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Gaseous effluents from the combustion of nanocomposites in controlled-ventilation conditions

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Abstract. Composite materials are more and more used every day. In order to further enhance their attractive mechanical and physico chemical performances, the last generation of these materials largely makes use of nanomaterials.
Various nanofillers are eligible for such a purpose, the best ones depending on the associated matrices. One favorite field of application of these nanomaterials is fire retardancy and fire behavior of nanocomposites. In the context of the ANR research project NanoFeu, various technical analyses have been performed [1]. One focuses on the characterization of the dispersion of nanofillers in the matrix; another deals with the characterization of the fire behavior of samples including the study of the composition of the gaseous effluents, the characterization of the emitted soot [2]. A third part of the work focused on molecular modeling of observed phenomena within the matrices. This paper focuses mainly on the combustion of nanocomposite samples under various ventilation conditions.
Tests have been performed with the Fire Propagation Apparatus (FPA). Samples are based on poly(methyl methacrylate); various nanofillers were used: carbon nanotubes, alumina and silica. Efficiency of fillers is compared to the classical ammonium polyphosphate in equal proportions. During testing, the ventilation-controlled conditions were obtained by adjusting the combustion air flow rate entering the apparatus. Gaseous effluents were analyzed by Fourier Transform Infra-Red spectrometer.
Fire behavior is characterized in terms of fire parameters and chemical composition of gaseous effluents. The influence of ventilation conditions is especially significant in terms of amount of gases released: much more important production of specific gases is generally observed in case of under ventilation regime as compared to the well ventilated case.

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1. Introduction

Nanotechnologies and the relating use of nanomaterials represent one of the major economic break-through for the developed societies today, with headways which have already allowed important evolutions in various domains such as health, energy, information, or transport… In the field of polymeric materials various types of additives are used to improve their behavior. Indeed, to respond to more stringent demands in terms of overall performances of plastic materials, including reaction to fire, new fire retardancy systems based on introduction of nanoparticles may become a suitable alternative to traditional approaches. The alternative brought by nanoparticles must also be assessed and confronted to the traditional systems, in terms of environmental impact. It is in this context that the NanoFeu project has been initiated. The objective of these works is to study the fire behaviour of materials containing nanoparticles, to define their role and their fate during the combustion. To perform this study, nanocomposites with a polymer matrix were elaborated; experiments were performed to assess the reaction to fire of the test samples and the composition of the emitted gaseous effluents. Section 2 presents the NanoFeu project; section 3 is devoted to the description of experimental devices. Main results are given in section 4; conclusion is presented in section 5.

2. The *NanoFeu* project

The elaboration of nanocomposites using a polymer matrix is one of the most active domains in nanomaterials development. The properties assigned to nanoparticles are highly varying and concern in particular the mechanical intensification, electrical and thermal conduction characteristics, the barrier properties to gases and liquids, as well as the fire behavior that is thought to result from barrier properties efficiency [3].

The ANR project called *NanoFeu*, started in 2008 for three years. It focused on the impact of fillers on the fire behavior of nanocomposites. Coordinated by INERIS (Institut national de l'environnement industriel et des risques), four other partners have taken part to the research consortium, namely: Laboratoire National de métrologie et d'Essais (LNE), Ecole des Mines d'Alès (EMA), Institut supérieur des matériaux et mécaniques avancés (ISMANS) and PlasticsEurope. PlasticsEurope supports this academic group as an association of nanocomposite and polymer producers.

The *NanoFeu* project focuses on nanofillers impact on the smoke composition (gases and aerosols), by comparing polymers own responses to the ones of polymers containing nanofillers and polymers containing both nanofillers and conventional flame retardant systems. Another aspect is to evaluate the morphological modifications of nanoparticles produced during the combustion of such materials and to assess relating potential health hazards. The consortium gathers experts in several fields like fire physics, chemistry and numerical modeling.

3. Fire behaviour tests

3.1. Samples composite setup

In order to evaluate the fire behaviour of nanocomposites, a series of formulations have been elaborated at Ecole des Mines d'Alès for this project. Dimensions of samples are 100 mm x 100 mm x 4 mm. Blends of polymers with nanofillers were compounded using a twin screw extruder (Clextral BC 21, L ¼ 1200 mm, L/D ¼ 48, 2.7 kg/h, 200 rpm). PMMA and commercial PMMA/MWNT 5%wt. masterbatches were mechanically mixed prior to feeding the extruder.

Main characteristics of samples tested in this paper are given in the following table:

Table 1. Table of samples

Sample	Formulation	Designation
1	Poly(methyl methacrylate);	PMMA
2	PMMA + 0.2%wt Carbon Nanotubes	PMMA - 0.2 CNT
3	PMMA + 1%wt Carbon Nanotubes	PMMA - 1 CNT
4	PMMA + 15%wt Silica	PMMA - 15 SiO_2
5	PMMA + 15%wt Alumina	PMMA - 15Al_2O_3
6	PMMA + 15%wt Ammonium Polyphosphate	PMMA - 15 APP
7	PMMA + 5% wt Alumina +10%wt Ammonium Polyphosphate	PMMA - 5Al_2O_3 – 10 APP

3.2. The Fire Propagation Apparatus

Fire behavior of nanocomposites is evaluated using a fire propagation apparatus (ASTM E2058:09, ISO DIS 12136 [4]). Under a thermal irradiance of 35kW/m², various samples are tested for ventilation controlled condition of air flows of 50L/min and 350 L/min.

Figure 1. The Fire Propagation Apparatus

3.3. The infrared spectrometer instrument

In order to analyze the composition of gases emitted during combustion, infrared spectroscopy is used with a Thermofisher Nicolet 6700. This spectrometer is equipped with a detector of type MCT-A cooled with liquid nitrogen, scanning a spectral range from 650 to 4200 cm^{-1}. Its spectral resolution is 0,5 cm, the cells of optical path of 2 meters and 10 meters are heated at 180°C. Data acquisition is performed every 4s. Gases at present measured for quantification are: H_2O, CO_2, CO, NO, NO_2, SO_2, N_2O, CH_4, C_3H_6, HBr, HCl, HF, HCN, NH_3. A semi-quantitative measure of following species is performed too: formaldehyde, acetaldehyde, ethylene, acetylene.

4. Experimental results

4.1. Fire behaviour of nanocomposites

For the various regimes of ventillation, combustion parameters are given in the following table. Variations for instance in terms of ignition time, effective heat of combustion and mass loss rates are noticed.

Table 2. Combustion parameters of sample

Formulations	Ignition Time		Effective heat of combustion				mass loss rates	
	s		kJ/kg		MJ/m^2		g/m^2/s	
Test condition	Well-ventilated	Under-ventilated	Well-ventilated	Under-ventilated	Well-ventilated	Under-ventilated	Well-ventilated	Under-ventilated
PMMA	52	45	24880	16120	121	78	34	29
PMMA-0.2 CNT	42	45	25100	15950	121	77	35	31
PMMA-1 CNT	39	42	24130	17220	116	83	28	25
PMMA - 15 SiO_2	47	43	24205	23964	109	108	18	16
PMMA-15 Al_2O_3	60	50	23878	23280	110	107	20	15
PMMA-15 APP	72	55	23840	18510	108	84	25	23
PMMA - 5Al_2O_3 – 10 APP	50	39	23745	20830	109	96	25	19

In the well-ventilated case, the latest ignition times are obtained with the formulations PMMA-15 Al_2O_3 and PMMA-15 APP. The heat of combustion obtained for the PMMA is in accordance with the 24±2 MJ/kg measured more recently with the fire propagation apparatus [5]. As compared to PMMA without any additive (first sample in table 2), all tested formulations including fillers and or fire retardants (except PMMA with 0.2%CNT) show in our tests lower values for the effective heat of combustion and for the average mass loss rate. Nevertheless, the most significant decrease of heat of combustion is about 6%. This value is lower than corresponding weight fraction of incorporated additives and is obtained for the formulation containing PMMA – 5% Al_2O_3 – 10% APP.

In the under-ventilated case, the variations are less significant as regard times of ignition. The most 'retarded' times of ignition are observed for the formulations PMMA-15 Al_2O_3 and PMMA-15 APP. The shortest time is obtained with the formulation combining alumina and ammonium polyphosphate. The highest effective heats of combustion are obtained with the formulations PMMA - 15 SiO_2, PMMA-15 Al_2O_3 and PMMA - 5Al_2O_3 – 10 APP. The most largest mass loss rates are obtained with formulations containing CNT.

The kinetics of heat release versus time is represented in figures 2 and 3. The peaks of HRR vary according to formulations, as well as the general shape of HRR overall responses.

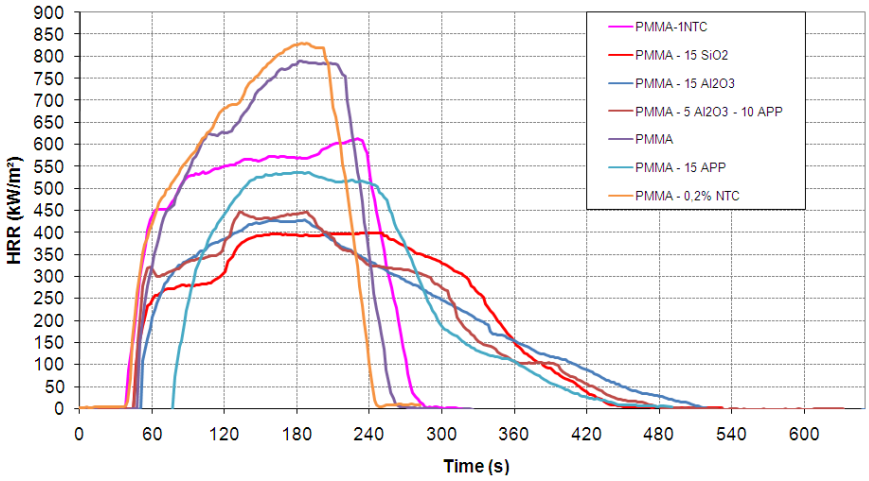

Figure 2. Heat Release Rate measuring during tests in well-ventilated conditions

The impact of nanoparticles, as well as APP on the decrease of peak of heat released (pHRR) during combustion is observed. Compared to PMMA with a pHRR include between 750 and 800 kW/m², the presence of CNT in concentration of 1%wt CNT decreases this peak of 25%. Our results are in agreement with Costache et al. who obtained a decreasing of 29% in the pHRR with matrix

containing 3%wt multiwall carbon nanotubes (MWCNT) [6]. On the other hand Kashiwagi et al. [7] have obtained a decrease superior to 50% with 1%wt singlewall CNT. They also showed that this decrease was depending on the quality of nanotubes dispersion into the matrix. Indeed, with 0,5% of nanotubes badly scattered, the relating decrease in the pHRR is only about 10%, and this value can reach up to more than 50% in the case of a good dispersion.

Identical tests are performed in the well-ventilated case.

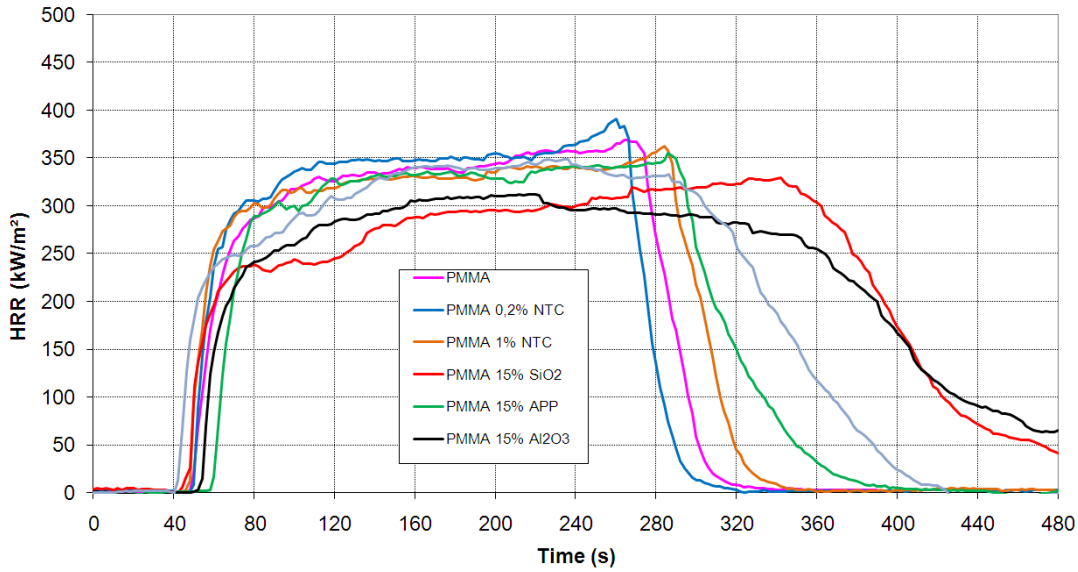

Figure 3. Heat Release Rate measuring during tests with under-ventilated conditions.

In this case, a significant decrease of HRR for some formulations is noticed, as well as a variation of the shapes of HRR curves.

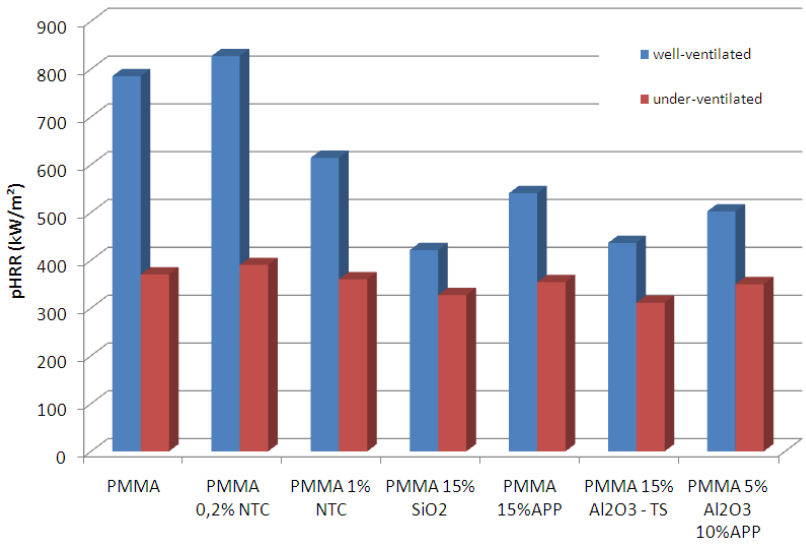

Figure 4. Comparison of pHRR for the test samples.

Figure 4. illustrates more particularly that for various formulations, a decrease more or less significant of pHRR is observed, according to the composition of nanofillers for combustion tests in the well-ventilated case. In the underventilated case, the peak of HRR vary in a very limited manner (between 300 and 400 kW/m²).

4.2. Composition of gaseous effluents

In addition to the observation of fire behavior of samples, the composition of gaseous effluents from combustion of nanocomposites is analyzed. The obtained results are given in the following figures for the various identified gases for the two regimes of ventilation. In fig. 5 to 10, THCs refer to overall hydrocarbons CxHy, including methane, as measured by a dedicated analysor (flame ionization detector).

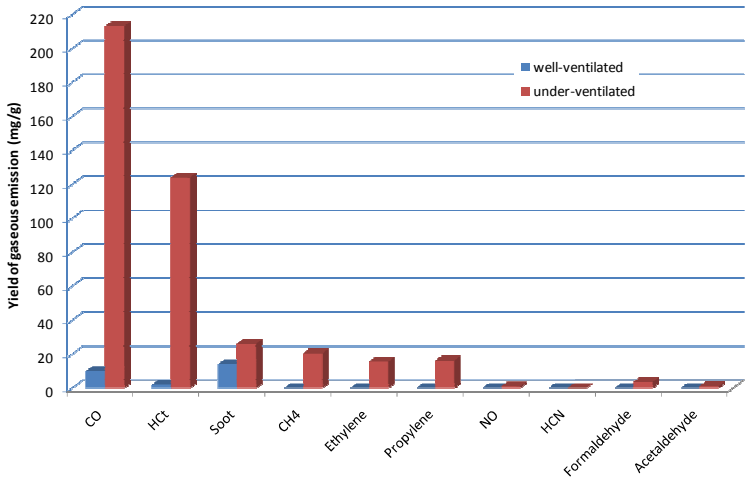

Figure 5. Emission yields of various gases from combustion of PMMA in controlled-ventilation conditions.

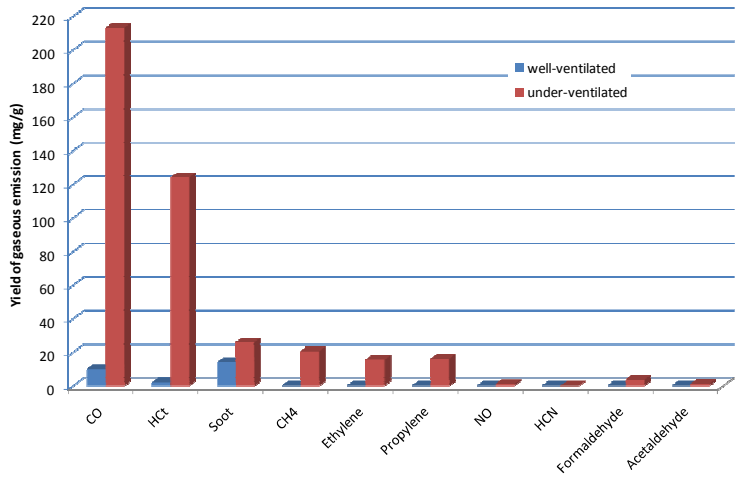

Figure 6. Emission yields of various gases from combustion of PMMA-0.2 CNT in controlled-ventilation conditions

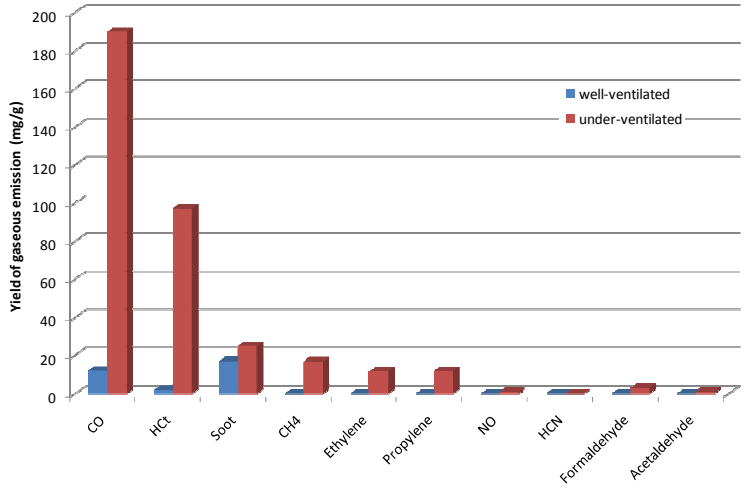

Figure 7. Emission yields of various gases from combustion of PMMA-1 CNT in controlled-ventilation conditions

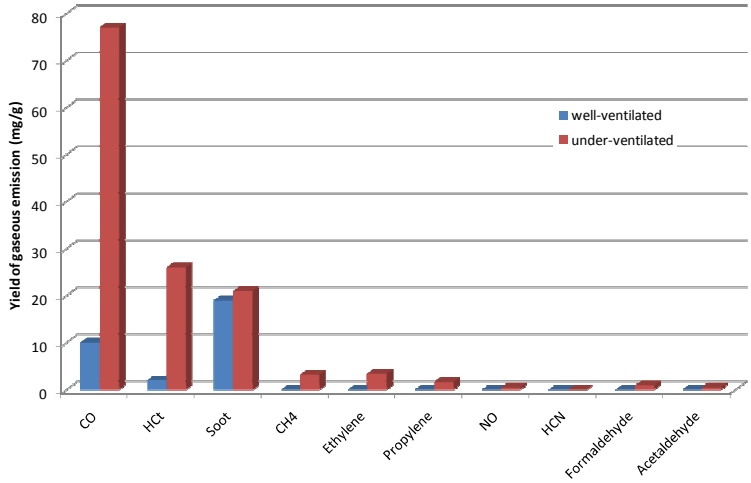

Figure 8. Emission yields of various gases from combustion of PMMA - 15 SiO2 in controlled-ventilation conditions

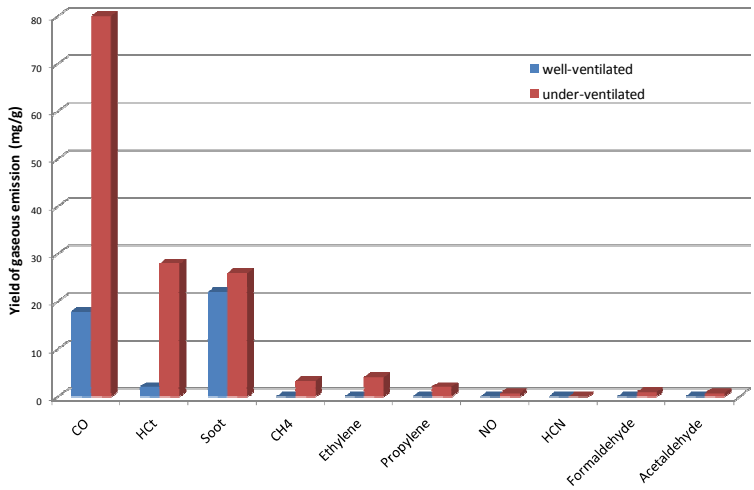

Figure 9. Emission yields of various gases from combustion of PMMA-15 Al2O3 in controlled-ventilation conditions

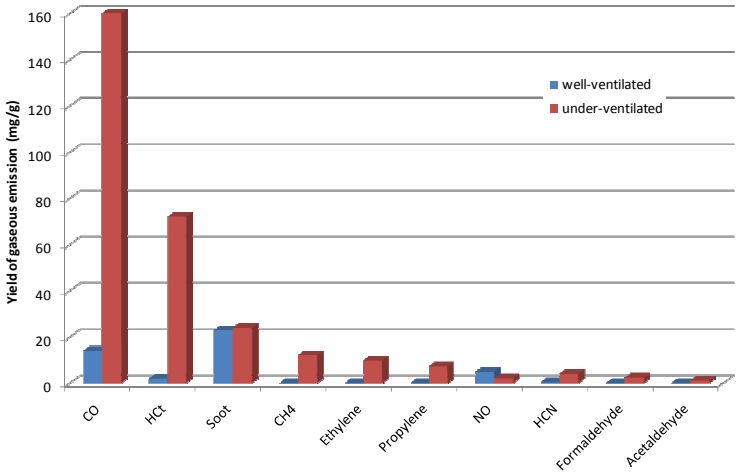

Figure 10. Emission yields of various gases from combustion of PMMA-15 APP in controlled-ventilation conditions

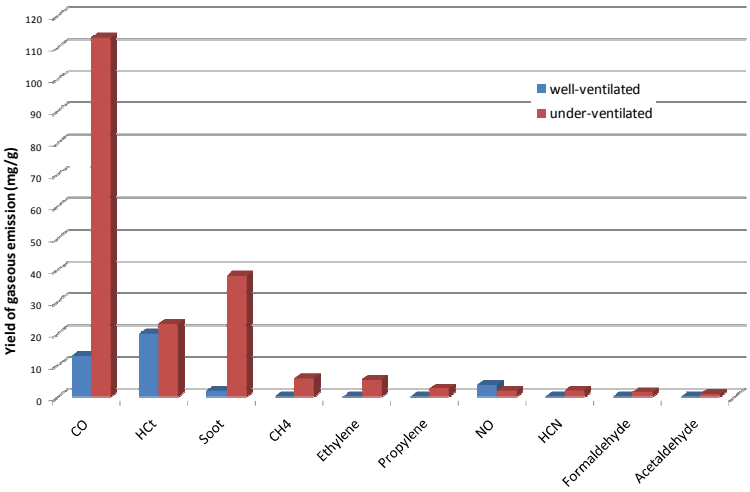

Figure 11. Emission yields of various gases from combustion of PMMA - 5Al2O3 – 10 APP in controlled-ventilation conditions

Significant concentrations in NO are obtained in presence of samples containing APP. A measurable value of HCN is also observed for samples containing APP. This statement highlights reactive processes that take place in gaseous phase involving the ammonia resulting of decomposition of APP and carbon monoxide produced by the combustion of PMMA. This production of HCN is lower for PMMA - $5Al_2O_3$ – 10 APP than for PMMA-15 APP.

In the under-ventilated case, the introduction of nanofillers in the PMMA matrix can significantively reduce the yield of CO emission. The more the samples contain nanofillers, the more significant the decrease is. This decrease is also observed for the yield of THCs (total hydrocarbons) emission. The yields of soots production are more significant for the formualtions PMMA-15 Al_2O_3, PMMA - 15 SiO_2 as well as for the PMMA - $5Al_2O_3$ – 10 APP.

Globally, from the overall gas emission sprectrum, 3 classes of combustion related emission yields are identified. The first one deals with the species CO, THCs and Soot: these species are emitted in relative large quantities whatever the samples and the combustion conditions are (say yields may reach more than 10 mg/g. The second class concerns the species CH_4, ethylene, propylene and NO that are globally produced in moderate yields for both well and under-ventilated regimes. The last class containing HCN, Formaldehyde and Acetaldehyde refers to toxic products emitted in a still lower yield than the other species during combustion. A global view of compared overall toxicity would

require however require a more detailed analysis integrating individual contribution of toxic species as well as cumulative effects that is out of scope of this paper.

5. Conclusion

Experimental tests for the combustion of nanocomposites samples have been performed in the context of *NanoFeu* project. Various regimes of ventilation have been tested in order to observe the influence of nanofillers on the composition of gaseous effluents.

Gaseous effluents spectrums have been established for the combustion of PMMA and PMMA containing nanofillers. Combustion parameters seem to be coherent with others references on the subject, the impact of the filler is observed in terms of HRR curves and peak of values. Nanofillers modified heat release rate in the two regimes of ventilation. pHRR values are less significant in under-ventilated case than in well-ventilated case. Concerning gaseous effluents, differences are observed between the two regimes. This difference is more or less significant for 3 classes of species identified during the combustion of samples, and that are ranked according to levels of mass yields observed. High emissions are expected for the first class (including CO_2, which yield is not given here), moderate ones for the second (light hydrocarbons + NO) and still significantly less for the last class (specific species like HCN). Nevertheless this observation does not completely inform about the global toxicity of gaseous effluents. Others complementary studies are in progress to further address the question.

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