Characterization of aerosol emitted by the combustion of nanocomposites

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Abstract. Day after day, new applications using nanoparticles appear in industry, increasing the probability to find these particles in the workplace as well as in ambient air. As epidemiological studies have shown an association between increased particulate air pollution and adverse health effects in susceptible members of the population, it is particularly important to characterize aerosols emitted by different sources of emission, during the combustion of composites charged with nanoparticles for example. The present study is led in the framework of the NANOFEU project, supported by the French Research Agency (ANR), in order to characterize the fire behaviour of polymers charged with suitable nanoparticles and make an alternative to retardant systems usually employed. To determine the impact of these composites on the emission of airborne particles produced during their combustions, an experimental setup has been developed to measure the mass distribution in the range of 30 nm – 10 µm and the number concentration of submicrometric particles of the produced aerosol. A comparison is performed on the aerosol emitted during the combustion of several polymers alone (PMMA, PA-6), polymers containing nanofillers (silica, alumina, and carbon nanotubes) and polymers containing both nanofillers and a conventional flame retardant system (ammonium polyphosphate). The results on the morphology of particles were also investigated using AFM.

1. Introduction

There is a growing interest of natural or synthesized nanoparticles due to the fact that nanoscale materials are known to exhibit significantly different physical, chemical, electrical, and optical properties, compared to their properties at the macroscale. From an industrial point of view, it is an opportunity to develop new products in various fields such as health, energy, information, and transport. However, there is a concern that nanoscale materials and nanomanufactured products may endanger human beings, as different public debates on the safety of nanosciences and nanotechnologies take place. Both assessments of these risks, preventive actions, and remediation, when needed, will rely on the measurements and characterization of nanoparticles. Consequently, it is necessary to improve our knowledge in this field to assess the potential toxicology risks of nanotechnology [1]. As epidemiological studies have shown an association between increased particulate air pollution and adverse health effects in susceptible members of the population, it is particularly important to characterize aerosols emitted by different sources of emission; for example during the combustion of composites filled with nanoparticles. The material in accidental fires could then become a new source of nanoparticles. In this context, we present this study, which is led in the framework of the NANOFEU [2] project, started in January 2008 for 3 years, supported by the French
Research Agency (ANR). In order to know the impact of these composites on the emission of airborne particles produced during their combustion, an experimental set-up has been developed to measure the mass distribution and the number concentration of the produced aerosol.

2. Experimental methods

The presented experimental methods deal with the determination of the nanofillers impact on the smoke composition of aerosols, by comparing polymers alone, polymers containing nanofillers and polymers containing both nanofillers and a flame retardant (ammonium polyphosphate). Three different nanofillers (silica, alumina, and carbon nanotubes) have been selected, with or without surface treatment based on silane. These nanofillers are incorporated in Polymethyl Methacrylate (PMMA) and Polyamide-6 (PA-6) matrices [3]. This work also focuses on the study of the influence of the matrix on such modifications.

An experimental setup has been developed to measure the mass distribution and the number concentration of the produced aerosol with a cone calorimeter according to standard ISO 5660-1 [4]. This setup is composed of a cascade impactor [5] and a Condensation Nuclei Counter (CNC) coupled with a cone calorimeter (see figure 1). The concentration of submicrometer particles was measured by a CNC [6]. The CNC used (TSI 3022) detects particles down to 7 nm (minimum particle size corresponding to an efficiency of 50%) at concentrations up to $10^7$ particles/cm$^3$ [7]. In our experimental conditions, the flow rate of the CNC is equal to 0.3 L/min. A Low Pressure cascade Impactor (DLPI: DEKATI, with the electrical configuration disabled) has been used to measure the mass distribution of the airborne particles in the range of 30 nm – 10 µm by post-gravimetric analysis.

The cone calorimeter main duct is modified in order to avoid the trapping of soot on the 90° angle of the exhaust duct, and also to allow sampling at a point where the flow of effluents can be considered as homogeneous and laminar. The heat flux is set at 50 kW/m$^2$ with a standardized ventilation rate. Two ventilation rates have been used depending on the associated metrology, equal to 38 L/s with the CNC alone (A, see figure 1) or equal to 24 L/s for the measurement with the Dilutor FPS (DEKATI) coupled at CNC (B, figure 1) and with the DLPI alone (C, figure 1).

An Atomic Force Microscope (AFM) is used to investigate the morphological differences of the particles produced during the combustion of the various formulations. To prepare appropriate samples for AFM measurements, particles were collected using the DLPI where polycarbonate circular filter membranes have been replaced by optical microscope glass cover slips. Those cover slips have been chosen for their particular dimensions: a glass square of 18 mm x 18 mm that perfectly fits into the impactor and the smallest thickness of 150 µm. The glass slip roughness is of a few nanometers. The cover slips were imaged using an AFM with a scan range of 90 µm x 90 µm x 8 µm and an accurate three-axis closed-loop (NanoMan VS from Digital Instruments equipped with the hybrid XYZ scanner). The AFM is protected with an acoustic/vibration isolation enclosure and equipped with a vibration isolation table. The system is placed on a massive concrete block dissociated from the building in a laboratory controlled in humidity and temperature (50 % Hr and 20°C). The measurements were conducted in air using tapping mode and OTESPA probes (Veeco probes). A low scan speed (2 µm/s) was applied to the scanner to get high quality and high resolution images. Topographic and phase images were recorded without real-time filter.
In the configuration where the CNC is directly linked to the cone calorimeter (A, figure 1), two constraints must be taken into account: not operating the CNC in ambient temperature above to 40°C and measuring an aerosol with a concentration below the limit concentration of $10^7$ particles/cm$^3$. To lower the temperature of the effluent, the length of the primary probe is increased of 80 cm. An experiment with a sample of PMMA with a dimension of 100 x 100 mm was used to check that the temperature doesn’t exceed 40 °C at the secondary probe sampling of the CNC. The ventilation rate is increased to 38 L/s in order to dilute the combustion aerosol and thus not saturate the detector of the CNC. The sampling probe (diameter) had been selected to be in isokinetic sampling conditions. A small quantity of the sample was chosen to reduce the amount of aerosol produced: an average mass of 1.4 g for samples of all formulations (with a dimension of 17x17x4 mm$^3$).

In the case of certain experiments, we observe that the concentration is above the limit concentration of the CNC. Thus, it was necessary to use a diluter in order to measure the emitted aerosol and compare the results obtained by different formulations of nanocomposite: a configuration with the Diluter FPS-4000 (DEKATI) coupled at CNC (B, figure 1). This diluter is adapted for combustion dilution with two-stages (double diluter setup), where the first diluter is heated and the second operates at ambient temperature. This system allows to dilute the aerosol avoiding the condensation and the particle perturbation with regard to a simple cold dilution. The nanocomposite sample size is fixed at 25x25x4 mm$^3$ (corresponding to 3 g of materials).

For the measurement with the DLPI linked to the cone calorimeter (C, figure 1), an external heating assembly has been used to prevent the effect of humidity on the aerosol size distribution. The experimental conditions (C, figure 1) are the following: the nanocomposite sample size is fixed at 50x50x4 mm$^3$ (12 g) and the sample flow rate is equal to 10 l/min for the DLPI, during 5 minutes. This multi-stage aerosol-sampling device separates particles by size, according to their inertial

![Diagram of experimental setup](image)
properties in a moving air stream. Each stage of the impactor is characterized by a “cut-off size” (D50%). DLPI has a 13-stages particles impactor (table 1).

Table 1. Cut-off diameter D50% of each stage of Low Pressure cascade Impactor (DLPI: DEKATI) for a sample flow rate equal to 10 l/ min.

| N°of stage | Cut-off size D50% (µm) |
|------------|-----------------------|
| 1          | 0.03                  |
| 2          | 0.06                  |
| 3          | 0.09                  |
| 4          | 0.16                  |
| 5          | 0.26                  |
| 6          | 0.38                  |
| 7          | 0.62                  |
| 8          | 0.95                  |
| 9          | 1.60                  |
| 10         | 2.39                  |
| 11         | 4.00                  |
| 12         | 6.69                  |
| 13         | 9.93                  |

The “cut-off size” corresponds to the aerodynamic diameter of trapped particles with an efficiency of 50% on a given stage. The aerodynamic particle diameter (d_{ae}) is defined as the diameter of a spherical particle with a reference density equal to 1000 kg.m^{-3} which has the same gravitational settling velocity as the particle under consideration [8].

The experiments were performed with the nanocomposite described in the table 2.

Table 2. Used Samples: polymers alone, polymers containing nanofillers and polymers containing both nanofillers and a conventional flame retardant system.

| Sample | Composition of the sample | Information on the nanofillers |
|--------|---------------------------|-------------------------------|
| A      | PMMA                      |                               |
| B      | PMMA containing nanofillers of 15 % wt.SiO₂ | Average primary particle size of 12 nm |
| C      | PMMA containing nanofillers of 15 % wt.Al₂O₃ | Average primary particle size of 13 nm |
| D      | PMMA containing nanofillers of 15 % wt.Al₂O₃ with a surface treatment (silane) | Average primary particle size of 13 nm |
| E      | PMMA containing nanofillers of 5 % wt.Al₂O₃ and 10 % of Ammonium Polyphosphate | Average primary particle size of 12 nm |
| F      | Polyamide-6 (PA-6) containing 1% wt.CNT | Multi – wall carbon nanotubes |

3. Result on the aerosol measurements

3.1. Results with the Low Pressure cascade Impactor

The aerosol size distribution is obtained by measuring the mass of the particles collected at each stage of the impactor with the balance Metler (with a 10 µg precision). The doubled weight gravimetric method is used: the gravimetric measurement of each filter before and after aerosol sampling is performed two times.

3.1.1. Discussion on the uncertainty of the mass distribution in the case of PA-6

Figure 2 presents the mass distribution obtained with the DLPI in the case of three combustions of a Polyamide-6 (PA-6) containing multi – wall carbon nanotubes (MWNT with 1%). This figure shows the distribution of the mass plotted on the logarithmic diameter scale. The Y – axis (dM/dlog (D_{ae}) ) represents the mass of the particles collected divided by the width in the logarithmic scale of various channels of measurement of the diameter, with the channel determined by the cut-off sizes (D_{50%}).
Figure 2. Mass distribution obtained with the DLPI in the case of three combustions of a PA-6 filled with 1% carbon nanotubes.

The results presented in figure 2 illustrate that the measurements are repeatable: we observe that the deviation obtained between different experiments could be explained by the standard deviation calculated only from the gravimetric measurement method. All the measured masses are significant for stages with a cut-off diameter between 0.1 µm and 4 µm. These results reveal an highlight presence in particle mass in these ranges. For other measurement channels above 4 µm, and below 100 nm, the calculated standard deviation of all the measurements couldn’t always determine the significant presence in mass. However, the measurements always give a positive difference between the masses of blank and loaded filters (filters before and after the aerosol sampling). These results seem to suggest the presence of particles in all the measurement range of 30 nm-10 microns. The aerodynamic diameter of each size class midpoint is determined by the square root of the multiplication of the two successive cut-off diameters.

Figure 3 presents the average mass distribution on the results of three replicates of combustion of a Polyamide-6 filled with 1% carbon nanotubes (MWNT).

Figure 3. Average mass distribution on the results of three combustion of a PA-6 filled with 1% carbon nanotubes.

The uncertainty presented in figure 3 in the mass of the particles deposed on each stage is calculated using an error propagation method on the three replicate measurements from the gravimetric measurement method. The results presented in figure 3 illustrate that the standard deviation calculated on three experiments allow to determine a significant presence in mass of the particles in the range of 30 nm to 10 µm. The modal diameter obtained is equal to 0.21 µm. Figure 3 shows that the aerosol obtained is mainly in the range of 0.1 to 2 µm.
3.1.2. Results on the mass distributions in the case of several formulations with PMMA

Results are given below for PMMA alone, PMMA without flame retardants, but containing nanofillers of SiO$_2$ or Al$_2$O$_3$. Figure 4 presents the mass distribution obtained with the DLPI in the case of the combustion of (A) PMMA alone, (B) PMMA containing nanofillers of 15% SiO$_2$ (with an average primary particle size of 12 nm), (C) PMMA containing nanofillers of 15% Al$_2$O$_3$ (with an average primary particle size of 13 nm) and (D) PMMA containing nanofillers of 15% Al$_2$O$_3$ with a silane surface treatment. Each mass distribution presented is the result of the average of three replicate of combustion.

![Figure 4](image-url)

**Figure 4.** Mass distributions obtained with the DLPI in the case of the combustion of (A) PMMA alone, (B) PMMA containing nanofillers of 15% SiO$_2$, (C) PMMA containing nanofillers of 15% Al$_2$O$_3$ and (D) PMMA containing nanofillers of 15% Al$_2$O$_3$ with a silane surface treatment.

Figure 4 shows that the aerosol obtained are not monodispersed. The modal diameter obtained, equal to 0.12 µm, is the same for the 4 types of PMMA. A comparison of the graphs obtained for all types of PMMA shows a more significant presence of larger particles, greater than 4 µm (three last size classes), in all formulations containing nanofillers of SiO$_2$, Al$_2$O$_3$ with and without silane surface treatment compared to the PMMA matrix alone. Our experiments show that the nanofillers with or without silane surface treatment could have an influence on the mass distribution in the range of 1 nm to 4 µm. A slight decrease is observed for class 1.13 µm in the case of PMMA containing nanofillers of 15% SiO$_2$ in regard to the results for PMMA alone. In the range of 30 nm - 1 µm, the form of the size distribution is the same in the four cases, whatever the formulation is. However, the value of the mode for PMMA with nanofillers is greater than the value of the mode for PMMA alone; the quantities in mass near the modal diameter (0.12 µm) are greater for PMMA with nanofillers compared to the PMMA matrix.

Figure 5 shows the cumulative distribution of mass for the 4 types of PMMA described above (A, B, C and D).
ultrafine particles (< 0.1 µm) are in the range of 75 – 92 % and 30 - 45 %. These results illustrate that submicrometric particles emitted for the 4 formulations of PMMA described above (A, B, C and D). The mass median diameter (50 %) is between 100 and 200 nm for the 4 types of PMMA (figure 5). The results show that respectively, the mass fractions of submicrometric particles (< 1 µm) and ultrafine particles (< 0.1 µm) are in the range of 75 – 92 % and 30 - 45 %. These results illustrate that the large mass quantities emitted have been obtained with submicrometric particles (close to 80 %) and ultrafine particles (close to 40 %).

3.2. Results with the CNC alone

Figure 6 presents the number concentration measured by the CNC as function of the time of nanocomposites combustion. This figure shows the kinetics of the number concentration of submicrometric particles emitted for the 4 formulations of PMMA described above (A, B, C and D).

**Figure 5.** Cumulative distributions of mass for the 4 types of PMMA with nanofillers and PMMA alone (A, B, C and D).

**Figure 6.** Number concentration measured by the CNC as function of the time of nanocomposites combustion (A, B, C and D).
The emission rate obtained for the PMMA matrix is very different from those obtained for other formulations. The presence of nanofillers has a significant effect on the rate of particle emission with a decrease of the number concentration of the submicrometric particles emitted. For all the formulations, a peak representing the emitted particles preceding or at the moment of the inflammation of the sample is observed around 40 s. At this peak, the number concentration is similar for all the formulations of PMMA. The comparison of graphics C and D illustrate the influence of the surface treatment on the same matrix composed of PMMA containing nanofillers of 15 % Al₂O₃. The surface treatment involves a decrease of the number concentration.

Another formulation with Ammonium Polyphosphate (APP) has been tested. However, a rapid saturation of the number concentration is observed. Thus, it was necessary to change the setup in order to characterize the airborne particles (setup B, figure 1).

3.3. Results with a Diluter coupled at CNC

Figure 7 illustrates the kinetics of the number concentration measured by the CNC coupled with the diluter as function of the time for the combustion of 3 g of PMMA without fillers and of PMMA containing nanofillers of 5 % Al₂O₃ and 10 % APP. The dilution ratio used, equal to 54, is taken into account in the results presented in this figure.

![Figure 7. Number concentration measured by the CNC coupled with the diluter as function of the time for the combustions of PMMA alone and of PMMA containing nanofillers of 5 % Al₂O₃ and 10 % APP.](image)

The comparison of figures 6 and 7 allows to illustrate the influence of the Ammonium Polyphosphate added in the matrix composed of PMMA containing nanofillers of Al₂O₃. The Ammonium Polyphosphate involves a strong increase of the number concentration of the particles emitted.

3.4. Results on the morphology of particles

Figure 8 presents the AFM images (2 µm x 2 µm) of the particles collected on the first stage of the impactor (cut off aerodynamic diameter: 30 nm) for two formulations: PMMA (1st column) and PMMA + Al₂O₃ + APP (2nd column) with the topographic image on top and the phase image on the bottom.
PMMA PMMA + 15% Al₂O₃ + APP

Topography

Phase

Figure 8. 2 µm x 2 µm AFM images of the particles collected on the first stage of the impactor (cut off aerodynamic diameter: 30 nm) for two formulations: PMMA (1st column) and PMMA + Al₂O₃ + APP (2nd column) with the topographic and phase images.

For the PMMA formulation, the surface is mainly populated with nanoparticles. The few present aggregates do not exceed a diameter of 200 nm. In the case of PMMA + Al₂O₃ + APP, the images seem to show that the population of nanoparticles has increased compared to PMMA alone. This highest density of particles observed on the impactor stage with a cut off aerodynamic diameter of 30 nm could be expected because the measurements obtained by the CNC, including all sub-micron particles (<1 um), showed a greater concentration in the case of PMMA + Al₂O₃ + APP (see figure 7). We also observe the physico-chemical modifications of the particles suspected as tar or liquid phase coalesce on particles.

4. Conclusion
As epidemiological studies have shown an association between increased particulate air pollution and adverse health effects in susceptible members of the population, it is particularly important to characterize aerosols emitted by different sources of emission; for example, during the combustion of composites charged with nanoparticles. The present study is led in the framework of the NANOFEU project, supported by the French Research Agency (ANR), in order to characterize the fire behaviour of polymers charged with suitable nanoparticles and make an alternative to usually employed retardant systems. To evaluate the impact of these composites on the emission of airborne particles produced during their combustion, an experimental setup has been developed to measure the mass distribution and the number concentration of the produced aerosol. In this paper, a comparison of the mass
distributions of the aerosol emitted during the combustion for several polymer alone (PMMA, PA-6), polymers containing nanofillers (silica, alumina, and carbon nanotubes) and polymers containing both nanofillers and APP as a flame retardant was presented. In the case of PMMA with and without nanofillers of SiO$_2$ or Al$_2$O$_3$, the results illustrate that the large mass quantities emitted have been obtained with submicrometric particles (close of 80 %) and ultra fine particles (close of 40 %). The presence of nanofillers in PMMA shows a significant effect on the rate of particle emission with a decrease of the number concentration of the emitted submicrometric particles. The results show that a silane surface treatment of the nanofillers contained in the PMMA matrix could involve a decrease of the number concentration of submicrometric particles. Conversely, the Ammonium Polyphosphate involves an high increase of this number concentration. The morphology of these particles collected by the impactor has been studied using Atomic Force Microscopy.

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