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FTIR–PCFC coupling: A new method for studying the combustion of polymers

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ABSTRACT

Gases released from pyrolysis and partial combustion of various polymers (low-density polyethylene, polystyrene, poly(parabromostyrene), pure and flame-retarded polypolyamide 6, cellulose, and chloroprene) were studied using a new coupling between Fourier transform infrared spectrometry (FTIR) and pyrolysis combustion flow calorimetry (PCFC). Combustion in PCFC was monitored by modifying the combustion temperature between 600 and 900 °C. Decreasing the combustion temperature in PCFC leads to partial combustion and the evolution of CO, but also of methane, acetylene, or ethylene when temperature is very low. The evolution of these gases depends also on the polymer and on the presence of a flame inhibitor, demonstrating that flame inhibition can be studied using this method. A correlation between FTIR–PCFC and FTIR–cone calorimetry coupling was attempted via the CO/CO_2 ratio. The first results show that an "isoconversion temperature" in the cone calorimeter test may be estimated. Polar gases such as chlorinated or brominated gases are not fully observed using this method due to possible adsorption in the transfer line before they reach the FTIR gas cell.

1. Introduction

When exposed to an intense source of heat, a polymeric material undergoes heating up to a temperature high enough to break covalent bonds, leading to pyrolysis. The release of combustible gases increases until combustion starts. Combustion can be complete or partial, depending on the temperature, the excess of oxygen, the nature of combustible gases, and the presence of flame inhibitors (generally halogenated compounds). The completeness of combustion can be estimated by the ratio between the effective heat of combustion (EHC) and the heat of complete combustion. This ratio is called combustion efficiency (χ). Effective heat of combustion (respectively heat of complete combustion) is defined as the heat of the oxidation (respectively complete oxidation) of gases released from the anaerobic pyrolysis of a polymeric material.

The more complete the combustion, the higher is the heat release. This heat release adds to the initial source of heat, entailing an increase of the pyrolysis rate. Combustion efficiency is monitored by several parameters that can slow down the combustion kinetics without modifying the equilibrium yields of reactions. Therefore, to predict the pyrolysis rate, it is necessary to know how the combustion efficiency changes with the temperature of combustion, the oxygen rate, and the presence of flame inhibitors.

A new technique has recently been developed for studying the combustion efficiency of polymers using pyrolysis combustion flow calorimetry (PCFC) [1]. PCFC was developed by Lyon from FAA and allows measuring the flammability of small samples (2–5 mg) [2]. The sample is heated under nitrogen flow at 1 K/s, typically up to 750 °C. The pyrolysis gases are sent to a tube furnace, where combustion occurs. Therefore, combustion and pyrolysis are well separated and the temperature and the oxygen rate can be monitored. The heat release is measured using an oxygen analyzer. According to the Huggett relation [3], 1 kg of oxygen consumed during the combustion corresponds to 13.1 MJ of released energy. Hence, it is possible to measure the combustion efficiency under well-controlled conditions. In recent papers, it was shown that the curve of combustion efficiency versus temperature of combustion changes according to the nature of the polymer and to the presence of a flame inhibitor [1,4–7]. A correlation with the cone calorimeter test was also proposed [1].

It could be suggested that the combustion efficiency profile is related directly to the nature of combustible gases released during the pyrolysis. For this purpose, we have equipped our pyrolysis combustion flow calorimeter with a FTIR spectroscopy apparatus. The analysis of gases released during the thermal degradation of a polymer is usually performed by two well-known couplings, namely FTIR–thermogravimetric analysis (TGA) and FTIR–cone calorimetry. The former method makes it possible to analyze the gases released during pyrolysis before combustion: TG analysis is

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generally performed under nitrogen flow. Even if pyrolysis is carried out in an oxidative atmosphere, the polymer is degraded at relatively low temperatures (most often lower than 500 °C) and combustion does not occur to a great extent. Examples of the use of FTIR–TGA coupling to determine the degradation pathway can be found in the work of Schartel and co-workers [8,9]. FTIR–cone calorimetry coupling allows analyzing gases after combustion, but this combustion is not controlled. Combustion efficiency is generally close to 1 (complete combustion) except when flame inhibitors are incorporated into the polymer. This coupling is used for industrial purposes to measure the amounts of some released gases using a calibration method. An example of the use of this method can be found in the work of Lyon et al. [10]. To the best of our knowledge, no work about FTIR–PCFC coupling has been published yet. FTIR–PCFC coupling was presented by Sonnier et al. [11] during BCC2013. Lyon and Walters [12] have also studied a coupling between PCFC and a CO–CO_2 analyzer.

As mentioned above, in the PCFC test, pyrolysis and combustion are well separated and the combustion conditions can be modified independently. Therefore, FTIR–PCFC coupling should yield additional information about the combustion mechanisms. We believe that such coupling is complementary to FTIR–TGA and FTIR–cone calorimeter couplings. In this article, we present the first analyses obtained using FTIR–PCFC coupling.

2. Materials and methods

Polymers and additives used in this study are described in Table 1. All products are commercially available. PA6/melamine cyanurate (MC) blend 75/25 was prepared using a corotative twin-screw extruder (Clextral BC21; temperature profile ranges between 225 and 235 °C). PA6 was dried at 80 °C for 4 h before processing.

PCFC tests were performed using a fire testing technology apparatus. Samples were heated under nitrogen flow up to 750 °C at a heating rate equal to 1 K/s. Gases were extracted and sent to a combustion chamber in the presence of N_2/O_2 (80/20) flow. For each experiment, sample weight was carefully selected in the range 2–5 mg with a precision of 0.01 mg to ensure that O_2 was always in excess. The temperature of combustion was monitored between 600 and 900 °C. Combustion efficiency at a temperature T is calculated as follows

$$\chi\ (T) = \Delta O_2 \text{ at the temperature } T/\Delta O_2 \text{ at } 900\,^{\circ}\mathrm{C}, \qquad (1)$$

where ΔO_2 at the temperature T is the mass or volume of oxygen consumed at the combustor set point temperature T, and ΔO_2 at 900 °C is the oxygen consumed by combustion of the pyrolysis gases at $T = 900$ °C. As said previously, 900 °C is generally enough to ensure complete combustion.

The heat release rate is calculated from the oxygen consumption according to Huggett's relation (1 kg of consumed oxygen corresponds to 13.1 MJ of released heat) [3]. Total heat release is equal to the area under the curve plotting the heat release rate versus the pyrolysis temperature. Therefore, combustion efficiency is practically calculated as follows:

$$\chi\ (T) = \text{total heat release at the temperature } T/\text{total heat release at } 900\,^{\circ}\mathrm{C}. \qquad (2)$$

Eqs. (1) and (2) are equivalent in this case.

It is noteworthy that pyrolysis conditions were never changed. Only the combustion efficiency of the gases released by pyrolysis was affected when the combustion temperature was modified. Repeatability of PCFC analyses is estimated to be 3% [2] and is experimentally confirmed for our apparatus.

A Nicolet iS10 FTIR spectrometer from ThermoFisher Scientific was coupled at the exhaust of PCFC via a 2-m heated transfer line. The temperatures of the line transfer and of the gas cell were fixed at 160 and 165 °C, respectively. FTIR spectra (400–4000 cm^{-1} range, resolution fixed to 0.5 cm^{-1}) were studied using Omnic software from ThermoFisher Scientific. The spectra acquisition uses a Gram–Schmidt vector of data orthogonalization, which is a particularly simple and direct approach. Gram–Schmidt processing can provide visualizations of spectroscopic imaging data in real time. A basis set consisting of background interferograms is established before the experiment is started. This basis set is then used to detect the presence of infrared-radiation-absorbing species in real time by comparing the sample interferograms to the basis set [13]. The Gram–Schmidt rebuilt from vector analysis of the acquired interferograms allows the total evolved gases detected by the spectrometer to be plotted. The detector signal has been plotted as a function of the pyrolysis temperature.

It must be noticed that gases are transferred from the tube furnace to the exhaust of the PCFC along a first nonheated transfer line including Drierite and an oxygen analyzer. As proved below, some gases adsorb before reaching the FTIR cell. Therefore, no accurate gas analysis is possible. Further work will be carried out to avoid the adsorption or condensation of gases and of water, which could solubilize some volatiles. Recommendations for a correct coupling system can be found elsewhere [14–16]. This work was done to develop the FTIR–cone calorimeter coupling. In particular, the choice of probe, filters, and sampling line (temperature, inner diameter, and length) was emphasized. Halogenated gases (HCl and even more extensively HBr) are subjected to strong adsorption. In particular, a minimum temperature of 150 °C along the entire sampling device is recommended [14]. It is not the case of our coupling and some gases are not detected (or only after a long unacceptable response time).

Cone calorimeter tests were performed using a FTT apparatus according to ISO 5660 standard. Irradiance was fixed at 35 kW/m^2. The samples were embedded in aluminum foil and positioned in the standard sample holder. No grid was used. Ignition was piloted using a spark igniter except when thermocouples were used. An Antaris IGS FTIR spectrometer (400–4000 cm^{-1} range) from ThermoFisher Scientific was coupled to the cone calorimeter using a 2-m transfer line heated to 160 °C. The sampling point was located on the stack just before the sampling point for the oxygen analyzer. Filters were positioned to trap soot particles. Temperature and pressure conditions in the gas cell were fixed at 165 °C and 650 Torr. FTIR spectra were studied using Omnic software from ThermoFisher Scientific.

Thermogravimetric analyses were carried out using a Pyris-1 Perkin–Elmer apparatus. The heating rate was fixed at 10 °C/min under nitrogen flow up to 750 °C.

Table 1
Polymers and additives used in this study.

Polymer or additive	Grade
Polystyrene (PS)	Lacqrene 1340 (Arkema)
Poly(parabromostyrene) (PS-Br)	Aldrich
Polyamide 6 (PA6)	Technyl C216 (Rhodia)
Low-density polyethylene (LDPE)	Riblene FL20 (Polimeri Europa)
Melamine cyanurate (MC)	MC15 (Melapur)
Cellulose	Arbocell BC 1000
Chloroprene	Baypren 116 (Lanxess)

3. Results and discussion

If some combustible molecules are not fully oxidized during combustion, CO is produced (instead of CO_2) and other not-fully-oxidized hydrocarbon gases could be released, such as methane. Nevertheless, in combustion, "the hydrocarbon is attacked by the O°, H° and OH° radicals. The larger alkyl radicals formed in this