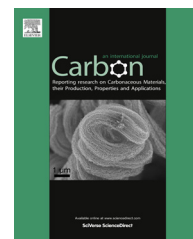


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Review

Release characteristics of selected carbon nanotube polymer composites



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ABSTRACT

Multi-walled carbon nanotubes (MWCNTs) are commonly used in polymer formulations to improve strength, conductivity, and other attributes. A developing concern is the potential for carbon nanotube polymer nanocomposites to release nanoparticles into the environment as the polymer matrix degrades or is mechanically stressed. Here, we review characteristics related to release potential of five sets of polymer systems: epoxy, polyamide, polyurethane, polyethylene, and polycarbonate. Our review includes consideration of general characteristics and use of the polymer (as related to potential MWCNT release) and its MWCNT composites; general potential for nanomaterial release (particularly MWCNTs) due to degradation and mechanical stresses during use; and potential effects of stabilizers and plasticizers on polymer degradation. We examine UV degradation, temperature extremes, acid–base catalysis, and stresses such as sanding. Based on a high-level summary of the characteristics considered, the potential for release of MWCNT with typical, intended consumer use is expected to be low.

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1. Introduction

Multi-walled carbon nanotubes (MWCNTs) possess unique physicochemical characteristics that in recent years allowed them to be projected into industries as a valuable component of polymer systems. With the addition of MWCNTs into polymer matrices, manufacturers can manipulate a material's conductivity, strength, flexibility/flowability, thermal stability/flame retardancy, static properties, weight, and need for other fillers. Despite continued exploration of this technology, there is a lack of widely-accepted methods for assessing the release of MWCNTs from polymer systems. Examining the release potential of MWCNTs is an important aspect of evaluating exposure potential as part of any environment, health, and safety risk assessment.

To assess the most useful methods for measuring the release of MWCNTs from polymer systems, it is essential for the materials to be commercially relevant and representative of a range of characteristics. Based on these criteria and others, the following set of polymer systems was chosen for initial focus [1]:

- Epoxy
- Polyamide (PA)
- Polyurethane (PU)
- Polyethylene (PE)
- Polycarbonate (PC)

An analysis was completed of existing knowledge of material characteristics that may affect release of MWCNTs from the chosen polymer systems. For each, the analysis included consideration of the following:

- General characteristics and use of the polymer (as relevant to potential MWCNT release).
- Use of carbon nanotubes (CNTs), particularly MWCNTs, in the polymer (purpose and applications).
- General potential for nanomaterial release (particularly MWCNTs) based on polymer properties and use applications.
- MWCNT traits that may affect release from the polymer system (i.e., type, alignment, dispersion, typical load, etc.).
- Potential effects of stabilizers and plasticizers on polymer degradation, if applicable.

Potential scenarios for release of MWCNTs from the polymer composite matrix have been recently considered by Nowack et al. [2]. Clearly the release potential depends on the handling, use, and environment at each of the stages of the life cycle. A few examples are discussed for the chosen polymer systems in the conclusions.

To address the scope of this review, significant considerations were given to specific end-products and applications, especially where direct consumer contact to released CNTs is probable during normal product use. For example, detailing uses of CNTs in automotive, electronics, and sporting goods applications was discussed due to market sizes and consumer bases. Applications in textiles and tires were also considered due to the potential for consumer contact with released CNTs. For example, CNTs have recently been incorporated into

“smart textiles” to add strain-sensing properties (see Polyurethane section as well as Zhang et al. [3]) or to improve flame retardancy, with the latter leading to an evaluation of the life cycle impacts of flame-retardant CNT textiles [4]. In the majority of cases, insufficient market and product performance data could be identified to substantiate an assessment of such specific uses. Ultimately, it was decided to focus on higher-level polymer and polymer-CNT properties, aiming for conclusions that would be broadly applicable to diverse products and extrapolated to other polymer matrices. Similar decisions were made about perspectives of different user groups of polymer-CNT composites. It was generally acknowledged that professional users such as those at formulation, master-batch, and assembly facilities, as well as military and defense personnel, could encounter CNT release products in their work. This review, however, will focus on general consumers of articles containing polymer-CNT composites since they represent a broader group and may not have the benefits of safety infrastructure and training that professional users have.

Conclusions and recommendations were based on the analysis and are summarized in Section 7. Data gaps were identified, which is not surprising considering that interest in CNT-polymer nanocomposites is relatively new. Further testing is needed to assess release potential for MWCNTs of each polymer system accurately, and measurement methods must be established and standardized. Therefore, recommendations in this report are not intended as a definitive indication of polymer systems that will have high/low release. For purposes of establishing release measurements, a “release potential” evaluation using existing data and expert opinion is sufficient.

1.1. General overview of CNTs in polymer matrices

CNTs exhibit exceptional mechanical, thermal, optical, and electrical properties. Combined with their low density and high aspect ratios, CNTs are ideal fillers for fabricating lightweight polymer composite materials with improved mechanical performance, electrical conductivity, and multifunctional properties. Properties of CNTs and their potential uses in diverse applications have been well documented in the academic literature [5,6] and will not be discussed in detail.

Global production of CNTs has already surpassed the kiloton level and is expected to more than double in the next 4 years as existing manufacturers increase production and new manufacturers emerge. This investment in CNT production is driven by rapidly increasing demands in numerous applications. Many current and near-term applications of CNTs involve their integration into polymer matrices to improve electrical, mechanical, and thermal properties. A summary of the use of CNT by major industry sector is presented in Fig. 1. The largest industry consumers of CNTs are the electronics, data storage, defense, aerospace, and energy sectors, which are early adopters of new materials and technologies. CNTs are also increasing penetration into diverse consumer goods markets such as sporting goods, packaging, and textiles. With continued advancements in cost reduction and production scale the number and diversity of products and technologies containing CNTs will continue to rise and the

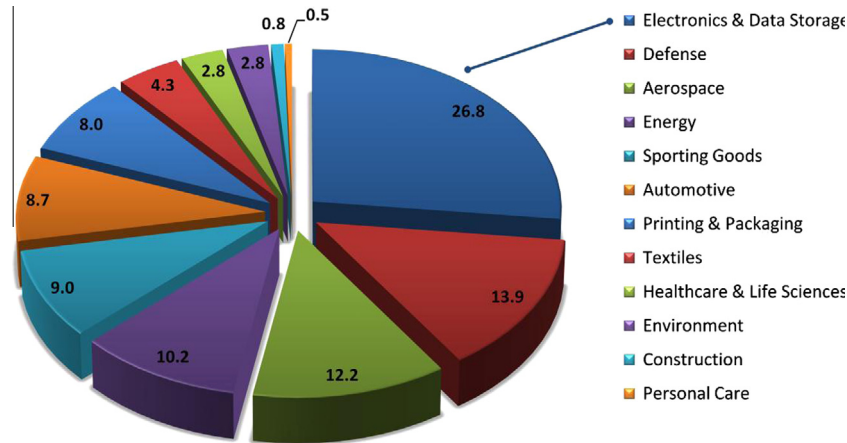


Fig. 1 – Global CNT demand by application. Percentage data are adapted from a market report by Nanoposts.com [7]. (A color version of this figure can be viewed online.)

CNT industry could compete with the carbon fiber industry and become a major additive for polymer-composite fabrication. Although the products and applications that can benefit from CNTs are nearly limitless, leveraging of their most straightforward properties, electrical conductivity and mechanical strength, has been most exploited in early commercial applications. Examples of commercial products containing CNT-polymer composites are listed in Table 1.

Many more applications are nearing commercial readiness, including structural aerospace composites, flame retardant composites, gas sensors, spun CNT fiber textiles, semiconductor interconnects, nano-electromechanical systems (NEMS), transparent electrodes, super-capacitors, photovoltaic devices, thermal management systems, sorbents, skincare products, and anti-microbial packaging.

There are currently limited market data available that quantify commercial use of CNTs in specific polymer types. Information on Internet sites of companies advertising CNT products, as well as anecdotal information from such companies, suggests that CNTs already have commercial uses in a variety of polymer matrices. There is evidence to suggest that a few types of polymer-CNT nanocomposites are being produced at larger volumes or with broader scopes of end-product use. In this subset, we identified CNT nanocomposites of epoxy resins, polycarbonates, polyamides, polyurethanes, and polyethylenes as having significant commercial use or potential use in consumer products, and these are the focus of this review.

The current and future commercial use of CNT has resulted in substantial academic interest in CNT-polymer composites, with extremely rapid progress in recent years. There are a number of literature reviews on the conductive and mechanical properties of CNT-polymer composites [8–20]. CNTs have also been investigated as additives in polymers such as epoxies, polycarbonates, polyurethanes, polyethylenes, polyamides, polyamides, polystyrene, and many others. Methods of incorporating the CNT vary greatly, as do observed impacts of the CNT on properties of polymers, from reduced performance to significantly increased mechanical properties and electrical conductivity. The main challenge has been achieving uniform dispersion of the CNT within the polymer matrix because improved dispersion leads to improved mechanical, electrical, and optical properties of composites. Optimizing interfacial adhesion between the CNT and polymer matrix has also been determined as an essential factor in extracting positive benefit from CNT additives. Functionalizing the CNT with specific chemistries optimized for a given polymer matrix is often necessary to achieve good CNT dispersion and improved polymer properties. In general, optimizing CNT chemistry and processing parameters to maximize dispersion and interfacial bonding in the polymer matrix can yield nanocomposites showing substantial improvements in strength, toughness, and modulus as well as electrical conductivity.

Table 1 – Current commercial applications of CNT-polymer composites.

Industry sector	CNT-polymer composite applications
Automotive	Fuel system components, electrostatically painted parts, lightweight structural components
Aerospace	Adhesives, electrostatic discharge and electromagnetic interference shielding
Defense	Anti-fouling coatings on naval vessels, conductive coatings for jet fighters, structural components for jet fighters, armor materials
Electronics	Antistatic packaging, scanning probe microscopy tips, conductive inks
Energy	Lithium-ion battery electrodes, transparent conductive films
Sporting goods	Baseball bats, skis, golf clubs, hockey sticks, tennis racquets, bicycle frames and components

1.2. Additional considerations influencing CNT release

The potential for CNT release from consumer products depends on many factors, including the physical and chemical properties of the polymer, the type of product, and how and in what environment it is used. Another consideration is the nature of the CNTs themselves. CNTs are not a single species; rather, they are a family of related materials with similar structures.

Although this report will focus exclusively on MWCNTs in polymers used for consumer applications, there remain many variables that characterize MWCNTs. They can be produced by processes that involve different precursor materials, catalysts, synthesis reactor technologies and conditions, and post-processing steps. The specific distributions of the structure and properties of a MWCNT product are also strongly dependent on the process and conditions under which they are produced. Properties that can vary between MWCNT suppliers include:

- *Composition:* catalyst metal and impurity carbon residue, residues from post-processing.
- *Physical properties:* length, average diameter, diameter distribution, number of walls, end cap configuration, degree of agglomeration, wall crystallinity and defect density, surface charge, orientation.
- *Chemical properties:* surface functionalization, solubility.

These properties also influence their incorporation into a polymer composite and the level of interaction with the polymer matrix, and can impact the release of CNTs from the polymer system. Information on the release of CNT from polymer systems is very limited and that which is available has assessed only a small number of CNT source materials under a few select release scenarios. The role of surface functionalization in CNT release is of particular interest since, in practice, the chemistry of the CNT is often adapted to be compatible with the polymer matrix being used and chemical bonding between the CNT and polymer will certainly influence the potential for CNT to be released from the matrix. Unfortunately, only a very small number of studies have examined the role of functionalized CNT in release scenarios, or presented data from which the role of functionalization might be inferred. To maintain a focused scope we have highlighted the studies that inform on the subject of CNT release in the sections below; for a more general overview of the subject of surface functionalization one may refer to recent review articles on this subject [21]. It is challenging to attempt to generalize these data, and those pertaining to other CNT properties, and make assessments and recommendations that are relevant to all CNT materials.

Most polymers used in commerce are formulations of the polymer plus additives to modify physical and chemical properties. Examples of physicochemical modifications include toughening, making compatible, promoting adhesion, increasing flexibility, and reducing friction. Additives used to achieve such modifications include plasticizers, stabilizers, surfactants, and polymerization modifiers. Wherever possible, assessment of the impact of CNT on polymer properties

and the potential for their release has accounted for such additives in commercial formulations to be as representative as possible of real materials in commerce. The assessments provided here represent a combination of the current state of knowledge in the field, including published literature, and expert opinion from numerous stakeholder groups.

2. Epoxy

2.1. Description of the polymer

Epoxy resins deliver outstanding adhesion, corrosion and chemical resistance, and toughness. They are found in a range of markets including construction, transportation, electronics, packaging, and industry, where they are used as protective coatings, as adhesives, in fiber-reinforced forms, and as structural materials. Global production of epoxy resins in 2009 was about 1,800,000 MT; the largest markets are in coatings and electronics, which account for nearly 80% of all epoxy resin use. Composites represent a minor use of epoxy resins (<4% globally, but 11% of US consumption). High performance markets for composites include applications such as automotive leaf springs and fiberglass pipe. Composites are also used in the aircraft/aerospace industry and have a growing presence in the wind turbine blade market. Epoxy resins are among the most frequently used in advanced composites where they are combined with glass fibers or carbon fibers to deliver excellent lifetimes. Most epoxy resins are based on the diglycidyl ether of bisphenol a (DGEBA), which accounts for 80–85% of worldwide consumption [22].

2.2. Uses in conjunction with CNTs

Epoxy resin consumption in the aircraft/aerospace sector increased from 2006 to 2009. In these various applications, CNTs are being explored as the next generation of advanced composites – either as replacement of carbon fiber or in combination with carbon fiber. The main incentive to move from carbon fiber to carbon nanotubes is the potential weight savings that is available [23]. Epoxy composites are particularly valuable to the aircraft and aerospace industries because of their high strength-to-weight ratio and high-temperature resistance. One example is their use in Lockheed's F-35, where carbon nanotube-reinforced epoxy will be used in wingtip fairings. Tomahawk[®] missiles and various military aircraft are using more composites. Military aircraft containing epoxy resin composites include the V-22 Osprey Tilt-Rotor aircraft, a vertical-takeoff and -landing aircraft. Carbon/epoxy composites account for 60–70% of its total weight [22]. Boeing's new passenger model, the 787, incorporates more carbon fiber composites than any previous model—an estimated three times more than in the 777. The Boeing 787 is made up of ~50% carbon composites, including the wings and fuselage. Airbus's rival plane is the A350-XWB, which has a full composite fuselage and more than 39% composites content, which is roughly comparable to Boeing's 787. Advanced epoxy composites can contain 60–70% by weight high-performance glass, aramid, carbon or boron fibers that are continuous and oriented to maximize performance.

Representative end uses for epoxy-glass composites include fuselage sections, wing skins, and fairings in certain military aircraft including the B-2 stealth bomber as well as numerous components for the Boeing 757 and 767 jetliners and cargo bay doors for the space shuttle. Epoxy-carbon and epoxy-aramid composites are employed as the rocket motorcase for many solid-fuel missiles and in structural uses for satellites.

Other uses for epoxy resin composites are in wind energy, electronic packaging, sporting goods, and adhesives. Epoxy resin composites are used in wind turbine blades; the majority of wind blade manufacturers use epoxy resin systems and either prepegs, vacuum-assisted resin transfer molding (VARTM), or a combination of both. Carbon nanotubes also have potential to act as electrically conductive fillers in polymers used in electronic packaging where they are fillers in electrically conductive epoxy adhesives. The aim is to improve performance of conductive adhesives compared to common products [24]. Epoxy-CNT composites also are used in golf clubs, badminton racquets (Applied Nanotech, personal communication, 2012; [25]), and bicycle frames.

2.3. Degradation and potential for release

2.3.1. UV degradation

Photodegradation of MWCNT/epoxy composite was investigated by exposure to artificial UV radiation at 50 °C and 75% relative humidity (RH) [26]. Analysis of chemical degradation, mass loss, and surface morphology showed the surfaces of both neat and CNT-enhanced epoxy undergo rapid photodegradation, with the rate for the MWCNT/epoxy being lower than the neat epoxy. Degradation of the matrix resulted in a gradual increase in concentration and aggregation of CNT

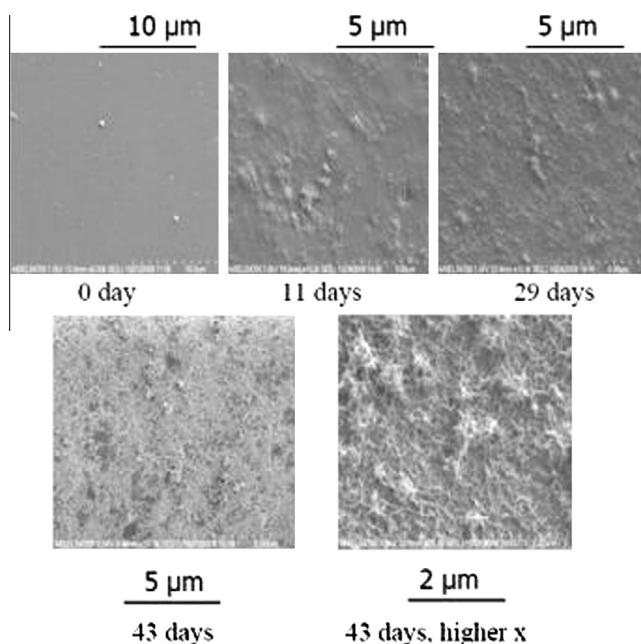


Fig. 2 – Field emission scanning electron microscopy (FE SEM) images of 0.72% MWCNT/epoxy composite exposed to UV/50 °C/75% RH, showing increasing amounts of CNTs on the composite surface with exposure time. Reproduced from Nguyen et al. [26].

on the surface (Fig. 2). This apparent accumulation is most likely attributable to receding of the polymer matrix, while more resistant MWCNTs remained and became exposed on the surface. This effect has also been observed with MWCNT/polyurethane composites [27].

2.3.2. Leaching

No literature reports were found in which leaching of CNTs from epoxy composites was studied, although there were studies of aging and degradation of fiber or glass reinforced epoxy resins. These studies provided information on the complex kinetics and diverse pathways involved in degradation of these composites. Degradation of glass fiber-reinforced epoxy resins was conducted to provide data on the long-term durability and service-life of these materials [27]. Some mechanisms relate to epoxy resins, but much of the chemistry was related to the glass fibers. Given the impact that the reinforcing material has on mechanisms of degradation, it may be difficult to use studies conducted with non-CNT composites to predict what will happen with CNT composites. In general, most leaching studies with epoxy materials focused on the potential release of monomers or other small molecules.

2.3.3. Temperature extremes

The cure kinetics and processing behaviors of epoxy resins can be influenced by nanoparticle additives [28]. Addition of unmodified MWCNTs has a negative effect on thermal stability due to the poor affinity of neat MWCNT and the epoxy matrix which increases voids in the nanocomposite. Conversely, use of amine-modified MWCNTs led to improved thermal stability and promoted flame retardancy of the epoxy; this suggests a better affinity for the polymer matrix. The stabilization effect of MWCNT may be explained by a barrier effect of the CNT which hinders diffusion of polymer degradation products into the gas phase. An increased interfacial interaction between MWCNT and the epoxy leads to increased degradation activation energy. Presence of carboxylated CNTs further stabilizes polycondensation polymers which restrict thermal motion of the macromolecules, resulting in increased thermal stability, with 2–5 wt% generally leading to the highest thermal stabilization. At higher nanoparticle content, aggregation causes deterioration of thermal stability because a microcomposite rather than a nanocomposite is formed, lessening the shielding effect of the nanoparticles. The general trend of increased thermal stability of epoxy-CNT nanocomposites suggests very limited potential for release of MWCNT with typical consumer use due to elevated temperatures.

2.3.4. Chemical resistance (including acids/bases)

Epoxy resins are generally highly resistant to solvents, acids, and bases. Given the wide variation in the resins, curing agents, and curing conditions, there is also variability in susceptibility of these resins to various conditions including exposure to acids or bases. Studies of the acid or base treatment of CNT epoxy composites have not been published. Exposure to high concentrations of mineral acids such as sulfuric or hydrochloric can have a significant effect on the epoxy resin. Base treatments have little effect on the resins. Exposure to weak, organic acids such as acetic acid had a

larger effect than mineral acids, with around 14% weight loss taking place over 120 days of exposure to acetic acid. In other cases, total decomposition of the resin after 28 days of exposure to acetic acid was observed. The extent of MWCNT release would likely be proportional to the degree of resin decomposition, with more susceptible resins having a greater propensity to release CNT.

2.3.5. Mechanical stresses (abrasion, deformation)

Functionalization of the CNT surface can enhance linkage with the epoxy to enable a stress transfer between the polymer and the CNT. Addition of carboxylic acid groups to the surface enabled better dispersion, but the stress transfer from the matrix to the tube is low and pull-outs were observed [29]. Further derivatization introduced amino functional groups which led to covalent bonds with the epoxy resin. TEM micrographs showed enhanced interfacial interaction in that the CNTs were completely covered with matrix and telescopic pull-out was observed; interaction of the outermost layer of the MWCNT remains in the matrix while the inner tubes, held only by van der Waals forces, pull apart. Fig. 3 shows a schematic representation of possible fracture mechanisms of CNT [30].

Continued efforts compared mechanical properties of several epoxy/CNT systems (Table 2) [30].

Two major conclusions related to potential release of CNT can be drawn from the results: 1) amino functionalization improves dispersion and integration of the CNTs into the epoxy network structure; and 2) agglomeration and higher filler contents can result in improper impregnation in the epoxy matrix and lead to composite failure.

Other studies have examined release of MWCNTs by abrasion. No free CNTs were released during cutting and sanding of an epoxy nanocomposite [31]. Release of CNTs from a DGEBA epoxy system was investigated using a Taber Abraser with an enclosure for particle collection [32]. Addition of CNT filler resulted in a 70- to 90-nm shift in the first mode of par-

ticle size distribution to the right, indicating larger abraded particles and a change in component properties. In contrast to similar studies, particles smaller than 100 nm were not observed by aerosol measurement tools. Moreover, this was the first study to report free-standing CNTs resulting from abrasion. The raw material CNTs added to the epoxy system had a length of $0.7 \pm 0.2 \mu\text{m}$, while the abraded CNT particles averaged $304 \pm 251 \text{ nm}$, which suggests that the CNTs were chopped during abrasion. This study also questions the ability of particle size distribution to show release of nanofiller since aerosol instruments used did not show an additional mode consistent with sizes of free-standing CNTs observed by TEM.

Hand sanding of a 2 wt% MWCNT/epoxy composite test stick produced particles exhibiting protrusions that appeared to be parts of the CNTs (Fig. 4) [33–35]. Observations of this sanding study were as follows:

- SEM showed that bulk CNT had protrusions similar to those on the sanding particle.
- Dark field TEM exhibited dark areas indicating elements of low atomic number (i.e., carbon), as well as bright areas indicating elements of high atomic number (i.e., metal catalyst residues from CNT production).
- Bright field TEM: dark areas revealed thicker regions or regions with a higher atomic number.
- EDS X-ray mapping: X-ray EDS peaks corresponded to electrons excited by the X-ray; multiple peaks for the same element corresponding to electrons in different energy shells; EDS mapped onto surface of images – turquoise color corresponds to carbon, red to iron, and blue to nickel. Protrusions seen from sanding dust particles had EDS X-ray signatures consistent with CNT.

There is no indication of significant nanoparticle release based on number concentration measured during this sanding process, as demonstrated in Table 3 [33]. There is, however, a significant increase of general respirable-sized

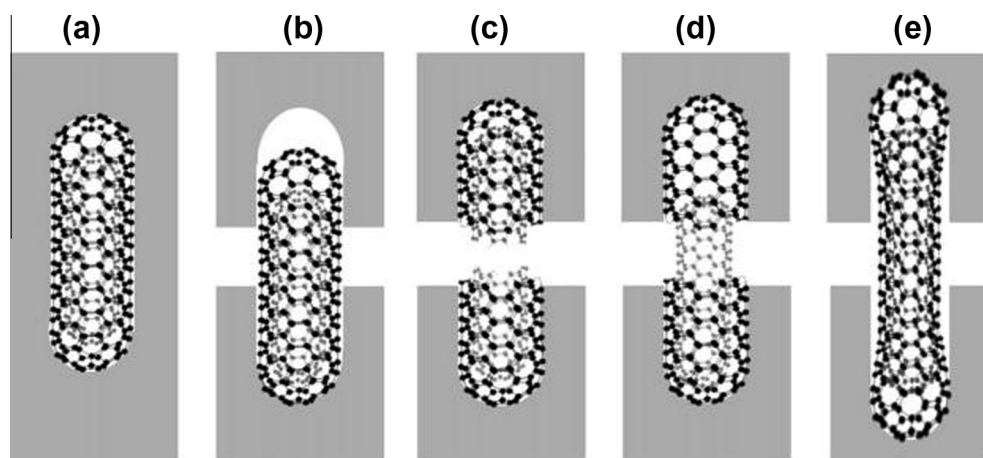


Fig. 3 – (a) Initial state of CNT in matrix. (b) Pull-out resulting from weak interfacial adhesion. (c) Rupture of CNT from strong interfacial adhesion plus extensive/fast local deformation. (d) Telescopic pull-out due to stronger interfacial bonding than van der Waals between the tube layers. (e) Crack bridging and partial debonding of the interface. Reprinted from Chem Phys Lett, vol. 370, Gojny FH, Nastalczyk J, Roslaniec Z, Schulte K, Surface modified multi-walled carbon nanotubes in CNT/epoxy-composites, p. 820–4. Copyright © 2003, with permission from Elsevier [30].

Table 2 – Mechanical properties of CNT/epoxy systems.

	Filler type/ content (wt%)	Young's modulus (MPa)	Ultimate tensile strength (MPa)	Fracture toughness K_{Ic} (MPa m ^{1/2})
Epoxy	0.0	2599 (±81)	63.80 (±1.09)	0.65 (±0.062)
Epoxy/CB	0.1	2752 (±144)	63.28 (±0.85)	0.76 (±0.030)
	0.3	2796 (±34)	63.13 (±0.59)	0.86 (±0.063)
	0.5	2830 (±60)	65.34 (±0.82)	0.85 (±0.034)
	0.05	2681 (±80)	65.84 (±0.64)	0.72 (±0.014)
Epoxy/SWCNT	0.1	2691 (±31)	66.34 (±1.11)	0.80 (±0.041)
	0.3	2812 (±90)	67.28 (±0.63)	0.73 (±0.028)
	0.1	2785 (±23)	62.43 (±1.08)	0.76 (±0.043)
Epoxy/DWCNT	0.3	2885 (±88)	67.77 (±0.40)	0.85 (±0.031)
	0.5	2970 (±29)	67.66 (±0.50)	0.85 (±0.064)
	0.1	2610 (±104)	63.62 (±0.68)	0.77 (±0.024)
Epoxy/DWCNT-NH ₂	0.3	2944 (±50)	67.02 (±0.19)	0.92 (±0.017)
	0.5	2978 (±24)	69.13 (±0.61)	0.93 (±0.030)
	0.1	2780 (±40)	62.97 (±0.25)	0.79 (±0.048)
Epoxy/MWCNT	0.3	2765 (±53)	63.17 (±0.13)	0.80 (±0.028)
	0.5	2609 (±13)	61.52 (0.19) ^a	^a
	0.1	2884 (±32)	64.67 (±0.13)	0.81 (±0.029)
Epoxy/MWCNT-NH ₂	0.3	2819 (±45)	63.64 (±0.21)	0.85 (±0.013)
	0.5	2820 (±15)	64.27 (±0.32)	0.84 (±0.028)

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^a High viscosity disabled degassing – composite contained numerous voids.

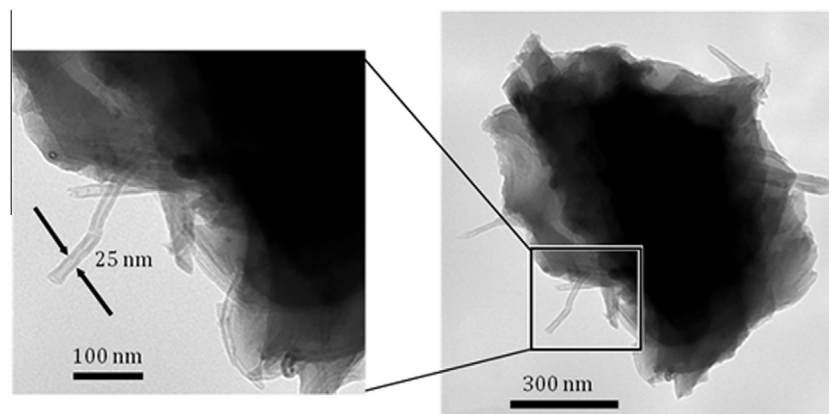


Fig. 4 – SEM images of sanded surface of particle of epoxy containing 2% by weight MWCNTs. More details are provided in the text of Section 2.3.5. Reprinted from J Occup Environ Hyg, vol. 8, Cena LG, Peters TM, Characterization and control of airborne particles emitted during production of epoxy/carbon nanotube nanocomposites, p. 86–92. Copyright © 2011 with permission from Taylor & Francis Ltd. (<http://www.tandf.co.uk/journals>) [33].

Table 3 – Impacts of sanding on release of nanoparticles from epoxy–CNT composite.

	Process	N	GM	GSD	Ratio to background
Number concentration (10 nm to 1 μm)	Sanding	100	3889 #/cc	1.48	1.04
Respirable mass concentration	Sanding	130	2.68 μg/m ³	6.57	5.90

Particle number and respirable mass concentrations observed during the sanding processes. N = number of data points logged by the instrument, GM = geometric mean, GSD = geometric standard deviation. Data are adapted from Cena [31].

particulates during sanding. These results suggest that the nanoparticles (in this case, MWCNT) are contained within the epoxy matrix during this specific abrasion event. Data

have begun to emerge on health effects associated with MWCNT protrusions on the surface of the sanding dust particles [36].

2.4. Composite traits that affect mechanical release

The most important factors of the MWCNTs that affect their release include their successful dispersion and incorporation into the epoxy matrix, length, and orientation of the MWCNT, and surface functionalization; for example, carboxylation of MWCNT achieved much better, more uniform dispersion in the epoxy matrix [37]. Effects of amine functionalization are discussed in Section 2.3. Another factor to consider is that formation of MWCNT-rich areas on the surface can help to protect the epoxy from UV degradation and reduce the potential for MWCNT release. This is in contrast to observations of silica particle-reinforced epoxy materials where silica particles were released after UV exposure [38].

2.5. Effects of stabilizers and plasticizers on degradation

Epoxy resin degradation in outdoor exposure environments is primarily due to water/humidity and solar ultraviolet radiation. Outdoor exposure data [39] from several locations suggest the strength loss on from natural exposure is ~25% over a 10-year period. UV-induced surface cracking of epoxy composite laminated in humid outdoor environments has been reported [40]. In this study by Sookay et al. [40], 20 weeks of exposure in South Africa led to extensive surface cracking of the epoxy. Although the depth of cracks was not enough to affect the strength of composite, it could allow release of any filler on the surface layer. The epoxy in the study did not use filler, but was reinforced at 50 wt% with glass fiber. In addition to light-initiated degradation epoxy resins degrade by autooxidation or inherent oxidation processes [41].

3. Polyamide

3.1. Description of the polymer

Polyamides are generally classified as non-nylon resins, polyamide elastomers, and nylons which can be resins or fibers. Consumption of polyamide elastomers is very minor, at about 18,000 MT per year [42]. The consumption of non-nylon polyamides is larger at ~130,000 MT, but is still much smaller than the global production and consumption of nylons [43]. Nylon resins are the largest volume of polyamides consumed, with a reported global consumption of about 2,000,000 MT in 2009 [44].

Nylons can be made via two pathways: by a combination of a diacid with a diamine, or by polymerization of an amine functional acid. The most common nylons, by far, are Nylon 6,6 and Nylon 6. Nylon 6,6 is made by polymerization of adipic acid with hexamethylene diamine (hence, each portion of the polymer is composed of a monomer having 6 carbons, leading to the 6,6 designation). Nylon 6 is prepared from caprolactam, which readily undergoes self-condensation. Manufacturing in the United States for Nylon 6 and Nylon 6,6 represents about 90% of the total production.

Polyamides are used in fibers and resins. The market for nylon fibers is mostly carpeting and textiles, with minor markets in paint brush bristles or toothbrushes or as filaments for fishing line and weed trimmers. As resins, nylons

are a member of engineering thermoplastics and are used in some of the same applications as epoxy resins, polycarbonate resins, and polyacetals; these are frequently used in filled or reinforced systems. Glass fiber reinforcement is common, as are mineral (clay) fillers; however, carbon black and carbon fiber are also used for some applications. Nylons are noted for their strength, toughness, and wear properties. While they are highly crystalline, they are less brittle than typical epoxy resins. Most nylon and reinforced nylon resins are injection molded, not extruded. Typical applications might be gears for the automotive and trucking industries. Reinforced nylons are replacing metal in many applications where they provide the required strength, wear, and impact resistance with fewer weight and corrosion concerns.

By far, the largest uses of reinforced nylon resins are in the automotive industry, including the following:

- *Body.* Side molding/cladding, exterior mirror housings, exterior door handles, window lift mechanism, grille/headlamp support, rear end panel, interior handles, or window latches.
- *Interior.* Instrument panel, airbag housing, interior steering column housing, interior speedometer components.
- *Powertrain and chassis.* Brake fluid reservoir, fuel vapor canister, fuel line, interior pedals, transmission components, wheel covers, windshield wiper components/tubing, wiring harness, connectors, switches/sockets, and fuse/junction systems.
- *Underhood/engine.* Intake manifold, air cleaner, radiator-fan shield, radiator-end tanks, radiator fan, air conditioner fan, coolant system heater core end, vacuum system, power steering reservoir, engine control system, engine oil pan, engine timing belt/torque chain, engine camshaft, gears.

Nylon resins have a high value; estimates place the content of recycled resin manufacturing scrap and off-spec materials at about 10% for nylons. These recycling efforts may not have much impact on the release of carbon nanotubes since the main feedstock is carpeting, which is not expected to provide a significant opportunity for CNT composites, unless contemplated for flame retardancy in carpet fibers.

3.2. Uses in conjunction with CNTs

CNT composites with nylons or polyamides have been made by melt compounding or in situ polymerization. Properties of examples made by both approaches are reviewed by Byrne and Gun'ko [45]. Polyamide composites with CNT are anticipated to deliver extended wear, lower friction resistance, increased load capacity, and mechanical strength. A three-fold improvement in Young's modulus at a loading of 1.5–2% CNT was reported in both melt processing and in situ polymerization.

Further research targets include flame-retardant materials [46], and conducting materials [47].

Commercial products of PA-6, PA-66, or PA-12 with carbon nanotubes are available with applications for the following [48]:

- Electrostatic Discharge (ESD) and electrically conductive parts.
- Electrical and Electronics (E&E) and Industrial.
- Injection molding, extrusion.
- Automotive fuel filters and connectors.

For example, the master-batch product PLASTICYL™ PA1503 is reported to have a CNT loading of 15 ± 1.0 wt% [49]. This technical data sheet also recommends using polymers with a high Melt Flow Index (MFI) to get well-dispersed CNT aggregates. Inferior dispersion could lead to pockets of unbound CNT that could be released following disturbance of the surrounding polymer.

3.3. Degradation and general potential for release

All evidence suggests that properly dispersed MWCNTs are tightly bound in the polyamide matrix. Although the relationship between degradation and MWCNT release is not well known, the potential for release is expected to increase as the polyamide undergoes structural or chemical changes. It is therefore anticipated that the most likely mechanism for release will come from degradation of the polyamide resins.

3.3.1. UV degradation

Samples of carbon fabric-reinforced Nylon 6 composite laminates, exposed for up to 600 h of UV radiation, showed considerable yellowing; however, they maintained structural integrity with no effects observed on the flexural or impact properties of the composite [50]. Although this exposure time is relatively short compared to what may possibly be encountered in many real-world uses of Nylon 6 composites, this suggests that significantly longer exposure times are needed to degrade the resin to the point that potential for release of CNTs from the composite increases. Aggregating exposure

conditions (e.g., UV in addition to moisture from outdoor humidity or rain) may also increase the potential for degradation and subsequent release. MWCNTs in composites with polyamide 6 slowed the UV degradation of the polymer matrix compared to the polymer itself [51]. The surface concentration of the MWCNT increased during the aging process.

3.3.2. Temperature extremes

Structure of the polymer matrix and interaction between CNTs and the matrix may be key factors for thermal degradation behavior of CNT-filled polymer composites. In a thermal degradation study of a multi-walled carbon nanotubes/polyamide 6 composite [52], the presence of MWCNTs was shown to improve thermal stability of PA-6 under air atmosphere, but had little effect on thermal degradation behavior under nitrogen atmosphere. The activation energy (E_a) value for degradation under air was 153, 165, and 169 kJ/mol for neat PA-6, purified-MWCNT/PA6, and amino-functionalized-MWCNT/PA6, respectively.

Another study [53] showed that adding up to 1.0 wt% MWCNT to PA-6 increased the onset temperature of thermal degradation measured by thermal gravimetric analysis. It suggests that the presence of MWCNTs lowers molecular mobility at the interface, improving thermal stability. Consequently, maximum degradation temperature has been shown to increase in PA 6.6/CNT systems, with the most significant improvement from 334 to 536 °C at 0.5% CNT loading and low heating rates, and increases further from 405 to 585 °C at higher heating rates (Fig. 5) [54].

Ribeiro et al. [54] also showed that neat PA 6.6 has lower activation energy, E_a , than its CNT-containing composites, again supporting that nanocomposites have higher thermal stability than pristine polymer. The curves in Fig. 5 indicate that higher energy is required for bond breaking as CNT is

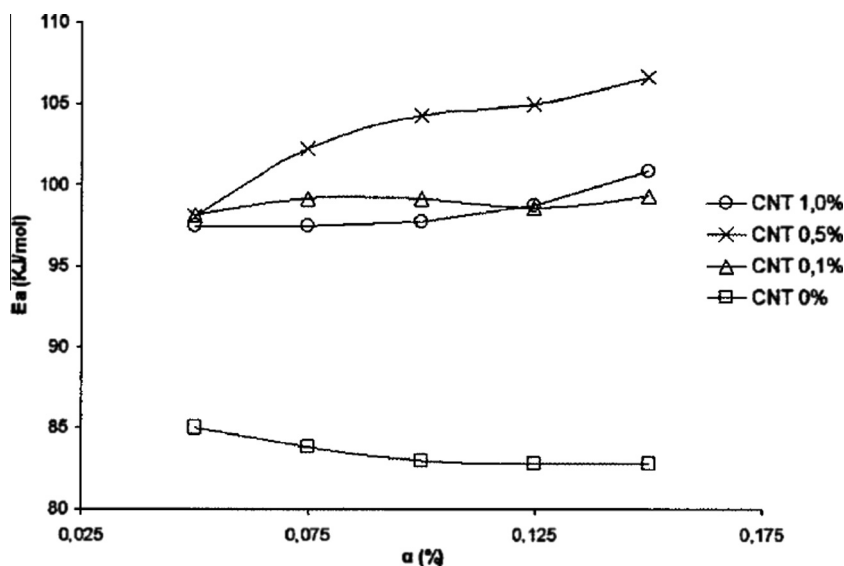


Fig. 5 – Activation energy (E_a) as function of the conversion degree (α) for the polyamide 6.6 (PA 6.6) and their nanostructured composites. Ribeiro B, Nohara LB, Oishi SS, Costa ML, Botelho EC. Nonoxidative thermal degradation kinetic of polyamide 6, 6 reinforced with carbon nanotubes. *J Thermoplast Compos Mater* [published online ahead of print March 25, 2012]. Copyright © 2012. Reprinted by permission of SAGE [54].

added to the polymer system, with 0.5% CNT loading being the optimal formulation. It is theorized that agglomeration behavior at CNT loading of 1.0% explains decreasing thermal stability of the higher CNT content. These data suggest that nanofiller loading should be optimized to create composites with less likelihood of releasing nanomaterials under thermal stress conditions.

3.3.3. Chemical resistance

Nylons are stable in many solvents and in most inorganic media, including liquid ammonia, sulfurous acid, and others, but may be eroded with oxidants such as hydrogen peroxide, concentrated inorganic acids, and chlorine-based decolorants. The resins are significantly resistant to alkaline solutions but are very susceptible to deterioration in some weak organic acids such as acetic acid and some alcohols including isopropyl alcohol [55,56].

Although data describing impacts of CNTs on chemical stability of nylon composites are not available, it is reasonable to expect that the potential for release of MWCNTs will increase in solvent media to which the resin has poor chemical resistance.

3.3.4. Mechanical stresses

In a study by Giraldo et al. [53] of tribological properties of PA-6 reinforced with up to 1 wt% MWCNTs, it was observed that scratch hardness increased significantly with introduction of MWCNT reinforcement. From sliding wear tests performed at loads from 5 to 25 N, the stiffness of the composite increased with the presence of MWCNT; however, there was no evidence of debris formation on the surface caused by the presence of MWCNTs. In a separate friction and wear study [57] of carbon nanotubes reinforced PA-6 composites, results showed that CNTs could improve wear resistance and reduce the friction coefficient of PA-6 considerably under dry and water-lubricated sliding conditions, due to effective reinforcing and self-lubricating effects of CNTs on the PA-6 matrix.

Given the improvements to mechanical properties of MWCNT-nylon composites, we conclude that mechanical wear represents a low probability pathway to release of MWCNTs. Further investigation is needed to quantify level of release and determine if there is any propensity to release free MWCNTs, or if nanotubes remain bound to polymer fragments.

3.3.5. Other factors (humidity and leaching)

Exposure to moisture can affect long-term structural durability and properties of polyamide composite materials, especially for the PA matrix that can absorb moisture up to 10% of its weight. Hydrolysis and plasticization strongly affect inter-laminar shear and impact resistance. A study of carbon fabric-reinforced Nylon 6 composite laminates, exposed to moisture at 100 °C, resulted in a 45% reduction of flexural strength where the main factor contributing to lowering of mechanical properties was plasticization of the matrix and attack on the fiber-matrix interface by the water [50]. No information was found on leaching of CNTs from composites with PA. Solvents capable of dissolving or softening the polyamide could favor diffusion and release of CNTs.

3.4. Composite traits that affect release

As with most CNT composites, effective dispersion of nanotubes in the polymer and strength of the interaction between polymer and nanotubes play key roles in developing desired properties. As identified by the resulting mechanical properties of Nylon 6 composites, aromatic amine-functionalized MWCNT resulted in superior dispersion, compared to pristine MWCNTs, and in situ polymerization was superior to melt blending [58]. Several other studies functionalized MWCNTs with amine groups using a grafting technique [52,59]. The fractured surface of MWCNT-NH₂/Nylon 6 composites showed uniform dispersion of MWCNTs and strong interfacial adhesion with the matrix, as evidenced by many broken, but strongly embedded MWCNTs in the matrix in the absence of debonding from the matrix. These factors are also likely to impact potential release of CNTs from nylon composites.

3.5. Effects of stabilizers and plasticizers on degradation

Properties of polyamide resins are typically modified by additives and many are added in far higher proportions than the typical 1% range of MWCNTs. One example of heat stable plasticizers with typical use levels of 5–20% are the sulfonamides sold by companies including Unitex (UniPlex 214 [60]) or Ferro-Plast ([61]). Ferro-Plast also offers master-batches of polyamides with various additives, including some with carbon nanotubes. For applications such as fishing line, grass-trimming line, and thread-bonding, a high degree of flexibility is required; up to 30% of the plasticizer may be added, which lowers chances of impact failure and stress cracking but increases surface abrasion potential.

Polyamides are more resistant to flame and ignition than many other polymers and are used in applications where a high degree of flame retardancy is required. They are then modified with halogenated or phosphorous based flame retardants. To reach the V-0 rating in the UL 94 class, one must use 20 wt% of brominated polystyrene with antimony trioxide or 14 wt% of red phosphorus or 18 wt% of Clariant Exolit OP 1312 organic phosphinate additive [62]. All of these additives reduce mechanical properties of polyamide composites.

UV stabilizers such as hindered amine light stabilizers (HALS) (e.g., from BASF and the former Ciba Chemical) are typically added in levels <0.5%. It is thus unlikely they will have much effect on the release of CNTs other than the intended one of reducing matrix degradation, thus lowering the probability of release by weathering.

Impact modifiers are used in cases where the polyamide is required to have good impact strength at low temperatures. Impact strength at or below 0 °C temperatures can be dramatically improved by adding these modifiers. Dow's Paraloid line of impact modifiers is one class used at levels up to 15%, or even 20%, if lower temperature performance is required [63]. Additives that reduce elongation at break and notched impact strength (certainly flame retardants and possibly heat stabilizers) are likely to increase the probability of CNT protrusions on sanding fragments and CNT release, which was identified as the critical parameter for CNT release by sanding on other matrices [27].

4. Polyurethane

4.1. Description of the polymer

Polyurethane (PU) is one of the most versatile and actively used polymers, with low-density foams (0.025 kg/l) up to compact materials, and highly elastic materials to highly cross-linked rigid materials. Current industrial uses of polyurethane foams include homopolymers and many different copolymer matrices (e.g., polyesters and polyethers) [64]. In global plastics consumption (230 million tons in 2005), PU holds a market share of 5.5%. Typical markets include consumer-relevant applications such as automotive, building, furniture, electronics, shoes, and sports.

Conventional PU is often sold as two-component precursors to be mixed, applied/shaped, and polymerized at the OEM customer: polyol and di- or polyfunctional isocyanate, which condenses to a thermoplastic, thermoset, or elastic urethane polymer. Tailor-made properties are possible by di- or polyfunctional monomers and by diverse particulate or dissolved additives, such as blowing or gelling catalysts, blowing agents, antioxidants, fire retardants, pigments, surfactants, and various fillers.

In order of increasing foam density, PU elastic foams are then sold as slabstock foams (for furniture) or as molded foams (for office or automotive seating). PU rigid foams mainly serve as thermal insulation in buildings. Flexible integral foams are used in shoe soles. Inline skate wheels are made from hot-cast PU elastomer (density 1 kg/l). Thermoplastic PU (TPU) (1.1 kg/l) is marketed as granulate, to be melt-processed into cable sheathing, plugs and terminations, spiral tubing, films, ski-boot shells, and technical moldings. TPU tensile strength is below 100 MPa and tear strength is below 100 kN/m, but the elongation at break reaches several hundred percent. Nanocomposites enable enhanced functionalities by incorporating a variety of fillers such as silica nanoparticles [65], clays [66], glass or carbon fibers [67,68], and graphene sheets [69] into the TPU matrix.

4.2. Uses in conjunction with CNTs

There is currently little information on CNT-PU composites in the marketplace and no information on production volume. Anecdotal information gleaned from the Internet indicates CNT-PU composites are available for industrial use. The Nanocyl website [48] includes studies on optimization of PU-CNT composites through melt modification and tracking of the composite's electrical, mechanical, and thermal properties. The company also has reports on PU-MWCNTs as efficient flame retardants. Bayer utilizes PU-CNT composites for wind turbine blades [70]. Media information indicates another MWCNT manufacturer, Zyvex Corporation, has developed MWCNT (and SWCNT) for easy dispersion into polyurethane matrices [71,72]. Similar information is available for Arkema (GraphiStrength), which has a line of PU-CNT master-batches that contain up to 45 wt% of CNTs for composites.

Limited literature indicates clear advantages of these composites over traditional PU systems. For example, Loos et al. found increased fatigue life of PU composites for wind blades, which included MWCNTs (Baytubes C150P), by 248% over historically used systems. A review by Köhler et al. [73] suggests that PU-CNT coatings have enhanced thermal mechanical and electrical properties. Song et al. [74] found an increase in coefficient of friction and high-wear resistance for PU-MWCNT films compared to traditional films. Studies have looked at effects of glass transition temperatures of neat PU and PU-MWCNT, finding dramatic differences between the two [75,76]. While the mechanisms of change in thermal stability remain largely unknown, a flux obstruction type hypothesis is the prevalent theory [75].

One PU variant that was used for evaluation of the release of CNTs is the thermoplastic PU (TPU) [27]. The commercial motivation for including CNTs is to achieve antistatic or conductive properties. The advantage over traditional fillers is that lower filler content is needed to reach percolation, such that mechanical properties are less downgraded than a carbon-black composite of equal conductivity.

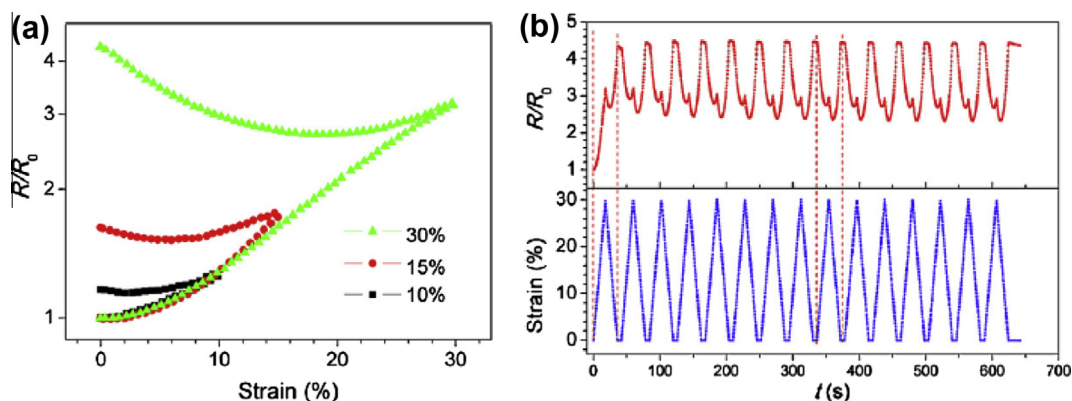


Fig. 6 – Sensor application of a CNT-TPU composite: (a) when mechanical strain is applied to the elastic TPU matrix, the resistivity R increases because the CNT network cannot follow the deformations entirely (weight% CNT is indicated); (b) the effect can be cycled several times with reproducible changes, highlighting the elasticity that sets it apart from CNT-polymer composites based on epoxy and other polymers, with implications for release probability. Reprinted from *Sensor Actuator A-Phys*, vol. 179, Zhang R, Deng H, Valenca R, Jin J, Fu Q, Bilotti E, et al. Carbon nanotube polymer coatings for textile yarns with good strain sensing capability, p. 83–9. Copyright © 2012, with permission from Elsevier [3]. (A color version of this figure can be viewed online.)

Based on the large number of reports examining the addition of CNT to polyurethanes, it is possible to state the following generalized characteristics of PU–CNT composites [65–68,75,77–87]:

- Tensile strength and modulus increase, with increase in wt% of CNTs.
- Tensile strength and modulus increase, with increased dispersion and alignment of CNTs.
- Thermal stability increase (higher decomposition temperature) with CNTs.
- Electrical conductivity increase with CNTs.
- Increased phase separation of PU with CNTs.

More advanced PU–CNT technologies include responsive materials where strain-sensitive resistivity of the CNT network (of vanishing elastic elongation) depends on the strain exerted on the (elastic) PU matrix (Fig. 6). Applications as electrically-read strain sensors for smart textiles are being developed [3,88] and even higher levels of system integration are targeted by shape-memory CNT-PU composites for smart actuators in micro-aerial systems [69].

4.3. Composite traits that affect release

Typical CNT loading levels in CNT–TPU composites are between 0.1 and 5 wt%. In terms of the matrix, there are studies that discuss degradation and biodegradation pathways of PU [81,89–91]. A recent study by Lattuati-Derieux et al. [86] indicates that PU foams (soft matrices of PU) are amenable to degradation from aging, with hydrolysis and photo-oxidation as the major pathways.

PU can be tailored to strong interfacial activity with CNTs as shown by Deka et al. [80], using hyper-branched PU–MWCNT composites (HBPU–MWCNT) made from *Mesua ferrea* L. seed oil; the duration and extent of dispersion of nanotubes in the matrix increased dramatically, according to TEM and SEM analysis (Fig. 7). This effect can possibly be attributed to functional groups added to the MWCNT to facilitate hydrogen bonds with the HBPU and thus better phase adhesion.

4.4. Degradation and general potential for release

4.4.1. UV degradation

The first study on weathering of a PU–nanocomposite addresses PU–graphene oxide [77] and indicates accumulation of graphene-oxide flakes on the sample surface under UV radiation. The authors found that the PU matrix underwent photodegradation, resulting in the emergence of graphene oxide nanoflakes on the substrate surface after 15 days in a 22-fold accelerated UV intensity. Presence of the nanofiller tended to slow photo-oxidation, but only as a % effect. After continued irradiation, agglomerates that were orders of magnitude thicker than individual flakes remained on the surface. Actual release after UV irradiation has not been studied.

A detailed study of a CNT–TPU composite matrix has been reported [27]. After weathering, the polymer matrix receded, while more resistant CNTs remained and became exposed as an entangled network on the surface; this is very similar to the effects observed on epoxy (Fig. 2). Presence of naked

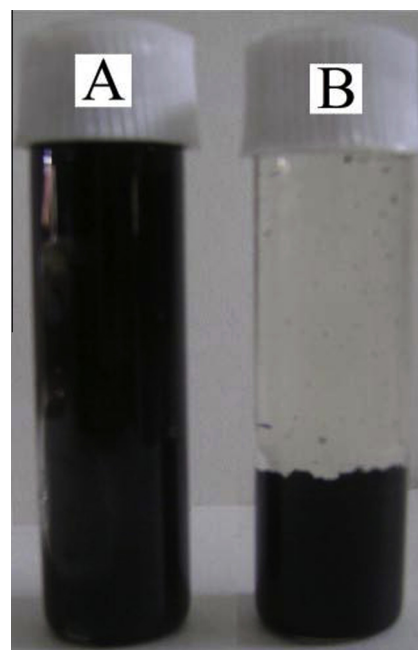


Fig. 7 – Sample of MWCNTs dispersed in a HBPU matrix (left) compared to a sample of MWCNTs dispersed in DMF (right). Sample A was dispersed adequately for over 7 months, while MWCNTs in sample B agglomerated within a week. Reprinted from Carbon, vol. 48, Deka H, Karak N, Kalita RD, Buragohain AK. Biocompatible hyperbranched polyurethane/multi-walled carbon nanotube composites as shape memory materials, p. 2013–22. Copyright © 2010, with permission from Elsevier [80]. (A color version of this figure can be viewed online.)

CNTs was confirmed by photoelectron spectroscopy (XPS) where it became evident that wet weathering is roughly a factor of 3 more progressive than UV-only weathering (Fig. 8). The carbon photoelectron spectra are selective for specific organic groups. The comparison to a positive control reference (bottom graph, Fig. 8) identifies the chemical bonding state and especially the contribution of CNTs. The TPU polymeric matrix obviously vanishes on the order of or below 1 μm per year; van der Waals forces hold the remaining CNT network together and keep it attached to protruding CNTs from the intact composite below. As hypothesized by Nguyen, these CNT networks collapse due to strong van der Waals attraction, form a dense layer, and do not release spontaneously. Using the same methods of induced release after weathering, it takes worst-case combinations of weathering plus ultrasonic wear to release CNTs from their network [35].

We conclude from indications of PU–graphene oxide [77] and TPU–CNT [27] that UV irradiation is a potential route of release of CNTs from PU if additional strong mechanical forces disrupt the collapsed CNT network [35]. It is expected that the physical and chemical properties of the CNT will influence the necessary force or energy thresholds.

4.4.2. Temperature extremes, acids/bases and biodegradation
Technical processing temperatures of neat polyurethanes reach up to 240 °C. There are limited reports of the thermal

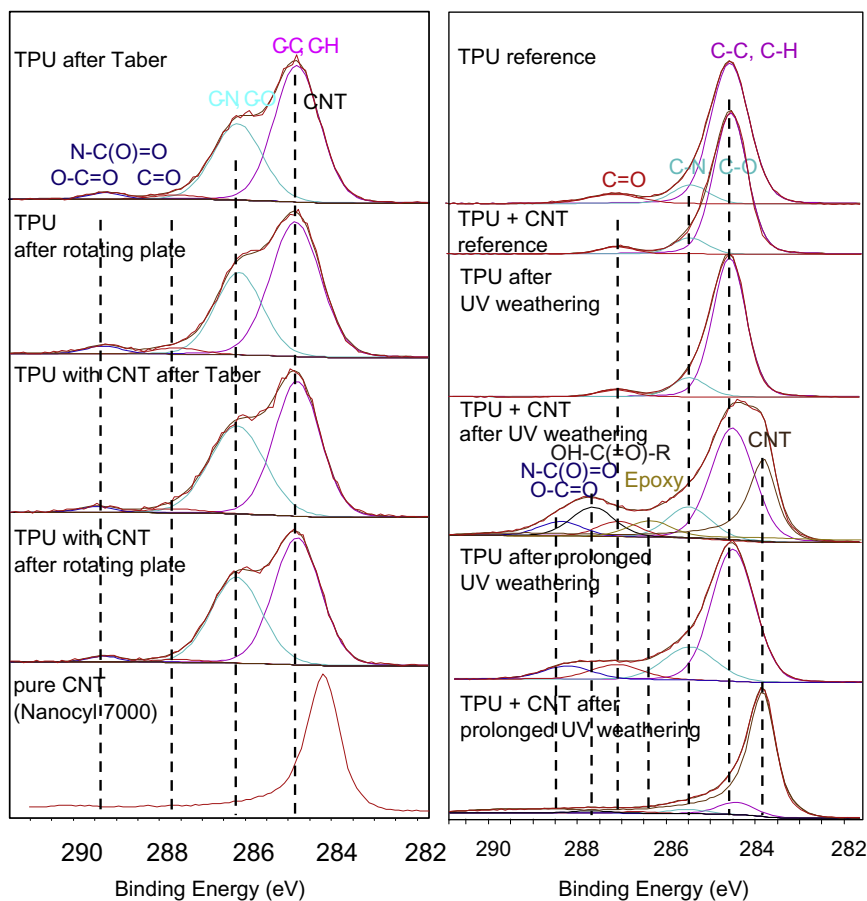


Fig. 8 – TPU + CNT lifecycle: Surface chemistry in the upper 10 nm after degradation. (Left column) Fragments collected after mechanical treatment by Taber Abraser or by sanding (rotating plate) by X-ray photoelectron spectroscopy (XPS). The CNT positive control is shown as the bottom panel. The C 1s detail spectra of fragments exhibit no signal from low binding-energy-photoelectrons that are characteristic for CNTs, regardless of the mechanical degradation scenario. (Right column) Nanocomposite surface after weathering. When the samples were exposed to UV irradiation only, matching 9 months' equivalent weathering, a shoulder that is characteristic for naked CNTs appears and cannot be explained by any other functional group. The remaining material after prolonged weathering is dominated by CNTs. Reproduced from Wohlleben et al. [27] with permission from The Royal Society of Chemistry. (A color version of this figure can be viewed online.)

properties of PU–CNT composites. Degradation temperatures are higher for PU–CNT composites, compared to neat PU. Neat hyper-branched polyurethane (HBPU) typically has various steps to degradation temperatures, although with HBPU–MWCNT composites only one degradation temperature was found [80]. Thermoset polyurethane (TPU) is attacked by concentrated acids and alkaline solutions, even at room temperature. Ketones (acetone, methylethylketone) are partial solvents; highly polar organic solvents such as DMF, DMSO, and THF dissolve the matrix. The potential for CNT release from TPU nanocomposites is, therefore, expected to be higher where they are exposed to such chemical environments.

PU is known to be susceptible to microbial degradation by microorganisms. This depends on polymers' properties such as the presence of functional groups, orientation, crystallinity, and cross-linking since these address the organism's accessibility to the polymer. Polyester-based PU is more susceptible to microbial attack than polyether-based variants [92].

4.4.3. Mechanical stresses (abrasion, deformation)

The nature of deformation for a large-scale PU–MWCNT composite is not unlike a neat PU elastomer, as determined by Koerner et al. [84], in which the composite persists to deform as unfilled PU does at various concentrations of CNTs; this suggests the mechanics of deformation are at least on a scale influenced by the PU matrix. This expectation was confirmed by a release study on PU and CNT–PU in which both sanding (high shear, machining simulation) and Taber Abraser (normal use simulation) were tested, aerosols monitored, and the released fragments assessed by a battery of techniques (SMPS, CPC, XPS, SEM, AUC, LLD). For both the nanocomposite and the TPU reference, the aerosol number concentration during machining was around 6000–8000 P/cm³. Positive evidence of free CNTs was not found in morphology (SEM, Fig. 9) by surface chemistry (XPS, Fig. 9) or by classification and size-selective quantification. The size-selective detection used both positive and negative controls and found amounts around 0.2 wt% in the range below 100 nm where free CNTs

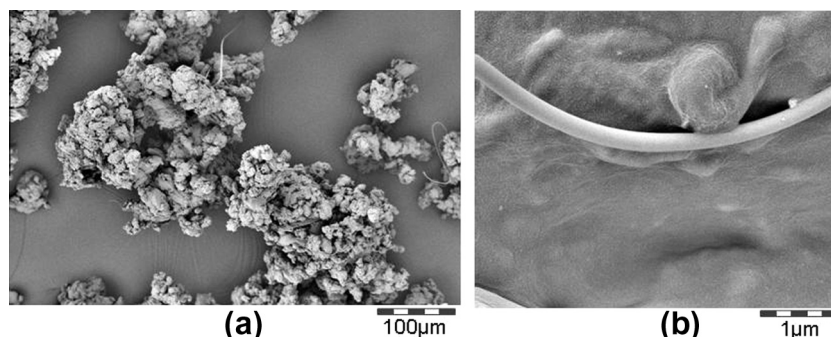


Fig. 9 – Debris after Taber Abraser degradation of TPU + CNT, showing large fragments of 10–100 μm , confirmed by laser diffraction. The fiber in (b) is one order of magnitude thicker than the CNTs present in the product. In accordance with chemical identification (Fig. 8), such fibers must be polymeric in nature; this observation indicates that the very soft matrix of TPU deforms under shear up to 600%, much more than CNTs. Adapted from Wohleben et al. [27] with permission from The Royal Society of Chemistry.

would appear, but the same content in this size range is found for the reference material without CNTs. Compare these numbers to the total content of 3 wt% CNTs in the sample. Tubular protrusions are not observed, in contrast to brittle epoxy degradation.

As a possibly generic phenomenon, it was hypothesized that the relative softness of the material actually enhances the embedding of CNTs in its degradation fragments because TPU elongates 600% before it breaks and flows around the embedded CNTs during shear. The same mechanism was observed for POM (30% elongation), but not for epoxy (5%) or cement (1%) [27].

We conclude that mechanical forces without matrix degradation do not lead to a significant probability of CNT release from TPU.

4.5. Effects of stabilizers and plasticizers on degradation

Additives are common practice for PU, including TPU: anti-static, flame retardant (halogen free), hard phase modifier, surface matting, UV stabilizer, plasticizer, and lubricant. Mechanical degradation will obviously change if hard phase modifier, plasticizer, or lubricants are compounded. Weathering degradation is controlled by UV stabilizers/antioxidants.

5. Polyethylene

5.1. Description of the polymer

Polyethylene (PE) is the most widely used plastic, with an annual production of ~ 80 million MT. It is a thermoplastic polymer that is a typical injection-molded material consisting of long chains produced by combining the ingredient monomer ethylene. PE has several grades with varying properties: the largest volume grades are high density polyethylene (HDPE), low-density polyethylene (LDPE), and linear low-density polyethylene (LLDPE). PE has multiple consumer uses that vary according to grade. Approximately 50% of PE demand is made up of HDPE, one-third by LLDPE, and the balance by LDPE. PE's inherent properties include strength, light weight, ease of processing, and resistance to chemicals, abrasion, and im-

pact. Industrial and consumer packaging accounts for over half of PE's use, followed by consumer/institutional uses for approximately one-fourth, and the balance in construction and other uses.

HDPE has a low degree of branching, thus stronger intermolecular forces and tensile strength, and is harder and able to withstand higher temperatures, compared to LDPE. It also has excellent resistance to moisture. Typical density values are 0.935–0.96 g/cm^3 . Global demand increased from 15.5 million tons in 2000 to 23.1 million tons in 2009, growing at a rate of 4.5% during the period. Typical processing methods include blow molding, extrusion, and rotational and injection molding. HDPE consumer uses are milk jugs, detergent bottles, margarine tubs, garbage containers, and paint “cans,” along with injection-molded toys and housewares. Industrial uses include automotive gas tanks and chemical storage containers. Construction applications include water pipes, fencing, decking, and playground equipment.

LDPE has a comparatively lower density range of 0.910–0.940 g/cm^3 that is related to the small amount of branching in the chain (on about 2% of the carbon atoms). LDPE is a branched homopolymer of ethylene and branching results in weaker intermolecular forces and lower tensile strength. It is another widely-used grade of PE at about 20 million tons in 2012. It is translucent to opaque, robust enough to be virtually unbreakable and simultaneously quite flexible. It has a variety of uses, but the most common are plastic bags, stretch wrap and shrink wrap film, some adhesives, and paperboard coating. Additional products include trays, general purpose containers, and corrosion-resistant work surfaces.

This grade of PE has a similar density to LDPE but contains only short branching. LLDPE is not a homopolymer, but a branched copolymer of ethylene with short chain (C4–8) alkenes. The global demand for LLDPE increased from 10.6 million tons in 2000 to 15.49 million tons in 2009. Packaging and construction industries are the major consumers. Like LDPE, LLDPE is used for plastic bags and sheets, plastic wrap, stretch wrap, pouches, toys, covers, lids, pipes, buckets and containers, cable covering, geomembranes, and flexible tubing including squeeze bottles. The majority of LLDPE is used in film form. It has higher tensile strength and higher impact

and puncture resistance compared to LDPE. It is very flexible and elongates under stress. It can be used to make thinner films with better environmental stress cracking resistance. It also has good resistance to chemicals and good electrical properties.

Ultra-high-weight polyethylene is of increasing importance due to its strength, toughness, and resistance to abrasion. Applications range from industrial to medical/orthopedics to high-strength fibers.

5.2. Uses in conjunction with CNTs

CNT-enhanced variants have the potential for rapid market adoption. The combination of exceptional conductivity (electrical and thermal), low density and mechanical properties of CNTs prompted exploration of their use in filled PE composites [11,12,17,93–104]. The electrical and thermal conductivity of PE is dramatically improved by the addition of CNTs (Fig. 10). Examples of uses of PE–MWCNT composites include automotive external body components, electrostatic dissipation materials, hot melt adhesives, materials and yarns and conductive plastics for surface resistivity. As in other polymer applications, the principal challenge is in their dispersion and the interfacial bonding between CNTs and the polymer

matrix. PE–MWCNT master batches are increasingly available in pelleted form for ease in downstream use. Producers include Arkema (Graphistrength C M4-30 Polyethylene Masterbatch, 30% by weight MWCNT in a low-density polyolefin matrix), Nanocyl (Plasticyl LDPE200, 20% by weight MWCNT; HDPE1501, 15% by weight MWCNT), and Hyperion Catalysis (HDPE MB 3520). As described in the Introduction, both single wall nanotubes (SWCNTs or SWNTs) and multi-walled nanotubes (MWCNTs) have been used in composites with PE. The literature that describes MWCNT–PE composites often does not specify the particular form of MWCNT used in the study.

5.3. Degradation and general potential for release

Several papers were recently published regarding possible pathways for release of nanomaterials from polymer matrices [106], including polymer MWCNT composites. Although they do not specifically address PE–MWCNT composites, their discussions remain relevant. Mechanical release via abrasion from smaller particles is one possible mechanism. PE generally is a flexible polymer that is less susceptible to abrasion than harder polymers being considered in this evaluation. Within the range of PE grades, the harder HDPE is most likely to release MWCNTs via this pathway; yet, the applications targeted are not typically subject to mechanical abrasion. Degradation appears to be the most likely pathway for release in PE–MWCNT composites. Degradation also generally changes the tensile strength of polymers and promotes fragmentation to smaller particles which, in turn, are more biologically degradable. Leaching of hydrophobic substances such as MWCNTs is not likely to be a significant release mechanism for undegraded material, however, once degraded; the potential is greater for leaching.

PE generally resists degradation by acids, bases, and microbial activity. This is illustrated by the fact that PE often is selected as the liner for long-term retention of waste in sanitary landfills. With exposure to light, the primary pathway for initial breakdown involves auto-oxidation by free radicals that include reactive oxygen species [107–110]. Auto-oxidation is mediated by chain-propagating processes that involve the intermediacy of hydroperoxides. This process is accelerated by exposure to UV radiation and increases in temperature. Most grades of PE contain trace amounts of substances that could eventually initiate auto-oxidation processes. Addition of pro-oxidants to the PE can accelerate its decomposition, especially when exposed to UV radiation. Carbonyl compounds build up in PE upon exposure to light and free radicals [111]. Photochemical cleavage of carbonyl moieties by Norrish Type I and Type II photoreactions contributes to further fragmentation of PE chains [108]. The light-induced breakdown into smaller fragments, coupled with changes in composition, greatly enhances susceptibility to biological degradation [108,112].

Often UV stabilizers and free radical scavengers are added to retard degradation [108]. In the case of light-initiated degradation, the stabilizers function in part by screening out UV radiation. PE itself is quite transparent to UV radiation and, in the absence of UV screening additives, effective wavelengths of light can penetrate the polymer matrix significantly. Antioxidants added to the polymer scavenge free

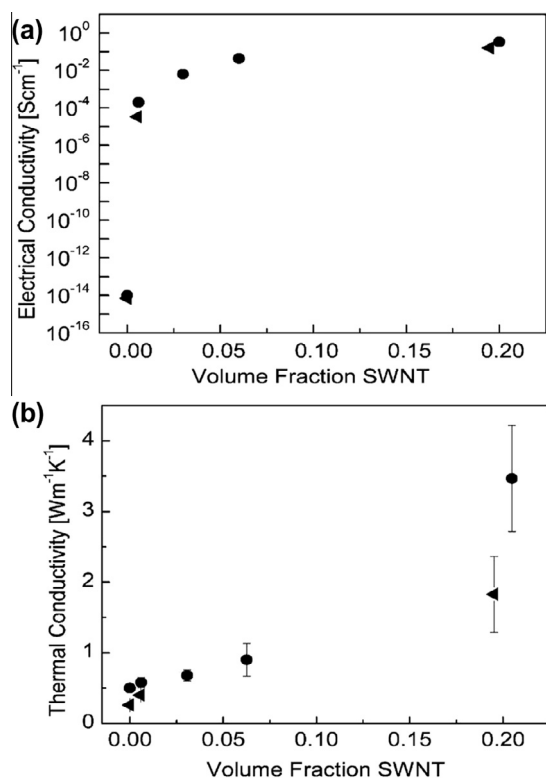


Fig. 10 – Comparison of (a) electrical and (b) thermal conductivity for isotropic (tilted filled triangles) SWNT/LDPE and (filled circles) SWNT/HDPE composites at various SWNT. Reprinted with permission from Haggenueller R, Guthy C, Lukes JR, Fischer JE, Winey KI. Single wall carbon nanotube/polyethylene nanocomposites: thermal and electrical conductivity. *Macromolecules* 2007;40:2417–21. Copyright © 2007 American Chemical Society [105].

radicals and inhibit degradation by breaking free radical chain reactions. MWCNTs could influence degradation of PE–MWCNTs composites by screening out UV radiation and/or by scavenging or producing reactive oxygen species that initiate degradation processes [38,113,114]. MWCNTs are a type of fullerene structurally related to SWCNTs and Buckminster fullerene, both of which produce and scavenge reactive oxygen species [115,116].

5.4. Composite traits that affect release

There are currently no studies available that have evaluated the release of MWCNTs from PE. As with other MWCNT–polymer nanocomposites, however, the degree of dispersion of CNTs and strength of the interfacial interaction between the polymer and nanotubes will greatly influence final properties of the composites. It is likely these same factors will impact potential release of carbon nanotubes from PE composites. The nature of the surface functionalization of the CNT and method of incorporation into the matrix will also strongly influence release potential.

6. Polycarbonate

6.1. Description of the polymer

Polycarbonates are an unusual, extremely useful class of high heat polymers known for toughness and clarity. The vast majority are based on bisphenol A (BPA) and sold under the trade names Lexan (GE), Makrolon (Bayer), Caliber (Dow), Panlite (Teijin), and Iupilon (Mitsubishi); many other producers and suppliers are also available. BPA polycarbonates have glass-transition temperatures (T_g) in the range of 140–155 °C, and are widely regarded for optical clarity and exceptional impact resistance and ductility at or below room temperature. Other properties such as modulus, dielectric strength, and tensile strength are comparable to other amorphous thermoplastics at similar temperatures below their respective T_g values. Whereas most amorphous polymers are stiff and brittle below their T_g values, polycarbonates retain ductility. Many important products are based on polycarbonate in blends with copolymers, branched resins, flame-retardant compositions, foams, and other materials. They are produced by more than a dozen companies, with global manufacture at just over 2 million tons annually. Polycarbonate is also the object of academic research due to its widespread utility and unusual properties. Research on polycarbonates has increased steadily over the past 2 decades, with over 5000 publications on the topic since 1995, and with nearly 20,000 patents globally (see Brunelle [117] and references therein).

6.2. Uses in conjunction with CNTs

No information for the production volume of CNT PC composites can be found, but it is known that companies such as Bayer, Hyperion, Carbon NT&F21, RTP, and Nanocyl currently produce CNT PC composites. According to a 2007 report [118], the largest North American producer, Hyperion, may produce 50 tons/year of masterbatch materials, i.e., CNTs dispersed in

monomer or polymer, and PC CNTs are part of this total volume.

Of the known uses of virgin polycarbonates [117], CNT PC composites could be used as replacements to improve properties for the following:

1. Electrical, electronic, and technical applications use polycarbonates for a variety of purposes. The worldwide market is ~160,000 tons annually.
2. Medical and health care-related applications consume ~30,000 tons of polycarbonate annually. Polycarbonate is popular because of its clarity, impact strength, and low level of extractable impurities.
3. Automotive applications account for ~150,000 tons of worldwide consumption annually, with applications for various components including headlamp assemblies, interior instrument panels, bumpers, etc.

It is expected that CNT PC will take over some of the market share of PC for the above uses. A few current uses of CNT PC are as follows:

1. Restricting electrical interference in electrical equipment and removing heat generated by electric circuits [119].
2. High strength, impact resistant materials [120].
3. Mechanical processing of soft material surfaces at the nanoscale [121].
4. Lightning strike protection for aircraft, cars, and wind turbines [122].

The form of polymer/composite used in bulk material, films, coatings, and fibers can be buckypaper sheets distributed in PC, bulk CNTs, or surface-modified CNTs distributed in PC.

MWCNTs are added to change the physical-chemical and mechanical properties of the PC. The distribution and form of CNTs in the PC matrix will have an effect on overall properties. As a result of increasing CNT content in PC, the following properties can be modulated: compressive strength, Young's modulus, ductility, viscosity, and conductivity.

6.2.1. Increasing compressive strength

As shown below (Fig. 11), the MWCNT-reinforced polymer has a higher compressive strength than virgin polymer. The lower molecular weight polycarbonate exhibited greater increase in compression strength with MWCNT reinforcement, than blending with higher molecular weight polymer.

6.2.2. Increasing Young's modulus

Manual stretching of the polycarbonate and CNT-reinforced polymer results in increased elastic strength [123]. The virgin polycarbonate lacks the entanglement and extensive bridging mechanism enabled by the carbon nanotubes. Bridging enhances toughness and structural integrity of the polycarbonate. Another study showed that adding 5% MWCNT reinforcement to virgin polycarbonate resulted in a 70% increase in the elastic modulus [124]. Surface modifications on CNTs have also been shown to affect mechanical properties of the polycarbonate. In fact, a 95% increase is seen in the

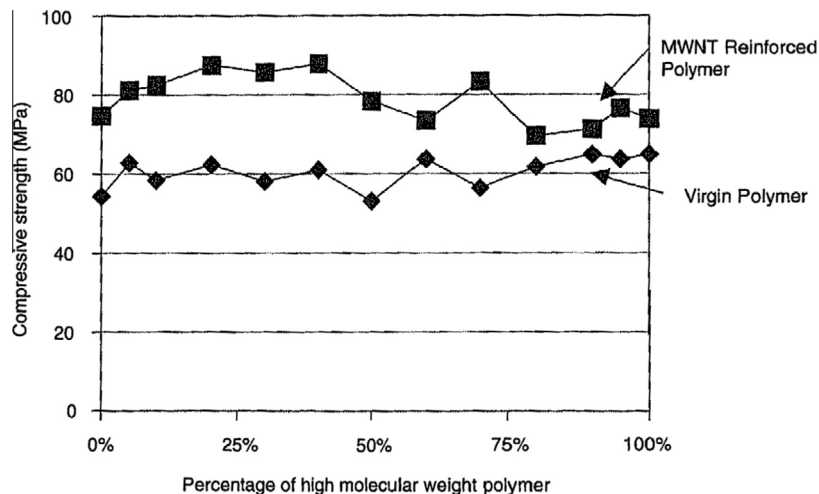


Fig. 11 – Compressive strength of virgin polymer mixtures and of VG-MWCNT-polymer mixture composites. Reproduced from Loutfy et al. Reprinted from *Perspectives of Fullerene Nanotechnology*, 2002, p. 317–25, Carbon nanotube-polycarbonate composites, Loutfy RO, Withers JC, Abdelkader M, Sennett M, Fig. 5, with kind permission from Springer Science and Business Media [120].

elastic modulus at a 5% epoxy surface-modified MWCNT loading to the virgin polycarbonate.

6.2.3. Ductility

Ductility of PC CNT composites is generally retained, compared to virgin PC, with the addition of up to 6 wt% MWCNT to the polymer [125]. Increasing MWCNT wt% in a polycarbonate CNT composite at 77 K increases rigidity and brittleness; however, there seems to be a threshold in CNT loading where ductility of the polymer composite decreases and, at a loading of up to 0.1% of MWCNT into the polycarbonate, the CNT acts more like an impurity. Thus, SEM observations show that with an increase in MWCNT content, fracture surfaces are rougher and grainier which is consistent with decreasing ductility, while increasing CNT content [126].

6.2.4. Increasing viscosity

With increasing CNT loading, increased viscosity is observed (Fig. 12). Furthermore, PC/MWCNT composites treated with hydrogen peroxide and freeze-dried show a further increase in viscosity due to better dispersion of MWCNT within the polycarbonate matrix. The increased dispersion is directly related to surface oxidation of the MWCNTs and results in more polar groups on the surface.

It is also noteworthy that the dynamic modulus was shown to increase with increases in compression strength, Young's modulus, and viscosity.

6.2.5. Increasing conductivity

Increasing CNT content enhances PC conductivity [127]. Treatment of the PC/MWCNT composite with hydrogen peroxide provides increased conductivity due to better dispersion of CNTs in the polymer matrix. The increased dispersion is directly related to surface oxidation of the MWCNTs, resulting in more polar groups on the surface.

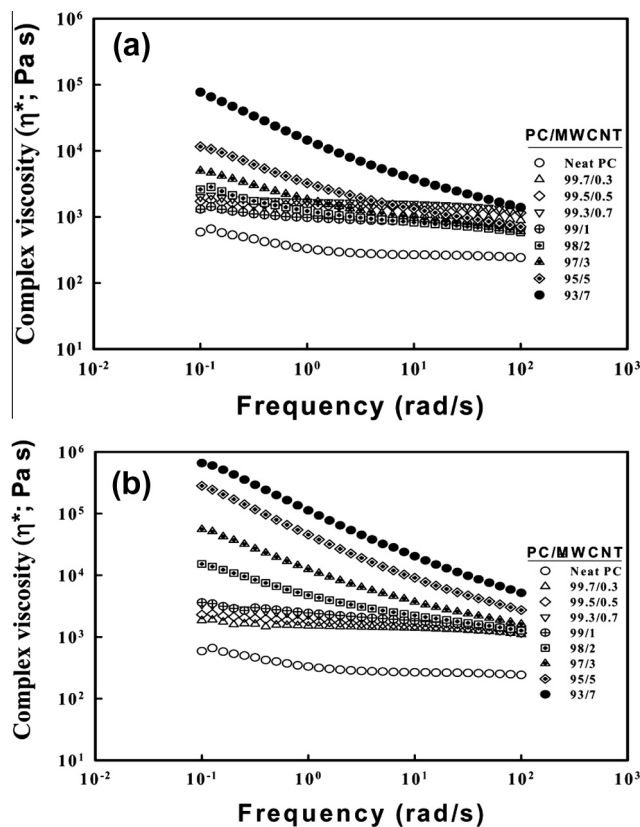


Fig. 12 – Complex viscosity (η^*) of PC/MWCNT composites with MWCNT content at 260 °C. (a) MWCNT was untreated. (b) MWCNT was freeze-dried after treatment with H_2O_2 . Reprinted from *Macromol Res*, vol. 17, 2009, p. 863–9, Effect of multi-walled carbon nanotube dispersion on the electrical, morphological and rheological properties of polycarbonate/multi-walled carbon nanotube composites, Han MS, Lee YK, Kim WN, Lee HS, Joo JS, Park M, et al. with kind permission from Springer Science and Business Media [127].

6.3. General potential for release

Release information for specific CNT/PC composites by various degradation pathways has not been extensively studied, but it is well known that sunlight, humidity, and oxygen cause PC to degrade (Diepens and Gijssman [128] and references therein). It has been argued that photo-oxidation is the dominant degradation pathway that leads to releases in polycarbonate, with minor contribution from the photo-Fries rearrangement (Diepens and Gijssman [128] and references therein). In Fig. 13 below, the mechanism for side chain oxidation reactions is depicted for bisphenol A polycarbonate.

It can be assumed that CNT/PC composites will also undergo degradation by a similar photo-oxidation mechanism as polycarbonate.

With growing interest in cryogenic systems for space, hydrogen storage, and superconductivity, the need for new, high strength, low weight, cost-effective cryogenic structural materials is clear and investigations into effects of low temperature on PC/CNT composites is an area of interest [126]. Oliver et al. elucidated the degradation mechanism at low temperature and it involves interfacial debonding (breaking of the weak van der Waals bonds between the polymer and the CNTs) where interfacial debonding increases at 77 K, especially with higher CNT concentration samples [126]. Increase in interfacial debonding is directly related to the coefficient of thermal expansion of CNTs, and CNTs will contract less than the PC.

It is also well known that polycarbonates are susceptible to degradation under basic conditions [129]. It can be expected that incorporating MWCNT will not hinder degradation of the PC matrix under basic conditions.

6.4. Composite traits that affect release

CNT formulation/incorporation techniques may affect overall releases of CNTs from polycarbonates (CNTs typically incorporated are those synthesized by arc discharge or chemical vapor deposition). Typical PC CNT incorporation techniques include solvent casting, melt mixing, and buckypaper impregnation.

To illustrate differences in the resulting storage modulus from different CNT incorporation techniques and loadings, see Table 4 below. Wang et al. imply that good CNT dispersion and higher loadings of CNT will lead to a higher storage modulus, as seen with their buckypaper impregnation method.

Thus, different formulations of CNT PC lead to changes in storage modulus, which in turn lead to different rates of release.

Table 4 – Variation in CNT incorporation technique and loading for polycarbonate–CNT composites with resulting storage modulus.

CNT Incorporation Technique	Weight% tubes	Storage modulus (GPa)
Buckypaper impregnation	SWNT: 20	6.2
Melt mixing	MWNT: 1.5–15	Approx. 1.0
Solution casting	SWNT: 0.05–0.25	1.6–2.1
	Functionalized SWNT: 0.5–2	2.35–2.52
	MWNT: 5–20	1.1–2.42

Data are adapted from Wang et al. [130] and references therein.

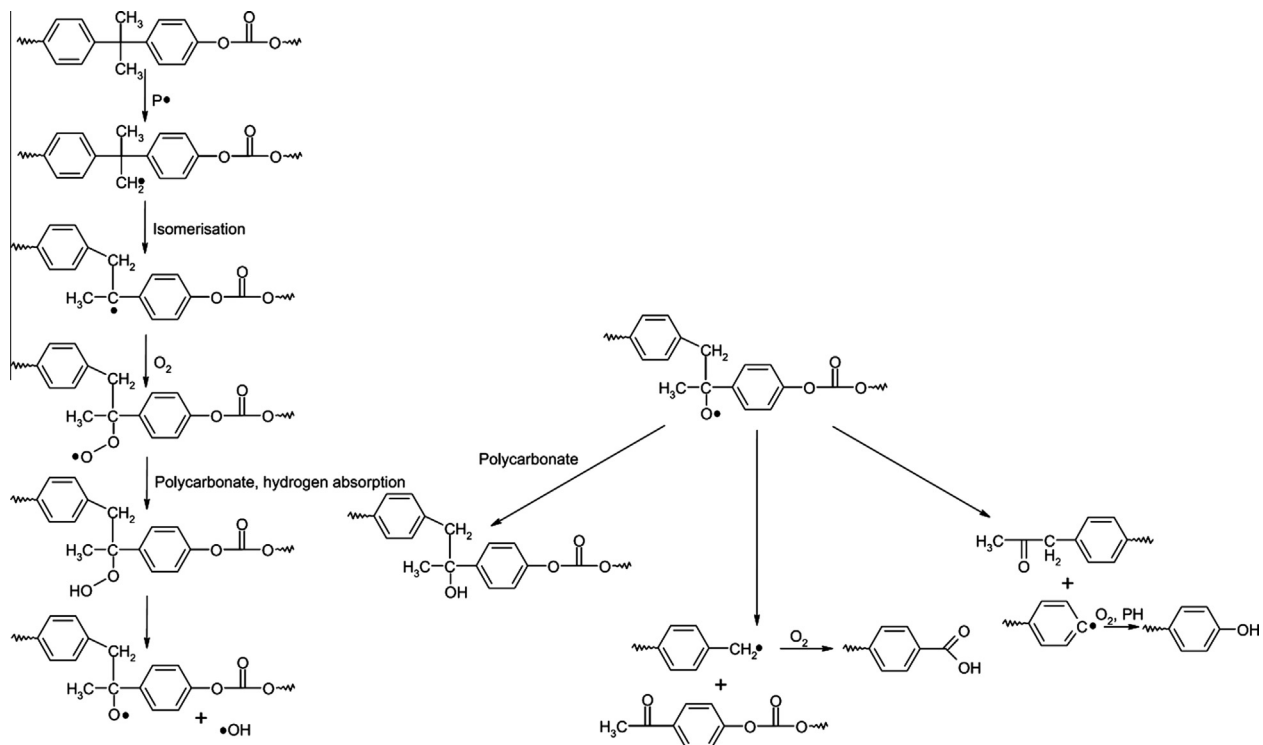


Fig. 13 – Photo-oxidation of bisphenol A polycarbonate. Reprinted from Polym Degrad Stabil, vol. 92, Diepens M, Gijssman P. Photodegradation of bisphenol A polycarbonate, p. 397–406. Copyright © 2007, with permission from Elsevier [128].

6.5. Effects of stabilizers and plasticizers on degradation

Polycarbonate is susceptible to photo-oxidation and antioxidants are necessary to maintain the low color and high transparency critical to end-use applications. Phosphites (0.1%) minimize color development during processing. The inherent stability of PC is related to the level of phenolic end groups. These can increase as a result of humidity-induced hydrolysis, catalyzed by acid. The phosphite chosen must be very stable to avoid generating catalytic amounts of phosphorus acids (Thomas et al. [131] and references therein).

It is not expected that CNT impregnation into the polycarbonate matrix would affect the rate of the various degradation pathways for the virgin polymer significantly; therefore, when degradation occurs, it is expected to release CNTs. More research is needed to verify this assumption.

7. Conclusions

A high-level summary of our assessment of the potential for CNT release from polymer composites and the impact of different polymer properties is presented in Table 5. Despite numerous differences between properties and end uses of the test-case CNT–polymer nanocomposite systems examined here, a number of common tendencies have been deduced with respect to potential for MWCNT release from consumer goods.

Polymer degradation represents the greatest potential for CNT release. Degradation can involve photoreaction, hydroly-

sis, oxidation, and thermolysis of the polymer matrix. Release of MWCNT by thermolysis at elevated temperatures is expected to result in low potential for CNT release, especially since CNTs have been shown to improve thermal stability of most polymer matrices into which they have been incorporated. Rates of degradation depend on structural features of the polymer as well as physical, chemical, or biological agents that drive the processes. For example, chemical agents such as acids or bases can accelerate the hydrolysis of PA, PU, and PC, but PE is not susceptible to hydrolysis. On the other hand, UV photodegradation appears to be a generally significant outdoor process for all polymers considered here.

As CNT–polymer composites move through various phases of their life cycles, changes in their chemical environments alter susceptibility to degradation and CNT release potential [2]. Limited life cycle analyses have been conducted of the polymer systems considered in this review. These analyses have indicated that highest potential for release occurs during the manufacturing and end-of-life phases. Nowack et al. [2] reached similar conclusions but also point out that exposure can be best controlled during the manufacturing phase. Several examples illustrate the usefulness of life cycle analyses:

- An analysis of the life cycle of epoxy resins and their nanocomposites as possible routes for exposure to respirable CNTs [132] found that the following four activities have the highest release potential:
 1. Bulk handling of CNTs where powder or dust is possible.

Table 5 – High-level summary of considerations for material characteristics of MWCNT–polymer systems (epoxy, PC, PA, PU, PE) as relevant to release potential.

	Epoxy	Polyamide	Polyurethane	Polyethylene	Polycarbonate
Mechanical Characteristics	Hard, brittle	Soft, ductile	Soft, ductile, elastomer	Soft, ductile	Hard but ductile**
Photodegradation	Rapid, CNT can stabilize	Susceptible	Susceptible	Low	Susceptible
Oxidation	Susceptible	Susceptible	Susceptible	Susceptible	Susceptible
Hydrolysis	Susceptible	Susceptible	Susceptible	Low	Susceptible (esp. when exposed to base)
Thermolysis	Low	Low	Low	Low	Low
Mechanical Degradation	Low	Low	Low	Low	Low
Lifecycle*	End of life processing	End of life processing	End of life processing	End of life processing	End of life processing
Summary	Low	Low	Low	Low	Low

Green – low susceptibility for release; yellow – moderately susceptible for release; red – high susceptibility for release.

*Life cycle stages most relevant for degradation which can influence release potential. The manufacturing stage is not considered in this report.

**Increasing brittleness with higher loading of CNT.

2. Polymer compounding where transfer of CNTs and dust from grinding may be present.
 3. Recycling operations in which grinding, milling, chemical treatment, or re-compounding may generate small particulates.
 4. Uncontrolled incineration which may destroy the epoxy but not the CNTs, presenting the risk of inhalation of these materials.
- Another general example involves potential release from thermoplastic polymer composites during the manufacturing process [133]. Production of composites often involves polymer melt processes with potential for thermal decomposition and polymer recondensation and/or mechanical processing that may generate fragments that contain CNTs. Standard industrial hygiene is effective to insure occupational safety.
 - Composites of PA and PC (e.g. in compact disc waste) likely will end up in a landfill. In both cases biodegradation coupled with hydrolysis could result in release of the CNTs occur over time. The CNTs themselves appear to exhibit very limited biodegradability, though a recent study suggests they may biodegrade very slowly under some conditions [134]. There is also a possibility that any released CNT may be transformed over time, depending on the local conditions.

During the use-phase of their life cycles, composites in consumer goods are designed to be resistant to degradation and release will occur slowly, if at all. Nevertheless, alternative use and misuse by consumers might expose CNT composites to incompatible chemical environments that accelerate degradation. Sufficient warnings, therefore, should be expressed by manufacturers about the hazards of using these nanocomposites under conditions for which they were not designed.

Of greatest interest here is the potential for MWCNT release via environmental degradation during consumer use. Breakdown of the polymer matrix by photoreaction, hydrolysis, oxidation, or other weathering mechanisms alters mechanical properties of the polymer and potentially weakens interfacial interactions with the CNT fillers, increasing the potential for release over the pristine nanocomposite. Products that are frequently used outdoors could display higher rates of decomposition than those used exclusively indoors although the potential for long-term dust generation from slow degradation indoors should not be ignored. Evidence suggests that CNT fillers help to stabilize polymers to environmental degradation, as demonstrated in UV-induced degradation of epoxy and PU systems; this stabilizing effect mitigates the potential for release. These studies further indicate that after weathering of the composites, the polymer matrix receded, while more resistant CNTs remain and become exposed as an entangled network on the surface. Unfortunately, there is insufficient evidence to indicate whether this is a broad trend across many types of polymer nanocomposites or merely isolated cases. In any case, it is recommended that manufacturers incorporate appropriate coatings and stabilizers for polymer–CNT nanocomposites for intended environments.

Mechanical degradation and wear appears to pose only a minor risk to MWCNT release for all polymers studied. This is attributed to the fact that commercially developed composite formulations for consumer applications have undergone a process of optimizing the chemistries and processing of integration of CNT into the polymer to achieve the level of dispersion and interfacial interaction necessary for desired properties of the nanocomposite. The result is a tendency for the polymer nanocomposite to resist release of free MWCNT, even under situations of significant mechanical stress and wear. Softer, more flexible polymer matrices such as PE and PU are expected to show stronger resistance to release of CNT due to mechanical degradation, while harder resins such as epoxies will have a higher potential for release. Evidence to date suggests that it is fairly unlikely that free MWCNT will be released, but that CNT embedded in or attached to small polymer fragments is the most likely form of release.

Limited information pertaining to commercial use of CNT in specific polymer matrices proved to be a significant obstacle to this review. Narrowing the scope of our work to polymers and sub-variants with strong present or near-term commercial presence for CNT nanocomposites in consumer goods was a primary goal at the outset. A lack of market data and direct industry feedback detailing the types and volumes of polymer–CNT nanocomposites in active commerce, however, represented a challenge to objectively assessing polymers upon which to focus directly. To bridge this gap, research relied on information available on the Internet sites of companies known to conduct commerce in this area, anecdotal information on known and suspected CNT–polymer composites in commercial production, and internal expert assessments to arrive at the present group of polymers.

Similarly, data specific to the release of CNT from polymer nanocomposites are very limited, and comparability between those studies is hindered by the variability in the methods and conditions that were used (e.g. timeframes, experimental conditions, sampling and measurement methods). This presented challenges in assessing release potential of CNT from polymers based solely on reported properties of the nanocomposites. Again, internal expert assessments were drawn upon when there were insufficient data. There is a significant need for work to quantify the degree of release of CNTs from polymer nanocomposites. Questions about the quantity and nature (free MWCNT, attached to polymer fragments, etc.) of CNT that can be released, as well as their correlation with properties of the nanocomposites are largely outstanding for most polymer matrices. Greater insight into the factors influencing the release of CNT from polymer matrices could also be attained if more similar methods could be used across different materials, thus improving direct comparability between studies.

Based on the available evidence, we have concluded that the potential for release of MWCNT from the selected types of polymer nanocomposites is low in typical consumer applications unless the nanocomposite is exposed to conditions which degrade the bulk integrity of the polymer matrix. Considerably more work is needed in this area to address the many challenges and uncertainties that are present.

Acknowledgments

The assessments provided in this article represent a combination of current knowledge in the field and expert opinion from numerous stakeholder groups. The information presented is as accurate and representative as possible; however, given the level of maturity of the study, CNT release, and the complexity of CNT as a polymer additive, it is possible that other release behaviors can be observed. Experts were convened and concepts developed for this paper by the NanoRelease Consumer Products Steering Committee (<http://www.ilsr.org/ResearchFoundation/Pages/NanoRelease1.aspx>). NanoRelease is funded by the US Environmental Protection Agency, the American Chemistry Council Nanotechnology Panel, Environment Canada, Health Canada, the American Cleaning Institute, the Society of Organic Chemical Manufacturers and Affiliates, the Adhesives and Sealant Council, and the ILSI Research Foundation. More than 60 experts listed on the NanoRelease CP web site from government, academia, industry, and civil society organizations have also contributed time and expertise in support of the project. We especially thank Eva Wong, U.S. EPA, and Lyubov Tsytsikova, ILSI, for their contributions to this work under the NanoRelease project, and to Christina West for editorial assistance in completing this manuscript. This article has been reviewed in accordance with the U.S. Environmental Protection Agency's (U.S. EPA) peer and administrative review policies and approved for publication. Mention of trade names or commercial products does not constitute an endorsement or recommendation for use by the U.S. EPA.

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