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journal homepage: www.elsevier.com/locate/envpolCarbon nanotube release from polymers into a food simulant[☆]Yining Xia^{a, b}, Ilke Uysal Unalan^{a, c, **}, Maria Rubino^{a, *}, Rafael Auras^a^a School of Packaging, Michigan State University, East Lansing, MI 48824, USA^b Institute of Quality Standard and Testing Technology for Agro-Products, Chinese Academy of Agricultural Sciences, Beijing 100081, China^c Department of Food Engineering, Faculty of Engineering, Izmir University of Economics, Izmir 35330, Turkey

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ABSTRACT

The release assessment of multi-walled carbon nanotubes (CNTs) was performed on two types of polymer-CNT nanocomposites: polypropylene (PP) and polyamide 6 (PA6) containing 3 wt% CNT. Nanocomposite films were prepared and then exposed to ethanol as a fatty-food simulant at 40 °C, and the amount of CNT release into ethanol was determined by ultraviolet-visible spectroscopy (UV-Vis) and graphite furnace atomic absorption spectrometry (GFAAS). The CNTs released into ethanol were visualized by transmission electron microscopy (TEM) and verified by Raman spectroscopy. UV-Vis analysis showed a very small amount of CNT release from the nanocomposite films into ethanol over 60 d: maximum CNT concentrations in ethanol were 1.3 mg/L for the PP-CNT film and 1.2 mg/L for the PA6-CNT film. GFAAS results indicated that the amount of CNTs released into ethanol after 12 d was over 20-fold higher than the results obtained by UV-Vis. Overestimation of CNT release by GFAAS suggested aggregation and poor dispersion of CNTs in the solvent. This assumption was verified by TEM images exhibiting the embedded CNTs in the polymer flakes, which could be poorly dispersed in the solvent. In general, CNT release from the nanocomposite films was considered a surface phenomenon, as indicated by detachment of CNT-containing polymer flakes from the film surface.

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1. Introduction

Carbon nanotubes (CNTs) exhibit extraordinary chemical, physical, and mechanical properties and they can be used as ideal fillers in polymers to significantly improve the material performance, even at small loadings. The creation of a polymer-CNT nanocomposite was first reported in 1994 (Ajayan et al., 1994). Since then, the variety and number of polymer-CNT nanocomposites has increased significantly. The presence of CNTs can improve polymer properties in multiple aspects such as tensile strength, stiffness, toughness, thermal stability, electrical conductivity and chemical resistance (Breuer and Sundararaj, 2004; Coleman et al., 2006; Moniruzzaman and Winey, 2006; Winey et al., 2007).

CNT use has expanded in recent years as advances in production technologies and mass production have greatly reduced the cost of CNTs. The global CNT market reached \$158.6 million (U.S.) in 2014, and the value is expected to be \$670.6 million in 2019, with a five-year compound annual growth rate of 24% (BCC Research). CNT use in polymers occupies the largest market share of CNTs (Nanowerk.com). Polymer-CNT nanocomposites have found applications in various industries such as automobile, aircraft/aerospace, electronics, energy, construction and packaging.

Concerns about CNTs have increased due to their potential risks to human health (Aschberger et al., 2010; Warheit, 2006; Zhao et al., 2008). Both pristine CNTs (hydrophobic) and oxidized CNTs (hydrophilic) have been proven to be harmful to living cells in culture studies (Bottini et al., 2006; Cui et al., 2005; Nerl et al., 2011). The toxicity of CNTs may depend on concentration, morphology, dimension, surface charge, and aggregation (Du et al., 2013; Liu et al., 2012). Human beings can be exposed to CNTs in the environment through different routes, including inhalation, and dermal and oral exposure. Therefore, the safety of polymer-CNT nanocomposites, especially the potential release of CNTs from polymers into the surrounding environment, must be assessed (Kingston et al., 2014). The potential release of CNTs from polymers

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has been addressed for polymer degradation (e.g., UV degradation, biodegradation) (Nguyen et al., 2009; Wohlleben et al., 2013) and mechanical stresses during use (e.g., abrasion, deformation). (Cena, 2011; Schlagenhauf et al.,) and their combination (UV + stress) (Wohlleben et al., 2016). However, studies on CNT release from polymers in contact with a solvent are scarce. A polymer-CNT nanocomposite is likely to be in contact with a solvent during its life cycle. The interaction between a polymer and a solvent may increase the potential for CNT release (Pillay et al., 2009). Such interaction involves the plasticizing and swelling effects of the polymer when it has poor chemical resistance to the solvent. It is critical to understand the release behavior of CNTs from the polymer, in order to develop safe polymer-CNT nanocomposites.

This study aimed to track and quantify the release of CNTs from polymer-CNT systems into a food simulant (i.e., ethanol). The outcome of this study will add to the understanding of the release behavior of CNTs from polymers in real-world applications. Two types of polymer-CNT nanocomposite films, polypropylene (PP) and polyamide 6 (PA6), compounded with CNTs, were selected as model systems to represent nonpolar and polar polymers, respectively. Release assessment of CNTs was conducted in accordance with ASTM D4754-11 (ASTM) by exposing the polymer-CNT nanocomposite films to ethanol. Ethanol was selected as it is a common organic solvent used in many industries and appears in different proportions in many consumer products (e.g., food, beverage, medical, personal care, and fuel). Absolute or 95% ethanol has been found to be an effective fatty-food simulant for polyolefins (although it appears to exaggerate migration for other food-contact polymers), according to U.S. Food and Drug Administration (FDA) recommendations on the migration testing of food contact substances (FDA). Ethanol was used for this. The release of CNTs from the nanocomposite films into ethanol was measured by an ultraviolet-visible spectroscopy (UV-Vis) method and verified by a graphite furnace atomic absorption spectrometry (GFAAS) method, and the results obtained by the two methods were compared.

2. Materials and methods

2.1. Materials

Multi-walled CNTs functionalized with a carboxyl group (–COOH) were purchased from Nanostructured & Amorphous Materials, Inc. (Houston, TX, USA) (>95% purity, 3.67–4.05% –COOH, outer diameter <8 nm, length 0.5–2 μm). 3-(2-Aminoethylamino) propyldimethoxymethylsilane (herein referred to as silane) was purchased from Sigma-Aldrich (>95% purity, St. Louis, MO, USA). The polymers used were polypropylene (PP; Profax 6523, LyondellBasell Industries, Houston, TX, USA), maleic anhydride-graft-polypropylene (MAPP; 1 wt% bound maleic anhydride, Polyram Co., Shelby Township, MI, USA), and polyamide 6 (PA6; Ultramid B40 01, BASF, Florham Park, NJ, USA).

2.2. Silylation of CNTs

A silylation procedure was carried out by grafting silane to the CNT for two purposes: a) to improve the compatibility of CNTs with the polymer, and promote CNT dispersion in the polymer matrix; and b) to enable CNT tracking and detection by using Si (part of silane) as a marker of the CNT. The grafting reaction (Fig. 1) was conducted by adding 0.6 g silane and 3 g CNT powder (silane:CNT = 1:5, w/w) into 100 mL of ethanol (200 proof) in a 250-mL round-bottom glass flask and then refluxing at the boiling point for 4 h. After the reaction, the solid sample was dispersed in deionized water, sonicated (3 min) in a model FS30 ultrasonic cleaner (35 kHz, Fisher Scientific Co., Pittsburgh, PA, USA),

centrifuged (5000 rpm, 3 min) at least 24 times, and then dried in an oven at 80 °C. To ensure that the unreacted silane was totally removed from the CNTs, the washing solution at each washing cycle was filtered with a Waters GHP filter (13 mm, 0.2 μm; Waters Co., MA, USA) and checked with the UV-Vis spectrometer set at 225 nm until no detectable silane was present in the solution.

2.3. Scanning electron microscopy (SEM)

The original CNTs and the silane-grafted CNTs (abbreviated as CNTs herein) were observed under a JEOL 6610LV scanning electron microscope (JEOL Ltd., Tokyo, Japan) equipped with an X-ray energy dispersive spectroscopy (EDS) detector. The instrument was operated at an accelerating voltage of 15 kV. CNT powder was spread on a carbon tape and a selected area of the tape was scanned in both secondary electron (SE) mode and EDS mode. The composition of the CNT was calculated in the EDS mode. Additionally, the silane-grafted CNTs were also examined by a JEOL JSM-7500F (cold field emission emitter) scanning electron microscope (JEOL Ltd.) operating at 3 kV to obtain more detailed structural information.

2.4. Raman spectroscopy

Raman spectra of the CNTs were recorded by a Raman 2000 spectrograph (Chromex, Inc., Albuquerque, NM) at an excitation wavelength of 532 nm through a 100 × objective, with scan times of 20 s and accumulation of 3 at room temperature. The CNT powder was deposited on a metal microscope slide and scanned in both the normal-frequency region (1000–3000 cm⁻¹) and the low-frequency region (100–600 cm⁻¹). Raman spectrum baseline extraction was also performed.

2.5. Preparation of polymer-CNT films

The PP-CNT nanocomposite was prepared by initially melt mixing the PP and MAPP resins in a Brabender Half Size mixer (C.W. Brabender Instruments, Inc., NJ, USA) at 180 °C and 60 rpm for 5 min; CNT powder was then added and further mixing was carried out at 180 °C and 100 rpm for 5 min. The PA6-CNT nanocomposite was prepared by melting the polymer resin (pre-dried in a vacuum oven at 100 °C for 8 h) in the Brabender Half Size mixer at 240 °C and 60 rpm for 5 min; CNT powder was then added and further mixed with the polymer at 240 °C and 100 rpm for 5 min. The final nominal composition of the PP-CNT nanocomposite was 79 wt% PP, 18 wt% MAPP and 3 wt% CNT, while the PA6-CNT nanocomposite was 97 wt% PA6 and 3 wt% CNT.

The two polymer-CNT nanocomposites prepared by melt mixing were further converted to films by using a 30-ton PHI Manual Compression Press (PHI-Tulip Co., CA, USA). The compression molding was performed at 180 °C and 5 tons for the PP-CNT films (thickness: 132.9 ± 5.8 μm), and 240 °C and 5 tons for the PA6-CNT films (thickness: 117.9 ± 5.9 μm) with a compression time of 5 min. The compressed films were water cooled to room temperature. Control films of both polymers (thickness: 127.9 ± 5.3 μm for PP, 115.2 ± 6.8 μm for PA6) were also prepared in the same manner without the addition of CNTs.

2.6. Characterization of polymer-CNT films

Thermal properties of both nanocomposite and control films (in triplicate) were characterized by differential scanning calorimetry. The melting temperature (T_m) and crystallinity (X_c) were determined with a Q-100 differential scanning calorimeter (TA Instruments, Inc., New Castle, DE, USA) in the first heating cycle from 40 to 220 °C for PP, and from 40 to 260 °C for PA6. The experiment

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