

CARBON NANOMATERIALS THERMAL DEGRADATION: POTENTIAL RISK OF NANOWASTE COMBUSTION

DANIHELKA Pavel¹, HASE Veronika¹, SCHREIBEROVÁ Lenka¹, LACH Karel², FILIPI Bohdan¹

¹VSB - Technical University of Ostrava, Ostrava, Czech Republic, EU

²Public Health Institute Ostrava, Ostrava, Czech Republic, EU

Abstract

New nanomaterials are used in nearly every industrial area and provide many benefits. Nevertheless, with new properties of new nanomaterials come new potential risks. Social demands to ensure the safety of nanomaterials enters to forefront, taking into account risks, caused by nanomaterials production and use, and are connected with whole nanomaterial life cycle. Potential risks associated with the end-of-life of nanomaterials are an issue that needs to be addressed. Nanoparticles or transformed nanomaterials can be released during disposal methods, enter environment and should be monitored.

Carbon based nanomaterials are interesting for incineration tests, because they might be eliminated totally. As the case study of nanoparticles (NPs) release potential during incineration, multiwall carbon nanotubes (MWCNTs) and carbon black were tested. The primary objective of tests described in this study consisted in validating, whether NPs can be released in the gas phase during the combustion in static air and low-oxygen atmosphere. NPs (28 - 462 nm) were released from 875°C, resp. 925°C, to 1000°C for two types of MWCNTs. A comparison of nanoparticles size distribution and raw MWCNTs diameters indicates that fibres disintegrate during combustion. The highest NPs concentrations were around 30 - 70 nm in diameter. In nitrogen atmosphere thermogravimetric experiments showed mass decrease. There is a hypothesis that even very low-oxygen concentration leads to mass loss, probably due to oxidation of nanomaterials. SEM analysis of nanomaterials residue showed modified and variously deformed fibres with conical ends. We hypothesized that needle-like fibre shapes of CNT are more toxic than other carbon nanomaterials.

Keywords: Carbon nanotubes, Carbon black, Nanoobject release, Nanosafety

1. INTRODUCTION

Nanotechnology is currently one of the fastest growing technologies. Rising quantity and number of types of produced nanomaterials express their importance. Nanotechnology significance is confirmed by being classified as Key Enabling Technologies (agreement EU, [1]), i.e. belonging among technologies that can maintain competitiveness. Simultaneously, with the new property of nanomaterials, there are concerns that their new properties can bring new risks as well. Social demand to ensure the safety of nanomaterials enters to forefront, taken into account that risks, caused by nanomaterial production and use, are connected with whole nanomaterial life cycle. Till now, only limited information exists about potential waste problems arising from nanomaterials released from products after the end of their functionality. This fact can lead to uncontrolled and with difficulties monitored environment contamination by original or transformed nanomaterials. Nanomaterials can be transformed by heat, chemical reactions as oxidation, mechanical or biological degradation of original composite or product with an incorporate nanomaterial. Thus, in the spirit of the fact that environmental laws prefer recycling and energy recovery from wastes, it is expectable that a significant proportion of products with nanomaterials will be burned [2]. Therefore, it is a need to examine whether we can expect NPs releasing to the environment during nanomaterials processing or their products incineration. The similar question arises when considering the special kind of unintentionally combustion - houses or industrial fires and firefighting.

Among many important groups of nanomaterials are carbon based NPs (fullerens, single- and multi-walled carbon nanotubes, graphens, amorphous forms of carbon contained in carbon black etc.), which are

combustible. CNTs have aroused a great deal of interest as their possible applications encompass many industrial sectors. CNTs' mechanical and electrical properties demonstrated to be remarkable in comparison with other well-known materials currently used in the industry. Composite materials reinforced by CNT fibres as a way to improve material strength, holding, and wear resistance, are used for automotive plastics and tires. The specific atomic structure of CNTs provides exceptional performances to composite materials, such as high electrical, thermal conductivity [3; 4], and high mechanical strength [5; 6].

CNTs are allotropes of carbon made of one or several graphitic carbon sheets rolled up into a cylindrical (helical) shape. The first TEM evidence for the tubular nature of some nanosized carbon filaments might have originated from Radushkevich and Lukyanovich (1952) [7], and a growth mechanism has been discovered by Iijima (1991) [7]. Depending on the number of rolled sheets (i.e. tubes), two main forms of the allotrope are distinguished: single-walled CNT (SWCNT) and multiwalled CNT (MWCNT). Both are classified in the hollow nanofiber family of nanomaterials (ISO/TS-27687 2008). The dimensions of CNTs can significantly vary, depending on the process synthesis. [7]

MWCNTs have been widely used to reinforce ceramic and metallic matrix composites due to their superior mechanical properties such as high elastic modulus, high tensile and bending strength, and high fracture toughness [8]. MWCNTs may be one of the most promising carbon sources replacing graphite flake in carbon containing refractories to increase their strength and thermal shock resistance, especially in the case of low carbon containing refractories [8]. These are only few areas of MWCNTs using. Recently the social demand about safety of nanomaterials enters to forefront and is connected with whole nanomaterial life cycle. Potential risks associated with the end-of-life of nanomaterials need to be solved. Waste elimination methods such as recycling, landfill and incineration are typical processes in the end of nanomaterials life. NPs or transformed nanomaterials can be released during these disposal methods and enter environment, what should be monitored. Although these materials are assumed to be completely oxidized in a perfect combustion process to carbon dioxide, this situation is not so clear in real situations, which involves frequently the incomplete combustion. This is important when we realize that incomplete combustion is a typical process for the production of carbon black. Also fullerenes are prepared by incomplete combustion in large quantities. These particles could be relative stable during incomplete combustion process and thus they will not be burned. It is well known that carbon based nanoparticles are produced during incomplete combustion of any carbon containing fuel, even if not originally containing nanoparticles, but this question of incidental release of NPs and this is not the topic of this paper.

The aim of this study is preliminary experimental investigation of either nanoparticles or transformed nanomaterial release during carbon nanomaterials combustion. At first sight this idea seemed to be very unlikely because CNTs is combustible material which can be easily transformed into CO or CO₂. The literature review of this subject is very scarce, only few researchers [7; 9; 10; 11], have concerned with this question.

2. MATERIALS AND METHODS

2.1. Multiwall carbon nanotubes (MWCNTs), carbon black

The CNT powders used in this study are constituted by thin multiwall carbon nanotubes (MWCNT4000, MWCNT4001). We also note the high degree of agglomeration, mainly through intertwined fibres forming entangled bundles of 40 - 110 nm in diameter with carbon purity between 90 to 99 % (the rest is probably composed of catalyst traces). The fluffy carbon black is aggregates consisting of 50 - 500 nm primary particles. These aggregates are formed by linked chains with 50 - 70 g/l bulk density. Basic characteristics of these powders are summarized in **Table 1**.

2.2. Thermal analysis

Thermogravimetric analysis (TGA) measures changes in weight of a sample with increasing temperature. Computer-based methods can be used to calculate weight percent losses. The dynamic thermogravimetric

experiments were carried out using a Mettler-Toledo simultaneous thermal analyser, model TGA/DCS 2, and STA 449 F1 Jupiter (Netzsch) allowing measurement of mass change and associated phase transformation energetics. The system employed for this work was equipped with a PtRh, resp. silicon carbide furnace operated to 1550 °C, the temperature being measured using type S thermocouple. The system is vacuum tight, allowing measurements to be conducted under controlled atmosphere. In these experiments, differential scanning calorimetry (DSC) measurements were also recorded to study phase transitions and exothermic/endothemic decompositions taking place in the samples investigated.

Table 1 Basic carbon nanomaterial characteristics

Description	Carbon nanomaterial		
	MWCNT 4000	MWCNT 4001	Carbon black
Appearance	Black powder		
C content	89.81 %	99.19 %	97.60 %
Diameter	13.6 nm	64.2 nm	50 - 500 nm
Length	846 nm	4048 nm	
Specific surface area	254 m ² /g	17.85 m ² /g	
Impurities or additives	Al, Fe, Co, Cu, Zn, Si, O	Zn, Cu, Si, O	O, H, N, S
Mean aggregate size			0.5 - 0.05 µm

The testing temperature can be programmed to allow for required heating ramps, and a differential temperature experimental setup (measurement of the difference between the reference and the sample temperature) is used to monitor the onset combustion temperature (T_{onset}) and the released heat (J/g). The mass reduction of the sample during combustion is monitored online, by measuring the weight of the sample.

TGA-DSC analyses were performed on small sample mass (about 1.5 to 3.5 mg), mounted on Al₂O₃ crucibles in a static air and inert (N₂) atmosphere (flow rate of reactive gas, 50 ml/min). The experiments were carried out by heating the samples from room temperature (25 °C) to 1000 °C (static air atmosphere), resp. 1250 °C (inert atmosphere) at a rate of 20 °C/min. (25 - 300 °C), 10 °C/min. (300 - 400 °C) and 5 °C/min. (400 - 1000, resp. 400 - 1250 °C). Faster heat rate from 25 to 400 °C was chosen because during these temperatures were not detected any changes in nanomaterials during preliminary tests. For online particle size distribution was used SMPS 3080 (TSI) in static air atmosphere for experiments to characterize the particles released during the combustion tests, as shown in **Fig. 1**. SMPS measured particle size distribution from 28 to 462 nm.



Fig. 1 Experimental setup. TGA + SMPS

3. RESULTS AND DISCUSSION

3.1. Preliminary thermogravimetric analysis

In our study the experiments were done under atmospheric pressure for synthetic air (mixtures oxygen and nitrogen with 21 % of oxygen), for combustion simulation in static air atmosphere (**Fig. 2**). Nanomaterials oxidation started around 550 °C for MWCNT 4000 and carbon black. MWCNT 4001 began oxidize at 760 °C. Other thermogravimetric data are summarized in **Table 2**. The influence of oxygen on MWCNTs was

investigated previously, e.g. Vignes et al. [12] and Bouillard et al. [7]. The onset temperatures for our carbon nanomaterials were higher - since 100 to 300 °C. MWCNT 4001 and carbon black showed the biggest mass changes. These nanomaterials did not burn completely, even that the crucibles looked empty. Only MWCNT 4000 had visible residue in crucible.

These carbon nanomaterials were tested in nitrogen (99.999 % N₂) too. In this low oxygen atmosphere we observed the mass loss, for MWCNT 4000 and MWCNT 4001 the mass started decrease around 740 °C, for black carbon around 875 °C. We suppose that carbon nanomaterials oxidized on carbon monoxide due to presence of very small oxygen amount.

Table 2 Thermogravimetric data of carbon nanomaterial combustion in static air atmosphere

Carbon nanomaterial	Temperature range of mass change (°C)	Mass change	T _{onset} (°C)	Released heat (J/g)
MWCNT 4000	400 - 700	86,4 %	541	17 198
MWCNT4001	650 - 875	98,7 %	760	16 390
Carbon black	475 - 690	96,2 %	577	19 783

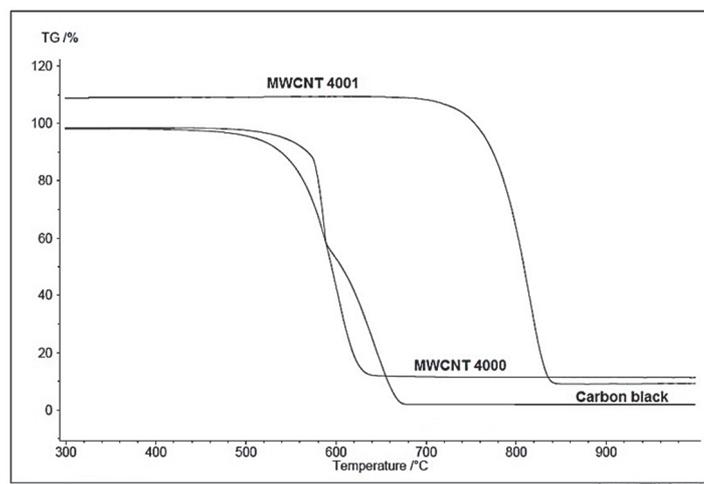


Fig. 2 Thermogravimetric measurement of carbon nanomaterial in static air atmosphere (21 % oxygen)

3.2. SEM carbon nanomaterial analysis

The raw carbon nanomaterials and residues after thermal degradation have been analysed by SEM techniques. The raw MWCNT 4000 had very distorted and interwoven fibres, so length determine was very difficult. Some fibres had up to 40 nm in diameter. The raw MWCNT 4001 had typically 50 - 60 nm in diameter. The total estimated variance was 40 - 110 nm in diameter (95 % of nanotubes), but there was an exception, around 200 nm in diameter. The fibres length exceeded 20 µm, some fibres had 50 µm, and there were obvious clusters (aggregates) of small-scale nanospheres. Both MWCNTs had visibly rounded ending.

In nitrogen atmosphere MWCNT 4000 were transformed to soot. MWCNT 4001 remained in the form of variously deformed and shortened carbon nanotubes. Interestingly, the lot of CNT's endings were conical to point. It was likely that fibres degradation extended from the ends. There were various-sized aggregates of mutually connected CNTs residues. In carbon black we observed the distorted rolls of deformed CNTs. Based on these findings we can suppose that MWCNTs 4001 are more resistant, while MWCNTs 4000 are oxidized to soot at very low oxygen concentration. MWCNTs 4001 remained as carbon nanotubes.

Shape of carbon nanomaterial is important factor for its toxicity. Some of the CNTs have the structural similarity to asbestos, raising concerns that widespread use of carbon nanotubes may lead to mesothelioma, cancer of

the lining of the lungs caused by exposure to asbestos. Especially, the needle-like fibre shapes of CNTs are more toxic than other carbon nanomaterials to human skin fibroblasts and other organs [13].

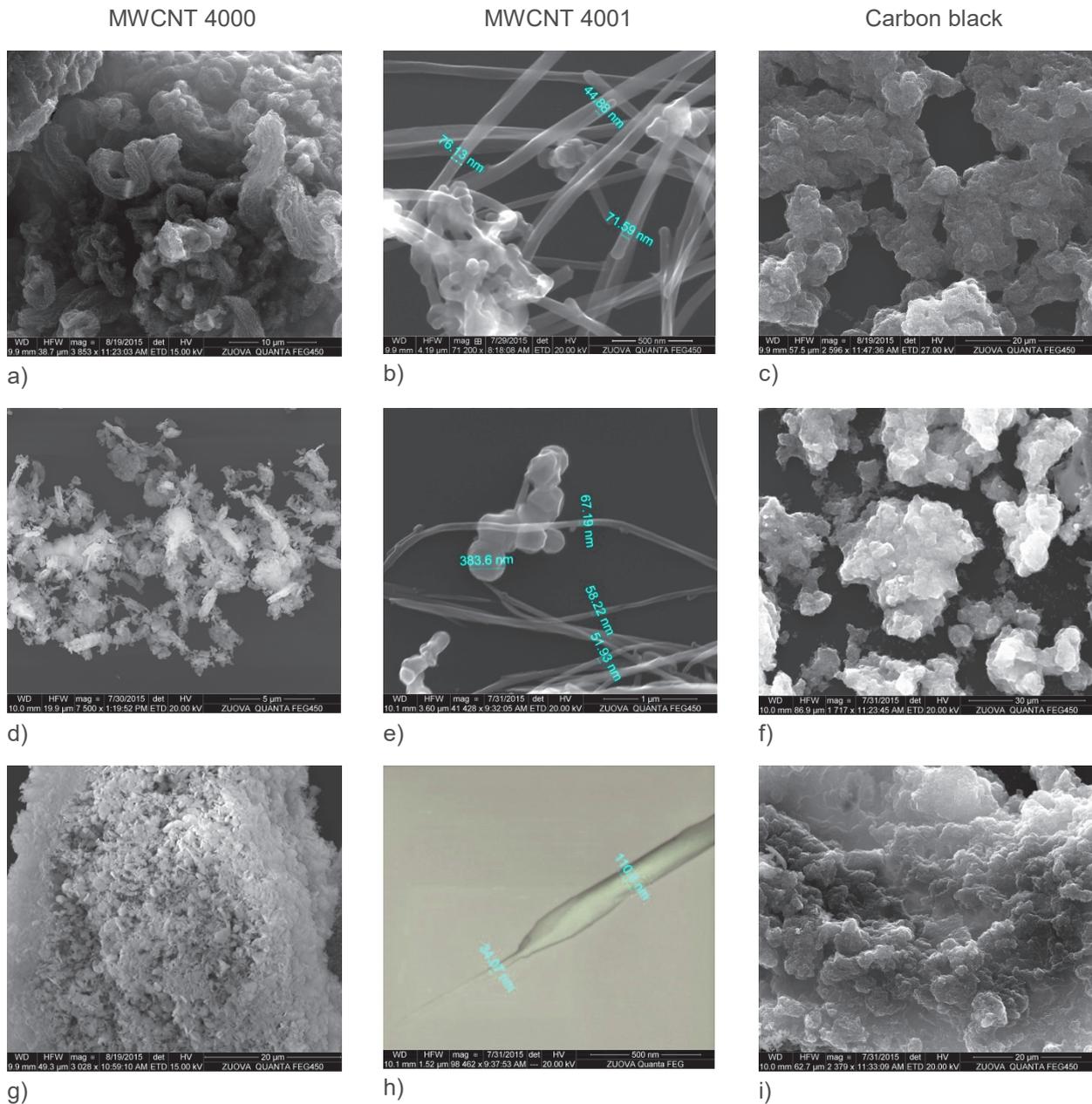


Fig. 3 SEM images of raw carbon nanomaterials and after thermogravimetric analysis in static air and nitrogen atmosphere. MWCNT 4000 (a - raw material, d - nitrogen atmosphere, g - air atmosphere), MWCNT 4001 (b - raw material, e - nitrogen atmosphere, h - detail of conical ending), Carbon black (c - raw material, f, i - nitrogen atmosphere)

3.3. Nanoparticles release analysis

Nanoparticles release analyses were done in the static air atmosphere. First nanoparticles (around 55 nm) started releasing in the end of nanomaterials combustion (around 685 °C for MWCNT 4000, 870 °C for MWCNT 4001). The highest nanoparticles production was from 900 to 1000 °C, for both MWCNTs. Nanoparticles with diameter 28 - 48 nm (MWCNT 4000) and 28 - 69 nm (MWCNT 4001) have been dominated (**Fig. 4**). Bouillard et al. [7] detected particles of sizes between 10 and 30 nm, which were mainly soot nanoparticles. MWCNT 4001 released nanoparticles with highest concentration than MWCNT 4000. We

suppose that the residual material have been raised in the air. This hypothesis is supported by detection of released nanoparticles, while MWCNT 4000 residue remained in crucibles after combustion. We can expect that some carbon nanotubes may stay in char residues or may be released in the flue gas phase.

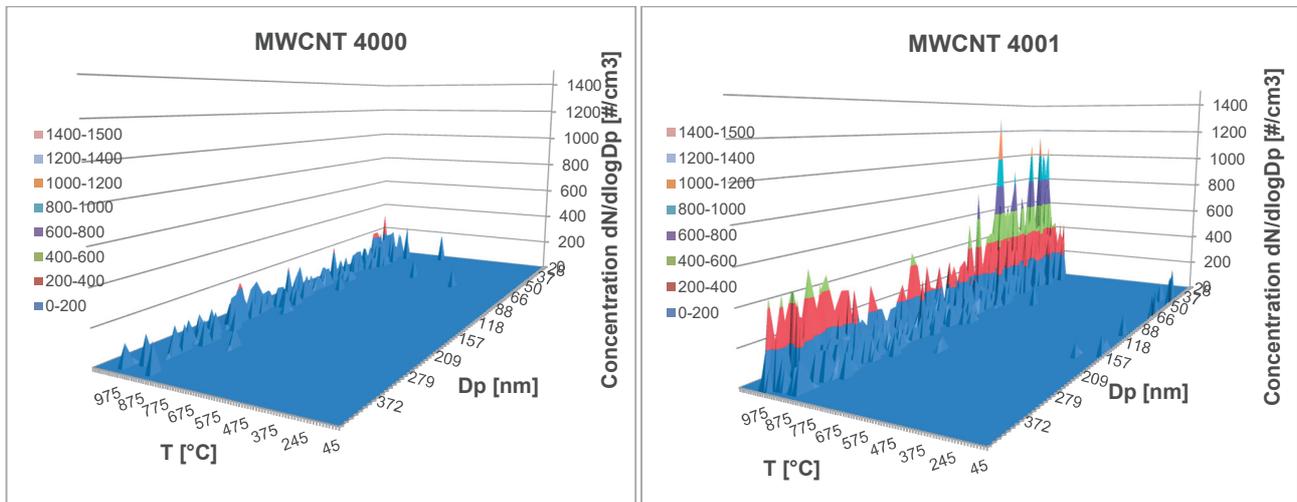


Fig. 4 Nanoparticles released during combustion in static air atmosphere

4. CONCLUSIONS

This study has shown that thermal degradation of carbon nanomaterial can lead to a risk of nanowaste combustion. Nanowaste combustion is one of waste elimination methods in the end of nanomaterial life. SEM analysis of nanomaterials residue from nitrogen atmosphere showed modified, deformed and shortened fibres with conical ends. We may hypothesized that needle-like fibre shapes of CNT are more toxic than other carbon nanomaterials and shorter fibres represent an increased risk of deposition in lung alveoli. Given the fact that MWCNT 4001 is more resistant and stay in form modified carbon nanotubes, there is a potential risk, due to the release of these NPs, and may be possible in the case of accidental scenarios.

The general conclusion, important for nanomaterials life cycle assessment, is that even fully combustible nanomaterials may be the source of environmental pollution. Carbon nanomaterials may be degraded only partly, i.e. other types of NPs are released.

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