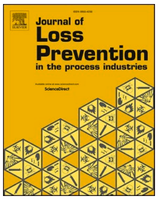
Journal of Loss Prevention in the Process Industries 94 (2025) 105541

Contents lists available at ScienceDirect

Journal of Loss Prevention in the Process Industries

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



Multicriteria approach to assess the fire behaviour of polymers in electrochemical energy storage

Benedetta A. De Liso, Gianmaria Pio, Ernesto Salzano *

Department of Civil, Chemical, Environmental, and Materials Engineering, University of Bologna, 40131, Bologna, Italy

ARTICLE INFO

Keywords:
Key performance indicators
Multicriteria approach
Batteries
Polymer
Calorimetry

ABSTRACT

An innovative and multicriteria procedure based on the experimental characterization of solid materials exposed to fire was developed in this work. The validity and potentialities of this approach were tested for the evaluation of polymeric materials of potential use in electrochemical energy storage systems. To this aim, different experimental techniques, including thermogravimetric analysis, differential scanning calorimetry, and cone calorimetry, were implemented to quantify fundamental-based key performance indicators (KPIs) accounting for environmental (e.g., toxicity), ignitability, and flame characteristics. The developed approach enabled us to thoroughly examine the implications of key variables, including sample thickness, thermal flux, and composition. Considering the analyzed scale, the flexibility in boundary conditions, and the variety of collected data, the use of bench-scale equipment such as the cone calorimeter is recommended for the implementation of the proposed procedure. Based on the combination of collected data an overall ranking in terms of sustainability was obtained, showing that PVC is the least-performing material among the ones investigated. Therefore, the presented methodology can be also intended as a powerful tool for the comparison of final products and materials, paving the way for a more informed decision-making process.

1. Introduction

The introduction of more stringent regulations limiting the emission of pollutants in the atmosphere together with the requirements for materials suitable for a wide range of applications and conditions have promoted the development of new solutions and compounds. In particular, the last decades have been characterized by terrific changes in polymer technologies to comply with the new requirements (Balart et al., 2020). Similarly, the current trend toward the electrification of industrial processes promoted the development of innovative solutions for effective electrochemical energy storage systems involving polymer-based materials as separators (Monisha et al., 2016). Among the others, polyethylene (PE), polypropylene (PP), and polyvinyl chloride (PVC) have been largely used as battery separators (Barbosa and Costa, 2020). Typically, polymeric materials are selected based on their technical characteristics, including maximum performance, limitations, and durability. Alternatively, techno-economic assessment and environmental analysis of the life cycle have been adopted for the evaluation of impacts related to production, utilization, disposal/recycling processes, and transportation (Ramesh and Vinodh, 2020). Considering the complexity of the analyzed systems and the interdisciplinary aspects involved in the occurring phenomena, a protocol supporting the decision-makers needs to account for possible oscillations of parameters, insufficient data, or unsuitable models (Yazdi et al., 2022). For these reasons, the definition and utilization of key performance indicators (KPIs) suitable for early design analysis is highly desirable (Zanobetti et al., 2023b). Indeed, KPIs can offer a quantitative evaluation of the suitability and sustainability of polymers regardless of the application and production route, unifying aspects related to different domains (e.g., economic, societal, technological, and environmental). The implementation of these strategies in the safety domain is mostly limited to the evaluation of the consequences and risks related to a possible accidental release of hazardous substances from an industrial plant or a specific equipment item (Andriani et al., 2024). Conversely, for the case of new technologies and products, KPIs are typically assessed under the assumptions of normal operation conditions and steady-state processes, focusing on the characterization of production processes and mechanical performance (Laurini et al., 2018). Notably, this type of analysis typically excludes considerations related to the fire safety of polymeric materials, although the relevance of safety in the determination of the

---

* Corresponding author.
E-mail address: ernesto.salzano@unibo.it (E. Salzano).

https://doi.org/10.1016/j.jlp.2024.105541
Received 3 October 2024; Received in revised form 10 December 2024; Accepted 28 December 2024

sustainability of technological solutions has been highlighted in the recent literature (Zanobetti et al., 2023a). Hence, the evaluation of safety-related KPIs based on material properties represents a new and desirable perspective on the use of KPIs in material and process industries, as suggested in the literature (Colla et al., 2011; Moncalero et al., 2017). In this sense, a limited availability of experimental data and numerical models suitable for the evaluation of the tendency to ignite, the main features of a flame, and the emission in the case of accidental fires can be observed in the current literature (Kim et al., 2022).

Under this impulse, a fundamental-oriented characterization of material response to external factors (e.g., thermal flux due to fire) is paramount either in terms of generated thermal power or material degradation as a function of the initial composition (Linteris, 2011). From a phenomenological perspective, the American Society for Testing and Materials (ASTM) defines thermal decomposition as a process of extensive chemical species change caused by heat (ASTM International, 2004). In the case of fire, thermal decomposition usually assumes a larger significance than thermal degradation, whereby the chemical decomposition of a solid material generates flammable vapors (Ray and Cooney, 2018). In the case of polymeric materials, the original material itself is essentially involatile because of the large molecular weight. A carbon-carbon bond break is a common activation step to produce smaller molecules that can vaporize (Krieg et al., 2022). Several stages can be identified either in the solid or gaseous phase. In most cases, a solid polymer breaks down into a variety of smaller molecular fragments made up of several different chemical species. Hence, each of the fragments has a different equilibrium vapor pressure (Fujita et al., 2019). The lighter molecular fragments vaporize immediately upon their production, whereas heavier molecules remain in the condensed phase (solid or liquid). These heavier molecules may undergo further decomposition into lighter fragments which are more easily vaporized. Although polymers can in principle break down completely with no solid residue, carbonaceous (char) and/or inorganic residues are largely observed (Matuszewska et al., 2022). Another important issue related to the decomposition of polymeric materials is the formation of toxic species, as demonstrated by the fatalities and serious injuries caused by fires involving polymer materials, mainly due to the content of CO within the smoke released during polymer combustion (Chow and Leung, 2006; Yang et al., 2021). Indeed, although low flammability is typically associated with polymers, the possible production of toxic gases developed during thermal decomposition/combustion plays a significant role in the case of fires, especially in enclosed spaces (Ogabi et al., 2021). Hence, the use of standardized and robust experimental techniques able to evaluate the fire response as well as the possible release of toxic compounds shall be preferred (Anderson et al., 2018).

Traditional small-scale thermal analysis methods, namely differential scanning calorimetry, and thermogravimetry, are extensively used in thermal degradation studies of polymers (Drzeżdżon et al., 2019), (Monteiro et al., 2012). However, these methods typically adopt a limited quantity of materials, posing reasonable questions on the validity of the obtained results on a larger scale. Besides, the typical size of the adopted experimental system promotes the utilization of a granular shape, which can be not representative of the final product or intermediate materials stored in large quantities. For this reason, bench scale tests, e.g., the performance-based cone calorimeter (CC), are recommended to compare and rank materials quantitatively for fire risks (e.g., heat release and time to ignition) and environmental impact (e.g., CO production, smoke production) (De Liso et al., 2024a). A cone calorimeter is a fire test apparatus that continuously measures the sample mass and the composition, temperature, and pressure of the exhaust gas produced during the experiments. To quantify the flammability and flame intensity, the material is exposed to an external radiation heat source. Several studies employing this technique for the characterization of polymeric materials have been mostly focused on the investigation of flame behavior once elevated external heat fluxes are provided to the samples (Patel and Wang, 2016), with a limited number of data on the ignitability and flame characteristics once milder conditions are of concern. The amount of heat released during each test is evaluated based on an online direct measurement of the oxygen consumption in the combustion process, providing relevant information on the severity of the fire (e.g., rate of fire growth) as well as on the ignitability of the material (e.g., time to flaming) (Lyon et al., 2018). The existence of a robust and accurate database of these parameters is a paramount step for advanced numerical simulations (e.g., computational fluid dynamic studies) involving reactive solid systems (Zhu et al., 2024).

Under these premises, the present work reports an innovative procedure combining newly collected experimental data and numerical analysis for the quantification of safety-relevant KPIs of polymeric materials, potentially used in batteries, under fire conditions. The use of KPIs in polymer classification can provide a standardized and reproducible framework, enabling informed material selection for applications where fire safety represents a relevant concern. The proposed approach also includes the evaluation of the effect of size and configuration on macroscopic parameters through a comparison of data collected by different techniques, such as cone calorimeter and classical calorimetry techniques (thermogravimetric analysis, TGA, and differential scanning calorimetry, DSC). Their integration in material testing will allow for a comprehensive understanding of the intrinsic characteristics and behavior of different polymer materials under specific conditions, ultimately enhancing the safety and sustainability of end products for a large set of applications and industrial fields.

2. Methodology

In this work, a methodology for the assessment of the performances of solid carbonaceous materials in the case of indirect exposition to fire conditions (i.e., proximity to an external heat source) was developed and applied for dedicated case studies. To this aim, KPIs representative of flame intensity, flame duration, ignitability, and toxicity aspects were defined and calculated based on newly collected experimental data. Several techniques were considered in this work as possible means of experimental characterization of polymeric materials, such as a cone calorimeter (CC), a thermal gravimetric analysis (TG), and a differential scanning calorimeter analysis (DSC). Different operative conditions were tested experimentally to obtain an in-depth physical characterization of the resulting fire as well as a chemical characterization of the produced exhaust gases, as will be presented in detail during the description of the case study. Specific information on the boundary conditions as well as on the procedures adopted in this work will be reported in dedicated sections in the following.

The collected data were classified and distinguished based on the investigated domains, as follows:

- Flame intensity. Mass Loss Rate (MLR) and Heat release rate (HRR) at the steady state were intended as the main properties associated with the flame intensity, being representative of the amount of material decomposed and the produced power in a given time, respectively. Similarly, the effective heat of combustion (EHC) was included within this domain to account for the chemical composition of the investigated species;
- Flame duration. Duration of the steady-state phase based on the measured flame intensity (t_{ss}) and the total heat released (THR) were assumed as KPIs for the flame duration.
- Ignitability. Time to autoignition (t_{au}) was used for the evaluation of the ignitability aspects, being representative of the minimum time required to obtain a stable flame. Besides, the efficiency of combustion (η), as defined in Eq. (1), was included in this domain since the provided definition of efficiency of combustion allows for the identification of the conditions leading to the transition from smoldering to flaming. More specifically, $\eta = 90$ % was assumed as the

threshold value for the transition between these regimes, in agreement with Ferek et al. (1998) (Ferek et al., 1998).

$$\eta = \frac{(C)_{CO_2}}{(C)_{CO} + (C)_{CO_2} + (C)_{HC} + (C)_{PM}} \tag{1}$$

where (C) represents the amount of carbon in mass due to the species reported as subscript (HC = unburned hydrocarbons, PM = particulate matter).

- Toxicity. Smoke production rate (SPR) and carbon monoxide production were considered for the environmental domain, because of the potential toxicity for humans and the environment. Moreover, these parameters allow for a robust comparison of the data collected with well-spread techniques and setups, regardless of the initial composition of the investigated compounds. However, they can be integrated with more specific parameters (e.g., SOx formation) if applicable and relevant to the analyzed case and materials;

For the sake of consistency, the use of data deriving from CC for the evaluation of the defined KPIs was prioritized because of the possibility of accurately capturing macroscopic physical phenomena as well as heat/mass transfer limitations, which is limited in small-scale systems. This approach guarantees an evaluation closer to the industrial-relevant cases. Nevertheless, the measurements deriving from TG and DSC were considered as preliminary characterization as well as for the comparison of overall reactivity (e.g., in terms of MLR) and crucial decomposition temperatures at different scales. By establishing generic parameters (*P*), it was possible to evaluate and rank the performance of different polymeric materials based on targeted attributes. To ensure a consistent comparison among properties having different units and scales, an internal normalization was performed. More specifically, the best-case values between the investigated materials were identified for each

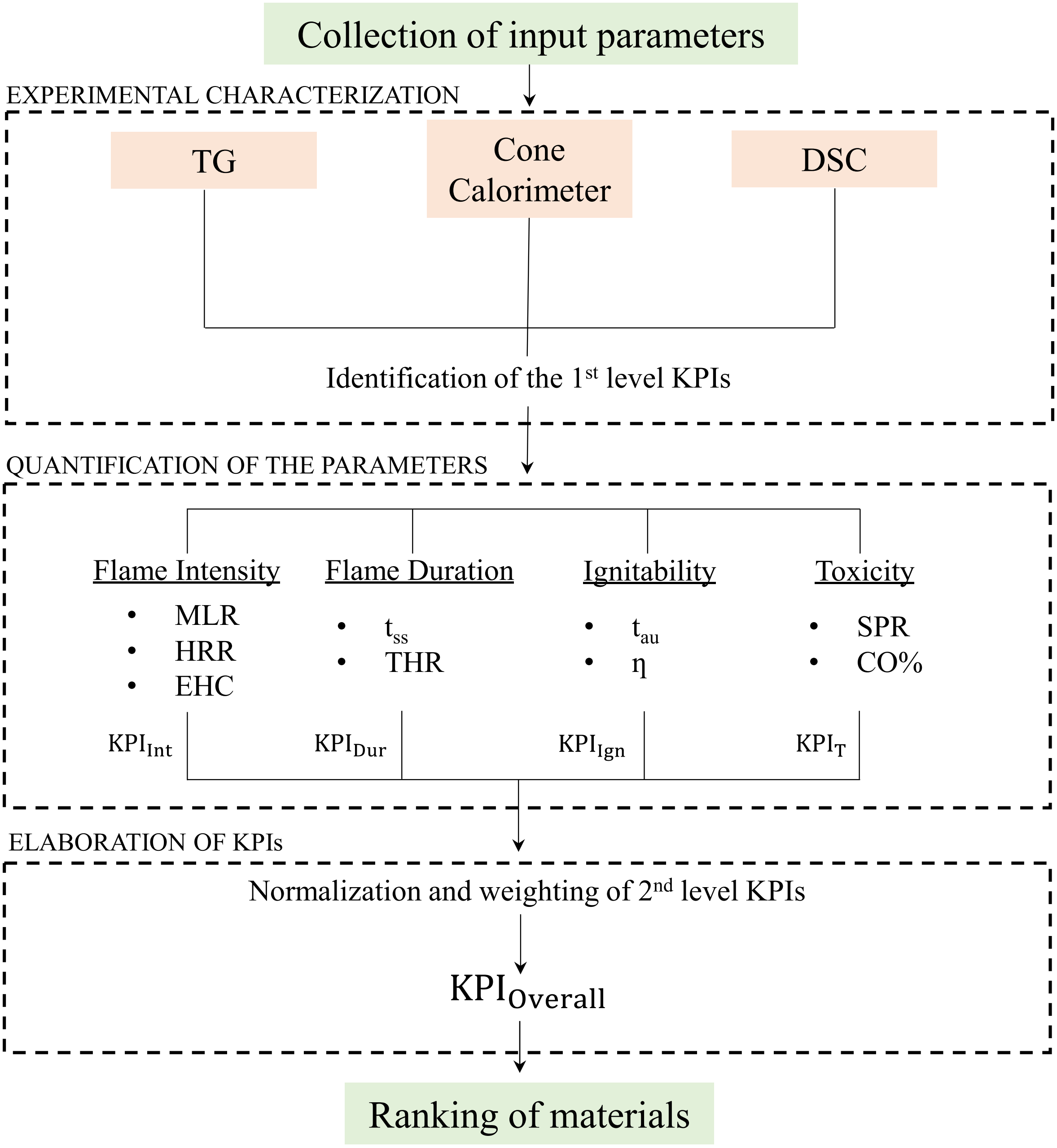


Fig. 1. Schematic representation of the methodology developed in the present work.

KPIs and employed for the sake of internal normalization. This step was designed to guarantee that KPIs fall within the range from 0 to 1 an increase in each normalized KPI corresponds to better material performance, meaning that the maximum value equal to 1 represents the best-case condition. Afterward, the second-level KPIs were defined by summing the normalized parameters included in the same domain with the assumption of equal weighting to produce a specific KPI for each domain. Eventually, a third level KPI ($KPI_{overall}$) was defined taking into account all domains through specific weighting factors (ω_i). The whole procedure can be summarized in Equation (2).

$$\mathrm{KPI}_{\mathrm{overall}} = \sum_{i}^{n} \omega_i \bullet KPI_i = \sum_{i}^{n} \omega_i \bullet \left(\sum_{j}^{m} \frac{\left(\frac{P_{b,i}}{P_j}\right)^a}{m} \right) \tag{2}$$

where n and m are the number of domains considered and the number of parameters (P) considered for each domain, a is equal to -1 if an increase in the parameter P implies better performances and is equal to 1 if a decrease in the parameter P implies better performances, the subscript i, j, and b stand for the generic domain, the index within the i-th domain, and the best case, respectively. Therefore, the overall performances of the investigated materials can be assessed and compared by ranking them through the obtained $\mathrm{KPI}_{\mathrm{Overall}}$. More specifically, the higher the value for $\mathrm{KPI}_{\mathrm{Overall}}$, the better the ranking.

The current literature proposes a set of possible weighting factors for the evaluation of the overall KPI (Collins et al., 2016), which can be related to trends in policy at company/corporate, national, and international levels as well as the type of decision-makers involved in the process. This aspect includes a possible source of uncertainties together with a case-oriented strategy. Therefore, the hypothesis of equal weighting was implemented in this work, meaning that ω_i was assumed as 0.25 per each domain. A schematic representation of the adopted method is shown in Fig. 1.

3. Case study

3.1. Investigated materials

The validity and potentialities of the proposed methodology were tested for polymeric materials of potential interest for the realization of energy storage systems, showing safety concerns and requiring evaluations on the overall sustainability (Chen et al., 2023). In this sense, a theoretical-based screening was conducted to populate a list of representative polymeric materials to carry out a classification based on their flammability properties and fire. The materials selected to conduct this study are respectively market grade Low-Density Polyethylene (LDPE), High-Density Polyethylene (HDPE), Polyvinyl Chloride (PVC), and Polypropylene (PP). Samples of LDPE, HDPE, PP, and PVC were collected following the Society of the Plastics Industry (SPI) (SPI Plastics Engineering Handbook of the Society of the Plastics IndustryInc., 1991) recycling standards, where each material is identified by a specific number, ensuring its proper classification in the recycling system. More specifically, the RIC 4 LDPE, RIC 2 HDPE, RIC 3 PVC, and RIC 5 PP were analyzed in this work. A single production batch was considered per investigated polymer to reduce the effects of a possible variation in the initial composition on the measured parameters. The selected materials were subjected to an initial characterization employing small-scale calorimetric techniques, followed by subsequent cone calorimetry tests under diverse experimental conditions.

3.2. Experimental systems

Thermal gravimetric analysis (TGA) was performed by using a TA Instruments Q500 (Fig. 2, a). Different heating rates were applied between 10 and 40 K/min. The maximum temperature was set to 873 K according to preliminary evaluations and data from the current literature (Makhlouf et al., 2017). Tests were conducted in a nitrogen environment with sample weights ranging from 20 to 50 mg. The differential scanning calorimetric (DSC) tests were carried out using a TA Instrument Q2000 (Fig. 2, b), working in a dynamic nitrogen atmosphere. A maximum temperature of 573 K was considered. Sample weights ranged from 30 to 50 mg.

Cone calorimeter tests were carried out following the standard ASTM E 1354/ISO 5660 (Marsh and Gann, 2013), by using the iCone + instrument of Fire Testing Technologies L.t.d, UK. A schematic representation of the experimental apparatus is reported in Fig. 3, highlighting the sampling and analysis sections of the instrument described above.

The specimen was conditioned at a temperature of 296 K and 50% humidity. It was mounted on a load cell which records the mass loss rate during combustion. Combustion gases are then collected in an exhaust hood and accompanying duct to characterize smoke production and measure temperature and pressure. The instrument features an IR analyzer for CO and CO_2, and a paramagnetic analyzer for O_2, which was suitable for the aim of the study due to the organic composition of the materials under investigation.

Smoke production is quantified based on the attenuation of a laser beam placed in the exhaust duct, whereas the temperature is measured by a series of thermocouples placed in the exhaust gas duct. Pressure is monitored by sensors preceding and following an orifice plate. The calculation of the heat release rate is performed by the instrument

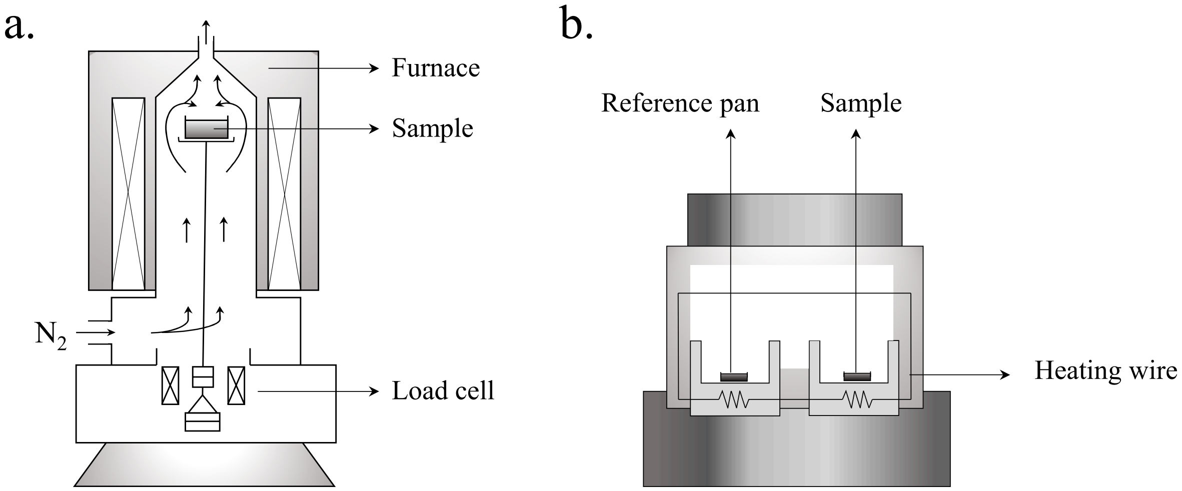


Fig. 2. Schematic representation of the Thermogravimetric analysis set-up (a) and the Differential Scanning Calorimetry equipment (b) used in this work.

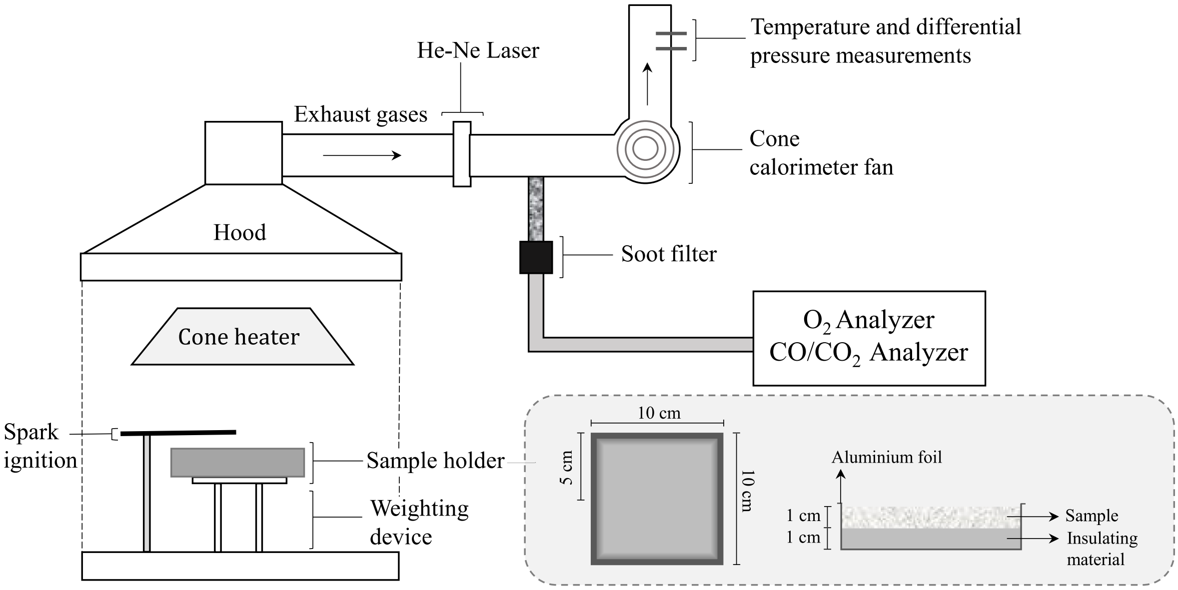


Fig. 3. Schematic representation of the experimental system used for the cone calorimetry.

through the C-factor, which represents a parameter determined through preliminary calibrations based on a well-defined methane flame, and the oxygen concentration in the combustion products. According to ASTM E1354 (2023) and ISO 5660 (2019), the equations used to calculate the C-factor and heat release rate are given below (Eq. (3), Eq. (4)).

$$C = \frac{\dot{q}_b}{\frac{\Delta h_c}{r_0} \bullet \frac{PM_{O_2}}{PM_{Air}}} \bullet \sqrt{\frac{T_e}{T}} \bullet \left(\frac{1.105 - 1.5\,X_{O_2}}{X^0_{O_2} - X_{O_2}} \right) \tag{3}$$

$$\dot{q}(t) = \left(\frac{\Delta h_c}{r_0} \right) \left(\frac{PM_{O_2}}{PM_{Air}} \right) C \sqrt{\frac{\Delta P}{T_e}} \bullet \frac{X^0_{O_2} - X_{O_2}}{1.105 - 1.5\,X_{O_2}} \tag{4}$$

where $\dot{q}(t)$ is the heat release rate in kW; $\Delta h_c/r_0$ is the ratio of the enthalpy of combustion of methane to stoichiometric oxygen assumed as 12.54 kJ/kg in this work; T_e is the absolute temperature of the gas in K; PM_{O2}/PM_{Air} is the molecular weight fraction of oxygen and air; $X^0_{O_2}$ is the average of the oxygen analyzer output measured during calibrations; X_{O_2} is the oxygen fraction detected during the tests; ΔP is the pressure drop at the orifice plate. Additional information on the experimental procedure adopted in this work can be found elsewhere (De Liso et al., 2024b).

The sample was placed under a cone-shaped radiant heater. Tests were carried out at various thermal fluxes (15, 25, 35, and 50 kW/m^2) and different sample thicknesses (0.02–0.01 m). Considering the possible variations in some boundary conditions (e.g., initial composition and sample thickness), each test was repeated three times and the average values were considered for subsequent analyses, reducing the impacts of experimental uncertainties on the resulting ranking. Comparable initial masses were studied to guarantee robust and consistent initial conditions. In addition, it is worth noting that most of the defined KPIs measured by the CC are weakly affected by a possible variation of the abovementioned parameters, which mostly influence the duration of the test and the response time. The robustness of the latter values was further enhanced through the comparison of the measured temperatures of the samples along the CC tests at the same boundary conditions and from the crucial temperatures collected by the small-scale tests. All samples were examined in a horizontal position with a surface area of 0.01 m^2. Each sample was exposed to an ignition source at regular intervals of 60 s until a stable flame was observed.

4. Results and discussion

Considering the differences in techniques and approaches adopted in this work, the structure of this section has been developed to distinguish the experimental characterization in the classical calorimetric approach and the bench scale experiments by the resulting evaluation of different levels of KPIs.

4.1. Experimental characterization

Fig. 4 presents the profiles obtained from TG analyses of an HDPE reference sample at various heating rates (left) and at a given heating rate for the investigated materials. For the sake of conciseness, the full set of data referring to different heating rates and materials can be retrieved in the supplementary material.

As can be seen at 10 K/min, HDPE exhibits a gradual reduction in mass as the temperature increases, showcasing the evolution of thermal transitions and potential degradation mechanisms. At the faster rates of 25 K/min and 40 K/min, the mass reduction occurs more rapidly, underlining a sharper thermal decomposition trend. This intricate interplay of mass change and temperature unveils the response of materials to escalating heat, with the supplementary material offering a comprehensive overview of these responses across diverse heating rates. The heating rate of 10 K/min will be considered as a reference point from now on since it represents a trade-off between the sensitivity and accuracy of the collected data. This rate has been used as a baseline for comparison to better understand differences in the thermal profiles of other materials. PP shows a rapid and continuous mass loss, indicating unique thermal degradation kinetics characterized by a single predominant process (Marcilla et al., 2003). Both HDPE and LDPE exhibit similar degradation patterns with gradual mass reduction (Awad et al., 2019; Dubdub and Al-Yaari, 2020). However, LDPE degrades slightly faster due to its more amorphous nature compared to the less crystalline HDPE. Polyvinyl Chloride (PVC) experiences two major weight loss steps: the first from the decomposition of hydrogen chloride (HCl) due to thermal instability, and the second at higher temperatures from the thermal decomposition of the polymer chain (Wu et al., 2024). These findings align with the previous characterizations of the investigated materials (Dubdub and Al-Yaari, 2020; Wang et al., 2018).

Starting from the collected data, Table 1 presents an insightful overview of the maximum degradation temperatures (T_d) for various polymer materials, along with corresponding temperatures at which 5%,

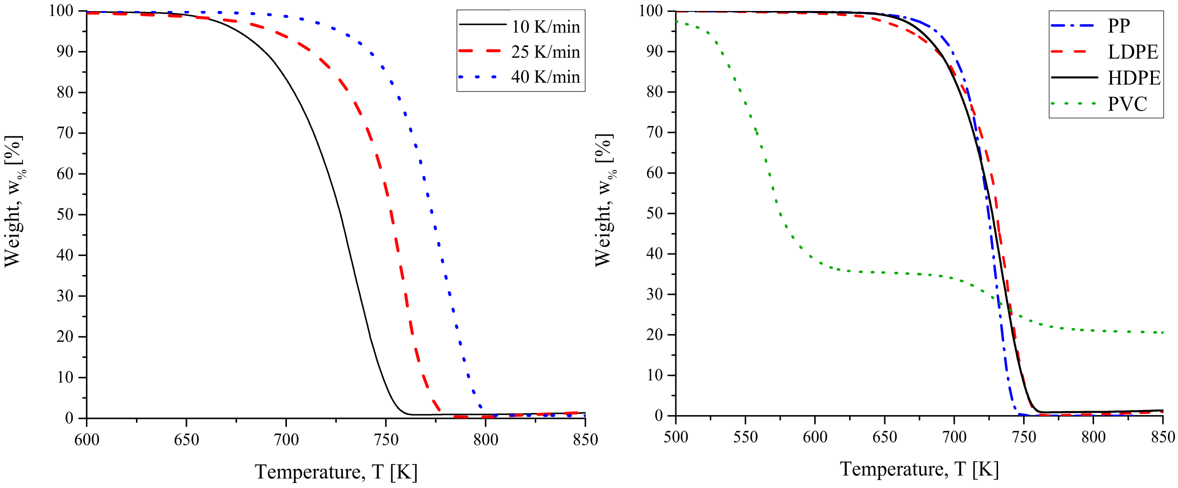


Fig. 4. TGA results for HDPE in nitrogen environment under different heating rate conditions: 10, 25, and 40 K/min (left) and for the investigated polymers at 10 K/min (right).

Table 1

Maximum temperature of degradation (T_d), temperature at which 5% mass is lost ($T_{5\%}$), temperature at which 10% mass is lost ($T_{10\%}$), and temperature at which 50% mass is lost ($T_{50\%}$) at different heating rates (HR) of different polymers.

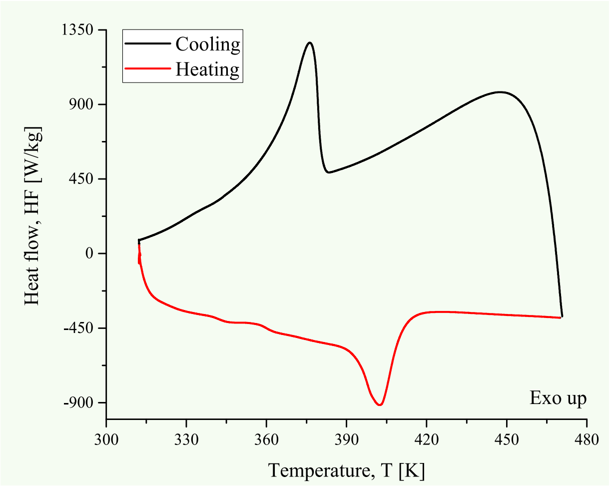
Material	HR [K/min]	T_d [K]	$T_{5\%}$ [K]	$T_{10\%}$ [K]	$T_{50\%}$ [K]
PP	10	730	686	698	724
	25	752	709	721	749
	40	762	676	698	747
LDPE	10	733	667	687	730
	25	760	695	715	754
	40	776	714	732	768
HDPE	10	732	675	689	727
	25	758	693	712	752
	40	777	726	741	773
PVC	10	523	521	532	574
	25	543	542	553	601
	40	555	552	563	614

10%, and 50% of weight loss occur. The data showcases also the influence of heating rates on the thermal behavior of the polymers.

PP encompassing heating rates of 10 K/min, 25 K/min, and 40 K/min, reveals a T_d range spanning 730 K–777 K. Notably, higher heating rates consistently yield higher degradation temperatures, highlighting the impact of chemical kinetics on the process. In comparison, Low-density polyethylene (LDPE) and High-Density Polyethylene (HDPE) demonstrate similar thermal degradation tendencies within temperature ranges of 733 K–776 K and 732 K–777 K respectively. The chemical structure of polypropylene imparts greater heat resistance relative to polyethylene, which, due to its linear structure and lack of polar groups, exhibits heightened sensitivity to elevated temperatures (Zhang et al., 2006). Additionally, the thermal behavior of PVC is significantly influenced by its chlorine content and C-Cl covalent bonds, resulting in a multi-stage decomposition process characterized by the release of HCl at lower temperatures, followed by carbonization, ultimately leaving behind a carbonaceous residue (Altenhofen Da Silva et al., 2011).

The DSC profiles of HDPE samples are presented in Fig. 5, highlighting key parameters for all tested materials. The temperatures and enthalpies for fusion and crystallization transitions are illustrated. The melting temperature of 402 K falls within the typical range of 393 K–413 K (Cai et al., 2018; Liu et al., 2002). The 26 K difference between melting and crystallization temperatures suggests variations in crystallization kinetics or nucleation complexities. It is worth noting that the measured ΔH_m of 24 kJ/kg while this value is not entirely atypical, does sit at the lower end of the spectrum when compared to the generally anticipated range for HDPE.

Similarly, for the cone calorimeter tests, HDPE was used as a



Material	T_m [K]	T_c [K]	ΔH_m [kJ/kg]	ΔH_c [kJ/kg]
PP	450	386	63	98
LDPE	400	368	35	100
HDPE	402	376	24	75
PVC	548	369	10	13

Fig. 5. DSC results for HDPE in a nitrogen environment at 10 K/min are shown on the left, while on the right the results which include the enthalpies and temperatures of fusion and crystallization for HDPE and the other materials under investigation.

reference to establish the optimal operating conditions to be applied for all other materials under testing and their effect. The provided data (Fig. 6) represents the heat release rate (HRR) profiles of HDPE for samples with different thicknesses (0.02 m and 0.01 m) under a 35 kW/m^2 external heat flux.

In the 10 mm thick sample, the HRR starts relatively low, increases gradually, and then shows a significant peak around 400 s which indicates the more intense combustion phase. Afterward, the HRR generally decreases as the combustion process stabilizes. In the 20 mm thick sample, a similar trend is observed. The HRR starts at a lower level, experiences a moderate increase, and then shows a peak around 800 s. However, the peak in this case appears to be less pronounced than in the thinner case. The larger difference in HRR between the two samples can be attributed to the different thermal capacity and thermal conductivity of samples with different thicknesses (An et al., 2015). More specifically, a thicker sample will be characterized by a longer time to reach a sufficiently high temperature to initiate the combustion process because of the thermal penetration (Torero, 2016). Based on the obtained results, the operational condition of 0.01 m thickness was selected as representative due to its capacity to offer insights into material behavior and its heightened sensitivity to subtle variations. Thinner samples, such as those at 0.01 m thickness, provide a closer approximation of how materials perform in practical applications, thus enhancing the relevance and applicability of the testing outcomes.

The heat release rate profiles of the HDPE under different external fluxes (left) and for different materials at an external heat flux of 35 kW/m^2 (right) were reported at this stage in Fig. 7.

As the thermal flux was increased, a distinctive trend became apparent, a shift from longer ignition times and lower HRR values to shorter ignition times and higher HRR values. Once the analyzed sample is exposed to an external thermal radiation of 15 kW/m^2, negligible HRRs are recorded for the whole length of the experiment. This observation implies that a critical flux larger than 15 kW/m^2 can be expected for HDPE, following the definition provided in the current literature (Tahmid Islam et al., 2023). This statement is supported by a numerical calculation based on the definition of critical heat flux (Rantuch et al., 2021), i.e., employing the ignition time at higher external fluxes to obtain by extrapolation a critical flux q_{cr}. Indeed, under the investigated conditions, an external heat flux of 16 kW/m^2 is required to have an infinite time necessary for initiation. This observation is in line with the crucial temperatures collected in a small-scale setup and previously reported in Table 1. Indeed, an external flux of 15 kW/m^2 corresponds to a temperature of ~750 K, thus insufficient to completely decompose the investigated materials. Nevertheless, based on the collected data on the production of CO and CO$_2$ an average combustion efficiency of 0.42 can be observed under these conditions, meaning that the smoldering phenomena cannot be neglected even though a transition to flaming conditions is not expected. Indeed, this aspect is particularly relevant for safety aspects because low-temperature reactions are still occurring, leading to the formation of pollutants including CO, with subsequent detrimental effects on indoor air quality, as well as a possible promotion of fire spread in the case of flammable materials in the surrounding of smoldering fires. To properly address the hazard introduced by the presence of smoldering fire, a case-specific study is recommended to define the required boundary conditions. For these reasons, a flaming regime will be considered for the comparison of the polymeric materials. Therefore, 35 kW/m^2 was chosen as a representative condition for this class of materials. Regardless of the investigated material, a common behavior can be observed. Indeed, each curve is composed of a pre-heating region, followed by the achievement of a peak value or (in some cases) a pseudo-steady state condition, further resulting in a decay phase and ultimately the extinction of fire. Based on this common structure, different key performance indicators representative of the ignition conditions and the magnitude of consequences can be identified.

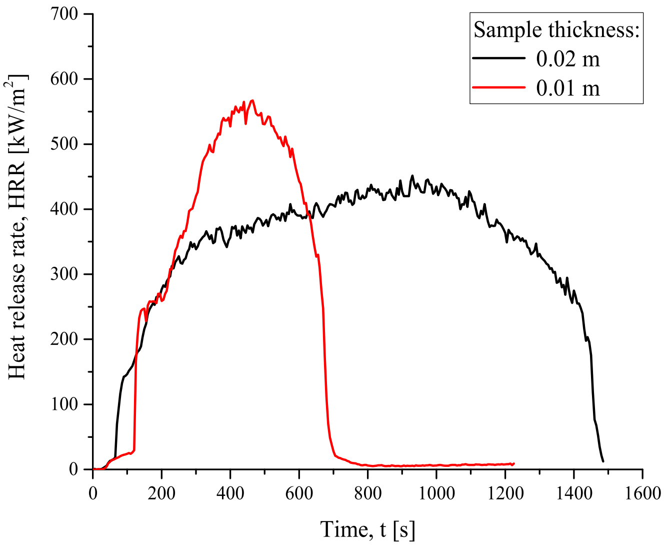


Fig. 6. Heat release rate of HDPE exposed to 35 kW/m^2 for different thicknesses.

4.2. Identification and quantification of key parameters

Based on the experimental data collected in this work via different techniques, optimized and representative boundary conditions for the evaluation of key parameters can be identified. Consequently, the parameters involved in the calculation of the defined KPIs were obtained for all the investigated species (Table 2).

Notable findings include the pronounced peak of heat release rate (pHRR) characteristic of LDPE, indicative of its heightened flammability. PVC presents a dichotomy of characteristics, with its apparent flame-retardant attributes elucidated by a reduced THR, aligned against an elevated total smoke production (TSP) value, thereby prompting consideration of potential smoke-related consequences. Furthermore, it is possible to observe a direct correlation between the melting temperature obtained from classical calorimetry analyses and the time of the peak of HRR. More specifically, the higher the melting temperature of the material, the greater the time to the peak, indicating that pyrolysis is the limiting step for the combustion process of a polymer. It is important to note that these parameters derive from cone calorimeter tests because this approach was identified as the most suitable approach for predicting the real-scale fire behavior of polymeric materials. Nevertheless, the abundance of experimental data on a small scale (i.e., collected by TGA and DSC) available in the current literature cannot be neglected. In this sense, the development of new correlations to extrapolate the most relevant parameters is encouraged.

The nature of ignition responses observed within the experimental campaign conducted in this work under different thermal flux conditions enabled the derivation of a comprehensive graph (Fig. 8) which illustrates the ignition time relative to the thermal flux, adopting a threshold of 120 s. Indeed, 120 s can be intended as the minimum evacuation time considering the perception, preparation, and evacuation times reported in the current literature (Ammar, 2019). Importantly, this graphical representation facilitated the classification of distinct zones. These delineated zones encompass three distinct regions: a non-combustible range even in the presence of an external ignition source (green zone), an inflammable zone susceptible to external ignition (orange zone), and a third region that becomes inflammable through auto-ignition processes (red zone). This methodology, thus, provides a robust framework for an in-depth understanding of the role of external conditions in the determination of ignition behavior and ignition modes.

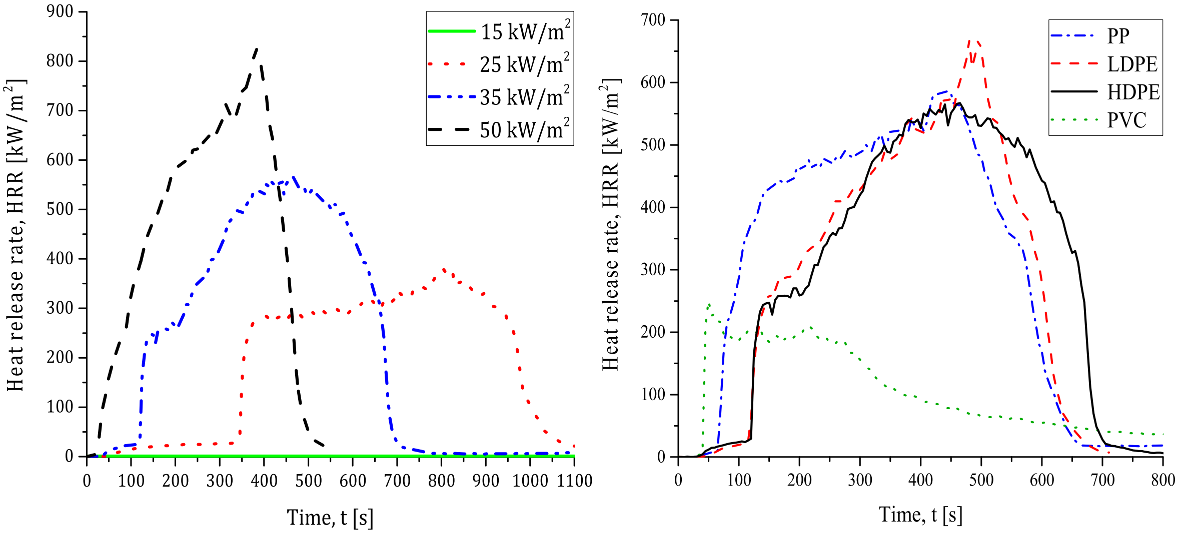


Fig. 7. Heat release rate of HDPE exposed to different external fluxes (left) and PVC, PP, LDPE, and HDPE at 35 kW/m^2 (right).

Table 2
Key parameters experimentally collected in this work for the investigated materials.

	LDPE	HDPE	PP	PVC
pHRR [kW/m^2]	587	669	567	251
mMLR [g/s]	0.17	0.15	0.16	0.15
mHRR [kW/m^2]	652	548	571	193
EHC [MJ/kg]	38.5	36.3	35.9	13.0
t_{ss} [s]	20	110	45	190
THR [MJ/m^2]	224	215	212	93
tp-HRR [s]	435	480	465	50
t_{au} [s]	70	115	120	40
SPR [m^2/s]	0.07	0.09	0.07	0.20
CO [%]	0.03	0.03	0.02	0.06
TSP [m^2]	28.33	22.53	24.48	46.27

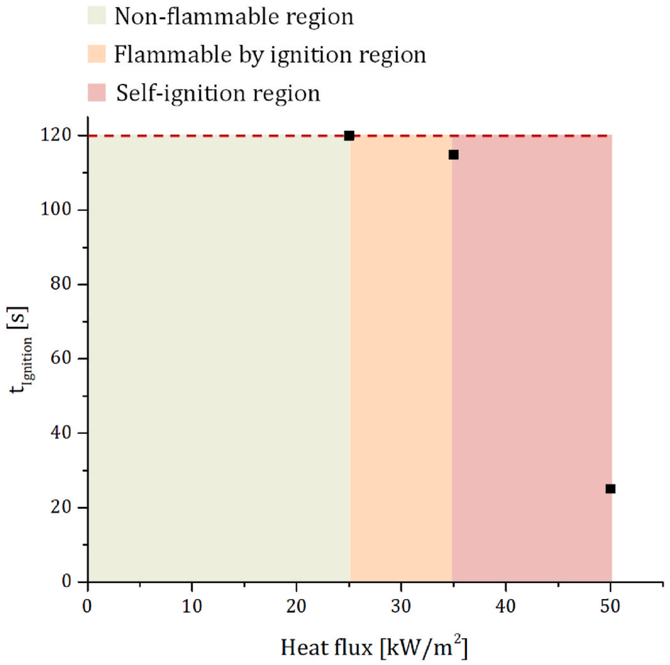


Fig. 8. Ignition time versus heat fluxes and the respective flammability zones identified in this work for different exposure times.

4.3. Normalization and aggregation of KPIs

Utilizing the data collected in this work, second-level KPIs were calculated (Fig. 9) based on the parameters reported in Table 3, which were adopted for the internal normalization step.

Based on the defined KPIs and obtained results, PVC exhibited the lowest flame intensity, which can be attributed to the presence of chlorine atoms in its polymer structure acting as flame retardants. Indeed, chlorine atoms inhibit the combustion process by releasing hydrogen chloride, which probably interferes with flame propagation. Conversely, LDPE, PP, and HDPE demonstrated significantly higher flame intensities, attributable to their hydrocarbon-rich structures that facilitate rapid and exothermic combustion reactions. Regarding flame duration, LDPE exhibited the shortest steady-state flame duration, likely due to its amorphous polymer structure, which allows for faster thermal decomposition and heat release. Conversely, HDPE shows lower values in terms of flame duration, in agreement with this hypothesis. PVC exhibited a longer flame duration, consistent with its flame-retardant properties that retard the combustion process. In terms of ignitability, LDPE requires the longest time to reach autoignition, which may be due to its crystallinity and relatively high melting point, delaying the onset of thermal degradation. On the other hand, PVC ignited more rapidly, likely due to the presence of additives that reduce the ignition temperature. In terms of toxicity, PVC produced the highest levels of smoke and carbon monoxide due to the release of hydrochloric acid and other toxic compounds from chlorine-based additives. In contrast, LDPE and HDPE emitted significantly less smoke and carbon monoxide, as their combustion primarily yields carbon dioxide and water vapor with fewer toxic by-products. This derives from the more complete combustion of LDPE and HDPE and the absence of chlorine, which reduces the formation of hazardous fumes. Through the aggregation of KPIs from each domain, an overall KPI value was derived as shown in Fig. 10.

Considering that larger areas imply higher performances in the corresponding domain, PVC can be identified as the least-performing material among those considered on a global scale. The poor ranking reported for PVC is due to the limited areas of ignitability and toxicity

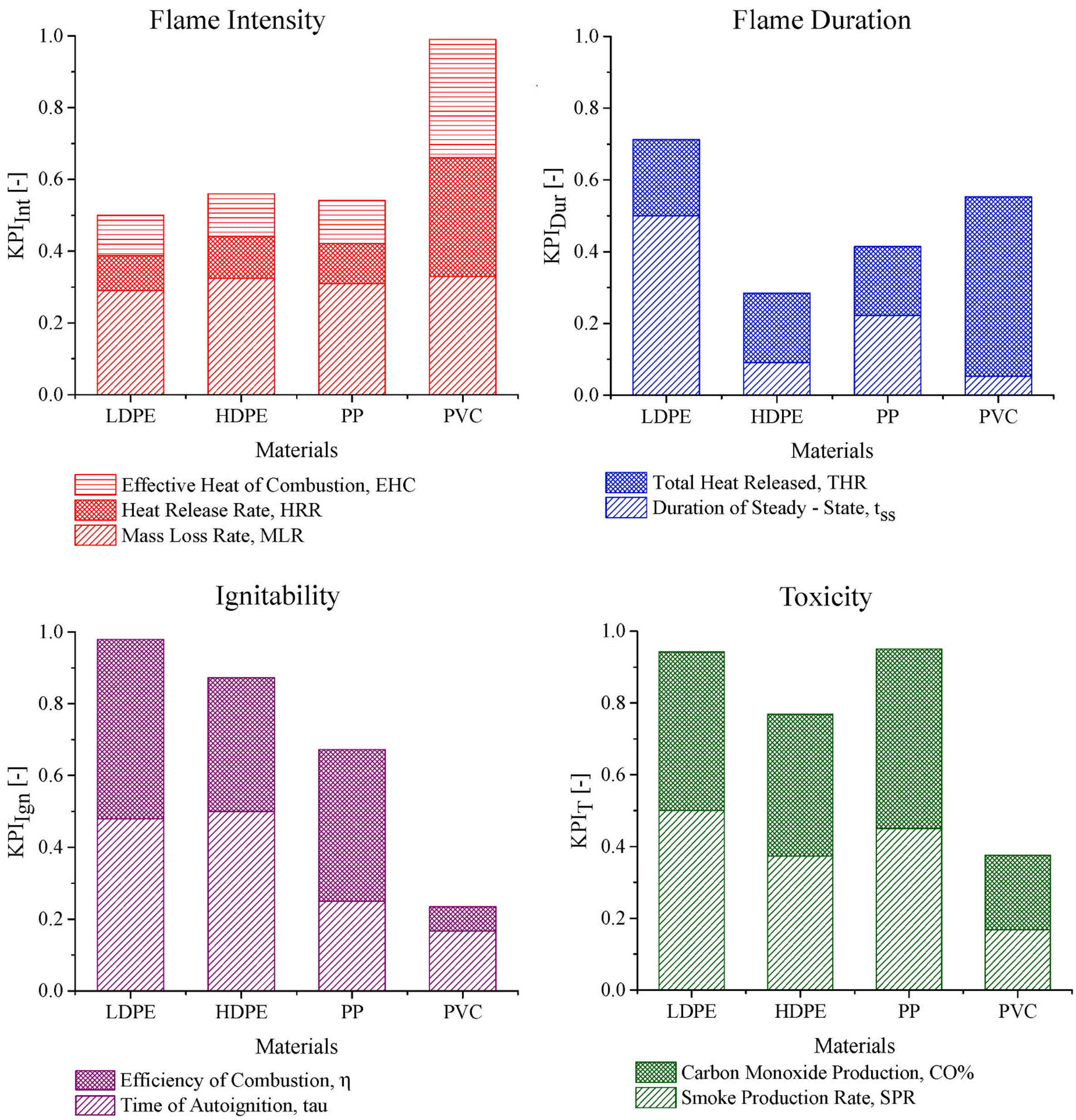


Fig. 9. Ranking of polymeric materials based on flame duration, flame intensity, ignitability, and toxicity KPIs.

Table 3
Normalization parameters and corresponding material considered in this work for the calculation of KPIs.

Domain	Parameter	Normalization	Material
Flame Intensity	HRR	193	PVC
	MLR	0.15	PVC
	EHC	13.0	PVC
Flame Duration	t_{ss}	20	LDPE
	THR	92.6	PVC
Ignitability	η	0.02	LDPE
	t_{au}	120	HDPE
Toxicity	SPR	0.07	LDPE
	CO%	0.02	PP

domains. This aspect is particularly relevant once the risk evaluation is of concern being the ignitability indicators linked to the likelihood of occurrence of fires and degradative phenomena and the toxicity typically associated with larger consequences than the one related to fire scenarios. Similarly, it is possible to observe that the performances of HDPE are mostly limited by poor values in flame duration. Although similar indexes can be observed for the other materials investigated in this work, based on the collected data, it is possible to rank them from the best to worst performing as follows: LDPE, PP, HDPE, and PVC.

Although the presented conclusions are based on small-scale and bench-scale experiments, it is worth mentioning that the proposed methodology is also applicable in the case of data deriving from large-scale experiments. Quite obviously, the implementation of this strategy implies a significant increase in the costs associated with the experimental campaign, thus it should not be recommended for early-stage design or preliminary screening, in contrast with small and bench scales. The consistency between the information gathered by the different systems adopted in this work indicates that a limited impact of the scale on the defined KPIs can be expected. Nevertheless, the possible source of uncertainties associated with the extrapolation of data from different sources/scales can be assessed through expert judgment as well as dedicated numerical methods (Zarei et al., 2024). In this sense, the use of a bench-scale setup appears to be a trade-off between accuracy, representativeness, and costs of the experimental campaign needed for

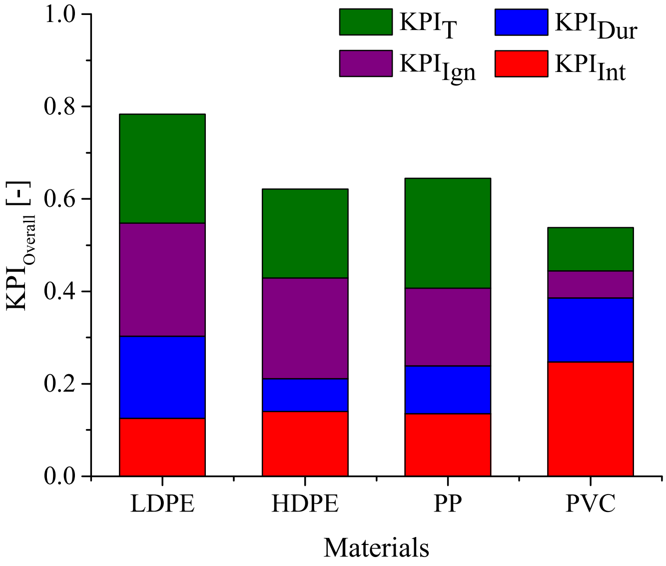


Fig. 10. Ranking of polymeric materials based on overall KPI.

the evaluation of KPIs. In addition, the cone calorimeter offers the possibility to adopt a standardized protocol and real-world geometries of structures, allowing for a robust comparison of data deriving from different studies as well as a good representation of industrial applications.

5. Conclusion

A tailor-made procedure was developed to assess the sustainability of solid materials suitable for energy storage systems in the case of fire, based on the utilization of dedicated experimental data. The effects of the size of the sample and the boundary conditions on the macroscopic properties were evaluated, combining different techniques such as thermogravimetric analysis, differential calorimetric analysis, and cone calorimetry. Sample thickness has emerged as a critical parameter, affecting the rate of thermal conduction and heat accumulation dynamics. Thermal flux, on the other hand, has shown a significant impact on the distribution and dissipation of heat within the samples. Composition has surfaced as a determining factor in the ability of a material to absorb, reflect, or retain heat. Based on collected and analyzed data, specific Key Performance Indicators (KPIs) were defined for each area of interest, accounting for flame intensity, flame duration, ignitability, and toxicity. An internal normalization of the obtained values followed by an aggregation step allowed for the production of a ranking based on global KPIs. The performed analysis shows that the combination of different aspects in partial contraposition as well as the complexity of the analyzed systems can lead to a trade-off condition. Hence, simplified tools and integrated approaches, such as the one presented in this work, can represent a powerful feature for objective, accurate, and standardized evaluations, facilitating comparisons and enabling better-informed decisions in material selection and development. Indeed, considering the posed hypothesis, the developed procedure can be implemented for the evaluation of the sustainability of materials fulfilling the same need as well as for the comparison of different production strategies or additives (e.g., flame retardant) to the same initial material.

CRediT authorship contribution statement

Benedetta A. De Liso: Writing – original draft, Investigation, Data curation. **Gianmaria Pio:** Writing – review & editing, Supervision, Methodology, Conceptualization. **Ernesto Salzano:** Writing – review & editing, Supervision, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jlp.2024.105541.

Data availability

Data will be made available on request.

References

Altenhofen Da Silva, M., Adeodato Vieira, M.G., Gomes Maumoto, A.C., Beppu, M.M., 2011. Polyvinylchloride (PVC) and natural rubber films plasticized with a natural polymeric plasticizer obtained through polyesterification of rice fatty acid. Polym. Test. 30, 478–484. https://doi.org/10.1016/j.polymertesting.2011.03.008.

Ammar, A.M., 2019. Fire Safety: Minimum Safe Distance.

An, W., Jiang, L., Sun, J., Liew, K.M., 2015. Correlation analysis of sample thickness, heat flux, and cone calorimetry test data of polystyrene foam. J. Therm. Anal. Calorim. 119, 229–238. https://doi.org/10.1007/s10973-014-4165-9.

Anderson, J., Boström, L., Jansson McNamee, R., Milovanović, B., 2018. Modeling of fire exposure in facade fire testing. Fire Mater. 42, 475–483. https://doi.org/10.1002/fam.2485.

Andriani, G., De Liso, B.A., Pio, G., Salzano, E., 2024. Design of sustainable reactor based on key performance indicators. Chem. Eng. Sci. 285, 119591. https://doi.org/10.1016/j.ces.2023.119591.

ASTM E1354, 2023. ASTM E1354-23 - Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter.

ASTM International, 2004. ASTM E176-15a Standard Terminology of Fire Standards.

Awad, A.H., Aly Abd El-Wahab, A., El-Gamsy, R., Abdel-latif, M.H., 2019. A study of some thermal and mechanical properties of HDPE blend with marble and granite dust. Ain Shams Eng. J. 10, 353–358. https://doi.org/10.1016/j.asej.2018.08.005.

Balart, R., Montanes, N., Dominici, F., Boronat, T., Torres-Giner, S., 2020. Environmentally friendly polymers and polymer composites. Materials 13, 1–6. https://doi.org/10.3390/ma13214892.

Barbosa, J.C., Costa, C.M., 2020. Polymer-Based Separators for Lithium-Ion Batteries.

Cai, Z., Dai, H., Fu, X., 2018. Investigation on the hot melting temperature field simulation of HDPE water supply pipeline in gymnasium pool. Results Phys. 9, 1050–1056. https://doi.org/10.1016/j.rinp.2018.04.019.

Chen, K., Bao, Q., Chen, G., Wu, S., Liu, Y., Wang, Q., 2023. Synergistic flame retardant linear low-density polyethylene based on piperazine pyrophosphate and melamine cyanurate. Fire Mater. 47, 979–989. https://doi.org/10.1002/fam.3142.

Chow, W.K., Leung, C.W., 2006. Necessity of testing fire behaviour of plastic materials under flashover. Polym. Test. 25, 853–858. https://doi.org/10.1016/j.polymertesting.2006.03.012.

Colla, V., Fornai, B., Amato, Alessandro, 2011. A novel Key Performance Indicator for measuring the competitiveness of materials production within the EU. Int. J. Bus. Compet. Growth 276–294.

Collins, A.J., Hester, P., Ezell, B., Horst, J., 2016. An improvement selection methodology for key performance indicators. Environ. Syst. Decis. 36, 196–208. https://doi.org/10.1007/s10669-016-9591-8.

De Liso, B.A., Pio, G., Salzano, E., 2024a. Small scale pool fires: the case of toluene. J. Loss Prev. Process. Ind. 92. https://doi.org/10.1016/j.jlp.2024.105430.

De Liso, B.A., Pio, G., Salzano, E., 2024b. Fire behaviour of liquid solvents for energy storage applications. Process Saf. Environ. Prot. 188, 726–734. https://doi.org/10.1016/j.psep.2024.05.153.

Drzeżdżon, J., Jacewicz, D., Sielicka, A., Chmurzyński, L., 2019. Characterization of polymers based on differential scanning calorimetry based techniques. TrAC - Trends Anal. Chem. 110, 51–56. https://doi.org/10.1016/j.trac.2018.10.037.

Dubdub, I., Al-Yaari, M., 2020. Pyrolysis of low density polyethylene: kinetic study using TGA data and ANN prediction. Polymers 12. https://doi.org/10.3390/POLYM12040891.

Ferek, R.J., Reid, J.S., Hobbs, P.V., Blake, D.R., Liousse, C., 1998. Emission factors of hydrocarbons, halocarbons, trace gases and particles from biomass burning in Brazil. J. Geophys. Res. Atmos. 103, 32107–32118. https://doi.org/10.1029/98JD00692.

Fujita, M., Izato, Y., Iizuka, Y., Miyake, A., 2019. Thermal hazard evaluation of runaway polymerization of acrylic acid. Process Saf. Environ. Prot. 129, 339–347. https://doi.org/10.1016/j.psep.2019.08.003.

ISO 5660, 2019. ISO 5660-1: 2019. Reaction-To-Fire Tests. Heat Release, Smoke Production and Mass Loss Rate Heat Release Rate (Cone Calorimeter Method) and Smoke Production Rate (Dynamic Measurement).

Kim, S.W., Park, S.G., Lee, E.J., 2022. Assessment of the explosion risk during lithium-ion battery fires. J. Loss Prev. Process. Ind. 80, 104851. https://doi.org/10.1016/j.jlp.2022.104851.

Krieg, T., Mazzon, C., Gómez-Sánchez, E., 2022. Material analysis and a visual guide of degradation phenomena in historical synthetic polymers as tools to follow ageing processes in industrial heritage collections. Polymers 14. https://doi.org/10.3390/polym14010121.

Laurini, E., Marson, D., Fermeglia, M., Pricl, S., 2018. Multimodel approach for accurate determination of industry-driven properties for Polymer Nanocomposite Materials. J. Comput. Sci. 26, 28–38. https://doi.org/10.1016/j.jocs.2018.03.002.

Linteris, G.T., 2011. Numerical simulations of polymer pyrolysis rate: effect of property variations. Fire Mater. 35, 463–480. https://doi.org/10.1002/fam.1066.

Liu, C., Wang, J., He, J., 2002. Rheological and thermal properties of m-LLDPE blends with m-HDPE and LDPE. Polymer 43, 3811–3818. https://doi.org/10.1016/S0032-3861(02)00201-X.

Lyon, R.E., Safronava, N., Crowley, S., 2018. Thermal analysis of polymer ignition. Fire Mater. 42, 668–679. https://doi.org/10.1002/fam.2521.

Makhlouf, G., Hassan, M., Nour, M., Abdel-Monem, Y.K., Abdelkhalik, A., 2017. Evaluation of fire performance of linear low-density polyethylene containing novel intumescent flame retardant. J. Therm. Anal. Calorim. 130, 1031–1041. https://doi.org/10.1007/s10973-017-6418-x.

Marcilla, A., Gómez, A., Reyes-Labarta, J.A., Giner, A., 2003. Catalytic pyrolysis of polypropylene using MCM-41: kinetic model. Polym. Degrad. Stab. 80, 233–240. https://doi.org/10.1016/S0141-3910(02)00403-2.

Marsh, N.D., Gann, R.G., 2013. Smoke Component Yields from Bench-Scale Fire Tests : 3. ISO 5660-1/ASTM E 1354 with Enclosure and Variable Oxygen Concentration. https://doi.org/10.6028/NIST.TN.1762. Gaithersburg, MD.

Matuszewska, A., Owczuk, M., Biernat, K., 2022. Current trends in waste Plastics' liquefaction into fuel fraction: a review. Energies 15. https://doi.org/10.3390/en15082719.

Moncalero, M., Signetti, S., Mazzanti, B., Bruzzi, P., Pugno, N.M., Colonna, M., 2017. Effect of material elastic properties and surface roughness on grip performances of ski boot soles under wet and icy conditions. Int. J. Ind. Ergon. 61, 62–70. https://doi.org/10.1016/j.ergon.2017.04.004.

Monisha, S., Selvasekarapandian, S., Mathavan, T., Milton Franklin Benial, A., Manoharan, S., Karthikeyan, S., 2016. Preparation and characterization of biopolymer electrolyte based on cellulose acetate for potential applications in energy storage devices. J. Mater. Sci. Mater. Electron. 27, 9314–9324. https://doi.org/10.1007/s10854-016-4971-x.

Monteiro, S.N., Calado, V., Rodriguez, R.J.S., Margem, F.M., 2012. Thermogravimetric behavior of natural fibers reinforced polymer composites-An overview. Mater. Sci. Eng. A 557, 17–28. https://doi.org/10.1016/j.msea.2012.05.109.

Ogabi, R., Manescau, B., Chetehouna, K., Gascoin, N., 2021. A study of thermal degradation and fire behaviour of polymer composites and their gaseous emission assessment. Energies 14. https://doi.org/10.3390/en14217070.

Patel, R.J., Wang, Q., 2016. Prediction of properties and modeling fire behavior of polyethylene using cone calorimeter. J. Loss Prev. Process. Ind. 41, 411–418. https://doi.org/10.1016/j.jlp.2015.11.009.

Ramesh, P., Vinodh, S., 2020. State of art review on life cycle assessment of polymers. Int. J. Sustain. Eng. 13, 411–422. https://doi.org/10.1080/19397038.2020.1802623.

Rantuch, P., Martinka, J., Ház, A., 2021. The evaluation of torrefied wood using a cone calorimeter. Polymers 13, 1748. https://doi.org/10.3390/polym13111748.

Ray, S., Cooney, R.P., 2018. Thermal degradation of polymer and polymer composites. Handb. Environ. Degrad. Mater. Third Ed, 185–206. https://doi.org/10.1016/B978-0-323-52472-8.00009-5.

SPI Plastics Engineering Handbook of the Society of the Plastics Industry, Inc., 1991. SPI Plastics Engineering Handbook of the Society of the Plastics Industry. Inc. https://doi.org/10.1007/978-1-4615-7604-4.

Tahmid Islam, M., Klinger, J.L., Toufiq Reza, M., 2023. Evaluating combustion characteristics and combustion kinetics of corn stover-derived hydrochars by cone calorimeter. Chem. Eng. J. 452, 139419. https://doi.org/10.1016/j.cej.2022.139419.

Torero, J., 2016. Flaming Ignition of Solid Fuels. SFPE Handbook of Fire Protection Engineering. Springer, New York, New York, NY, pp. 633–661. https://doi.org/10.1007/978-1-4939-2565-0_21.

Wang, Z., Wei, R., Wang, X., He, J., Wang, J., 2018. Pyrolysis and combustion of polyvinyl chloride (PVC) sheath for new and aged cables via thermogravimetric analysis-fourier transform infrared (TG-FTIR) and calorimeter. Materials 11. https://doi.org/10.3390/ma11101997.

Wu, J., Papanikolaou, K.G., Cheng, F., Addison, B., Cuthbertson, A.A., Mavrikakis, M., Huber, G.W., 2024. Kinetic study of polyvinyl chloride pyrolysis with characterization of dehydrochlorinated PVC. ACS Sustain. Chem. Eng. 12, 7402–7413. https://doi.org/10.1021/acssuschemeng.4c00564.

Yang, S., Huo, S., Wang, Jun, Zhang, B., Wang, Jingsheng, Ran, S., Fang, Z., Song, P., Wang, H., 2021. A highly fire-safe and smoke-suppressive single-component epoxy resin with switchable curing temperature and rapid curing rate. Compos. Part B Eng. 207. https://doi.org/10.1016/j.compositesb.2020.108601.

Yazdi, M., Zarei, E., Adumene, S., Abbassi, R., Rahnamayiezekavat, P., 2022. Uncertainty Modeling in Risk Assessment of Digitalized Process Systems, pp. 389–416. https://doi.org/10.1016/bs.mcps.2022.04.005.

Zanobetti, F., Pio, G., Jafarzadeh, S., Muñoz Ortiz, M., Cozzani, V., 2023a. Decarbonization of maritime transport: sustainability assessment of alternative power systems. J. Clean. Prod. 417. https://doi.org/10.1016/j.jclepro.2023.137989.

Zanobetti, F., Pio, G., Jafarzadeh, S., Ortiz, M.M., Cozzani, V., 2023b. Inherent safety of clean fuels for maritime transport. Process Saf. Environ. Prot. 174, 1044–1055. https://doi.org/10.1016/j.psep.2023.05.018.

Zarei, E., Yazdi, M., Moradi, R., BahooToroody, A., 2024. Expert Judgment and Uncertainty in Sociotechnical Systems Analysis, pp. 487–530. https://doi.org/10.1007/978-3-031-62470-4_18.

Zhang, J., Jiang, D.D., Wilkie, C.A., 2006. Thermal and flame properties of polyethylene and polypropylene nanocomposites based on an oligomerically-modified clay. Polym. Degrad. Stab. 91, 298–304. https://doi.org/10.1016/j.polymdegradstab.2005.05.006.

Zhu, X., Wu, J., Bai, Y., Wang, D., Zhang, J., 2024. Integrating FBN and FDS for quantitative risk assessment of cable fire in utility tunnel. J. Loss Prev. Process. Ind. 88, 105266. https://doi.org/10.1016/j.jlp.2024.105266.