Thermal decomposition of nano-enabled thermoplastics:

Possible environmental health and safety implications

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Submitted to:

Journal of Hazardous Materials

16 February 2017

1 **ABSTRACT**

2 Nano-enabled products (NEPs) are currently part of our life prompting for detailed investigation of potential
3 nano-release across their life-cycle. Particularly interesting is their end-of-life thermal decomposition
4 scenario. Here, we examine the thermal decomposition of a widely used NEP, namely thermoplastic
5 nanocomposites, and assess the properties of the byproducts (released aerosol and residual ash) and possible
6 environmental health and safety implications. We focus on establishing a fundamental understanding on the
7 effect of thermal decomposition parameters, such as polymer matrix, nanofiller properties, decomposition
8 temperature, on the properties of byproducts using a recently-developed lab-based experimental integrated
9 platform. Our results indicate that thermoplastic polymer matrix strongly influences size and morphology of
10 released aerosol, while there was minimal but detectable nano-release, especially when inorganic nanofillers
11 were used. The chemical composition of the released aerosol was found not to be strongly influenced by the
12 presence of nanofiller at least for the low, industry-relevant loadings assessed here. Furthermore, the
13 morphology and composition of residual ash was found to be strongly influenced by **the presence of**
14 **nanofiller**. The findings presented here on thermal decomposition/incineration of NEPs raise important
15 questions and concerns regarding the potential fate and transport of released engineered nanomaterials in
16 environmental media and potential environmental health and safety implications.

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18 *Keywords:* life cycle assessment, incineration, nano-EHS, nanotechnology, aerosol

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1. INTRODUCTION

Consumer products containing nanostructured materials (so-called nano-enabled products, NEPs) have already been in the market for decades for commodities such as car tires, paints, sunscreens, to name a few [1-3]. Due to the unique advantages that nanotechnology may offer in terms of products performance at limited cost, industry has recently shifted towards the incorporation of engineered nanomaterials (ENMs) in a variety of other products, such as toners [4] for printing equipment, building materials [5] and cosmetics [6]. This exponential expansion of NEPs makes human exposure to ENMs inevitable [7].

During the last decade there has been a great effort and numerous studies aiming to understand the bio-nano interactions and potential adverse health effect of ENMs in the emerging field of “nanotoxicology” [8]. In such studies, typically the pristine, raw ENMs are investigated *in vitro* and at a lesser extent *in vivo*. Several reports show that such materials may exhibit enhanced adverse effects when compared to their larger counterparts mostly attributed to their small size and large surface-to-volume ratio [7,9-15].

Both risk assessors and industry are struggling with the fact that most of the nano-environmental health and safety (nano-EHS) data focus on the pristine (raw) ENMs rather than impacts associated with NEPs across their life-cycle and in particular during consumer use and disposal at their end-of-life during thermal decomposition/incineration. Furthermore, there is limited understanding on release mechanisms and properties of released particles throughout the NEP life span which may or may not contain the ENMs used in its synthesis [16]. This important knowledge gap has been recently emphasized in both the National Research Council report as well the National Nanotechnology Initiative’s strategy on nano-EHS [17-18]. More importantly, it impedes public health assessors from addressing nano related risk issues and discourages industry from exploring the ocean of nanotechnology applications.

The end-of-life scenario of NEPs is of particular interest and raises concerns of a possible emerging nano-waste problem from the resulting byproducts of such a process. Recent studies on the material flows of ENMs through society indicate that 60-80% of all ENMs end up in landfills and approximately 9,000 metric tons/year end up in incineration facilities [19]. Additionally the use of ENMs in building materials and furnishings and other products commonly found in the built environment, raises concerns on the implications of incidental fires in the built environment. Therefore, the thermal decomposition/incineration of NEPs raises important questions and concerns regarding the fate and transport of released ENMs in environmental media and potential EHS implications. However, very little is known on the release and potential transformation of

ENMs during this thermal process. The limited literature on the thermal decomposition of NEPs focuses on either pristine, raw ENMs[20] or nanoparticle-spiked waste [21], while most focus lies on the particle size and concentration of the released aerosol from the thermal decomposition of nanocomposites [22-26].

Furthermore, there is a lack of a fundamental understanding on the thermal decomposition process of NEPs and the potential nano-release that might occur during this process. More specifically, nanofiller-specific effects, effects of thermal decomposition conditions (*i.e.* temperature, residence time), and the role of NEP matrix and their impact on the physicochemical properties of the released byproducts need to be assessed and linked to potential toxicological implications in order to facilitate safer by design approaches.

Recently, a standardized, versatile and reproducible integrated exposure generation system (INEXS) that allows for the systematic physicochemical and toxicological characterization of the thermal decomposition of NEPs was developed by the authors (Supporting Information, Scheme S1) [27]. The developed methodology allows for the real-time *in situ* monitoring of the released aerosol (size, concentration, composition) while it also facilitates the collection of size-fractionated released aerosol using the compact cascade impactor (CCI) [28] for *ex situ* detailed physicochemical and toxicological characterization. Furthermore, the residual ash may also be collected and further evaluated in terms of its properties and fate and transport in environmental media.

Here, a systematic investigation on the thermal decomposition of one of the most widely used industry-relevant family of NEPs, namely thermoplastic polymer nanocomposites, and using a variety of inorganic and organic nanofillers (Table 1 and Figures S1 and S2 in Supporting Information), is performed using the above mentioned methodology [27]. The investigated nanofillers were based on a priority-driven selection for industry-relevant thermoplastics. The target of this study is to obtain a fundamental understanding on the parameters that govern the thermal decomposition of NEPs and decipher their effect on the physicochemical properties of the byproducts, rather than merely simulating the combustion process of industrial incineration facilities. We choose such thermoplastics with controlled composition instead of real waste materials in order to have a fine control over their chemical composition that will facilitate us to link the properties of the byproducts to the materials used in the NEP synthesis. Such an approach also enables a systematic investigation by changing synthesis parameters such as nanofiller loading and matrix and will help in understanding which parameters affect the release of ENMs and properties of by products. Figure 1 shows a schematic of the integrated study design. Thermal decomposition of NEP will generate two main solid

1 byproducts: the released aerosol and the residual ash. Exposure to both of these byproducts may occur to
2 professionals (e.g. incineration facilities employees, fire fighters) or to consumers (e.g. from incidental fires).
3 Furthermore, the residual ash will also be disposed in landfills further raising questions regarding possible
4 nano-release in environmental media and subsequent ecotoxicity. Ultimately, the release mechanisms and
5 toxicological properties will be linked to both thermal decomposition parameters as well as the properties of
6 matrix and ENMs used in the synthesis of NEPs. Both the generated data and developed methods are of
7 paramount importance in addressing life-cycle EHS implications of NEPs. It will also facilitate the
8 development of safer-by-design [10,29] NEP approaches and exposure control practices. More importantly,
9 risk assessors will use the data and regulate risks not on the “raw” ENM toxicological properties but based
10 on actual exposures and associated toxicological properties of byproducts.

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12 2. MATERIALS & METHODS

13 Organic pigment Red 254 is a **highly** transparent and saturated diketo-pyrrolo-pyrrole (CAS-Nr = 84632-
14 65-5, TEM diameter = 26 nm, BET surface = 94 m²/g, see Figure S1 in Supporting Information), well suited
15 for automotive effect finishes and produced by BASF, while the Pigment Red 101 (CAS-Nr. = 1309-37-1,
16 TEM diameter = 32 nm, BET surface = 30 m²/g) is an **iron oxide (Fe₂O₃)** inorganic pigment with extremely
17 fine particles for coatings with highest fastness to weathering such as wood stains for outdoor use or
18 automotive effect coatings. Both are marketed as “transparent” pigments in the sense that it is possible to
19 achieve high transparency with low light scattering (as is normally achieved only for molecularly dissolved
20 dyes), but still to retain the fastness and light stability advantages of particulates (pigments). The pigments
21 were dispersed at 10% in a LDPE masterbatch, then melt-dispersed into HDPE at 2.5kg/h through a ZSK 18
22 twin-screw extruder at 250 °C, 28 bar, 300 rpm, and cut into granulates. These granulates were used for
23 incineration experiments. Final parts (**e.g. automotive exterior mouldings**) for the automotive industries are
24 produced from re-melting the same granulates and injection moulding (Figure S1a in Supporting
25 Information). The HDPE polymer matrix is M80064 (SABIC), a high density polyethylene injection
26 moulding grade with a narrow molecular weight distribution with tensile stress at yield of 32Mpa (ISO 527-
27 2).

28 Polyurethane (PU) was synthesized via a prepolymer process. Chemtura Prepolymer Adiprene LF 930
29 and Ethacure 300 as chain extender are mixed thoroughly to produce cast PU. The nanoparticles used are

1 MWNTs NC 7000 from Nanocyl. Synthesis of PU-CNT nanocomposites were carried out in two-steps
2 process as follows. First, CNTs were added to prepolymer heated at 80 °C and mechanically stirred for 15
3 min at high shear of 2000 tr/min. At the second stage, a calculated amount of curative was added to the
4 prepolymer nanocomposite and mixed again for one minute. The final mixture is degassed for one additional
5 minute and poured in open mold at 100 °C to crosslink in 30 min and postcure in 20 hours. The final CNT
6 concentration is 0.09 wt%. The CNT dispersion in the PU matrix was evaluated by TEM of thin slices of the
7 nanocomposites obtained by cryomicrotome (-140 °C) (Figure S2 in Supporting Information).

8 The thermal decomposition experiments were carried out in a recently developed from our group
9 integrated exposure generation system [27]. In brief, this system consists of a tube furnace in which the
10 thermoplastic polymer nanocomposite is placed in the form of pellets (~10 mm³). The temperature and
11 heating rate in the tube furnace is precisely controlled up to 500 and 800 °C (10 °C/min) such as to examine
12 two temperatures: one below and one above the full decomposition of the polymer matrixes. The released
13 aerosol is then guided to an array of *in situ* real-time measurements for its particle concentration and size
14 (after 100 dilution (either with a Dekatti rotating disk diluter or a TSI aerosol diluter depending on the
15 following instrument) and measured with SMPS and APS, both TSI). The released aerosol is also collected
16 using the Harvard CCI [28] and size-fractionated to PM_{0.1}, PM_{0.1-2.5} and PM_{2.5-10}.

17 The released aerosol and residual ash were characterized in detail by scanning electron microscopy
18 (SEM, Supra55VP field emission microscope equipped with energy dispersive X-ray spectrometer - EDX)
19 and transmission electron microscopy. The samples were imaged by transmission electron microscopy
20 (TEM) using a Tecnai Osiris machine (FEI Company, Hillsboro, USA) operated at 200 keV under bright-
21 field (BF) conditions. Images were evaluated using the iTEM (Olympus, Tokyo, Japan, version: 5.2.3554),
22 and TIA (FEI, version: 4.1.202) software packages. For the TEM analysis of the released aerosol, TEM grids
23 were placed in the corresponding CCI stages. The elemental carbon/organic carbon (EC/OC) content was
24 determined by gas chromatography/mass spectrometry and the elemental analysis by magnetic sector field
25 inductively coupled plasma mass spectrometry (ICP-MS) following published protocols [30-31]. One-
26 dimensional proton nuclear magnetic resonance (1-D ¹H-NMR) spectroscopy was also applied to
27 characterize the chemical content of the organic carbon from the released aerosol [27,32]. Briefly, ¹H-NMR
28 spectra were obtained in deuterated dimethylsulfoxide (DMSO; (CD₃)₂SO) containing 1% v/v
29 tetramethylsilane (TMS-d₁₂) on a Bruker Avance 500 MHz instrument equipped with a 5 mm double

resonance broad band (BBFO Plus Smart) probe at 298K with 8,192 scans. Thermogravimetric analysis coupled with Fourier-Transform infrared spectroscopy of the decomposition products in the off stream (TGA-FTIR, Netzsch-Proteus) was performed and compounds were identified by an automated fingerprinting analysis (Omnic software). The decomposition was performed under parameters adjusted to be as similar as possible to the developed methodology experiments: 30 mg of thermoplastic in an Al_2O_3 crucible, 5 K/min heating rate under air. FTIR spectra were selected at times just before the onset of the characteristic CO peak, in analogy to the peak emission of particulate matter as observed in the INEXS.

X-ray diffraction (XRD) patterns for the raw Fe_2O_3 nanofiller, PE- Fe_2O_3 nanocomposite, and residual ash at $T_d = 500$ and 800°C were collected using synchrotron-based XRD as the Stanford Synchrotron Radiation Lightsource (SSRL) on Beamline 11-3. Incident X-rays ($0.9744 \text{ \AA}$, 12735 eV) were focused using a bent cube-root I-beam Si(311) monochromator. A MAR345 Imaging Plate, 345 mm diameter, detector was positioned 150 mm downstream of the sample and was used to collect diffraction scans with a dwell time of 30 s. The collected images were calibrated and radially integrated using the program *WxDiff- Diffraction Imaging Analysis Software* (version 1.19) (SSRL). Crystal structures were determined through peak matching using PANalytical X'Pert HighScore.

3. RESULTS AND DISCUSSION

3.1 Morphology of released aerosol: Aerosol constitutes a major byproduct from the thermal decomposition of polymer nanocomposites. Figure 2 shows the released aerosol particle concentration after 100 times dilution (black lines) over time for the PU- (a,b) and PE-based (c,d) thermoplastic nanocomposites for two different final decomposition temperatures ($T_{d,\text{final}}$, red dotted lines) of 500 (a,c) and 800°C (b,d). The particle number concentration reaches maximum values at about $400 - 450^\circ\text{C}$ independent of the thermoplastic material, filler and $T_{d,\text{final}}$. This indicates that the heating rate does not strongly influence the thermal decomposition and neither does the presence of the nanofiller, at least at the loadings and nanocomposites investigated here. It is evident that the released aerosol particle number concentrations is dominated by the thermoplastic matrix and there is no nanofiller-specific effect observed here.

Furthermore, mass particle size distributions show that most released particles lie by in the nanoscale size regime for the whole duration of the thermal decomposition (Supporting Information, Figure S3) with lower mass fraction in the $\text{PM}_{0.1-2.5}$ and $\text{PM}_{2.5-10}$ range (Supporting Information, Figure S4), typical for aerosols

1 made by combustion processes [21,33]. Electron microscopy analysis of the *in situ* collected released aerosol
2 also reveals that these particles are mostly spherical in shape, indicative of the formation by homogeneous
3 nucleation of released gases [34]. It is worth noting that there are no significant differences among the
4 samples with different nanofillers from the same thermoplastic matrix. For example, Figure 2 shows the
5 released PM_{0.1} size fraction from the thermal decomposition at T_{d,final} = 800 °C from PU-CB (e), PU-CNT (f),
6 PE-Fe₂O₃ (g) and PE-org. (h) which exhibit similar features for all (highlighted by the red arrows). Further
7 electron microscopy images from the aerosol released from other samples at all examined conditions exhibit
8 similar morphology. This further indicates that the morphology and size of the released aerosol is dictated by
9 the thermoplastics matrix, while the nanofillers, if any, play only a minor role for the decomposition of
10 nanocomposites at the low filler loadings investigated here.

11

12 3.2 Nanofiller release during thermal decomposition: It should be noted that there were no nanofillers
13 detected by electron microscopy in the released aerosol for all size ranges (PM_{0.1}, PM_{0.1-2.5}, and PM_{2.5-10}) and
14 conditions for all NEPs studied here but one (case of Fe filler). This may also be verified by the elemental
15 analysis of the released aerosol. For example, by detecting the presence of Al (that is used as catalyst for the
16 CNT manufacture) in the released aerosol from the PU-CNT samples, the quantification of possible released
17 CNT can be investigated (assuming that there is no alteration of the Al concentration during the TD of the
18 NEP). There was no Al presence in the released aerosol for all PU-CNT samples, further indicating that no
19 CNT “escape” to the released aerosol, as also shown previously [27]. One should be cautious, however, of
20 such indirect quantification of CNTs in thermally-treated samples using the Al content as a surrogate
21 because Al and the CNTs might behave differently at elevated temperatures. Further analytical techniques
22 could be carried out for the CNTs quantification as performed recently by monitoring the C(1s) electron
23 band with X-ray photoelectron spectroscopy [5]. On the other hand, the CNTs concentration here is rather
24 low, which makes its accurate quantification in the residual ash a technical challenge. The absence of CNTs
25 and organic filler in the aerosol indicates that for the NEPs investigated in this study, the thermal
26 decomposition might be the result of: i) thermal decomposition of the nanofillers upon their release; and/or ii)
27 the nanofillers partially remain in the residual ash for some of the thermal decomposition scenarios (*i.e.*
28 lower temperature).

1 For the case of PE-Fe₂O₃, however, minimal contents of elemental Fe were found in the released aerosol
2 (Table 1) for both T_{d,final} conditions indicating that there is some nanofiller-related release, even though at
3 this point it is unclear whether the Fe undergone chemical and morphological transformations during the
4 thermal decomposition conditions. Therefore, the nanofiller properties may influence the elemental
5 composition of the released aerosol and more specifically, depending on these properties a nanofiller-related
6 compounds may be released in the aerosol. It is worth noting that the rather small Fe content in the released
7 aerosol for both T_{d,final} (<0.03 wt%), however, renders it difficult to detect by microscopy whether it is
8 present as solid nanoparticle (e.g. Fe₂O₃) or as ionic complex. In summary, organic nanofillers such as CNTs
9 and organic dyes most likely will not be released in the air during the thermal decomposition process while
10 inorganic fillers may be present in the released aerosol.

11

12 3.3 Chemical composition of released aerosol: The released aerosol consists of primarily organic
13 carbonaceous compounds (Table 1). This OC content reaches rather high values (>99 %) independent of the
14 thermoplastic matrix or the nanofiller material. Such OC compounds may also exhibit potential adverse
15 health effects [35]. It remains to be seen of course in future toxicological studies the nanofiller-specific effect
16 for the released aerosol.

17 The chemical composition of the released aerosol is further assessed using an independent setup of direct
18 coupling of thermogravimetric analysis with Fourier-Transform infrared spectroscopy of the decomposition
19 products in the off stream (TGA-FTIR, Netzsch-Proteus). Complete three-dimensional datasets of
20 absorbance vs. temperature (or time or mass loss) vs. wavenumber are plotted in Figure S5 in the Supporting
21 Information. A simple inspection of this complex dataset indicates that for the case of PE-Fe₂O₃, the matrix
22 decomposition might be influenced by the nanofiller Fe₂O₃, for which we observe that the main
23 decomposition peak around 460°C splits in two peaks at 410 °C and 478 °C respectively (data not shown).
24 Furthermore, the corresponding TGA traces of mass loss vs. temperature indicate that 4.1 ± 1 % of mass
25 remain from PE-Fe₂O₃ at 800°C, in agreement with the gravimetric results of this sample presented in Table
26 1, whereas the remaining mass is practically zero for all other materials.

27 In the gaseous off-stream, we observe only minor differences in the FTIR spectra of PU, PU-CNT and
28 PU-CB (Figure 3a). Fingerprint IR lines identify besides CO₂, CO and H₂O, significant traces of THF,
29 methane, ethylene and aldehydes, both for the pure PU and for PU-CNT and PU-CB. In contrast, we observe

1 significant differences in the FTIR spectra of PE vs. PE-Fe₂O₃ (Figure 3b). The pure PE decomposes into
2 CO₂, H₂O, CO, methanol, methane, and significant traces of ethylene and ketones. Fingerprinting
3 identification of a difference spectrum between the FTIR spectra of the mass loss peaks at 410°C and 478°C,
4 we derive that the earlier onset of decomposition with the PE-Fe₂O₃ releases preferentially methanol and
5 ethylene already at 410°C. This release then transforms at 478°C into a complete decomposition with more
6 dominant CO₂ peaks around 2360 cm⁻¹ than from the pure PE. Only the PE-Org. spectra are virtually
7 identical to spectra from the pure PE decomposition. The presence of Fe₂O₃ as nanofiller in the PE
8 thermoplastics might accelerate the polymer thermal decomposition similar to catalytic thermal
9 decomposition of other Fe₂O₃-containing polymer nanocomposites [36]. The different FTIR spectra of the
10 PE-Fe₂O₃ in comparison to the pure PE might be attributed, therefore, to the catalytic combustion
11 characteristics of Fe₂O₃ nanoparticles [36].

12 The chemical content of the organic carbon from the released aerosol collected from the CCI is further
13 investigated by NMR for the case of PU-based NEPs. Figure 3b shows the NMR spectra of the released
14 aerosol (PM_{2.5}) from pure PU at T_{d,final} = 500 (red line) and 800 °C (green line) as well as from PU-CNT at
15 T_{d,final} = 800 °C (blue line). Figure 3b also shows the determined [27] quantitative analysis from these spectra
16 regarding the detected total organic H. The non-exchangeable organic hydrogen concentrations were
17 computed by integrating NMR resonance signals based on the known concentrations of the internal standard
18 (*i.e.* TMS). Even though the total amount from the pure PU at 500 °C is lower than that from both PU and
19 PU-CNT at 800 °C (80.6 vs 241.1 and 224.3 μmol m⁻³, respectively), the corresponding relative fractions
20 from each organic H component have similar values and consisted of approximately 75% H-C and H-C-C=.

21 The above TGA-FTIR and NMR provide the following indications: (i) the T_{d,final} has little influence on
22 the chemical composition of the released aerosol, (ii) the chemical composition of the released aerosol might
23 depend on the specific nanofiller (e.g. for the case of PE-Fe₂O₃ there were differences while in the presence
24 of organic filler, CNTs and carbon black there were no significant differences). The TGA-FTIR findings
25 along with the NMR analysis support the hypothesis that particulate matter from thermal decomposition
26 being mainly composed of VOCs from recondensed polymer fumes. This has also been confirmed when the
27 released aerosol is treated chemically *in situ* passing through a thermal denuder and thus the semi-volatile
28 and volatile organic compounds were removed [27].

It should be noted that a subsequent treatment of the released aerosol strongly influences its properties. For example, with the developed INEX platform here the released aerosol may pass through a thermal denuder or a thermal conditioner (Supporting Information, Scheme S1, Routes II and III, respectively). The thermal denuder removes volatile and semi-volatile organic compounds [27] while the thermal conditioner facilitates the further combustion of carbonaceous compounds as the released aerosol is brought and maintained at 800 °C for a 5 s residence [37]. Indeed, the particle concentration is reduced significantly when passed through a thermal denuder (Supporting Information, Figure S6a,b) and further minimized when passed through the thermal conditioner (Supporting Information, Figure S6c,d). This is expected, since the released aerosol consists mainly from carbonaceous compounds as verified above.

3.4 Residual ash chemical composition and morphology: The presence of nanofillers in the residual ash is also investigated along with nanofiller specific effects on its properties. Organic compounds in general fully decompose at 800 °C so there is no residual ash at this $T_{d,final}$ for the pure thermoplastic polymers (both PU and PE) as also verified by TGA (Figure 3a). However, the inorganic nanofillers should be present in the residual ash at both $T_{d,final}$ conditions investigated here (500 and 800 °C). This is the case for the PE-Fe₂O₃ sample, that indeed yields residual ash close to its initial nominal concentration in the nanocomposite (~4 wt%, Table 1). In fact, upon the elemental analysis of the residual ash from PE-Fe₂O₃ at both $T_{d,final}$, the only element that is detected is Fe (Table 1). For the case of PU-CNT, even though pure CNT decompose at $T_{d,final}$ = 800 °C, there should be some residual ash originating from the catalysts metal and metal oxide nanoparticles used in the CNT synthesis. The rather low CNT loading, however, in the initial sample (0.09 wt%) renders the gravimetric detection of any residual ash at this $T_{d,final}$ impossible. A mass balance of the CNTs nanofillers in the residual ash at the thermal decomposition conditions used here has been established [27].

All samples yield residual ash at $T_{d,final}$ = 500 °C (Table 1) since the pure thermoplastic polymers do not fully decompose at these temperature as also indicated by the TGA results (Figure 3a). The residual ash mostly consists of EC (75 - 85 %) independent of the thermoplastic matrix or the presence or absence of nanofillers, except the residual ash from PE-Fe₂O₃. In that case, there was no EC detectable, with some minor OC amount, and elemental analysis revealed the presence of Fe. This is in agreement with the differences that were observed in the FTIR spectra of the gaseous off-stream of pure PE and the PE-Fe₂O₃

samples (Figure 3b) and a potential catalytic role of Fe_2O_3 nanoparticles [36], accelerating the thermal decomposition of the polymer matrix.

Electron microscopy images of the residual ash from all samples at $T_{d,\text{final}} = 500\text{ }^\circ\text{C}$ are shown in Figure 4. The residual ash morphology is similar from all PU-based nanocomposites, however, from the PU-CNT sample the presence of CNTs is detected (Figure 4c) and further quantification by the Al content shows that all CNTs remain in the residual ash [27]. The CNTs are distributed evenly within the residual ash with some CNTs surfaced with the brittle degraded thermoplastic matrix holding them together. Furthermore, the residual ash from PE- Fe_2O_3 shows distinctly different morphology than the pure PE and the PE-org. nanocomposites. In fact, it appears that the residual ash from PE- Fe_2O_3 consists only from inorganic Fe_2O_3 nanofiller with no residual degraded thermoplastic matrix in contrast to the pure PE and the PE-org. This might be attributed to the catalytic activity of Fe to decompose carbonaceous compounds and accelerate combustion [36] or to a local temperature increase around the nanofillers due to their higher thermal conductivity than the polymer matrix. This indicates that the presence of nanofiller may significantly influence the morphology and chemical composition of the residual ash.

Figure 5 shows four XRD patterns of raw Fe_2O_3 nanofiller, PE- Fe_2O_3 nanocomposite, and the residual ash at $T_d = 500$ and $800\text{ }^\circ\text{C}$. The crystal phase of the raw Fe_2O_3 is hematite $\alpha\text{-Fe}_2\text{O}_3$ (red line). For $T_d = 800\text{ }^\circ\text{C}$ (blue line), the ash contains only the $\alpha\text{-Fe}_2\text{O}_3$ phase, indicating that the phase of the nano-filler is unchanged upon combustion at this temperature. However, at $T_d = 500\text{ }^\circ\text{C}$ the $\alpha\text{-Fe}_2\text{O}_3$ phase has partially transformed to maghemite and/or magnetite (green line). Magnetite and maghemite are indistinguishable by XRD because both have the same cubic structure and their lattice parameters are almost identical [38]. In the dry state, maghemite transforms to hematite via rearrangement of the crystal lattice in the temperature range $370\text{--}600\text{ }^\circ\text{C}$ [38]. However, the more common synthesis process involves the reduction of hematite to magnetite, and then the oxidation to maghemite. Conversion of hematite to maghemite has been reported, but this required high-energy ball milling with ethanol for 96 hours [39]. The reduction of hematite (Fe_2O_3) to magnetite (Fe_3O_4) can occur under reducing conditions at $300\text{ }^\circ\text{C}$ [38]. It might be possible during the combustion process that the polymer plastic serves as a reducing agent, converting the hematite (Fe_2O_3) to magnetite (Fe_3O_4). The magnetite is then oxidized to the observed maghemite.

4. CONCLUSIONS

1 In summary, the life-cycle transformations of nanomaterials released at their end-of-life by thermal
2 decomposition were investigated here with **six** industry-relevant NEPs using both inorganic and organic
3 nanofillers. The main focus of this study was to obtain a fundamental understanding on the parameters that
4 govern the thermal decomposition of NEPs and identify whether there are nanofiller-specific effects on the
5 physicochemical properties of the generated byproducts during the thermal decomposition process. The
6 released aerosol is polydisperse in nature. For the materials and conditions studied here, the presence of
7 nanofiller did not influence the particle concentration and size **of the released aerosol**, nor the chemical
8 composition of the organic and elemental carbon. There were no nanofiller observed in the released aerosol
9 by microscopy for the case of organic nanofillers, however, in the case of Fe_2O_3 , minimal amounts of Fe
10 were detected in the released aerosol further indicating the potential nano-release from this material and
11 further raising concerns regarding other inorganic materials with lower melting/boiling point. The use of
12 high efficiency filters and wet scrubbers is thus essential to prevent release from waste combustion plants
13 [20]. It remains to be seen in future studies, the toxicological effect of the released nanofiller .

14 The effect of the nanofiller was more prominent in the physicochemical properties of residual ash at both
15 final decomposition temperatures. The majority of the nanofiller, if not all, remains in the residual ash for the
16 case of CNTs, while the presence of inorganic Fe_2O_3 nanofiller drastically changed the residual ash
17 composition and morphology. More specifically, the Fe_2O_3 nanofiller promoted the decomposition of the
18 thermoplastic polymer matrix leaving no polymer residue in contrast to the blank polymer and polymer filled
19 with organic nanofiller, essentially leaving the pure nanofiller in the residual ash. At elevated temperatures
20 relevant for waste combustion, residual ash was zero from all organic and carbon-based NEPs, and retained
21 almost the entire inorganic nanomaterial. Furthermore, the TGA-FTIR temporally resolves the splitting of
22 mass loss peaks and shifted composition that result from the catalytic action of nano- Fe_2O_3 on PE
23 decomposition, as confirmed by the chemical and structural analysis of the remaining ashes by SEM and
24 EC/OC ratio. In summary, the degradation of thermoplastic matrix results to brittle residual ash with surface
25 exposed nanofillers. This raises questions for potential release of nanofillers in environmental media from
26 further weathering given the fact that residual ash from incineration processes may end up in landfills around
27 the world [19]. Future work should investigate the effects of nanofiller loading, polymer matrix and thermal
28 process conditions to the properties of the generated byproducts. Obtaining this understanding will be crucial
29 for the sustainability of nanotechnology industry as a whole and will help in bridging major knowledge gaps

1 and facilitating risk assessment based on real word exposures and toxicological profiles across the life-cycle
2 of NEPs.

3

4 **5. ACKNOWLEDGEMENTS**

5 We thank the FP7-MARINA consortium for kind provision of the thermoplastic materials. We kindly thank
6 Dr. Martin Shafer (Univ. Wisconsin-Madison) for the EC/OC and ICP-MS measurements. This research was
7 supported by NSF (grant nr. 1436450), NIH (grant nr. P30ES000002) and BASF SE. This work was
8 performed in part at the Harvard Center for Nanoscale Systems (CNS), a member of the National
9 Nanotechnology Infrastructure Network (NNIN), which is supported by the National Science Foundation
10 under NSF award number ECS-0335765. Georgios A. Sotiriou gratefully acknowledges the Swiss National
11 Science Foundation for the *Advanced Researcher* fellowship (grant nr. PA00P2_145392). Portions of this
12 research were carried out at the SSRL beamline 11-3, a national user facility of the Department of Energy,
13 Office of Basic Energy Sciences.

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Table 1. Summary of all nano-enabled products (NEPs) analyzed in this study along with the main results regarding the yield, the EC/OC content as well as the Fe content for both the released aerosol and the residual ash.

NEPs				released aerosol										residual ash					
				500 °C					800 °C					500 °C				800 °C	
				yield (%)		EC (%)	OC (%)	Fe (wt%) ^b	yield (%)		EC (%)	OC (%)	Fe (wt%) ^b						
				PM _{0.1}	PM _{0.1-2.5}				PM _{0.1}	PM _{0.1-2.5}									
sample ID	filler	size (nm)	loading (wt%)	PM _{0.1}	PM _{0.1-2.5}				PM _{0.1}	PM _{0.1-2.5}				yield (%)	EC (%)	OC (%)	Fe (wt%) ^b	yield (%)	Fe (wt%) ^b
PU	-	-	-	1.65	0.44	0.9	99.1	-	3.41	1.07	0.8	99.2	-	5.0	84.9	15.1	-	-	-
PU-CB	CB	50-100	0.09	3.61	1.09	0.6	99.4	-	2.96	0.79	0.7	99.3	-	4.0	76.5	23.5	-	-	-
PU-CNT	CNT	10 ^a	0.09	4.04	0.93	0.7	99.3	-	3.64 ^c	1.84	0.9	99.1 ^d	-	6.1	82.1	17.9	-	-	-
PE	-	-	-	4.08	3.66	0.4	99.6	-	3.46	3.25	0.3	99.7	-	0.9	78.2	21.8	-	-	-
PE-Fe ₂ O ₃	Fe ₂ O ₃	50-100	4	2.77	0.74	0.3	99.7	0.004	1.46	1.60	0.3	99.7	0.026	3.9	-	-	74.5	3.9	77.3
PE-org.	Org. pigm.	50-100	0.2	3.29	0.90	0.3	99.7	-	2.66	0.63	0.4	99.6	-	1.0	75.0	25.0	-	-	-

PU: polyurethane, CB: carbon black, CNT: carbon nanotube, PE: polyethylene, Org: organic pigment Red 254, EC: elemental carbon, OC: organic carbon

^asize corresponds to diameter, ^bmeasured by ICP-MS, ^cstandard deviation of 3 independent measurements: 1.4%, ^dstandard deviation of 3 independent measurements: 0.2%.

FIGURE CAPTIONS

Figure 1. Schematic of the integrated approach for the investigation of the thermal decomposition of nano-enabled products. The products consists of nanofillers (e.g. CNTs, Fe_2O_3). After the consumer use the products reaches its end-of-life by thermal decomposition generating two particulate byproducts, the released aerosol and the residual ash. Exposure to these byproducts might occur to both professionals and consumers. The residual ash might end up in landfills further raising questions regarding its fate and transport to the environment.

Figure 2. Released aerosol particle concentration and size. The particle concentration over time for PU-based (a,b) and PE-based (c,d) thermoplastics at two final decomposition temperatures $T_{d,\text{final}} = 500$ (a,c) and 800°C (b,d). TEM images of *in situ* collected released aerosol particles from PU-CB (e), PU-CNT (f), PE- Fe_2O_3 (g) and PE-org. (h).

Figure 3. Chemical composition of released aerosols. TGA-FTIR spectra are at times just before the onset of characteristic CO peak for the PU-(a) and PE-based nanocomposites (b). (c) NMR spectra of pure PU decomposed at $T_{d,\text{final}} = 500$ (red line) and 800°C (green line), as well as PU-CNT decomposed at $T_{d,\text{final}} = 800^\circ\text{C}$ (blue line) along with their corresponding total organic H content and composition.

Figure 4. Residual ash morphology at $T_{d,\text{final}} = 500^\circ\text{C}$. SEM images of the residual ashes for PU (a), PU-CB (b), PU-CNT (c), PE (d), PE- Fe_2O_3 (e) and PE-org. (f). The presence of CNTs as well as pure Fe_2O_3 nanoparticles is detected. At $T_{d,\text{final}} = 800^\circ\text{C}$, only Fe_2O_3 nanoparticles, but no residual ash remains from all other materials.

Figure 5. XRD patterns of PE- Fe_2O_3 nanocomposite (black line), raw Fe_2O_3 nanofiller (red line) residual ash at $T_d = 500$ (green line) and 800°C (blue line).

FIGURES

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5