Characterization of airborne particles released by the combustion of Nanocomposites

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ABSTRACT

The technological advances in nanomaterials have allowed the development of new applications in industry, increasing the probability of finding these particles in the workplace as well as in ambient air. It is thus important to characterize aerosols emissions from different sources, for example, during the combustion of composites charged with nanoparticles. This study is undertaken within the framework of the NANOFEU project, supported by the French Research Agency (ANR, Agence Nationale de la Recherche), in order to characterize the fire behaviour of polymers charged with suitable nanoparticles and to provide an alternative to the retardant systems usually employed. To determine 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 in the range of 30 nm–10 µm, the number concentration of submicrometric particles and the morphology of the aerosol produced.

Keywords: nanocomposites, combustion, aerosol, nanofillers, emission

1 INTRODUCTION

The experimental study deals with the determination of the impact of nanofillers on aerosol emissions during the combustion of several polymers alone such as Polymethyl Methacrylate (PMMA) and Polyamide-6 (PA-6), polymers containing nanofillers (silica, alumina, and multi wall carbon nanotube) with or without surface treatment based on silane and polymers containing both nanofillers and a conventional flame retardant system (ammonium polyphosphate).

This study is undertaken within the framework of the NANOFEU [1] project which began in January 2008 for a 3-years period and is supported by the French Research Agency (ANR). In order to establish the impact of these composites on the emission of airborne particles produced during their combustion, an experimental set-up has been developed to determine the mass distribution and the number concentration of the aerosol produced [2]. Some of the results were presented at the recent NANOSAFE 2010 conference [3].

There is a general lack of knowledge regarding the question of nanoparticles released by the accidental or deliberate burning of materials containing nanoparticles. In a survey of the literature, only one study (a research program launched in 2009 by NIST [4, 5]) has provided any results on particles realeased by the combustion under controlled conditions of polyurethane foams containing carbon nanofibers (CNFs). Authors found that CNFs were effectively destroyed in the flames and observed that the major hazard sources for nanoparticle exposure were the char and residues, rather than the smoke.

The results in this field are of major significance for industry and the general public and therefore require further studies to be performed.

2 EXPERIMENTAL METHODS

An experimental set-up composed of a cascade impactor [6] and a Condensation Nuclei Counter (CNC) coupled with a cone calorimeter according to the ISO 5660-1 standard [7] has been developed. This set-up enables the mass distribution and the number concentration of the airborne particles released by the combustion of nanocomposites to be measured.

The morphology of the airborne nanoparticles collected by the impactor has been studied using Atomic Force Microscopy (AFM).

The concentration of submicrometer particles was measured by a CNC [8] (TSI 3022) which detects particles down to 7 nm (minimum particle size corresponding to an efficiency of 50%) at concentrations up to 10^7 particles/cm^3 [9]. A low pressure cascade impactor (DLPI: DEKATI, with the electrical configuration disabled) was used to measure the mass distribution by post-gravimetric analysis of the airborne particles in the range of aerodynamic diameter 30 nm – 10 µm [10].

The cone calorimeter main duct was modified to avoid the soot being trapped in the 90° angle of the exhaust duct. Point sampling was performed where the flow of effluents can be considered as homogeneous and laminar [3]. The incident heat flux onto the sample surface was set at 50kW/m². Two ventilation rates were used depending on the associated metrology, equal to 38 L/s with the CNC alone or equal to 24 L/s for the measurement with the

Dilutor FPS (DEKATI) coupled at CNC and with the DLPI alone.

3 RESULTS

A comparison [2] was performed on aerosol emissions during the combustion of several polymers alone (PMMA, PA-6), polymers containing nanofillers (silica, alumina, and carbon nanotubes) with or without surface treatment based on silane and polymers containing both nanofillers and a conventional flame retardant system (ammonium polyphosphate).

In the case of all formulations of PMMA or PA-6 whether modified or not, and with or without nanofillers of SiO_2, MWCNT, or Al_2O_3, the results obtained with DLPI illustrate that the mass fraction for the submicrometric particles (< 1 µm) is close to 80%.

In this paper, we will present only the comparison between the results of mass distribution with MWCNT nanofillers for two matrix PMMA and PA-6. Figures 1 and 2 respectively illustrate the average mass distribution for the results of three replicates of combustion of the PMMA alone and PMMA filled with 1% wt. multi wall carbon nanotubes (MWCNT). Figure 3 presents the mass distribution in the case of a PA-6 alone (a) and PA-6 filled with wt.1% MWCNT (b).

The uncertainty presented in figures 1, 2 and 3 on the mass of the particles deposed on each stage is calculated using an error propagation method on three replicate measurements from the gravimetric measurement method. The standard deviation calculated on three experiments enables us to determine a significant presence of particle mass in the range of 30 nm to 10 µm.

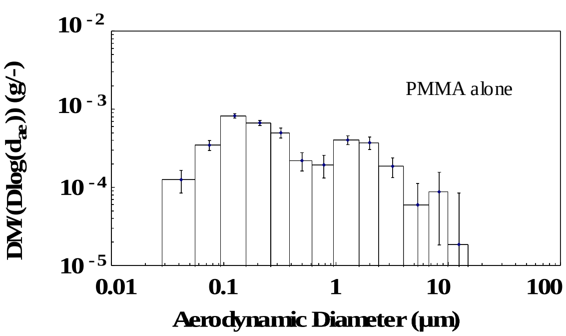


Figure 1. Mass distributions obtained with the DLPI in the case of the combustion of PMMA alone.

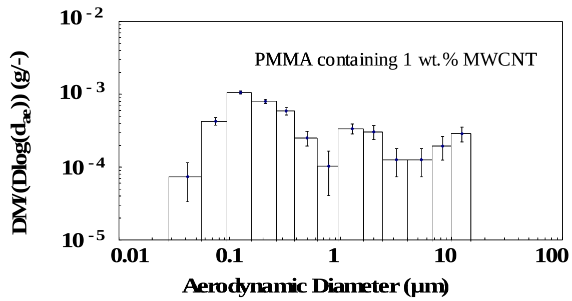
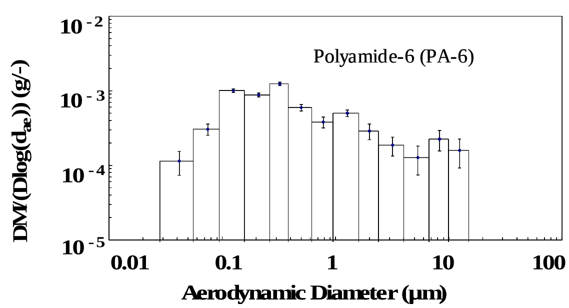


Figure 2. Mass distributions obtained with the DLPI in the case of the combustion of PMMA filled with 1% wt. carbon nanotubes MWNT.

The PMMA with and without nanofillers presents the same polydispersed distributions except for the 3 last stages at around 10 µm, with a higher amount for the PMMA with MWCNT. In both cases, the aerosol seems to be composed of at least two populations having their own lognormal distribution with a first mode in the range 0.1 to 0.2 and the second mode in the range 1 to 2 µm. 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) is greater for PMMA with nanofillers compared to the PMMA matrix.

a)



b)

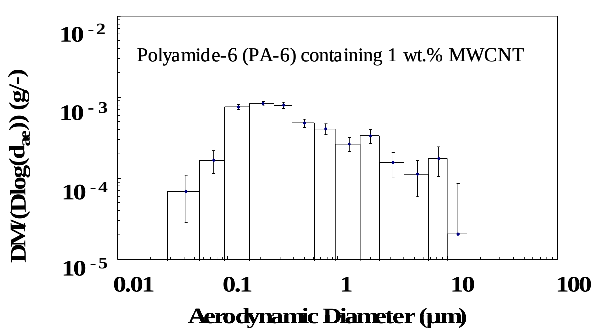


Figure 3. Mass distributions obtained with the DLPI in the case of the combustion of PA-6 alone (a) and the combustion of PA-6 filled with 1 wt.% MWCNT(b).

The DLPI results of PA-6 with or without nanofillers seem to show mono-modal distributions with mode diameter between 0.1 µm and 0.4 µm with regard to uncertainties. Figure 3 shows that aerosol mass obtained is mainly in the range of 0.1 µm to 2 µm.

The airborne particles released by the combustion collected at the first stage of the impactor (cut-off aerodynamic diameter of 30 nm) were observed by AFM in order to determine the morphology of these particles. We have found [2] that in the case of the nanocomposite PA-6 with 1 wt.% MWCNT, the nanotubes are clearly observable, in comparison with the effluent issued from the formulation of PMMA with 1wt. % MWCNT, where no carbon nanotube has been observed.

A recent study in 2011 also presents some results for carbon nanotubes filled in polymer matrix that can be released during a combustion process [11].

4 CONCLUSION

With regards to the potential risks associated with nanoparticles and nanomaterials, it is particulary important to characterize aerosol emissions from different sources, for example, during the combustion of composites charged with nanoparticles.

A comparison of the airborne particles released by the combustion of different nanocomposites has been performed [2, 3]: several polymers alone (PMMA, PA-6), polymers containing nanofillers (silica, alumina, and carbon nanotubes) and polymers containing both nanofillers and APP as a flame retardant were used in this study.

In order to make a conclusion about the influence of the matrix on the airborne nanoparticles released, further experiments will be necessary such as the morphology and chemical studies on other stages of the low pressure impactor.

The results of the airborne nanoparticles released depend on a variety of factors such as the matrix used, the nanofillers, the combustion process, the sampling, etc. In order to answer the question of the potential risks associated with the burning of nanocomposites, it seems necessary to work on different round-robin tests looking into this issue.

As a next step, using a Differential Mobility Analysing System (DMAS), we will measure the count size distribution of aerosol emissions during the combustion of different formulations of polymers containing nanocomposites. These measurements will enable us to determine the kinetics of aerosol size distribution according to the different kinds of polymers burned during the experiments.

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