

New Evidence Towards the Release of Airborne Carbon Nanotubes when Burning Nanocomposite Polymers

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ABSTRACT

This study investigates the potential release of carbon nanotubes from nanocomposites product during accidental or incomplete combustion. It was shown that at low temperature, the combustion of nanocomposite polymers using the polymeric compound ABS (Acrylonitrile Butadiene Styrene polymers) as matrix with a blend of 3% of MWCNT releases CNTs fibers into the fumes. Our findings are important to assess the environmental impact and the potential harmful consequences of accidental scenarios, e.g. release of nano-objets during a fire. In such instances, the release of those materials may induce environmental risks.

Keywords: Carbon nanotubes, combustion, polymer, nanocomposites, risk, release.

1 INTRODUCTION

Nanotechnology is a fast-growing industry that produces numerous materials enabling various innovative applications. The plastics industry is considered to be one of the main field in which the new nanotechnologies can play a key role. For many decades now, common polymeric materials have been reinforced with suitable additives to prepare reinforced plastics and polymer composites. If the possibility to incorporate engineered nanomaterials can represent a major breakthrough, these nanomaterials seem to be associated to health hazards which can result in new risks during the life cycle of the product, in case of release from the polymer matrix [1,2]. This study focuses on the potential release of airborne carbon nanotubes (CNTs) during the combustion of injection-molded nanocomposite polymers.

2 EXPERIMENTAL SETUP

Our experiment relies on new home-made demonstrator system that was setup at INERIS specifically for assessing the release of nanoparticles during combustion of polymeric products. It is composed of three made building blocks, as shown in Figure 1. The detail of the equipment is proprietary and is therefore not explained herewith. The

combustion regime thought is a substoichiometric regime that has proper characteristics so as to exploit the release of nano-objects. This demonstrator allows the emissions of nanoparticles and nanofibers of composites made of nanomaterials. A high performance filtration system allows removing gas mixtures from the combustion reactors to meet environmental compliances.

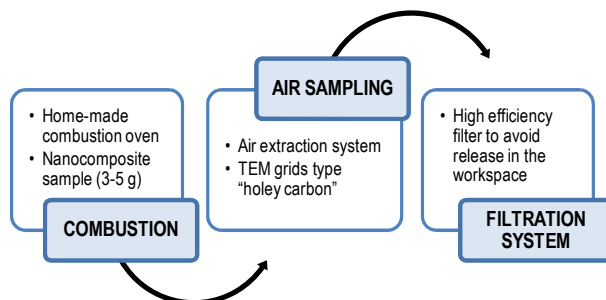


Figure 1. Functional block diagrams of INERIS demonstrator for the identification of nano-objects released from combustion.

A specific oven, of a proprietary nature was developed¹. The dimensions and design were devised to be able to run in specific combustion regimes (mainly in low temperature substoichiometric conditions). It is conceived with proper mass and heat transfer controls so as to provide good conditions for the release of nano-objects was developed. Such conditions may be encountered when accidental scenarios are to be considered which therefore warrant the need of such demonstrator. It reproduces experimental conditions close to an incomplete combustion or an accidental fire.

2.1 Measurement and sampling strategy

Differential thermal analysis measurement helped to monitor the combustion kinetics. In parallel the particle size distribution was recorded via direct measurements devices and aerosol sampling was performed by doing a picking straight into the combustion fumes.

The particle number concentration was recorded using an electrical low pressure impactor (ELPI). Sampling was

¹ Specific details of the systems will be found in INERIS patents being developed.

performed using a new device (aspiration based TEM sampler) that enables retrieving the morphological and the chemical composition of airborne particles by the analysis of TEM grids. The aspiration TEM sampler consists of a 6 mm inner diameter hollow tube where a TEM grid holder had been soldered perpendicularly to the tube section near one of its capped tips. This size-selection can be tuned by adjusting the two airflows of the device. In our experiment the primary and secondary airflows were calibrated to 10 L/min and 0.3 L/min, respectively. A similar technique was recently illustrated by INERIS in [3] for sampling CNT from workplaces to assess worker exposures. The grids used to perform the sampling are made of a holey carbon films lying on a nickel mesh grid. This type of medium, composed of many holes of different sizes, enable good capture efficiencies on a large range of particle diameter. This is particularly convenient in our case, i.e. when the sampling duration cannot be well estimated because the airborne particle concentration and the capture efficiency are not known precisely. Indeed, this guarantees that there is a location on the grid where the sampling conditions may be close to an optimum.

After sampling, the grids are post-analyzed via a transmission electronic microscope (TEM) equipped with a X-ray probe, to get back both chemical and morphological information. A large number of random locations are analyzed to evaluate statistically the nature of the collected particles.

2.2 Tested materials

Nanocomposites materials composed by a polymer matrix filled with CNTs have been used. This material was prepared on a Haake PTW24/40 twin-screw extruder at 240° C. The polymer matrix chosen is a special grade of ABS (acrylonitrile-butadiene-styrene, ref. BASF Terluran® HH112), with high temperature stability. The nanotubes were added in powder form using thin Multi Wall Carbon Nanotubes (ref. Arkema Graphistrength™ C100 [4]) produced via a catalytic carbon vapor deposition process (CCVD). This CNT production process uses metallic catalysts (Fe and Al compounds), usually leading to inclusion of nanometer-scale metallic particles at the surface of the nanotubes [2]. The CNTs powder have a purity of 90% (i.e. 90% of the weight is made of graphitic carbon), the rest being mainly composed of aluminum and iron oxides (Al_2O_3 and Fe_2O_3 , respectively). The other properties of the CNTs are the following: a diameter within 10-15 nm, a length ranging within 0.1-10 μm and a number of walls comprise between 5 and 15. The powder is constituted by agglomerates (entangled bundles) having a size of several hundred micrometer and has an apparent density of roughly 100 kg/m^3 . The CNTs powder is dosed and injected inside the extruder using a calibrated metering feeder in order to produce a final nanocomposites material containing 3wt% of CNTs. The electronic microscopy

analyses indicate that the final product (granules obtained after the extrusion process) is composed by two polymer phases: a continuous CNT-free matrix surrounding a CNT-rich polymer phase (see Figure 2).

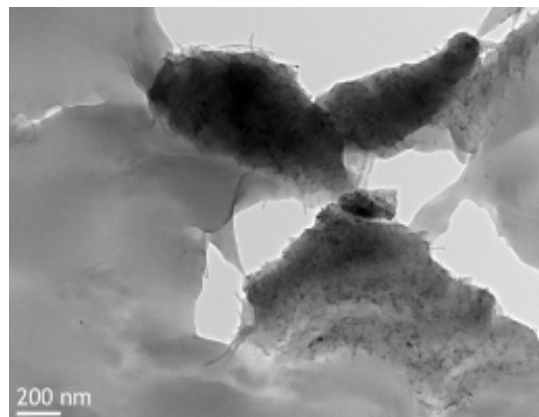


Figure 2. The SEM analysis reveals CNT bundles dispersed here and there in the polymer matrix.

Near a temperature of 200°C, the polymer will become liquid and sink to the bottom of the oven, cancelling the experiment. As a consequence, nanocomposites granules have been mixed with an equal weight of diatomite earth for increasing the viscosity and avoiding flowing. The diatomite earth is a soft siliceous solid composed of skeletons of small aquatic organisms. It is composed mainly of silica and may contain a significant proportion of cristobalite. Prior the experiments, this specific product has been incinerated, washed with acid and dried to destroy any organic matter, metallic compounds and water. Analysis have been performed on this material and confirm a very pure composition (SiO_2 concentration is higher than 99% by weight) which avoid any confusion in further result interpretations.

3 RESULTS

3.1 Direct measurements

The combustion kinetics recorded is coherent with those of a regular (unfilled) polymer (a blank test has been performed). The total particle concentration was monitored during the combustion. The results reveal two peak of emission at 300°C and 400°C. The second peaks is strongly correlated with sample temperature increase, which simply traduces that the polymer sample is burning (Figure 3). The results confirm a massive release of nanoparticles into the fumes. However they do not enable to identify the potential presence of airborne CNT in the smoke which is mainly made of carbon and exhibits a high particulate concentration (no difference is noticed between the unfilled polymer and the nanocomposite sample).

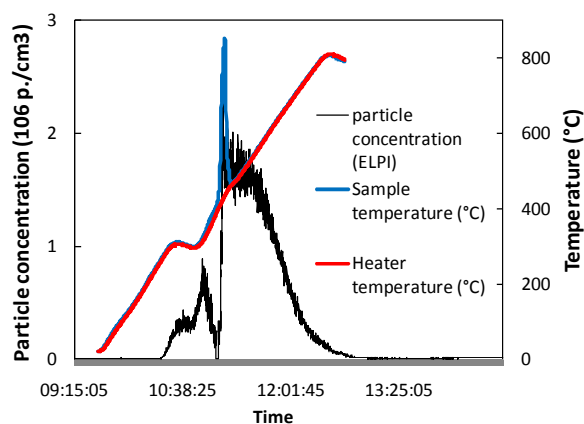


Figure 3. Combustion kinetics (temperature monitoring) and particle concentration recorded during the combustion of the nanocomposite sample.

3.2 TEM analysis of grid samples (fumes)

To go further in the analysis, TEM imaging was used to identify the kind of nanoparticles released. Although the analysis of the samples performed on the control material (blank polymer) has not revealed any carbon nanotubes (as expected), the sampling analysis of the nanocomposites has revealed several CNTs released through the combustion fumes. Despite a slightly altered structure, the metallic catalysts (Fe and Al compounds) are still attached to their ends (see Figure 4). This result demonstrates that CNT filled in a polymer matrix can be released during a combustion process, addressing a new kind of safety issues in regard to the combustion of nanocomposites. The analysis has also disclosed the release of some agglomerated CNT into the fumes, whose catalysts are still present.

This indicates that the uncontrolled incineration of fiber-containing products may release fibers in the environment. This can be a critical issue in the development of this technology and has a strong impact in disposal strategies.

Our observations are coherent with those of Chivas-Joly *et al.* in [6], since their experiment was conducted with a very different experimental setup (cone calorimeter connected to an ELPI device). Similarly, our results seem not contrary to the results of Nyden and Marsh [5] since their test setup was strongly different from ours (temperature control, aerodynamics and no sampling device).

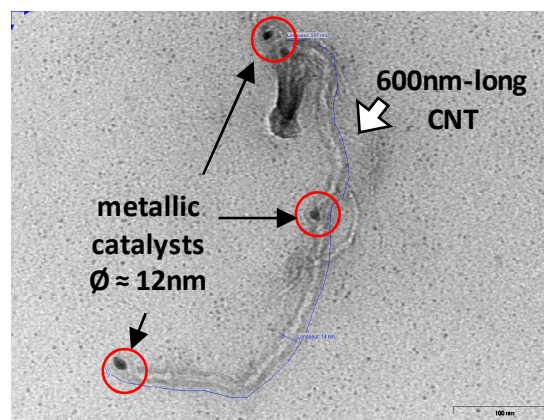


Figure 4. CNT isolated fibers sampled in the combustion fumes (TEM analysis, scale: 100 nm).

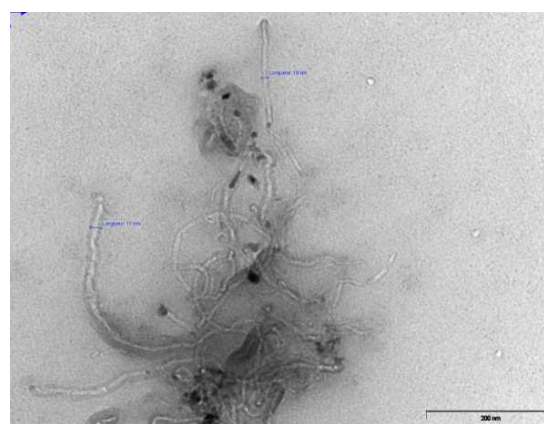


Figure 5. CNT agglomerate sampled in the combustion fumes (TEM analysis, scale: 200 nm).

3.3 SEM analysis (ashes)

In both cases (pure polymer or nanocomposite), 50% of weight is lost during the combustion process. This means that almost all the polymer sample has been burned and released into the combustion fumes. The residue is mainly composed of diatomite earth that remains quite unchanged after the combustion (insensitive to the oxidation process). The composition of the residues is almost the same from the sample to the blank test (pure polymer plus an equal weight of diatomite earth). The analysis show mainly SiO₂ with some metallic traces of Fe, Al and Mg compounds. However, the residues of the CNT-filled polymer contain several red clusters that can be isolated and analyzed separately (Figure 6).

The SEM analysis of the residual ashes has been conducted on both the control material (unfilled polymer) and on the nanocomposite sample. Although no CNT have been discovered in both samples, the observation of the residual ashes discloses red clusters, which can be related to metallic catalyst residues after all carbonaceous matter

(polymer and CNTs) has burned off (see Figure 7). The X-ray analysis reveals that these clusters are mainly composed of Al and Fe metallic oxides (probably Al_2O_3 and Fe_2O_3), a signature which fits well with the composition of the catalysts. This result evidences that a fraction of CNT (probably the less volatile part, e.g. heavy bundles) are not released in the fumes during the combustion. They probably burn with the matrix due to the high temperature elevation during the test (up to 600°C).

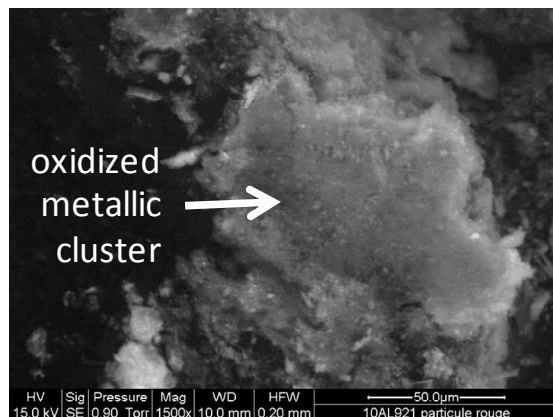


Figure 6. Oxidized metallic clusters are found in the ashes (SEM analysis, scale: $50\text{ }\mu\text{m}$).

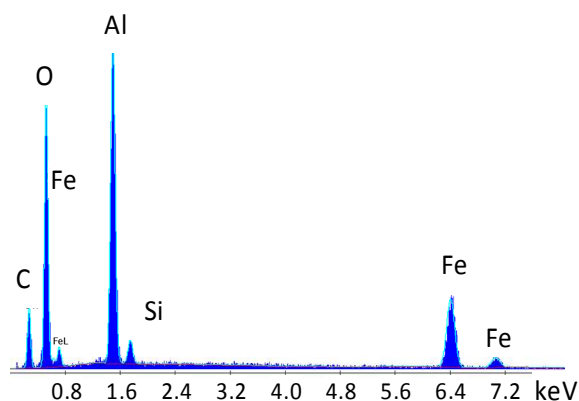


Figure 7. X-ray microanalysis (arbitrary units) of the red clusters found in the ashes: the spectrum reveals the presence of Fe and Al oxidized compounds.

CONCLUSION

Our results demonstrate that, during the combustion of the tested polymer nanocomposite, a fraction of CNTs is released in the fumes while the other fraction is destroyed by the oxidation process, thus releasing their catalysts in the ashes. This addresses a new kind of safety issues in regard to the combustion of these products. Our conclusions is not contrary to the recent literature [5,6] as this observation relies on a careful adjustment of the test parameters

(temperature, aerualics) and the use of a sampling device especially designed for this kind of experiment. However, at this time our strategy does not enable a quantitative assessment of the number of CNTs released, and then it is not yet possible to estimate the corresponding emission factor.

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