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Linking Pyrolysis Kinetics and Heat Release Behavior of Polymers: A Focused Review of TGA/DSC and MCC Approaches

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Abstract - Understanding the relation between polymer decomposition kinetics and flammability is essential for predicting fire hazard and for design of flame-retardant materials. This focused review critically examines the kinetic and thermochemical basis of polymer thermal decomposition with particular emphasis on integration of thermogravimetric and calorimetric analysis (TGA/DSC) with microscale combustion calorimetry (MCC). The theoretical background of solid-state reaction kinetics, Arrhenius modeling, and isoconversional methods is first reviewed, followed by analysis of the principles governing heat release measurements based on oxygen consumption calorimetry. The review highlights recent efforts to correlate activation energy, characteristic decomposition temperatures, and reaction mechanisms with key flammability parameters, including heat release capacity, peak heat release rate, and total heat of combustion. The synthesis indicates that, although significant progress has been achieved in coupling mass loss kinetics with heat release behavior, important challenges still remain in treatment of multi-step degradation, char-forming systems, and heating-rate effects. Overall, the integration of kinetic and thermochemical analyses provides a promising framework for linking polymer pyrolysis mechanisms to flammability performance and for improving the predictive capability of fire hazard assessment.

Keywords - Polymer thermal decomposition; Pyrolysis kinetics; Thermogravimetric analysis; Microscale combustion calorimetry; Flammability characterization

1. Introduction

The rapid growth of the global population, together with accelerated urbanization, industrial expansion, and changing consumption patterns, has resulted in an unprecedented increase in municipal solid waste (MSW) generation worldwide. At present, more than two billion tonnes of MSW are produced annually, and this amount is expected to rise considerably in the coming decades if current management practices continue [1]. Figure 1 shows the typical composition of municipal solid waste (MSW) on a global basis, providing insight into the relative proportions of major waste fractions. The organic portion, especially food and green waste, constitutes the largest single category, accounting for approximately 44% of total MSW. This dominant share reflects the global prevalence of biodegradable materials from households and food services. Paper and cardboard follow with about 17%, indicating ongoing use of paper products in packaging and communication materials. Plastics make up roughly 12% of the waste stream, a significant share given the environmental concerns

associated with plastic pollution and the challenges of recycling mixed polymer wastes. Smaller fractions include glass at about 5%, metals at around 4%, wood and rubber each near 2%, and the remainder classified as other materials such as textiles and mixed waste streams [2,3]. This distribution underscores the complexity of managing MSW due to its heterogeneous nature and highlights the particular importance of strategies that can address both high-organic and plastic components, including emerging thermochemical treatments such as pyrolysis. The composition profile cited here aligns with recent global assessments indicating similar constituency percentages for MSW across diverse regions and economic contexts [4].

Plastic waste represents a significant fraction of the global MSW stream, mainly due to the extensive use of single-use and short-lived plastic products, especially for packaging applications. Despite ongoing improvements in waste management systems, global plastic recycling rates remain critically low, while most plastic waste is still landfilled, incinerated, or improperly managed [5,6]. These practices cause serious environmental impacts, including greenhouse gas emissions, contamination of soil and water resources, and marine pollution. Conventional mechanical and chemical recycling routes face several economic and technical limitations, particularly when treating mixed or contaminated plastic waste streams. As a result, increasing attention has been directed toward advanced thermochemical conversion technologies, such as pyrolysis, which provide a promising route for converting plastic waste into valuable fuels and chemicals. In this global context, the development and optimization of sustainable waste-to-energy solutions are considered essential for supporting circular economy strategies and reducing dependence on fossil resources while mitigating climate-related impacts [7,8].

The study of the combustion and pyrolysis of polymeric materials includes several components like the study of the chemical reaction mechanism (Chemistry), accounting for heat transfer (Energy transfer), and gas flows (Gas flow). Both chemical and physical changes occur when a polymeric material is exposed to excessive heating. Once the polymer is heated, it starts to decompose, and the carbon backbone is cracked into shorter carbon chains. Begins yielding volatile products that are usually combustible. Additionally, the polymer can melt before decomposition what depends on the degree of crosslinking and its stability[9–11]. Polymer decomposition can occur through different mechanisms, and it can be chemical or thermal crack. And it happens by exposed polymers by the amount to heat, which causes the breakdown of the polymer chain and releases volatile gases and light compounds. The energy required for a particular chemical reaction to occur is referred to as the activation energy. According to **Fig. 2**, the initial energy needed to free molecules from the polymer chain is higher than the enthalpy ΔH, and these molecules get their energy to release and undergo reaction[12,13].

The chemical mechanism study is based on the determination of the kinetic parameters of the ongoing reaction, such as the order of the reaction, activation energy, preexponential factor, and conversion depth. Depending on the experiments' conditions, pyrolysis (oxygen-free thermal degradation) and oxidation of volatiles are isolated see Fig. 3. The Arrhenius equation gives a strong framework for understanding how temperature affects chemical reaction rates as in Eq. 1, connecting the rate constant (k) to the activation energy (Ea) through an exponential function of absolute temperature (T) [1,2].

$$K = Ae^{\frac{-E_a}{RT}} \quad (1)$$

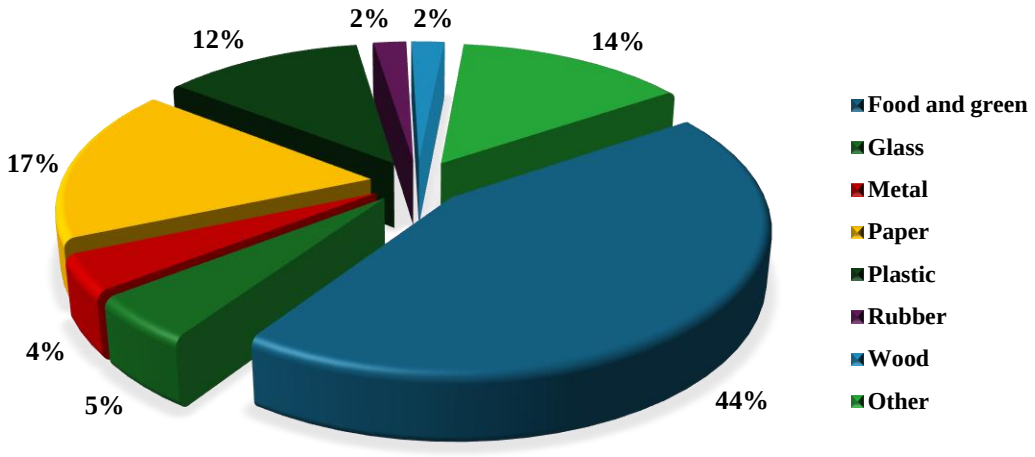


Fig. 1 Typical composition of municipal solid waste (MSW) on a global scale[1]

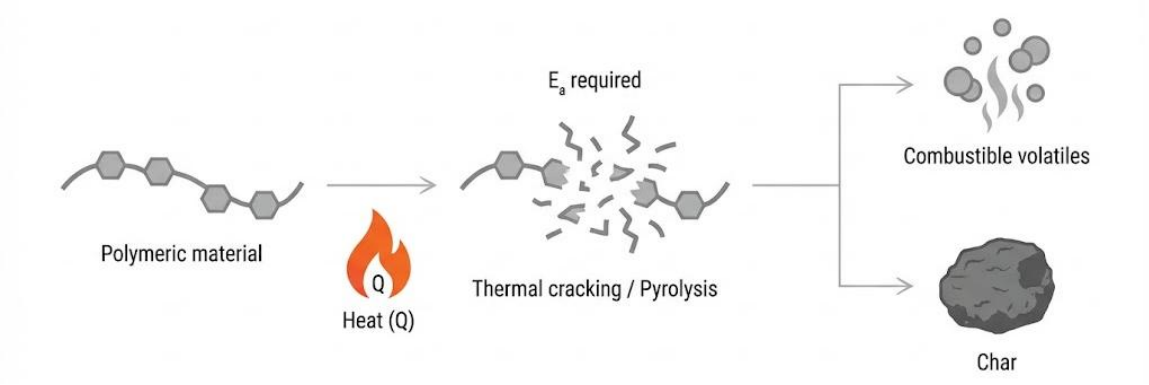


Fig. 2 The energy required for a particular chemical reaction

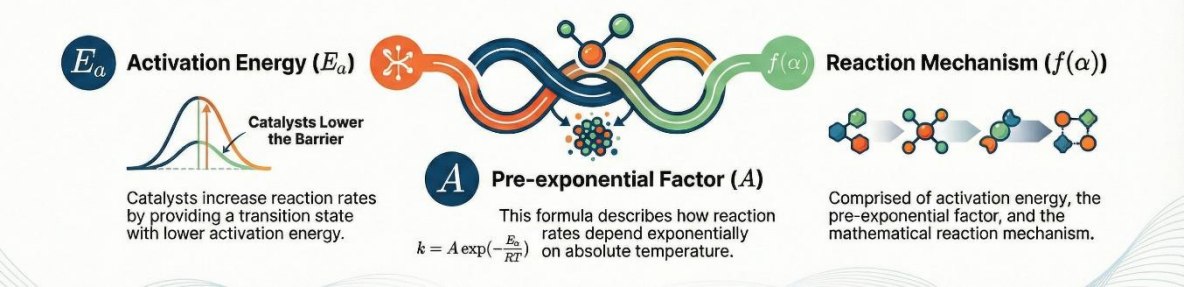


Fig. 3 a guide reaction analysis for kinetic triplet

When temperature rises, the energy distribution of molecules spreads according to Maxwell–Boltzmann statistics, so more molecules have sufficient energy to overcome the activation barrier. This explains why many reactions are very sensitive to temperature: for reactions with usual activation

energies ($Ea \gg RT$), even small increases in temperature can strongly increase the rate, sometimes doubling or tripling the rate for each 10 °C rise [14]. In experiments, the Arrhenius equation is often linearized by plotting $\ln k$ versus $1/T$, which allows easy determination of kinetic parameters like the pre-exponential factor (A) and the activation energy (Ea). The slope of the line gives Ea/R, and the intercept represents $\ln A$, providing insight into both the energy barrier and frequency of productive collisions [15]. This method remains essential in chemical kinetics and is widely applied to predict reaction behavior under different thermal conditions. Nevertheless, deviations from ideal Arrhenius behavior often occur in complex systems. Solid-state reactions, polymer degradation, or biomass pyrolysis sometimes do not follow a single exponential temperature dependence because of multi-step mechanisms, diffusion effects, or phase changes [16,17]. To handle these complexities, modified Arrhenius equations, are used to include weak temperature dependence of the pre-exponential factor. Also, isoconversional approaches, like Friedman, KAS, or OFW methods, are helpful when the reaction model is unknown, which is often the case in heterogeneous or non-isothermal processes [18,19].

3. Thermal analysis

As with any physical modeling, kinetic models represent an approximate description of the entire system and are fundamentally based on experimental data. Therefore, careful acquisition and preparation of these data, following the structured scheme for kinetic model development, form the first and most critical step in building a reliable model [20]. The chemical mechanism study is based on the determination of the kinetic parameters of the ongoing reaction, such as the order of the reaction, activation energy, preexponential factor, and conversion depth. Depending on the experiments' conditions, pyrolysis (oxygen-free thermal degradation) and oxidation of volatiles are isolated. Standard methods of thermal analysis, from the point of view of the scale of the samples used, can be conditionally divided into three types: spectroscopic techniques, which ensure the study of materials at the atomic and molecular levels (10^{-4}-10^{-22} m), tests for the explosion (fire-tests), which are carried out with materials whose weight exceeds 0.1 kg., and tests carried out using the so-called. Laboratory samples (1-10 mg) are shown in Fig.4. Each method has its benefits, depending on the purpose. Thermal properties, including glass transition temperature, crystalline melting point, thermal stability, thermal decomposition, are measured using dedicated instrumentation. These instrumentations like thermogravimetric analysis (TGA), differential thermal analysis (DTA), differential scanning calorimetry (DSC), and evolved gas analysis (EGA), Microscale Combustion Calorimeter [21,22]

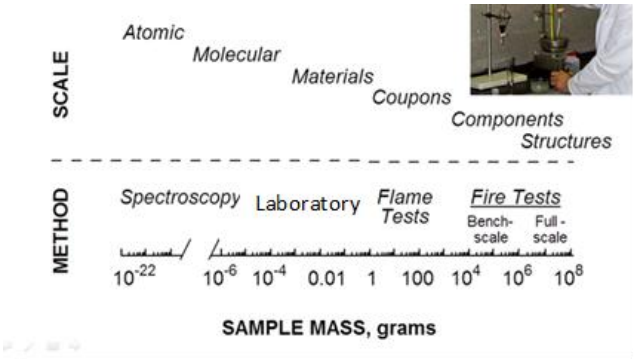


Fig. 4 The Scale of methods depending on sample sizes

4. Instrumentation for Thermal Analysis

Several dedicated instruments are used to measure thermal properties, including glass transition temperature, crystalline melting point, thermal stability, and thermal decomposition. These instruments include see **Fig. 5**. Thermogravimetric Analysis (TGA): Measures the change in mass of a sample as a function of temperature or time. TGA is used to determine the thermal stability, decomposition kinetics, and composition of materials. Differential Thermal Analysis (DTA): Measures the temperature difference between a sample and a reference material as a function of temperature or time. DTA is used to detect phase transitions, such as melting, crystallization, and

glass transition. Differential Scanning Calorimetry (DSC): Measures the heat flow into or out of a sample as a function of temperature or time. DSC is used to determine the heat capacity, enthalpy of fusion, and glass transition temperature of materials. Evolved Gas Analysis (EGA): Identifies and quantifies the volatile products released during thermal degradation. EGA is often coupled with TGA or DSC to provide a comprehensive understanding of the thermal decomposition process. Microscale Combustion Calorimeter (MCC): Measures the heat release rate of small samples during combustion. MCC is used to assess the flammability and fire behavior of materials.

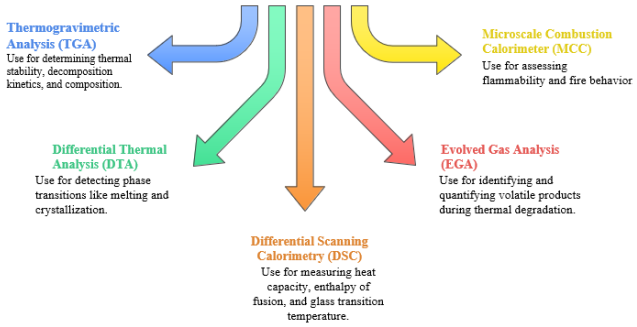


Fig. 5 Different thermal analysis techniques used to study the polymer degradations

4.1 Thermogravimetric Analysis (TGA)

Thermogravimetry is a thermal analysis technique that records the change in sample weight as a function of temperature or time while the sample temperature, in a specified atmosphere, is programmed. Allows one to judge the thermal stability and composition of the sample, the residue, and substances formed at the intermediate stages of the process. In particular, the TG signal's derivative (the rate of change in mass) makes it possible to establish the point in time or temperature at which the weight change occurs most rapidly with enthalpy changes that cannot be detected by the use of this technique. When the process progress is monitored, as a change in mass by TGA, α (reactant conversion) is determined as a ratio of the current mass change, Δm, to the total mass change, Δm_{tot} occurred throughout the process in Eq. 2, where m_0 and m_f, respectively, are the initial and final masses in **Fig. 6**.

$$\alpha = \frac{m_o - m_t}{m_o - m_f} = \frac{\Delta m}{\Delta m_{tot}} \qquad (2)$$

The thermal analyzer consists of a high-precision balance with crucibles (usually platinum). This device allows you to continuously determine the sample's mass depending on temperature, placed in a small chamber electric furnace **Fig. 6**. For example, there is a control thermocouple near the sample that measures the temperature with high accuracy under the bottom of the crucible. The furnace chamber can be filled with an inert gas to prevent oxidation or other undesirable reactions. A computer is used to control the measuring equipment and take readings[23].

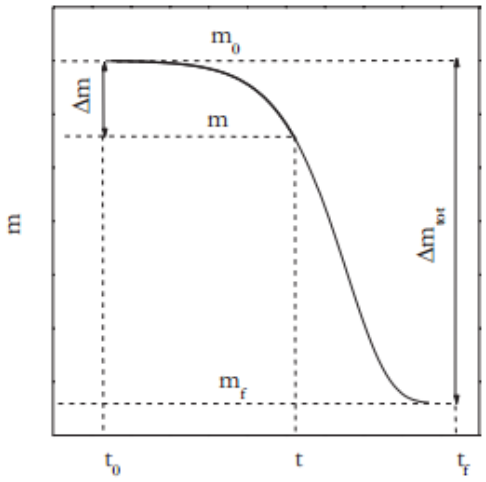


Fig. 6 Evaluation of conversion from TGA curve[23].

During the thermogravimetric analysis (TGA), the sample may be heated or cooled at a predetermined rate or held under isothermal conditions at a constant temperature. In typical experiments, the sample mass is recorded while heating the furnace at rates ranging from 5 to 20 °C/min, which are most commonly used for solid-state or polymeric materials [24]. Maintaining a constant and reproducible heating rate is critical, as any deviation from linear heating can distort the shape and onset temperatures observed in the TG curve. The maximum temperature achievable depends on the

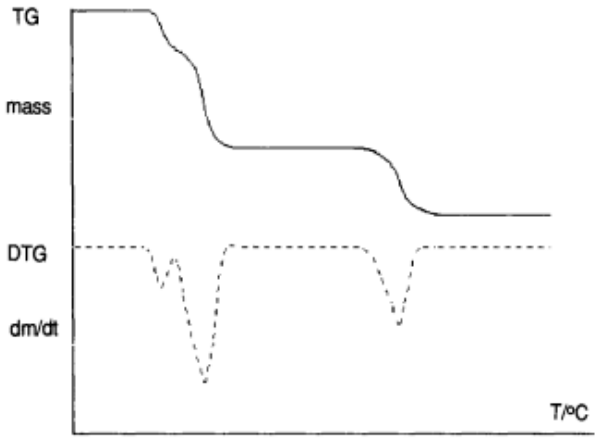
instrument design and usually reaches 1000–1500 °C for high-temperature TGA systems. Despite such high furnace temperatures, the external surface remains below 50 °C due to effective thermal insulation, ensuring operator safety during experiments [25].

The TGA method is useful when the sample releases volatiles because of various physical and chemical processes. Simultaneously, the most widespread use of TGA refers specifically to the field of research of polymeric materials: comparison of relative thermal stability, investigation of the effect of the type and content of various additives, and moisture on thermal stability, research of oxidation resistance. When studying thermo-oxidative destruction using thermogravimetry, it is possible to determine the rate constants, reaction order, frequency factors, and activation energies of the destruction process. The derivative thermogravimetric (DTG) trace is frequently drawn to enhance the steps in the thermogravimetric curve. Remember that this is the plot of mass change rate, with time, dm/dt [22,26].

4.2 DTA and DSC

The concept of DSC was initially derived from earlier DTA instruments[26–36]. For that, let's define first DTA, the differential thermal analysis (DTA) measures a difference in sample temperature and reference material temperature, they are heated in one furnace, with measure the differential temperature between the sample and the reference material during the control heating program, and differential Scanning Calorimetry (DSC) measures the change of the difference in the heat flow rate to the material (sample) and to reference material. At the same time, they are subjected to a controlled temperature program. The experimental curve of the DTA method is shown in Fig. 7.

Differential Scanning Calorimetry (DSC), on the other hand, measures the change in the difference in the heat flow rate to the material (sample) and to the reference material. Similar to DTA, the sample and reference material are subjected to a controlled temperature program. However, instead of measuring the temperature difference directly, DSC measures the amount of heat required to maintain the sample and reference at the same temperature see .



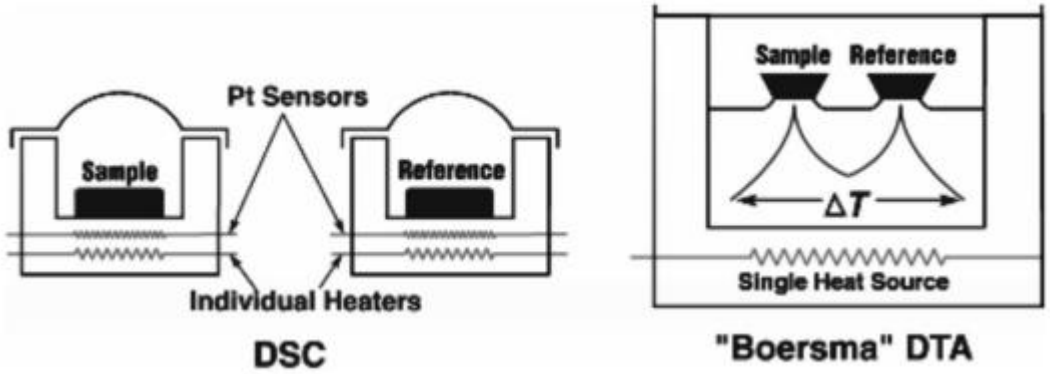


Fig. 7 Typical TGA (solid) and DTG (dashed) curves, Schematic layout of the DSC apparatus: PC-DSC and quantitative [32]

Fig. 8 Comparing between the DTA and DSC

While the temperatures of the sample and reference are maintained equal, both are placed on heaters that increase temperature at a constant rate, typically 10 °C per minute. The calorimetric cells are designed to be as symmetrical as possible, using identical crucibles, equivalent sensors, and equal spacing from the heater. During the experiment, the time-dependent temperature difference between the sample cell and the reference cell is continuously recorded, as illustrated in **Fig. 9**.

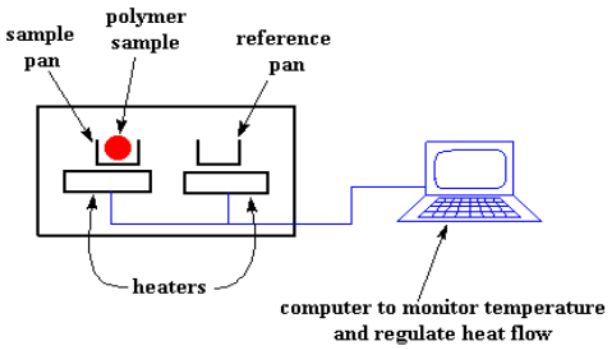


Fig. 9 Schematic diagram of the DSC method setup[29]

Differential scanning calorimetry (DSC) allows you to register the heat flux - the derivative of heat over

time (hence the term "differential" in the name), which characterizes the changes occurring in a substance as a result of heating or cooling. Heat fluxes are measured by the temperature difference at two points of the measuring system simultaneously [27,29]. Their internal structure and properties determine the presence of peaks in the DSC curve for polymers; therefore, the curve's character is different for different polymers. Phenyl groups, which are part of polystyrene, prevent the ordered arrangement of macromolecules and crystalline formations. Therefore, polystyrene does not crystallize, and the lower peak goes to infinity. The experimental curves presented in **Fig. 10** illustrate the variation of the heat flux, dQ/dt, as a function of temperature, providing insight into the thermal transitions of the polymer. Upward peaks in the curves indicate endothermic processes, corresponding to an increase in enthalpy, such as the melting transition (Tm), while downward peaks represent exothermic events, such as crystallization (Tc). The initial feature observed at lower temperatures is associated with the glass transition (Tg) of the polymer, reflecting the onset of molecular mobility in the amorphous regions. Analysis of these thermal events allows for characterization of the polymer's phase behavior, crystallinity, and thermal stability. Moreover, the relative magnitudes and positions of the peaks provide information about the kinetics of the transitions, enabling correlation with heating rate and sample history. Such interpretations are fundamental for understanding the polymer's performance under processing or operational conditions, and they also form the basis for modeling its thermal behavior in kinetic studies [37].

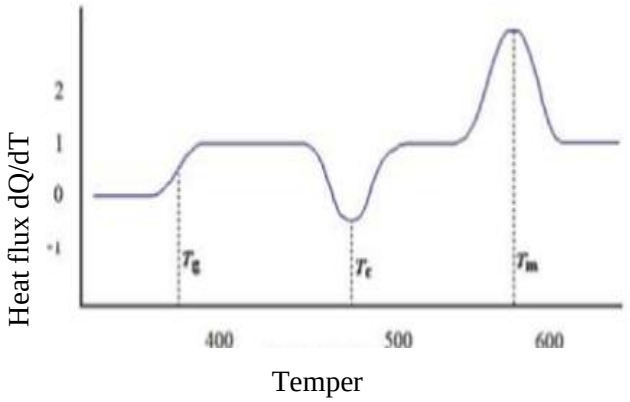


Fig. 10 Experimental curve of the DSC method [37]

Analysis of the DSC curve provides valuable information on various parameters related to the thermal behavior and decomposition of polymers. These include phase transition temperatures, such as melting (Tm) and the glass transition (Tg), specific heat capacity over a wide temperature range, degree of crystallinity or amorphousness, enthalpy changes associated with transitions or reactions, thermal stability, and oxidation resistance. In addition, DSC can assist in identifying decomposition or reaction products by their characteristic thermophysical signatures. In practical applications, DSC is often combined with thermogravimetric analysis (TGA) on the same sample, forming a combined thermal analysis (CTA) approach. The simultaneous use of TGA allows separation of the contributions from fillers, resin, and other additives, providing a more comprehensive understanding of the material. Furthermore, TGA data offer direct insights into polymer thermal stability and enable quantitative evaluation of the effectiveness of additives in enhancing thermal performance. This integrated analysis is essential for both fundamental studies and the design of polymers with tailored thermal and mechanical properties [38,39].

4.3 Microscale Combustion Calorimeter

The Pyrolysis Combustion Flow Calorimeter (PCFC), also known as Micro Combustion Calorimeter (MCC) [40–49] apparatus, is utilized to determine the flammability characteristics of polymeric materials using combustion calorimeter on a micro-scale. Initially, MCC was used as a

thermal analysis tool for polymer and composite materials used in the aircraft industry. As a result, because of the significant expansion of capabilities and several advantages over standard techniques, this method became widespread. In 2007, a standard of the American Society for Testing Materials had approved its use: ASTM D7309-07 "Standard Test Method for Determining Flammability Characteristics of Plastics and Other Solid Materials Using MCC"[50]. Pyrolysis-combustion flow calorimetry is an applicable method to calculate the material combustion parameters by using milligram samples. It measures quantities include the specific heat release rate under simulated fire conditions, the heat of combustion of the fuel gases, the heat of combustion of the solid, and a derived quantity called the heat release capacity. With experiments, it showed the heat release capacity as an indicator of fire hazard [51].

The principle of the PCFC/MCC, as illustrated in **Fig. 11**, separates the combustion process of the test material into two stages: pyrolysis under an inert gas flow (typically N2) and the subsequent oxidation of the volatile products released from the decomposing material. In this way, a small-scale simulation of the fundamental combustion process is achieved, where the polymer's decomposition products are burned in oxygen. The system includes a pyrolysis zone and a combustion chamber that are spatially separated, allowing precise measurement of the combustion behavior [52].

A comparison between MCC and TGA results is shown in Fig. 12, demonstrating the complementary information obtained from the two techniques. Thermogravimetric analysis provides quantitative insight into mass loss as a function of temperature, allowing identification of the onset, rate, and extent of thermal degradation. In contrast, MCC directly measures the heat release rate associated with the oxidation of volatile decomposition products generated during polymer pyrolysis. When used together, these methods offer a more comprehensive description of the polymer's thermal and combustion behavior, including degradation pathways, flammability characteristics, and the influence of fillers or additives. By correlating mass loss profiles from TGA with heat release data from MCC, specific thermal events can be more clearly distinguished, and both thermal stability and energetic potential of the material can be evaluated under controlled conditions. This combined interpretation improves the reliability of thermal characterization and provides valuable input for material design and fire-safety assessment.

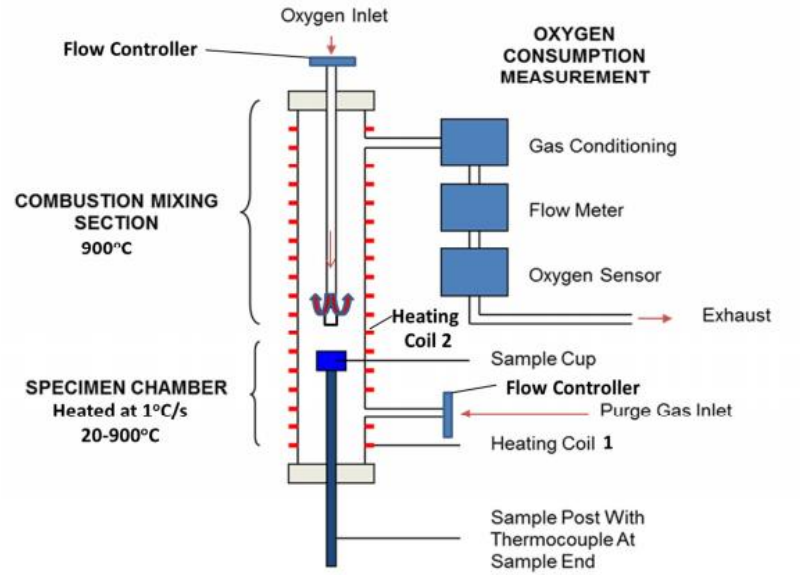


Fig. 11 Schematic view of MCC [52]

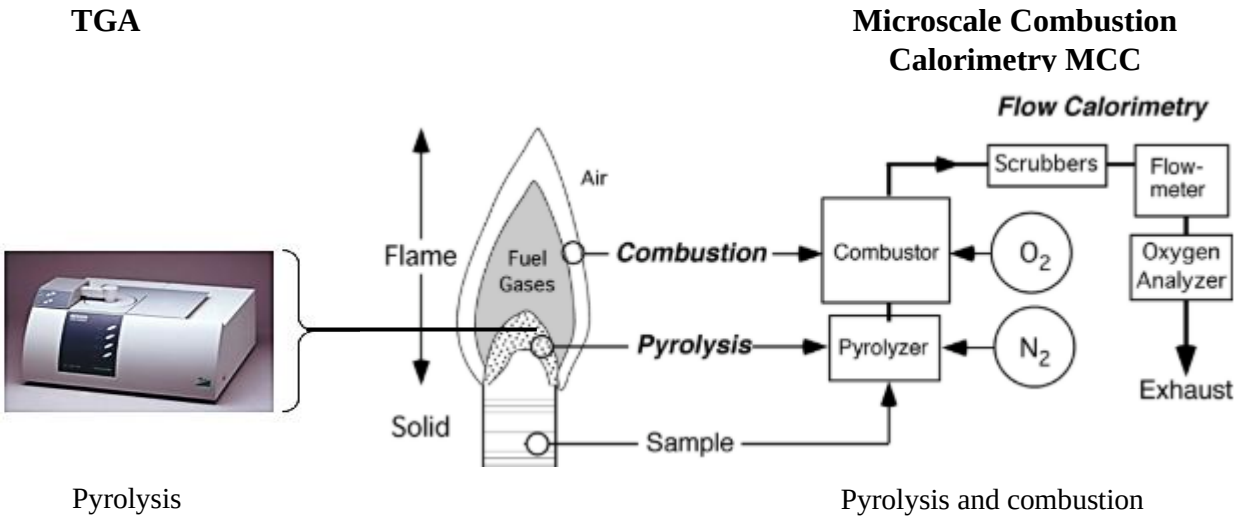


Fig. 12 MCC principle in comparison with TGA

The complementary nature of MCC and TGA results, as discussed above, is particularly relevant when interpreting heat release behavior based on oxygen consumption principles. According to Thornton [53], the actual value of complete combustion can be determined by measuring the rate of oxygen consumption during the oxidation of volatile products, which is then multiplied by the average thermal effect of complete combustion of organic carbon to obtain the heat release rate. In this context, TGA provides essential information on the temperature-dependent mass loss and the generation rate of volatile species during polymer decomposition, while MCC quantifies the corresponding heat release associated with their oxidation. By linking the mass loss profiles obtained from TGA with the oxygen consumption–based heat release measured by MCC, a direct relationship can be established between decomposition kinetics and combustion energetics. This combined interpretation enables a more accurate assessment of polymer flammability and thermal stability, as it couples the physical degradation process with the fundamental combustion parameter defined by Thornton's rule.

$$C = 419 \pm 19\,\mathrm{kJ/mol},\ O_2 = 13.1 \pm 0.6\,\mathrm{kJ/mol.\,O} \qquad (3)$$

This value does not depend significantly on the burning material's chemical composition and applies to a wide range of fuels with an accuracy of about 5% [51]. The heat of combustion is defined as the liberated heat per unit time t, which is limited by thermal decomposition solid and generates the fuel gas in the PCFC. Where the heat release rate proportional to the formation mass of volatiles rate, According to Eq. 4. we find the heat release rate dQ/dt in PCFC/MCC is proportional to the mass generation rate of volatile fuel or the mass loss rate of the solid:

$$\dot{Q}_c(t) = \frac{dQ_c(t)}{dt} = h^0{}_{c,v}(t)\frac{dm_v(t)}{dt} = -h^0{}_{c,v}(t)\frac{dm_s(t)}{dt} \qquad (4)$$

where $h^0{}_{c,v}$is the enthalpy heat of complete combustion of the volatile pyrolysis products of mass m_v, and m_s the instantaneous residual mass of solid. Considering the oxygen consumed during this reaction Δm_{o_2}:

$$dm_v(t)h^0{}_{c,v}(t) = \Delta m_{o_2}(t) \qquad (5)$$

Then, substituting the time derivative of Eq. 4 into equation Eq. 5, and transforming it:

$$\frac{dQ(\dot{t})}{dt} \equiv Q_c(t) = -h^0{}_{c,v}(t)\frac{dm_s(t)}{dt} = C\frac{d\Delta m_{o_2}(t)}{dt} = C\Delta m_{o_2}(t) \quad (6)$$

The heat release rate by the combustion of fuel gases, which produce from the thermal degradation polymer obtained by measuring the mass of oxygen consumed, with notice, is independent of the composition of the fuel. Then, the total heat of combustion of the volatiles is returning to zero as the pyrolysis process is complete, and no more volatile gases and the rate of consumption oxygen back to zero, which is obtained by simple integration over time of Eq. 6

$$\dot{Q}_c = \int_0^\infty \dot{Q}_c\,(t)dt = C\int_0^\infty \Delta m_{o_2}(t) \quad (7)$$

While Eq. 7 the total consumption oxygen, which relates to the total heat release rate of products degradation polymer, and the heat release rate required to measure the downstream of oxygen consumption, and need to synchronize with volatiles gases produce, or the mass-loss history of the sample in the pyrolizer. But there are smears of the oxygen signal because the flow of combustible gases from the pyrolizer to the oxygen analyzer is distorted. On the other hand, this distortion doesn't affect the total heat of combustion, which results in the heat release rate not related to the fuel generation rate of the sample [54–57]. The calculated heat release rate from the product of mass loss rate and the heat of combustion determines from Eq. 6 to compare with the heat obtained from the oxygen consumption history in the MCC, it needs to deconvolute the oxygen signal to valid for instrumental broadening. For this, a mixed model of a microcalorimeter [51] is used: the rate of heat release of solids is expressed in units (W/g) in terms of the change in oxygen concentration Θ. Taking into account the response time of the device τ, the heat release rate in Eq. 6 is represented as:

$$\dot{Q}_c(t) = C\rho F\left(\Theta + \tau\frac{d\Theta}{dt}\right) \quad (8)$$

where ρ and F are the density and volumetric flow rate of the gas, respectively. Dividing Eq. 8 by the initial sample mass m_0 (g), we obtain the Specific Heat Release Rate (W/g) Eq. 9:

$$\dot{q}_c(W\,g^{-1}) = \frac{\dot{Q}_c(t)}{m_0} = \frac{C\rho F}{m_0}\left(\Theta + \tau\frac{d\Theta}{dt}\right) \quad (9)$$

Since pyrolysis in the MCC method carried out under conditions of linear heating of the sample with a constant, preset rate of temperature change β (K / s), and char fraction, the sample thermal decomposition occurs in one stage, the maximum heat release related to the pyrolysis kinetic parameters. The heating rate and which known as the heat Release Capacity (HRC, W/g.K).

$$\eta_c \equiv \frac{\dot{q}_c^{max}}{\beta} = \frac{C\rho F}{\beta m_0}\left(\Theta + \tau\frac{d\Theta}{dt}\right)|_{max} = \frac{h^0_{c,s}}{e}\frac{E_a}{R}\frac{}{T_p^2} \quad (10)$$

where Ea is the total activation energy of pyrolysis, T_P is the temperature corresponding to the maximum rate of mass loss, e and R are the natural numbers, and universal gas constant respectively, $h^0_{c,s} = (1-\mu)h^0_{c,v}$ the heat of combustion of the fuel gases per unit initial mass of solid, μ is the pyrolyzed substance fraction. The resulting expression in Eq. 10 is a set of thermochemical properties, which have units of measurement of the power of heat release capacity η_c and depend only on the composition of the material. MCC method evaluates objective indicators of material flammability and provides information for building a kinetic model of thermal decomposition. The setup's essential advantages are objectivity, high reproducibility of experiments, and a wide range of controlled input data. Finally, the PCFC/MCC method's main output is all thermochemical characteristics determined from the oxygen consumption during the degradation polymer.

The MCC method has the advantage of obtaining the thermochemical features by an insensitive parameter to endothermic processes in the pyrolysis zone, such as the chemical destruction of solid material of melting or evaporation of moisture. Also, the MCC data are is a quantitative technique characterized as a result that does not depend on the size of the test sample and is highly reproducible. It

is also worth noting the advantage in time and safety of the experiments carried out compared to the DSC and TGA methods.

The thermoanalytical techniques summarized in Table 1 provide complementary information that is essential for a comprehensive understanding of the thermal behavior and decomposition mechanisms of polymeric materials. TGA is primarily used to quantify mass loss associated with thermal degradation, volatilization, and oxidation processes, enabling the determination of degradation temperatures, residue content, and kinetic parameters. However, TGA alone does not directly distinguish between physical and chemical transformations occurring during heating.

DTA and DSC extend this analysis by identifying endothermic and exothermic events associated with phase transitions, such as glass transition, melting, crystallization, and chemical reactions. While DTA offers qualitative insight through temperature differences, DSC provides quantitative heat flow data, allowing accurate determination of enthalpy changes and heat capacity. The combination of mass and thermal information in STA improves data reliability by ensuring that both signals originate from the same sample under identical conditions, which is particularly important for materials containing fillers, additives, or multicomponent phases.

Despite their strengths, conventional thermoanalytical techniques are limited in their ability to directly assess combustion-related properties. In this context, MCC serves as a powerful complementary method by directly quantifying flammability parameters, such as heat release rate and total heat release, under well-controlled conditions. Unlike DSC and TGA, MCC focuses on the oxidation of volatile pyrolysis products, providing information that is directly relevant to fire behavior and thermal decomposition kinetics. Therefore, the combined use of TGA, DSC/STA, and MCC enables a more complete and reliable evaluation of polymer thermal stability, decomposition pathways, and combustion characteristics.

Table. 1 Summary of thermos analytical techniques commonly used for polymer characterization

Analytical Technique	**Measured Parameters**	**Main Analytical Significance / Typical Applications**
Thermogravimetric Analysis (TGA)	Mass change as a function of temperature or time under a controlled heating program and atmosphere	Evaluation of thermal stability, degradation steps, decomposition temperatures, residue content, filler or ash fraction, and kinetic parameters of thermal decomposition.
Differential Thermal Analysis (DTA)	Temperature difference between sample and reference subjected to the same thermal program	Qualitative identification of endothermic and exothermic processes such as melting, crystallization, phase transitions, and chemical reactions.
Simultaneous Thermal Analysis (STA)	Simultaneous mass change (TGA) and thermal effects (DTA or DSC)	Correlation between mass loss and thermal events; improved interpretation of overlapping degradation and phase-transition processes in complex materials.
Differential Scanning Calorimetry (DSC)	Heat flow as a function of temperature or time required to maintain sample and reference at the same temperature	Quantitative determination of glass transition temperature, melting and crystallization temperatures, enthalpy changes, specific heat capacity, and degree of crystallinity.

Microscale Combustion Calorimetry (MCC)	Heat release rate, total heat release, and combustion efficiency of pyrolysis gases	Assessment of material flammability, fire behavior, and combustion characteristics; quantitative input for kinetic modeling of polymer thermal decomposition.

5. Conclusions

This focused review has synthesized the kinetic and thermochemical foundations of polymer thermal decomposition with particular emphasis on integrating TGA/DSC-based kinetic analysis with microscale combustion calorimetry. The analysis shows that while classical kinetic parameters provide essential insight into degradation mechanisms, their coupling with heat release and flammability indices obtained from MCC is necessary for a comprehensive assessment of fire hazard. The reviewed models and formulations demonstrate the feasibility of establishing quantitative links between mass loss kinetics and heat release behavior, although important challenges remain in treating multi-step degradation, char formation, and heating-rate effects. Overall, the integration of thermoanalytical kinetics and microscale combustion calorimetry offers a robust framework for advancing both the fundamental understanding of polymer pyrolysis and the predictive evaluation of flammability performance.

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