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Revisited investigation of fire behavior of ethylene vinyl acetate/aluminum trihydroxide using a combination of mass loss cone, Fourier transform infrared spectroscopy and electrical low pressure impactor

F.E. Ngohang [a,b], G. Fontaine [b], L. Gay [a], S. Bourbigot [b,*]

[a] MFEE/EDF R&D, 6 quai Watier, 78400 Chatou, France
[b] UMET/ENSCL, Avenue Dimitri Mendeleëv, CS 90108, 59652 Villeneuve d'Ascq, France

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A bench scale test combining mass loss cone, Fourier transform Infrared Spectroscopy and Electrical Low Pressure Impactor (MLC/FTIR/ELPI) was developed to assess simultaneously heat release rate (HRR), evolved gases (qualitatively and quantitatively) and particles (size distribution and concentration) in the smoke from fire. It was evidenced (external heat flux of 35 kW/m^2) with ethylene vinyl acetate copolymer as reference material a good repeatability on qualitative and quantitative analysis of evolved gases and particles out of the flame. The tests on neat ethylene vinyl acetate (EVA) and filled EVA with aluminum trihydroxide (EVA/ATH) show as main results, high concentration of evolved acetic acid before the ignition of EVA, high concentration of water before the ignition of EVA/ATH, and the evolution of acetone during the combustion of EVA/ATH assigned to the catalytic effect of alumina transforming acetic acid into acetone. In the two cases (EVA and EVA/ATH) the size distribution of particles in the smoke lies in similar range mainly made of ultrafine (<0, 1 μm) and submicron particles (<1 μm). It is noteworthy that peaks of particles of 16 nm (almost 3. × 10^7 particles per cm^3) and 93 nm (2. × 10^7 particles per cm^3) are observed in the smoke of EVA. In the case of EVA/ATH, particles of 6 nm (around 5. × 10^6 particles per cm^3) are detected and of 54 nm (3. × 10^7 particles per cm^3) while they are not measured in the case of neat EVA. The evolved mass of particles out of the flame have shown a maximum of 50 g/m^3 (close to the flame out) from fire of EVA and a maximum of 6 g/m^3 (before the piloted ignition) from fire of EVA/ATH. These results show the interest and the efficiency as well as the reliability of coupling MLC/FTIR/ELPI as alternative bench test to expand simultaneous analysis of fire behavior of materials.

1. Introduction

Fire has an important place in the classification of risks in industrial facilities, public transportation, or building. One of the issues of fire is the generation of smoke constituted by toxic and/or corrosive gases and also, by particles able to be transported far away from the fire origin. In unfortunate circumstances, they have been recognized as the main cause of injury or death [1]. Their effects on the safety of electric or electronic devices have already raised some concerns such as loss of contact, shorts circuits, corrosion effect in mid or long term which may induce facilities immobilization with strong economic consequences [2–4]. So, the qualification and quantification of gases and particles release during fire should permit to assess and/or to understand effects of smoke as hazard for human being, electronic devices, etc. Methods involving small scale tests including Thermogravimetry/Gas Chromatography/Infrared spectroscopy [5], Thermogravimetry connected to Fourier Transform Infrared spectroscopy [6], or Simultaneous Thermal Analysis interfaced to Fourier Transform Infrared spectroscopy [7] have been used to characterize gases of material. However, as far as we know there are no published data and experimental bench scale test which permits simultaneous analysis of gas (qualitatively and quantitatively), particles (size distribution and concentration), combined with heat release rate measurement. It is the main goal of this paper to focus on the development and validation of an alternative bench test allowing to assess in real time and simultaneously HRR, gas (identification and quantitative concentration), and particles in the smoke to expand investigations of fire behavior of combustible fuels.

* Corresponding author. Tel.: +33 (0) 3 20 43 48 88; fax: +33 (0) 3 20 43 65 84.
E-mail address: serge.bourbigot@ensc-lille.fr (S. Bourbigot).

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In this paper, the Mass Loss Cone (MLC) will be used as fire model to perform calorimetric study on neat ethylene vinyl acetate copolymer (EVA) and filled EVA with aluminum trihydroxide (EVA/ATH). MLC will be connected to Fourier Transform Infrared spectroscopy (FTIR) to characterize (qualitatively and quantitatively) the decomposition gases and to Electrical Low Pressure Impactor (ELPI) [8] to analyze particles out of the flame. The process of this work will be as follows: (i) to get a coupling of MLC/FTIR/ELPI as an applicable and reliable experimental bench test, (ii) to develop qualitative and quantitative analysis methods of evolved gases and particles, and (iii) to validate the efficiency and the repeatability of coupling MLC/FTIR/ELPI using known flame retarded systems (EVA and EVA/ATH).

2. Experimental

2.1. Materials

Ethylene-vinyl acetate copolymer containing 28% of vinyl acetate (EVA) supplied by Arkema, and aluminum trihydroxide (ATH) in white powder supplied by Martinswerk (Bergheim, Germany) were used as raw materials to make plates of virgin EVA, and of EVA filled with ATH.

2.2. Processing

EVA/ATH was prepared using a Brabender mixer 350/EH with a shear rate of 50 rpm and at 180 °C. EVA was melted for 5 min, afterward ATH was incorporated and the formulation was mixed for 15 min (total duration of 20 min). EVA/ATH formulation is composed of 35 wt% polymer, and 65 wt% ATH respectively. Neat EVA and EVA/ATH were pressed in an appropriate mold ($100 \times 100 \times 4$ mm^3) at 200 °C under pressure of 20 kN for 3 min, followed by 5 min under 40 kN, and finally cooling down to room temperature and demolding.

2.3. Experimental bench

2.3.1. Mass loss cone

MLC from Fire Testing Technology (FTT) was used to perform measurements of HRR and piloted ignition time (t_{ig}) of sample undergoing an external heat flux of 35 kW/m^2 (which corresponds to a mild fire scenario) according to ISO 13927 [9]. This equipment is identical to that used in oxygen consumption cone calorimeter according to ISO 5660 [10], except that a thermopile into a chimney (straight linked to the cone heater and collected all the smoke evolved during the fire) is used to assess HRR measuring the temperature change of mass flow air [11,12] rather than oxygen depletion.

2.3.2. Fourier transform infrared spectroscopy

A Thermo Nicolet iS10 FTIR spectrometer equipped with nitrogen MCT (Mercury Cadmium Telluride) detector, 0.2 L volume gas cell, and 2 m optical path-length, was set to get the best quality of gases spectra. Acquisitions were performed in mid infrared (from 4100 to 650 cm^{-1}) with high spectral resolution (set at 0.5 cm^{-1}) and a scan number of one (NS = 1) (each scan was taken at 1.61 s and at 0.5 cm^{-1} as spectral resolution). Note that we used NS = 20 for the acquisition of quantitative calibration gases to enhance the signal/noise ratio, but in the case of the combustion experiments we preferred to reduce NS to get faster acquisition and so, to monitor potential fast changes of gases' concentration.

2.3.3. Electrical low pressure impactor

An Electrical Low Pressure Impactor (ELPI^{+}™) from Dekati was used to measure in real time size distribution and concentration of particles in the smoke from fire. Less known than MLC and FTIR, the principle of ELPI can be summarized in three consecutive steps: (i) particles are charged into a known charge level in the corona charger, (ii) the charged particles enter the low pressure cascade impactor into which they are size classified according to their aerodynamic diameters in 14 stages, covering the size range from 6 nm to 10 μm and (iii) charges carried by particles on each impactor stage are measured continuously with sensitive electrometers and the measured current values are inverted to yield particles' number (per cm^3) or mass concentration (mg/m^3) using transfer functions provided by manufacturers [8,13].

3. Results and discussion

3.1. Conception of coupling MLC/FTIR/ELPI

The experimental design of coupling MLC/FTIR/ELPI is depicted in Fig. 1. Initially, the chimney of mass loss cone was slightly extended to 250 mm in order to put two smoke retrieval probes just above the thermopile (50 mm). So, we can reasonably assume the flow of smoke stream is homogeneous and laminar (Reynolds number $<$ 2000 considering smoke as air in the chimney). Then, to monitor simultaneously gases release during MLC fire test, a sampling system from one probe into the MLC chimney to the FTIR gas cell was set up. It consists in a first cylinder ceramic filter (10 μm) close to the probe linked by 6 m of polytetrafluoroethylene (PTFE) transport line and in a second filter (2 μm) connected to the FTIR gas cell by 1 m PTFE line. This part of gases sampling system (shown on the right side of Fig. 1) and the FTIR gas cell are heated at 180 °C to avoid condensation of volatiles. Note that two additional thermocouples (type K, 0.38 mm diameter) were inserted into the chimney to measure the temperature change of smoke at sampling point (close to the thermopile). Furthermore, a pump (equipped with a flow meter and valve) to get controlled and constant flow (3.5 L/min) was put after the FTIR spectrometer and a pressure gauge with regulating valve to keep constant pressure (650 ± 5) [14] was set into the gas cell. Filters 1 and 2 (previously presented) are intended to remove particles to protect FTIR gas cell (beam and mirror) against soot. To the simultaneous analysis of particles with ELPI, another sampling system (shows on the left side of Fig. 1) was also set up. It consists in the second retrieval probe connected to an antistatic PTFE line to prevent static electricity during the transfer of smoke and a vacuum pump located after the ELPI to regulate isokinetic flow rate (10 L/min) in the particles analyzer. In the same way, the ELPI sampling system was heated at 180 °C to prevent effects of condensed humidity on the measurement.

Finally, an FTIR gas calibration was additionally developed to assess quantitatively gases evolved from MLC fire test. It consists in multiple compressed gas cylinders having a given concentration certified by Messer Supplier (top of right side of Fig. 1). These gas cylinders are linked to a mixing gas platinum (divider/diluter) made of specific mass flow meters for each gas of interest. These mass flow meters controlled via an automatic computer system allow to deliver a precise amount of mixed gases (nitrogen as diluting gas) to get calibration points.

3.2. Validation

The efficiency and repeatability of coupling MLC/FTIR/ELPI as an applicable and reliable experimental bench scale test is assessed in this section with EVA and EVA/ATH as reference materials. Those materials have been selected because they are widely used in