Journal of Hazardous Materials 340 (2017) 57–66

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Assessment of nanoparticles release into the environment during drilling of carbon nanotubes/epoxy and carbon nanofibres/epoxy nanocomposites

Kristof Starost[a], Evelien Frijns[b], Jo Van Laer[b], Nadimul Faisal[a], Ainhoa Egizabal[c], Cristina Elizextea[c], Maria Blazquez[d], Inge Nelissen[b], James Njuguna[a,*]

[a] Centre for Advanced Engineering Materials, School of Engineering, Robert Gordon University, Aberdeen, AB10 7GJ, United Kingdom
[b] VITO NV, Boeratang 200, 2400 Mol, Belgium
[c] TECNALIA, Mikeletegi pasealekua, 2 E-20009, Donostia Spain
[d] INKOA SISTEMAS, SL. Ribera de Axpe 11, Edificio D1, Dpto 208. 48950, Erandio, Bizkaia Spain

HIGHLIGHTS

- Real-time nanoparticle release quantification from life-cycle scenario.
- Particle number concentration, size distribution and mass concentration of particles released.
- Hazardous nanoparticles released significantly exceed recommended exposure limits.
- Comparison and effect of carbon nanofibers and nanotubes to neat epoxy matrix.
- Demonstrated nanoparticle release methodology without background particles within detection limits of the CPC.

ARTICLE INFO

Article history:
Received 22 November 2016
Received in revised form 22 June 2017
Accepted 23 June 2017
Available online 27 June 2017

Keywords:
Nanoparticle release
Carbon nanotubes
Carbon nanofibers
Drilling emissions

ABSTRACT

The risk assessment, exposure and understanding of the release of embedded carbon nanotubes (CNTs) and carbon nanofibers (CNFs) from commercial high performance composites during machining processes are yet to be fully evaluated and quantified. In this study, CNTs and CNFs were dispersed in epoxy matrix through calendaring process to form nanocomposites. The automated drilling was carried out in a specially designed drilling chamber that allowed elimination of background noise from the measurements. Emission measurements were taken using condensed particle counter (CPC), scanning mobility particle sizer (SMPS) and DMS50 Fast Particulate Size Spectrometer. In comparison to the neat epoxy, the study results revealed that the nano-filled samples produced an increase of 102% and 227% for the EP/CNF and EP/CNT sample respectively in average particle number concentration emission. The particle mass concentration indicated that the EP/CNT and EP/CNF samples released demands a vital new perspective on CNTs and CNFs embedded within nanocomposite materials to be considered and evaluated for occupational exposure assessment. Importantly, the increased concentration observed at 10 nm aerosol particle sizes measurements strongly suggest that there are independent CNTs being released at this range.

1. Introduction

The recent developments in understanding and improved manufacturing techniques of nanoparticles have rapidly introduced engineering nanomaterials (ENMs) across the commercial industry. The ability to incorporate nanofillers within polymers has permitted extensive research and progress in targeting specific material properties with great control and precision. This capacity has shown that epoxy based nanocomposite materials for uses in high-performance lightweight applications where carbon nanotubes (CNTs) and carbon nanofibers (CNFs) provide significant enhancements in properties: mechanical [1,2], electrical [3,4], thermal [5,6], and fire retardant [7,8] properties. As a result, worldwide CNT production capacity of CNT's has increased at least 10-fold since 2006 [9] and according to a report by Global Industry Analysts Inc. [10], the global market for nanofibres is projected to reach US$1 billion by 2020.

* Corresponding author.
E-mail addresses: j.njuguna@rgu.ac.uk, njugunajak@yahoo.co.uk (J. Njuguna).

http://dx.doi.org/10.1016/j.jhazmat.2017.06.057
0304-3894/

Despite the beneficial material properties of CNTs and CNFs, the nanofillers have shown conceivable health risks and toxicity to humans and the environment. The use and introduction of these materials into the workplace can be hazardous when human exposure is concerned [11]. Studies have validated that certain concentrations of CNT exposure has shown to induce cytotoxicity and apoptosis [12,13], genotoxicity [14,15], systemic immune function alterations [16] and pulmonary damage, inflammation and granuloma lesions [17–19]. Review papers have been released in an attempt to quantify various CNT attributes to the level of toxicity. Many studies with varied types of CNTs, different evaluation methods and different exposure conditions have shown conflicting results as presented by Liu et al., [19]. Consequently, we are still, at present, unable to classify and gauge exact level of toxicity factors such as size, shape, purity and functionalisation to CNT toxicity [20,21]. However, in the findings from Aschberger et al. [22], studies suggest that chronic occupational inhalation; especially during activities involving high CNT release and uncontrolled exposure are the main risks for humans.

Equally, CNFs are increasingly being investigated for toxicity. Studies have shown inhalation or exposure to a varied concentration of CNFs to cause respiratory tract and pulmonary inflammation [23–25], DNA damage [26] cell proliferation inhibition and cell death [27]. Despite the evidence of toxicity and widespread use of CNFs, most studies have investigated CNTs. However, additional to offering economic benefits over CNTs with a better cost to strength ratio, some studies have suggested that CNFs show less toxicity than CNT's [23,28,29].

Already established within industry and it is acknowledged that throughout its lifecycle, epoxy nanocomposites will undergo drilling during assembly operations where the nanofillers could unintentionally be released and exposed to workers and/or consumers. An Airbus A350 will undergo 16000 holes drilled per composite wing set [30]. Various studies have considered nanoparticle release due to various mechanical processes such as cutting [31], abrasion [32], sanding [33], sawing [34] and drilling [35] just to name a few. However, there is still a lack of understanding and being able to link the release of the embedded hazardous nanoparticles to exposure [36]. Kuhlbusch et al. [37] reviewed the current studies in nanoparticle exposure in workplaces and found nanomaterials of <100 nm to be released in only a few cases, but a regular release of >300 nm was observed in another review. Froggett et al. [38] summarised the existing release studies from mechanical scenarios, highlighting the current gap in knowledge with only 54 publications covering the release from solid non-food nanocomposites. From the experimental studies, 96% demonstrated release of nanoscale debris from the nanocomposites [38]. Both review articles agreed on a lack of systematic harmonised methods to compare the results and identified the need of a standardised method to test or characterise the release and exposure of nanoparticles from nanomaterials during a lifecycle scenario.

Studies in the open literature have investigated various life cycle mechanical processes which generate airborne material release which could potentially expose workers to the nanoparticles. Drilling is a fundamental and significant machining process used during assembly operations. In a review on the effects of drilling on nanocomposites, three studies were identified to have investigated the release of nanoparticles from nanocomposite materials [39,40]. All three studies demonstrated nanoparticles to be released. In one of the studies by [41], nanosilica filled nanocomposites demonstrated 56 times on the nano-emissions than conventional fibre reinforced composites. In a study by Bello et al. [42], collections of CNTs were revealed in the emissions after drilling on CNT-alumina and CNT-carbon nanocomposites. With a similar study using cutting, drilling demonstrated significant differences and an increase in overall nanoparticle release [43]. In contrast, another study by Sachse et al. [41] displayed a reduction in the number of airborne nanoparticles by a factor of 20 when nanoclays were added to neat PA6. However, the concentration of deposited nanoparticles doubled for the nanocomposite.

Along accessing the cost to performance ratio and with a better understanding or reduction of toxicity introduced from nanocomposites, materials can be manufactured to be safer by design. Data collected for nanoparticle release can be used towards developing materials which will reduce or potentially not release the toxic nanoparticles and hence, safer for workers and consumers. It is now recognised that safer by design allows bridging the gap between the rapid developments in nanotechnology and nanosafety assessment [44].

The aim of this study is therefore to investigate and characterise the effect CNTs and CNFs have on nanoparticle release from industrial nanocomposites due to drilling. The studies on drilling on nanocomposites thus far have revealed that nanoparticle fillers do influence nanoparticle emissions but have been unable to determine the risk and exposure. Little is known on the full potentially hazardous effect drilling polymer nanocomposites reinforced with CNTs and CNFs have on nanoparticle release. This study thus examines industrial used epoxy nanocomposites filled with CNTS and CNFs. The sampling and methodology undertaken were developed as a part of a controlled drilling protocol within the European Commission Life project named Simulation of the release of nanomaterials from consumer products for environmental exposure assessment (SIRENA, Pr. No. LIFE 11 ENV/ES/596) [45,56,57], with the sole intention of testing these nanocomposites for nanoparticle release into the environment from the composite matrix system during machining processes. The study is part of a wider project aimed at developing a standardised test method for the release of nanoparticles from industrial nanomaterials at various stages of material development.

2. Experimental methods

2.1. Materials and fabrication

A commercially available bi-component epoxy resin system MVR444R from CYTEK Solvay Group (former ACG) was reinforced with unmodified multi-walled carbon nanotubes with an average diameter of 10–15 nm (Multi-walled Graphistrength C100 from ARKEMA Inc.) and unmodified carbon nanofibres with an average fibre diameter of 100 nm (PYROGRAF PR24-XT-LHT from APPLIED SCIENCES INC) due to their electrical properties. A concentration of 2 wt.% of CNT and 2 wt.% of CNF were dispersed in the epoxy matrix through calendaring using a commercially available laboratory scale three-roll mill (EXAKT 80E, EXAKT Technologies Inc.) and cured in an oven process. The process involves employing repeated high shear stresses generated by the gap within the three rollers to disperse the CNTs and CNFs homogeneously in the epoxy. Manufactured sample measuring 70 mm × 45 mm × 5 mm were prepared for the drilling tests. Corresponding samples of 90 mm × 70 mm × 2 mm sample size were also fabricated for the standard DC resistance or conductance testing of moderately conductive materials using ASTM D4496 [46] and for insulating materials ASTM D257 [47].

2.2. Nanoparticle release setup – automated drilling method, instrumentation and measurement procedure

The materials were tested using a purpose built controlled test chamber that allows direct measurement of nanoparticles emitted during drilling. The process is developed and initiated by the SIRENA Life project –an acronym for Simulation of the