Polymer Degradation and Stability 154 (2018) 304–311

Contents lists available at ScienceDirect

Polymer Degradation and Stability

journal homepage: www.elsevier.com/locate/polydegstab

Characterization of in-flame soot from balsa composite combustion during mass loss cone calorimeter tests

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ARTICLE INFO

Article history:
Received 2 November 2017
Received in revised form
30 March 2018
Accepted 25 June 2018
Available online 30 June 2018

Keywords:
Soot
Cone calorimeter
Electron microscopy
Multi-scale morphology
Balsa composite

ABSTRACT

Soot is one of the degradation products of material burning, having the fingerprints of the conditions in which it is formed. In this work, in-flame soot was probed from flaming combustion of balsa core and its sandwich composite at different heat flux scenarios during mass loss cone calorimeter tests. Soot probing was performed by thermophoresis. Electron microscopy was performed to analyze the size of the particulate media at multiscale. The size of the aggregates and the primary particles were found to be inherent to scenarios, i.e. materials specifications and heat flux rates. Nanoscale structure of in-flame soot was consistent with the results of thermogravimetric analysis of emitted-deposited soot. This semi-quantitative study contributes to soot observations in fire scenarios and constitutes the first application of soot probing by thermophoresis in a bench-scale fire scenario simulated by cone calorimetry. Technique shall be used in future to support emitted soot and smoke data.

1. Introduction

For fire research and safety, the fire phenomenon and the response of materials exposed to it are examined through the properties of materials, their degradation pathways, physical and chemical properties, together with flame properties. In a fire scenario of polymer burning, the decomposition products in the gaseous phase include volatiles, condensables and particulate media [1]. An in-depth understanding of those products of combustion is essential both for experiments and simulations.

In general terms, soot represents carbon-rich material issued from the decomposed unburnt fuel molecules. In molecular stage, gaseous precursors are presumed to cluster until the nucleation of solid particulates and formation of aggregates, together with oxidation and surface growth reactions depending on the fuel and flame dynamics [2]. Soot is therefore one of the particulate degradation materials from combustion indicating the degree of incomplete burning in the gaseous phase. Its formation and morphology is directly dependent on the fuel type. In the gas phase of fire, soot clearly affects the thermal conditions because it is the major heat source and sink element. On the other hand, the nanoscale and mesoscale order of soot were reported to provide satisfactory information on the source identification in combustion systems [3]. During a fire, the potential modifications in the mechanisms of soot formation are caused by the presence of additives, protective layers or by the external thermal constraints; the decomposition process of the materials and subsequent combustion dynamics are thus affected.

The exact soot formation pathways are still unknown for various types of fuels. So, the ex-situ observation of individual soot particles is a complementary tool to in-situ techniques in order to assess the flame dynamics, the fuel type and source identity [4]. Soot probing by thermophoresis [5] is capable of providing single soot aggregates/agglomerates using microscopy observations. While this technique is widely used in combustion flames, its utilization is less common in fire domain. Some examples reported in literature are the flame soot analyzed from simulated and outdoor pool fires [6–8]. Very few studies reported multi-scale observations [6], and, so far, the in-flame soot from fires of polymeric materials has never been characterized at multiscale.

In bench-scale fire scenarios, soot emissions were reported for polymers and their fire retardant formulations in terms of the effect of fire retardancy on the emitted soot aerosols [9], while some works reported the effect of additives [10,11] and nanofillers [12]. Those studies were performed for soot in aerosol (i.e. emitted) form because most of the studies focused on the environmental deposition or the toxic effects of the particulates. Nonetheless, the probing of in-flame soot is an interesting alternative as it enables to

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https://doi.org/10.1016/j.polymdegradstab.2018.06.013
0141-3910/

probe the particulate media as close as possible to the production source. In earlier attempts on flame retarded (FR) ethylene vinyl acetate and FR polyamide, fingerprints of flame retardancy were evidenced by their in-flame soot aggregates probed in cone calorimeter tests [13], and the primary particle size distributions complied with the combustion of the gaseous hydrocarbon decomposition products of polymers formerly reported [10,14,15]. Technique enables single probing at specific instants instead of massive collection through filtering, preventing the restructuring of soot, hence providing more reliable data to comment on dynamics. In-flame probing is thereby a complementary approach to emitted soot and gases, enabling to trace the source, to comment on dynamics and on thermal conditions during testing. Note that soot particles are subject to modifications once they are outside the combustion process. This is especially true for the emitted type of soot because the particles can react with gases, or can adsorb them, once they are out of the flame and cooled down with exhaust gases. In that case, the particle collection through gaseous extraction is prone to errors if the denuding/filtration/dilution processes were not correctly set up while separating the gaseous media from particulate media [16]. Direct probing is advantageous because high temperature treated soot does not undergo considerable morphology modification or surface reaction once outside the flame, if it has been stored properly in an isolated and moisture-free environment at ambient temperature, according to the reported protocols [16].

As a natural polymer, balsa material has a wide range of applications and research interests, such as sandwich composites used as structural components in marine applications [17]. Balsa based flame retardant composites were also recently investigated [18,19]. Compared to bare polymeric materials, composites with laminate skins exhibit more complex structural and thermal behaviors [20]. Therefore, the main goal of this work aims at providing complementary data for further description of degradation materials from balsa, in order to trace the effects of thermal constraints and material intrinsic properties. To that end, balsa core and balsa sandwich composites were submitted to fire tests for soot probing and analyses. In this study, the particulate media were probed inside the flame during mass loss cone calorimeter tests, at 35 kW/m^2 and 50 kW/m^2 external heat flux rates mimicking mild and developed fires. For balsa composite testing, mass loss cone calorimeter tests were reported to provide good flammability data, even if they were reported not being completely representative of realistic fire conditions such as direct exposure to flame [17]. Nevertheless in mass loss cone calorimeter tests, the external heat source is only radiative: evolved gases and soot products are completely inherent to degradation conditions and intrinsic to the material, contrary to hydrocarbon flame experiments where the material is subjected to an external flame. We will thereby examine the multiscale soot morphology to address the following questions: how are the flame soot particles affected when exposed to different external heat flux rates and to different constraints by addition of a skin layer (polyester resin filled in with glass fibers); how will the flame soot probing method of combustion be adjusted to bench-scale fire testing; how can the morphology of particulates be observed at multiscales.

2. Materials and methods

2.1. Virgin material

Specimens tested in this study were obtained from commercial balsa composite: (1) a balsa core and (2) its composite form, having a core protected with skin layers made of glass fibers (non-woven) embedded in polyester resin, with a core of 12 *mm* thickness and skins of 6 *mm* on both sides. All samples have a surface of 10×10 cm^2. In studies mimicking the real life application of balsa composites, the core layer thickness is much higher than in our study [19]; in this work, observations were performed on a relatively thin balsa core to obtain a rapid burning of the material in mass loss cone calorimeter configuration for soot extraction, in order to minimize the time shift in probing times between the skin protected and the bare specimens.

2.2. Fire testing

The reaction to fire testing of materials was performed on a mass loss cone calorimeter (MLCC) from Fire Testing Technology (FTT) according to standards ISO 13927 or ASTM E906. The samples were tested under the incident heat flux rates of 35 kW/m^2 and 50 kW/m^2 as depicted in Fig. 1. At least two MLCC experiments were performed on each material in order to ensure repeatability within the error margins of ±10%.

2.3. Particle sampling

Soot samples were probed inside the flame by impaction and thermophoresis on TEM (transmission electronic microscopy) grids [5], as illustrated in Fig. 1. Lacey or holey carbon coated copper TEM grids were used. Probing was performed approximately 10 s after the peak heat release rate (pHRR) on the output curve. The user indeed determines the probing instant during MLCC testing by actively monitoring the HRR curve. The time step of HRR data acquisition was 5 s. Therefore, the user can detect the pHRR at 'pHHR+5 s'. Then, user can perform probing at 'pHHR+10 s'. Probing instants of scenarios are illustrated in Fig. 2a.

2.4. Microscopy

Soot imaging was performed using Scanning Electron Microscopy in transmission mode (SEM/STEM) and Transmission Electron Microscopy (TEM). STEM images were taken using a JEOL 7800 FEG LV scanning electron microscope at 30 kV and 7 mA, using a retractable bright and dark field SEM STEM detector completed with Deben Gen5 electronics and a 12 position TEM grid holder. TEM and high-resolution (HRTEM) images were taken using a

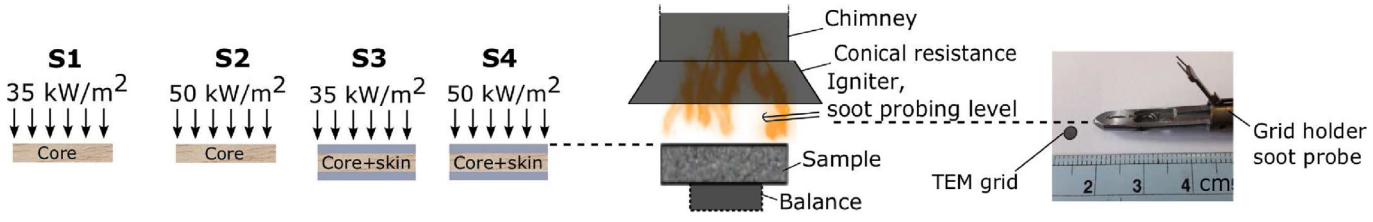

Fig. 1. Illustration soot probing during scenarios 'S' in MLCC tests. The probing is performed on TEM grids, at mid-height of the gap between conical resistance and the sample surface.