

Experimental Characterization of the Oxidation of PHBV in Flammable Solvents

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Highlights

- Identification of mixtures of flammable solids and liquids in the biopolymer industry
- Experimental characterization of PHBV – toluene mixture under fire conditions
- Comparison of heat release rate and mass loss rate evolution in time
- Evaluation of the most relevant reactions and physical phenomena

1. Introduction

Several applications within the chemical and process industries deal with multi-phase mixtures (e.g., gas-solid, gas-liquid, and liquid-solid) potentially forming flammable atmospheres in an oxidative environment, with clear implications on the safety and sustainability aspects of the whole process [1]. With specific reference to the solid-liquid mixtures, most of the studies on the subject available in the current literature provide a large emphasis on the characterization of the dynamics of solid particles during the transportation and/or reactive phase for the sake of process intensification and equipment design [2]. The formation of flammable conditions can derive from the co-existence of a flammable solid in an inert/non-flammable liquid, a non-flammable solid in a flammable liquid, or a flammable solid in a flammable liquid. The first case (i.e., flammable solid in inert liquid) can originate a mitigated scenario due to the heat sink action of the liquid compared with the pure solid case [3]. Conversely, the presence of inert porous media soaked by flammable liquids leads to more effective reactions [4], generating a larger amount of heat power as well as abrupt variations in the temperature and pressure of industrial systems. Indeed, the coupled effect of liquid permeation, enhanced heat transfer coefficient between liquid and solid, mass transfer capillarity effects, and micro-scale structures significantly affect the resulting flame properties [5]. Therefore, once dealing with the latter case (namely flammable solid and flammable liquid), a vigorous synergistic effect on the fire behaviour can be also expected. This aspect is particularly relevant given the ongoing energy transition. Indeed, alternative processes within the energy supply chain have introduced innovative combinations of flammable hybrid mixtures [6]. Among the others, toluene–PHBV (Poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) mixtures are conveniently used within the production and refinement processes of this biopolymer [7]. For a comprehensive characterization of the chemical behaviour of liquid-solid mixtures, the evaluation of the mass loss rate has been identified as one of the most relevant parameters [8]. Previous studies have indicated the use of a cone calorimeter as the most convenient option for the direct measure of the mass loss rate (MLR), together with the heat release rate (HRR) and time to flaming of species in a condensed phase [9]. For these reasons, this work discusses newly collected experimental data for the sake of the characterization of hybrid mixtures containing PHBV and toluene by using a cone calorimeter.

2. Methods

In this work, a cone calorimeter as described in dedicated standards, e.g., ISO 5660 [10], was adopted for the experimental characterization of a mixture containing Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) (PHBV) and toluene. A horizontally oriented heater placed at 0.025 m from the sample holder was adopted. Different solid-to-liquid ratios were tested. The influence of an external power supply was investigated by proving a constant radiative heating flux between 7 – 50 kW/m².

3. Results and discussion

Figure 1 reports the collected data in terms of MLR and HRR as a function of time for pure PHBV, Toluene, and 1:1 mixture in mass at 25 kW/m², exclusively. Homologous data were collected at different temperatures, showing similar trends. A gradual decomposition is observed for PHBV, whereas Toluene exhibits distinct rapid combustion peaks indicative of its highly flammable nature. The soaked sample

presents a compelling synergy in both HRR and MLR. The duration of the first peak in HRR is smaller than pure Toluene because of the decrease in liquid initial content. Conversely, the second peak, associated with PHBV is shorter and more intense for the soaked sample than the pure PHBV, revealing that the impregnation process not only amplifies reactivity but also significantly influences the overall ignition of the material. MLR profiles show trends in line with the discussion reported above, suggesting that negligible variations in the exhaust gas composition can be expected, because of the similarity in HRR to MLR ratios, which are related to the generated enthalpy per unit of area.

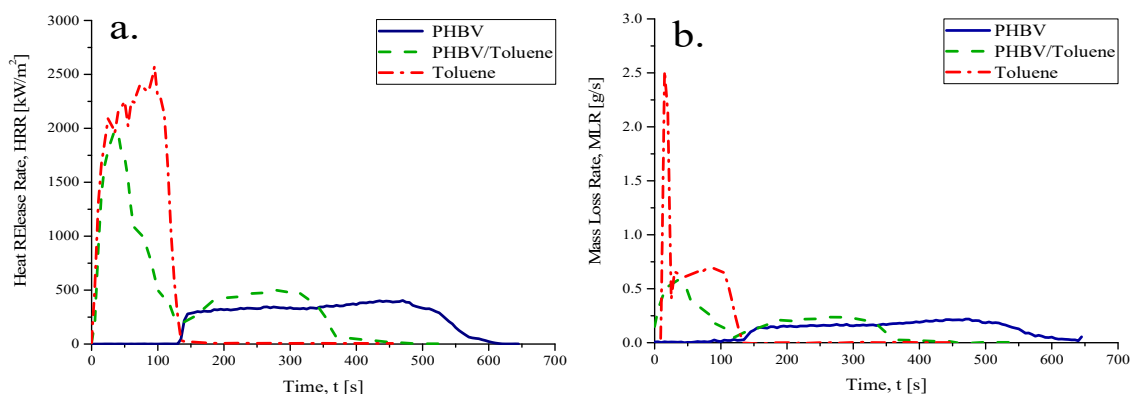


Figure 1. Heat release rate (a.) and Mass loss rate (b.) profiles of PHBV, Toluene and PHBV/Toluene (1:1) at 25 kW/m².

4. Conclusions

This work presents an experimental campaign devoted to the characterization of soaked PHBV in flammable solvents utilizing a cone calorimeter. The collected data elucidate the possible interactions between the investigated species in the view of their coexistence in industrial steps within the supply chain of biopolymers, debottlenecking a robust, optimized, and safe design of more sustainable industrial processes.

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Keywords

Biopolymers; Liquid Solvents; Safety; Cone Calorimeter.