440_131286.

Conflicts of Interest

The authors declare no conflicts of interest.

References

- 1. Coleman, J.N.; Khan, U.; Gun'ko, Y.K. Mechanical reinforcement of polymers using carbon nanotubes. *Adv. Mater.* **2006**, *18*, 689–706.
- 2. Coleman, J.N.; Khan, U.; Blau, W.J.; Gun'ko, Y.K. Small but strong: A review of the mechanical properties of carbon nanotube-polymer composites. *Carbon* **2006**, *44*, 1624–1652.
- 3. Sun, L.Y.; Gibson, R.F.; Gordaninejad, F.; Suhr, J. Energy absorption capability of nanocomposites: A review. *Composit. Sci. Technol.* **2009**, *69*, 2392–2409.
- 4. Giraldo, L.F.; Brostow, W.; Devaux, E.; Lopez, B.L.; Perez, L.D. Scratch and wear resistance of polyamide 6 reinforced with multiwall carbon nanotubes. *J. Nanosci. Nanotechnol.* **2008**, *8*, 1–8.
- 5. Huang, H.; Liu, C.T.H.; Wu, Y.; Fan, S. Aligned carbon nanotube composite films for thermal management. *Adv. Mater.* **2005**, *17*, 1652–1656.
- 6. Hollertz, R.; Chatterjee, S.; Gutmann, H.; Geiger, T.; Nueesch, F.A.; Chu, B.T.T. Improvement of toughness and electrical properties of epoxy composites with carbon nanotubes prepared by industrially relevant processes. *Nanotechnology* **2011**, *22*, doi:10.1088/0957-4484/22/12/125702.
- Kashiwagi, T.; Grulke, E.; Hilding, J.; Harris, R.; Awad, W.; Douglas, J. Thermal degradation and flammability properties of poly(propylene)/carbon nanotube composites. *Macromol. Rapid Commun.* 2002, 23, 761–765.
- 8. Breuer, O.; Sundararaj, U. Big returns from small fibers: A review of polymer/carbon nanotube composites. *Polym. Composit.* **2004**, *25*, 630–645.
- Kingston, C.; Zepp, R.; Andrady, A.; Boverhof, D.; Fehir, R.; Hawkins, D.; Roberts, J.; Sayre, P.; Shelton, B.; Sultan, Y.; Vejins, V.; Wohlleben, W. Release Characteristics of Selected Carbon Nanotube Polymer Composites. *Carbon* 2014, *68*, 33–57.
- Muller, L.; Riediker, M.; Wick, P.; Mohr, M.; Gehr, P.; Rothen-Rutishauser, B. Oxidative stress and inflammation response after nanoparticle exposure: Differences between human lung cell monocultures and an advanced three-dimensional model of the human epithelial airways. J. R. Soc. Interface 2010, 7, S27–S40.
- 11. Xia, T.; Li, N.; Nel, A.E. Potential Health Impact of Nanoparticles. *Annu. Rev. Public Health* **2009**, *30*, 137–150.
- 12. Helland, A.; Wick, P.; Koehler, A.; Schmid, K.; Som, C. Reviewing the environmental and human health knowledge base of carbon nanotubes. *Environ. Health Perspect.* **2007**, *115*, 1125–1131.
- Pulskamp, K.; Diabate, S.; Krug, H.F. Carbon nanotubes show no sign of acute toxicity but induce intracellular reactive oxygen species in dependence on contaminants. *Toxicol. Lett.* 2007, 168, 58–74.

- Ma-Hock, L.; Treumann, S.; Strauss, V.; Brill, S.; Luizi, F.; Mertler, M.; Wiench, K.; Gamer, A.O.; van Ravenzwaay, B.; Landsiedel, R. Inhalation Toxicity of Multiwall Carbon Nanotubes in Rats Exposed for 3 Months. *Toxicol. Sci.* 2009, *112*, 468–481.
- Palomaki, J.; Valimaki, E.; Sund, J.; Vippola, M.; Clausen, P.A.; Jensen, K.A.; Savolainen, K.; Matikainen, S.; Alenius, H. Long, Needle-like Carbon Nanotubes and Asbestos Activate the NLRP3 Inflammasome through a Similar Mechanism. *ACS Nano* 2011, *5*, 6861–6870.
- Thurnherr, T.; Brandenberger, C.; Fischer, K.; Diener, L.; Manser, P.; Maeder-Althaus, X.; Kaiser, J.P.; Krug, H.F.; Rothen-Rutishauser, B.; Wick, P. A comparison of acute and long-term effects of industrial multiwalled carbon nanotubes on human lung and immune cells *in vitro*. *Toxicol. Lett.* 2011, 200, 176–186.
- 17. Koehler, A.R.; Som, C.; Helland, A.; Gottschalk, F. Studying the potential release of carbon nanotubes throughout the application life cycle. *J. Clean. Prod.* **2008**, *16*, 927–937.
- 18. Wardak, A.; Gorman, M.E.; Swami, N.; Deshpande, S. Identification of risks in the life cycle of nanotechnology-based products. *J. Ind. Ecol.* **2008**, *12*, 435–448.
- 19. Abbott, L.C.; Maynard, A.D. Exposure Assessment Approaches for Engineered Nanomaterials. *Risk Anal.* **2010**, *30*, 1634–1644.
- 20. Gottschalk, F.; Nowack, B. The release of engineered nanomaterials to the environment. *J. Environ. Monit.* **2011**, *13*, 1145–1155.
- Petersen, E.J.; Zhang, L.W.; Mattison, N.T.; O'Carroll, D.M.; Whelton, A.J.; Uddin, N.; Nguyen, T.; Huang, Q.G.; Henry, T.B.; Holbrook, R.D.; *et al.* Potential Release Pathways, Environmental Fate, And Ecological Risks of Carbon Nanotubes. *Environ. Sci. Technol.* 2011, 45, 9837–9856.
- Nowack, B.; Ranville, J.F.; Diamond, S.; Gallego-Urrea, J.A.; Metcalfe, C.; Rose, J.; Horne, N.; Koelmans, A.A.; Klaine, S.J. Potential scenarios for nanomaterial release and subsequent alteration in the environment. *Environ. Toxicol. Chem.* 2012, *31*, 50–59.
- 23. Fissan, H.; Horn, H.G.; Stahlmecke, B.; Wang, J. From nanoobject release of (Bio)nanomaterials to exposure. *BioNanoMaterials* **2013**, *14*, 37–47.
- 24. Vorbau, M.; Hillemann, L.; Stintz, M. Method for the characterization of the abrasion induced nanoparticle release into air from surface coatings. *J. Aerosol Sci.* **2009**, *40*, 209–217.
- Wohlleben, W.; Brill, S.; Meier, M.W.; Mertler, M.; Cox, G.; Hirth, S.; von Vacano, B.; Strauss, V.; Treumann, S.; Wiench, K.; *et al.* On the Lifecycle of Nanocomposites: Comparing Released Fragments and their In-Vivo Hazards from Three Release Mechanisms and Four Nanocomposites. *Small* 2011, 7, 2384–2395.
- 26. Golanski, L.; Gaborieau, A.; Guiot, A.; Uzu, G.; Chatenet, J.; Tardif, F. Characterization of abrasion-induced nanoparticle release from paints into liquids and air. *J. Phys. Conf. Series* **2011**, *304*, 012062.
- Schlagenhauf, L.; Chu, B.T.T.; Buha, J.; Nueesch, F.; Wang, J. Release of Carbon Nanotubes from an Epoxy-Based Nanocomposite during an Abrasion Process. *Environ. Sci. Technol.* 2012, 46, 7366–7372.

- 28. Wohlleben, W.; Meier, M.W.; Vogel, S.; Landsiedel, R.; Cox, G.; Hirth, S.; Tomovic, Z. Elastic CNT-polyurethane nanocomposite: synthesis, performance and assessment of fragments released during use. *Nanoscale* **2013**, *5*, 369–380.
- 29. Koponen, I.K.; Jensen, K.A.; Schneider, T. Sanding dust from nanoparticle-containing paints: Physical characterisation. *J. Phys. Conf. Series* **2009**, *151*, doi:10.1088/1742-6596/151/1/012048.
- Koponen, I.K.; Jensen, K.A.; Schneider, T. Comparison of dust released from sanding conventional and nanoparticle-doped wall and wood coatings. *J. Expo. Sci. Environ. Epidemiol.* 2011, 21, 408–418.
- 31. Gohler, D.; Stintz, M.; Hillemann, L.; Vorbau, M. Characterization of Nanoparticle Release from Surface Coatings by the Simulation of a Sanding Process. *Ann. Occup. Hyg.* **2010**, *54*, 615–624.
- 32. Kuhlbusch, T.A.J.; Asbach, C.; Fissan, H.; Goehler, D.; Stintz, M. Nanoparticle exposure at nanotechnology workplaces: A review. *Part. Fibre Toxicol.* **2011**, *8*, doi:10.1186/1743-8977-8-22.
- Mazzuckelli, L.F.; Methner, M.M.; Birch, M.E.; Evans, D.E.; Ku, B.K.; Crouch, K.; Hoover, M.D. Identification and characterization of potential sources of worker exposure to carbon nanofibers during polymer composite laboratory operations. *J. Occup. Environ. Hyg.* 2007, *4*, D125–D130.
- Bello, D.; Wardle, B.L.; Yamamoto, N.; deVilloria, R.G.; Garcia, E.J.; Hart, A.J.; Ahn, K.; Ellenbecker, M.J.; Hallock, M. Exposure to nanoscale particles and fibers during machining of hybrid advanced composites containing carbon nanotubes. *J. Nanoparticle Res.* 2009, *11*, 231–249.
- Bello, D.; Wardle, B.L.; Zhang, J.; Yamamoto, N.; Santeufemio, C.; Hallock, M.; Virji, M.A. Characterization of Exposures to Nanoscale Particles and Fibers During Solid Core Drilling of Hybrid Carbon Nanotube Advanced Composites. *Int. J. Occup. Environ. Health* 2010, *16*, 434–450.
- 36. Bello, D.; Wardle, B.L.; Yamamoto, N.; deVilloria, R.G.; Hallock, M. Exposures to Nanoscale Particles and Fibers During Handling,Processing, and Machining of Nanocomposites and Nanoengineered Composites Reinforced with Aligned Carbon Nanotubes. Proceedings of the 17th International conference on composite materials (ICCM), Edinburgh, Scotland, July 27–31, 2011.
- 37. Cena, L.G.; Peters, T.M. Characterization and Control of Airborne Particles Emitted During Production of Epoxy/Carbon Nanotube Nanocomposites. *J. Occup. Environ. Hyg.* **2011**, *8*, 86–92.
- Methner, M.; Crawford, C.; Geraci, C. Evaluation of the Potential Airborne Release of Carbon Nanofibers During the Preparation, Grinding, and Cutting of Epoxy-Based Nanocomposite Material. J. Occup. Environ. Hyg. 2012, 9, 308–318.
- Ogura, I.; Kotake, M.; Shigeta, M.; Uejima, M.; Saito, K.; Hashimoto, N.; Kishimoto, A. Potential release of carbon nanotubes from their composites during grinding. *J. Phys. Conf. Series* 2013, 429, doi:10.1088/1742-6596/429/1/012049.
- Golanski, L.; Guiot, A.; Pras, M.; Malarde, M.; Tardif, F. Release-ability of nano fillers from different nanomaterials (toward the acceptability of nanoproduct). *J. Nanoparticle Res.* 2012, *14*, doi:10.1007/s11051-012-0962-x.
- 41. Hellmann, A.; Schmidt, K.; Ripperger, S.; Berges, M. Release of ultrafine dusts during the machining of nanocomposites. *Gefahrst. Reinhalt. Luft* **2012**, *72*, 473–476.

- 42. Huang, G.; Park, J.; Cena, L.; Shelton, B.; Peters, T. Evaluation of airborne particle emissions from commercial products containing carbon nanotubes. *J. Nanoparticle Res.* **2012**, *14*, 1231.
- 43. Mailhot, B.; Morlat-Thérias, S.; Bussière, P.O.; Gardette, J.L. Study of the Degradation of an Epoxy/Amine Resin, 2. *Macromol. Chem. Phys.* **2005**, *206*, 585–591.
- Mailhot, N.; Morlat-Theias, S.; Ouahioune, M.; Gardette, J.L. Study of the degradation of an epoxy/amine resin, 1 photo- and thermo-chemical mechanisms. *Macromol. Chem. Phys.* 2005, 206, 575–584.
- 45. Zhang, Y.; Maxted, J.; Barber, A.; Lowe, C.; Smith, R. The durability of clear polyurethane coil coatings studied by FTIR peak fitting. *Polym. Degrad. Stab.* **2013**, *98*, 527–534.
- 46. Nguyen, T.; Pellegrin, B.; Bernard, C.; Rabb, S.; Stuztman, P.; Gorham, J.M.; Gu, X.; Yu, L.L.; Chin, J.W. Characterization of Surface Accumulation and Release of Nanosilica During Irradiation of Polymer Nanocomposites by Ultraviolet Light. *J. Nanosci. Nanotechnol.* **2012**, *12*, 6202–6215.
- 47. Celina, M.C.; Dayile, A.R.; Quintana, A. A perspective on the inherent oxidation sensitivity of epoxy materials. *Polymer* **2013**, *54*, 3290–3296.
- Barkoula, N.M.; Paipetis, A.; Matikas, T.; Vavouliotis, A.; Karapappas, P.; Kostopoulos, V. Environmental degradation of carbon nanotube-modified composite laminates: A study of electrical resistivity. *Mech. Composit. Mater.* 2009, 45, 21–32.
- 49. Starkova, O.; Buschhorn, S.T.; Mannov, E.; Schulte, K.; Aniskevich, A. Water transport in epoxy/MWCNT composites. *Eur. Polym. J.* **2013**, *49*, 2138–2148.
- 50. Popineau, S.; Rondeau-Mouro, C.; Sulpice-Gaillet, C.; Shanahan, M.E.R. Free/bound water absorption in an epoxy adhesive. *Polymer* **2005**, *46*, 10733–10740.
- 51. Liu, W.; Hoa, S.V.; Pugh, M. Water uptake of epoxy-clay nanocomposites: Model development. *Composit. Sci. Technol.* **2007**, *67*, 3308–3315.
- 52. Liu, W.; Hoa, S.V.; Pugh, M. Water uptake of epoxy-clay nanocomposites: Experiments and model validation. *Composit. Sci. Technol.* **2008**, *68*, 2066–2072.
- 53. Nguyen, T.; Pellegrin, B.; Mermet, L.; Shapiro, A.; Gu, X.; Chin, J. Network aggregation of CNTs at the surface of epoxy/MWCNT composite exposed to UV radiation. In Proceedings of the Nanotechnology 2009: Fabrication, Particles, Characterization, MEMS, Electronics and Photonics—Technical Proceedings of the 2009 NSTI Nanotechnology Conference and Expo, NSTI-Nanotech, Houston, TX, May 3-7 2009; Volume 1, pp. 90–93.
- Nguyen, T.; Pellegrin, B.; Bernard, C.; Gu, X.; Gorham, J.M.; Stutzman, P.; Stanley, D.; Shapiro, A.; Byrd, E.; Hettenhouser, R.; Chin, J. Fate of nanoparticles during life cycle of polymer nanocomposites. *J. Phys. Conf. Series* 2011, *304*, 012060.
- Petersen, E.J.; Lam, T.; Gorham, J.M.; Scott, K.C.; Long, C.J.; Stanley, D.; Sharma, R.; Alexander Liddle, J.; Pellegrin, B.; Nguyen, T. Methods to assess the impact of UV irradiation on the surface chemistry and structure of multiwall carbon nanotube epoxy nanocomposites. *Carbon* 2014, 69, 194–205.
- 56. Bocchini, S.; Di Blasio, A.; Frache, A. Influence of MWNT on Polypropylene and Polyethylene Photooxidation. *Macromol. Symp.* **2011**, *301*, 16–22.

- Hirth, S.; Cena, L.; Cox, G.; Tomović, Z.; Peters, T.; Wohlleben, W. Scenarios and methods that induce protruding or released CNTs after degradation of nanocomposite materials Technology Transfer and Commercialization of Nanotechnology. *J. Nanoparticle Res.* 2013, *15*, doi:10.1007/s11051-013-1504-x.
- Asmatulu, R.; Mahmud, G.A.; Hille, C.; Misak, H.E. Effects of UV degradation on surface hydrophobicity, crack, and thickness of MWCNT-based nanocomposite coatings. *Prog. Org. Coat.* 2011, 72, 553–561.
- Orlov, A.; Ramakrishnan, G.; Ging, J.; Hubert, A.; Feka, P.; Korach, C.S. Evaluating safety and stability of CNT nanocomposites exposed to environmental conditions. In Proceedings of the Technical Proceedings of the 2012 NSTI Nanotechnology Conference and Expo, Santa Clara, CA, June 18-21, 2012; pp. 335–337.
- Vilar, G.; Fernández-Rosas, E.; Puntes, V.; Jamier, V.; Aubouy, L.; Vázquez-Campos, S. Monitoring migration and transformation of nanomaterials in polymeric composites during accelerated aging. J. Phys. Conf. Series 2013, 429, doi:10.1088/1742-6596/429/1/012044.
- Busquets-Fité, M.; Fernandez, E.; Janer, G.; Vilar, G.; Vázquez-Campos, S.; Zanasca, R.; Citterio, C.; Mercante, L.; Puntes, V. Exploring release and recovery of nanomaterials from commercial polymeric nanocomposites. *J. Phys. Conf. Series* 2013, 429, doi:10.1088/ 1742-6596/429/1/012048.
- Ging, J.; Tejerina-Anton, R.; Ramakrishnan, G.; Nielsen, M.; Murphy, K.; Gorham, J.M.; Nguyen, T.; Orlov, A. Development of a conceptual framework for evaluation of nanomaterials release from nanocomposites: Environmental and toxicological implications. *Sci. Total Environ.* 2014, 473–474, 9–19.
- 63. Chin, J.; Byrd, E.; Embree, N.; Garver, J.; Dickens, B.; Finn, T.; Martin, J. Accelerated UV weathering device based on integrating sphere technology. *Rev. Sci. Instrum.* **2004**, *75*, 4951–4959.
- 64. Chen, W.; Auad, M.L.; Williams, R.J.J.; Nutt, S.R. Improving the dispersion and flexural strength of multiwalled carbon nanotubes-stiff epoxy composites through beta-hydroxyester surface functionalization coupled with the anionic homopolymerization of the epoxy matrix. *Eur. Polym. J.* **2006**, *42*, 2765–2772.
- 65. Kashiwagi, T.; Grulke, E.; Hilding, J.; Groth, K.; Harris, R.; Butler, K.; Shields, J.; Kharchenko, S.; Douglas, J. Thermal and flammability properties of polypropylene/carbon nanotube nanocomposites. *Polymer* **2004**, *45*, 4227–4239.
- 66. Kashiwagi, T.; Du, F.M.; Douglas, J.F.; Winey, K.I.; Harris, R.H.; Shields, J.R. Nanoparticle networks reduce the flammability of polymer nanocomposites. *Nat. Mater.* **2005**, *4*, 928–933.
- Kashiwagi, T.; Mu, M.; Winey, K.; Cipriano, B.; Raghavan, S.R.; Pack, S.; Rafailovich, M.; Yang, Y.; Grulke, E.; Shields, J.; Harris, R.; Douglas, J. Relation between the viscoelastic and flammability properties of polymer nanocomposites. *Polymer* 2008, *49*, 4358–4368.
- 68. Schartel, B.; Pötschke, P.; Knoll, U.; Abdel-Goad, M. Fire behaviour of polyamide 6/multiwall carbon nanotube nanocomposites. *Eur. Polym. J.* **2005**, *41*, 1061–1070.
- Verdejo, R.; Barroso-Bujans, F.; Rodriguez-Perez, M.A.; Saja, J.A.d.; Arroyo, M.; Lopez-Manchado, M.A. Carbon nanotubes provide self-extinguishing grade to silicone-based foams. *J. Mater. Chem.* 2008, 18, 3933–3939.

- 71. Fu, S.; Song, P.; Yang, H.; Jin, Y.; Lu, F.; Ye, J.; Wu, Q. Effects of carbon nanotubes and its functionalization on the thermal and flammability properties of polypropylene/wood flour composites. *J. Mater. Sci.* **2010**. *45*, 3520–3528.
- Zammarano, M.; Krämer, R.H.; Harris, R.; Ohlemiller, T.J.; Shields, J.R.; Rahatekar, S.S.; Lacerda, S.; Gilman, J.W. Flammability reduction of flexible polyurethane foams via carbon nanofiber network formation. *Polym. Adv. Technol.* 2008, 19, 588–595.
- Nyden, M.R.; Harris, R.H.; Kim, Y.S.; Davis, R.D.; Marsh, N.D.; Zammarano, M. Characterizing particle emissions from burning polymer nanocomposites. Tech. Proc. 2010 NSTI Nanotechnol. Conf. Expo 2010, 1, 717–719.
- Uddin, N.; Nyden, M.R.; Davis, R.D. Characterization of Nanoparticle Release from Polymer Nanocomposites Due to Fire. In Proceedings of the Nanotech 2011 Conference and Expo, Boston, MA, June 13-16, 2011.
- 75. Dittrich, B.; Wartig, K.A.; Hofmann, D.; Mülhaupt, R.; Schartel, B. Carbon black, multiwall carbon nanotubes, expanded graphite and functionalized graphene flame retarded polypropylene nanocomposites. *Polym. Adv. Technol.* **2013**, *24*, 916–926.
- Bouillard, J.; R'Mili, B.; Moranviller, D.; Vignes, A.; Le Bihan, O.; Ustache, A.; Bomfim, J.S.; Frejafon, E.; Fleury, D. Nanosafety by design: risks from nanocomposite/nanowaste combustion. *J. Nanoparticle Res.* 2013, 15, 1–11.
- Coleman, J.N.; Cadek, M.; Blake, R.; Nicolosi, V.; Ryan, K.P.; Belton, C.; Fonseca, A.; Nagy, J.B.; Gun'ko, Y.K.; Blau, W.J. High Performance Nanotube-Reinforced Plastics: Understanding the Mechanism of Strength Increase. *Adv. Funct. Mater.* 2004, *14*, 791–798.
- Cai, H.; Yan, F.Y.; Xue, Q.J. Investigation of tribological properties of polyimide/carbon nanotube nanocomposites. *Mater. Sci. Eng. a-Struct. Mater. Prop. Microstruct. Process.* 2004, 364, 94–100.
- Gupta, A.; Choudhary, V. Thermal and mechanical properties of poly(trimethyelene terephthalate)/acid-treated multiwalled carbon nanotube composites. *J. Mater. Sci.* 2013. 48, 7063–7070.
- Seyhan, A.T.; Tanoglu, M.; Schulte, K. Tensile mechanical behavior and fracture toughness of MWCNT and DWCNT modified vinyl-ester/polyester hybrid nanocomposites produced by 3-roll milling. *Mater. Sci. Eng. a-Struct. Mater. Prop. Microstruct. Process.* 2009, 523, 85–92.
- 81. Zhu, J.; Kim, J.D.; Peng, H.Q.; Margrave, J.L.; Khabashesku, V.N.; Barrera, E.V. Improving the dispersion and integration of single-walled carbon nanotubes in epoxy composites through functionalization. *Nano Lett.* **2003**, *3*, 1107–1113.
- 82. Gojny, F.H.; Nastalczyk, J.; Roslaniec, Z.; Schulte, K. Surface modified multi-walled carbon nanotubes in CNT/epoxy-composites. *Chem. Phys. Lett.* **2003**, *370*, 820–824.

83. Mueller, N.C.; Buha, J.; Wang, J.; Ulrich, A.; Nowack, B. Modeling the flows of engineered nanomaterials during waste handling. *Environ. Sci. Process. Impacts* **2013**, *15*, 251–259.

© 2014 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (http://creativecommons.org/licenses/by/3.0/).