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Techniques for Assessing the Combustion Behaviour of Polymeric Materials: Some Current Perspectives and Future Directions

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Summary: Polymers are increasingly being used in domestic, commercial and in public environments as components of fabrics, surface coatings and moulded articles. Most of these polymeric components are synthetic, are based on hydrocarbon intermediates, and are highly flammable, thus resulting in unwanted fires. Combustion of polymeric materials is a complex phenomenon that involves the solid phase, gaseous phase and the interphase. To fully characterize the flammability attributes of a polymeric material is not a straightforward task, and therefore several analytical techniques and other prescriptive tests (small-, medium-, and large-scale) were developed over the years. However, the actual behaviour of these materials in a real fire scenario can be quite different from the inferences that we get, especially, through the small- and medium-scale tests, and that there is often a lack correlation among the tests. In this paper, we attempt a critical appraisal of the various evaluation methods and test regimes that are currently used to characterize the combustion behaviours of polymeric materials.

Keywords: thermogravimetric analysis; flame retardance; flammability tests; smoke and toxic gases; char residue; correlation of test results

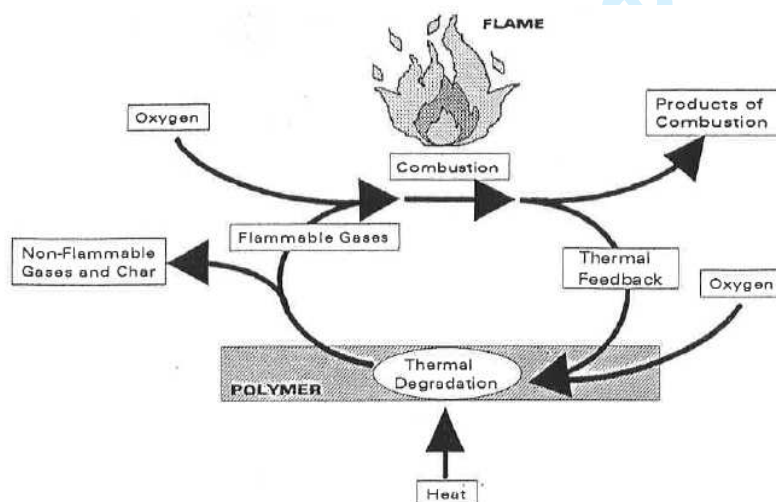
Introduction

Combustion is the term given to the overall exothermic reactions, of an oxidative character, which have the ability to propagate throughout the phase concerned. When the combustion process becomes uncontrolled, it is often described by the term fire.^[1] Combustion processes usually involve two reactants, a fuel and an oxidant, and in the case of a fire these reactants are generally a condensed phase fuel and a gaseous phase oxidant. Flames are light-emitting combustion reactions in which both the fuel and the oxidant are present in gas phase, but they are also found during the combustion of solid fuels such as organic polymers, which break down to give gaseous products. Flames may be initiated in a combustion system as a result of ignition, which can take place either spontaneously or

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3 following an application of an external source of energy. Ignition is the auto-acceleration
4 of an oxidation reaction, leading to glow, flame or explosion.
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7 When subjected to a sufficient heat flux for a sufficiently long time, all organic polymeric
8 materials undergo thermal degradation. In the absence of oxygen, these processes are
9 referred to as pyrolysis, which is usually exothermic in nature. In the presence of oxygen,
10 the overall process is referred to as oxidative pyrolysis, or thermo-oxidative degradation.
11 This can be either endothermic or exothermic. The susceptibility of a polymer to thermal
12 degradation is determined by its chemical constitution and affected by the presence of
13 fillers, pigments, stabilizers, plasticizers, and flame retardants.^[2] In most cases
14 decomposition occurs via free radical chain reactions, initiated by traces of oxygen or
15 other oxidising impurities in the polymer matrix, and give rise to various decomposition
16 products depending on the constitution of the polymer.
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20 If the gaseous mixture resulting from the mixing of degradation volatiles with air is within
21 the flammability limits and the temperature is above the ignition temperature, then
22 combustion begins. The combustion of a polymeric material is a highly complex process
23 involving a series of interrelated and/or independent stages occurring in the condensed
24 phase and the gaseous phase, and at interphases between the two phases. Flaming
25 combustion proceeds if the exothermic gas phase combustion reactions generate sufficient
26 energy, in the form of heat transferred back to the condensed phase, to decompose the
27 polymer further, thus producing more fuel and so maintaining the combustion cycle
28 (Figure 1).^[3]
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Figure 1. The combustion cycle.

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3 The flammability and resulting destruction of property are not the only problem. Fire
4 fatalities are essentially due to the evolved smoke and toxic gases, exacerbated in some
5 cases by poisonous fumes emitted from synthetic organic polymers.^[4] In addition, many of
6 the thermoplastic materials tend to melt and flow under heat/fire, and this can constitute a
7 very serious secondary hazard in fire scenarios involving them. For example in situations
8 where polymeric materials are used in the construction of doors, windows, ceilings and
9 roofs, etc.

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11 Successful strategies to reduce the flammability of a polymeric material involve breaking
12 into the complex stages of the combustion cycle (Figure 1) at one or more stages to reduce
13 the rate and/or change in the mechanism of combustion at that point.^[5] From a practical
14 point of view, this is achieved either by the mechanical blending of a suitable flame
15 retardant compound with the polymeric substrate (i.e. as an *additive*) or by the chemical
16 incorporation of the flame retardant into the polymeric molecule by a simple
17 copolymerization or by chemical modification of the preformed polymer (i.e. as a
18 *reactive*).^[6] Both additives and reactives can interrupt the burning cycle of a polymer in
19 several ways: by altering the thermal decomposition mechanism of a polymer; by
20 quenching the flame; or by reducing the heat transferred from the flame back to the
21 decomposing polymer. It is common practice, especially from a commercial point of view,
22 to use a combination of flame retardants for polymeric materials. In many cases, these
23 flame-retardant mixtures can give an enhanced performance at low cost.^[7,8] In recent
24 years, there has also been an increase in the use of multi-component intumescent systems,
25 and novel molecularly dispersed nano-scopeic fillers, such as clays, double metal
26 hydroxides, carbon nano-tubes, etc.^[9]

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28 Basically, there are two fundamental modes of action for flame retardant compounds,
29 namely vapour-phase inhibition and condensed-phase inhibition.^[3] If the radical
30 intermediates of the combustion process which exist in the gas phase are intercepted by a
31 flame retardant, it is said to exert vapour-phase inhibition. On the other hand, if a flame
32 retardant and/or its pyrolytic product(s) affect the solid state degradation mechanism of a
33 polymeric substrate in such way to reduce the supply of flammable volatile into the flame
34 zone thus interrupting the combustion cycle at this point, it is said to exert a condensed-
35 phase action. In majority of cases, the flame retardant(s) in question often can exert its
36 influence in both phases; however, the relative predominance in each phase is likely to
37 vary depending on its actual physio-chemical attributes.^[10] The ultimate selection criteria
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3 of a flame retardant for a particular polymeric material is also governed by the physical
4 and chemical properties of the polymer as well.
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7 8 **Testing procedures** 9

10 As a consequence of the complex nature and poor reproducibility of fire, there are many
11 traditional techniques for evaluating the degradative behaviours and for estimating the
12 flammability features of polymeric materials.^[11,12] Each technique often concentrates on
13 certain characteristics of the complex combustion process; for example, the ease of
14 ignition of the material, the flame propagation, the rate of heat release, the smoke
15 obscuration, etc. Generally, there are three main categories of test procedures: small-scale
16 tests in which a small amount of the sample is burnt and the combustion behaviour is
17 observed; medium-scale techniques involving calorimetric measurements, tunnel tests and
18 radiant panel test; and the large-scale room and corridor experiments. Although the large-
19 scale test are very comprehensive and give closest representation of a real fire situation,
20 they are expensive and difficult to control, and thus small and medium-scale tests are often
21 more practical.^[12] In any case, the first port of call is the thermogravimetric analysis
22 (TGA) where *ca.* 5-10 mg of a material is gradually heated, at a fixed heating rate (usually
23 10 or 20 °C/min) in a predetermined atmosphere (generally under nitrogen or in air) from
24 the room temperature to about 800 to 1000 °C. Such an approach, and the results obtained
25 therein, should be considered as quite aloof from what is actually happening to a material
26 in a real fire scenario. Nevertheless, TGA measurements can shed valuable information
27 regarding the thermal and thermo-oxidative behaviours of polymeric materials, and the
28 amounts of residues obtained through the runs are indicative of the propensity of the
29 material to form char, and thus reflects on the fuel production tendencies of the material
30 under a thermal insult.
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46 The following sections briefly describe the various techniques, including the TGA and the
47 associated 'hyphenated' measurements, to gauge the flammability attributes of polymeric
48 materials. These include: Limiting Oxygen Index (LOI) measurements; Underwriters
49 Laboratory (UL-94) tests; cone calorimetry; Pyrolysis Combustion Flow Calorimetry
50 (PCFC); smoke density and toxic gases measurements; 'hyphenated' techniques to study
51 the volatiles; analytical techniques to characterize solid residues; etc. In the final section,
52 correlations, if present, amongst the various test methodologies are discussed.
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Thermogravimetric analysis (TGA)

Thermo-analytical techniques are widely used for the study of polymer decomposition processes, but they cannot accurately represent the very complex process of polymer combustion. Furthermore, there is no simple correlation between the flammability of different organic polymers and their thermal stability. Thermal analysis can, however, be used to extract kinetic parameters governing step-wise/multi-step degradation of a polymeric material, undergoing thermal or thermo-oxidative degradation reactions, either under dynamic or static heating regimes. The thermograms, where generally the mass loss (as wt.%) is plotted against the temperature, can also provide valuable information regarding the change in the overall degradation profile, and associated char yield, of a particular polymer system and or the modified one with fire retardant compound(s), either by a reactive or by an additive route. In order to decipher more clearly the temperature, or its range, where subtle but definite changes in the profile of the thermogram is needed, a first derivative plot can be very useful.

The overall reproducibility of thermograms is quite satisfactory, however, they can slightly vary according to the sample size and morphology. In addition, and depending on the nature of the polymer under question, some salient features of the thermograms can vary according to the heating rates and/or depending on the atmosphere employed (i.e. air or nitrogen). The former can be accounted by the relative predominance of the possible individual degradation reactions and latter to the difference in purely thermal *versus* thermo-oxidative pathways of degradation. Generally, the amounts of char residue obtained for typically char-forming polymers (such as polyacrylonitrile, polyvinyl chloride, polymers containing char-forming precursor structures and certain thermosets) are higher in nitrogen than in oxygen, as secondary oxidation reactions of the carbonaceous char, especially above *ca.* 600 °C, are possible in the latter case. Furthermore, the quantity of char obtained for a polymeric material upon flaming combustion might correlate more readily with the actual amount of char residue formed from it owing to a fire, especially in under-ventilated conditions prevailing in typical enclosures.

The actual chemical steps, during decomposition of a polymer in a TGA run, leading to the formation of volatiles may differ in electronic nature, i.e. radical *versus* ionic. The three schemes common to most polymer degradations are given below.^[6]

1. Random chain cleavage followed by chain unzipping is characterized by high monomer yields in the degradation products and a slow decrease in molecular

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3 weight of the product (examples: polymethyl methacrylate, poly (α -methyl)styrene,
4 polytetrafluoroethylene, etc.).

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2. Random chain cleavage followed by further chain scission is characterized by low monomer yields in degradation products and a rapid drop in molecular weight (examples: polyethylene, polypropylene, etc.).
 3. An intra-chain chemical reaction is followed by a cross-linking reaction and formation of a carbonaceous residue, or random chain cleavage. This process generates a relatively high yield of volatiles from the inter-chain reaction, produces very little monomer, and produces no or only a very slight drop in molecular weight during the initial stages of degradation (examples: polyacrylonitrile, polyvinyl chloride, etc.).

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At least in some cases, several of these schemes occur simultaneously, depending on the sample size, heating rate, pyrolysis temperature, environment, and presence of any additives.

In a thermo-gravimetric experiment, the mass of *ca.* 5-20 mg of polymeric substance is accurately measured whilst it is either heated at a constant temperature, or at a fixed heating rate (usually 10, or 15, or 20 °C/min) from the room temperature up to about 1000 °C. Accordingly the thermograms can either plot of mass, or weight percentage, against time or temperature. Given that TGA experiments involve multiphase, and sometimes multi-component, materials and that often the degradation pathways of polymeric substrates can also involve multiple steps with competing parallel reactions, the extraction of kinetic parameters from these experiments are not straight forward.^[13] In this respect the reliability of kinetic parameters, especially obtained through a single thermo-gravimetric curve recorded at a certain heating rate, should be treated with caution. Here the kinetic parameters obtained cannot be used to predict the polymer degradation behaviours in conditions other than those corresponding to the thermogram in question. Generally, a set of curves, recorded at different heating rates, can furnish correct information regarding the degradation kinetics of a polymeric material, and the underlying equation denotes a single step kinetic process.^[14-16] However, it should be also noted here that weight loss measurements alone cannot provide the chemical and mechanistic parameters in complex organic polymer thermal degradation pathways. In fact, mechanisms need to be studied through the identification of the products of degradation and their rate of production under isothermal conditions.

The Limiting Oxygen Index (LOI) test

The most widely used laboratory test is the limiting oxygen index (LOI: ASTM-D-2683) technique, a very convenient, precise and reproducible test developed by Simmons and Wolfhard in 1957 and initially extended to polymers by Fenimore and Martin in 1966.^[17,18] The polymer sample, in the form of a small plaque or thin film, is ignited in an atmosphere of oxygen and nitrogen using a butane torch, and the oxygen to nitrogen ratio is varied, keeping the total gas flow rate to a constant level, so that the gas mixture supports candle-like combustion of the sample, for at least three minutes, or until a 5 cm length of the polymer is consumed. The limiting oxygen index is then expressed as the volume percentage of oxygen in the gas mixture. This value therefore, enables the combustibility of a polymer to be expressed and compared with that of the other materials. LOI values can be measured with a standard deviation of below 10% as shown by inter-laboratory testing (ASTM-D-2863).^[19]

Unambiguous identification of a flame retardant mechanism is difficult through LOI measurements, although it is possible to identify in which phase a particular kind of flame retardant is acting. Information concerning the type of mechanism involved with a particular flame retardant can be obtained by using a different oxidising medium such as nitrous oxide (NOI test).^[20] It is assumed that a flame retardant acting in the condensed phase works independently of the chemical oxidant, where as a change in flammability is observed with a change in oxidant for a flame retardant acting in the vapour phase. The Elevated-Temperature Oxygen Index module (TOI) sometimes is used alongside the LOI to determine the oxygen index at temperatures up to 125 °C. Elevated temperature at which materials will burn in air could be a better determinant of combustibility than is obtained through conventional LOI measurements. Ideally, the LOI values for a particular polymeric material should fall when the gas temperatures are increased. A typical LOI instrument can be modified so that elevated test temperatures are set by pre-heating the gas flow stream by an adjustable glass furnace. The temperatures of both heated sections are continuously displayed on the TOI control unit. When experiments are being carried out using different oxygen levels, gas conservation is achieved by using air from an integral quiet running pump between tests. Bottled nitrogen and oxygen supplies are only switched into the system for testing. The TOI at elevated temperature are determined in accordance with ISO 4589 Part 3 or the UK Naval Engineering Standard NES 715.

Underwriters Laboratory test (UL-94)

UL-94 test is widely used as an industrial standard, and basically is a vertical burning test on a solid plaque of the material, where ignition source is applied at the bottom of the hanging material in a chamber of ambient air. Depending on the orientation of the ignition source, with respect to the bottom tip of the specimen, the UL-94 test can be classified either as a horizontal burning test (HB test: ASTM D 635) or as a vertical burning test (VB test: ASTM D 3801). Generally, the latter orientation is employed, and the test leads to a pass/fail criterion of the material in terms of classifications, such as: V-0; V-1; V-2; etc. In addition, the melt/drip behaviour of the polymer, and the propensity of its drops to ignite surgical cotton placed at the bottom of the test chamber, is also gauged. Typically, for a material to pass this test (i.e. for a V-0 rating), the following criteria applies: 1) the specimens may not burn with flaming combustion for more than 10 seconds after either application of the test flame; 2) the total flaming combustion time may not exceed 50 seconds for the 10 flame applications for each set of 5 specimens; 3) the specimens may not burn with flaming or glowing combustion up to the holding clamp; 4) the specimens may not drip flaming particles that ignite the dry absorbent surgical cotton located 300 mm below the test specimen; 4) the specimens may not have glowing combustion that persists for more than 30 seconds after the second removal of the test flame.

Whilst UL-94 test results can be ambiguous in terms of the combustion behaviour of a polymeric material and are of not much use with regard to identifying the mechanism(s) of flame retardance, or development of fire safe materials, the ranking through the test can be used to assess the fire propagation risk. The latter can be serious secondary hazard in fire scenarios involving polymeric materials, for example, if present as component parts of the ceiling in an enclosure. In recent years, more quantitative attempts to measure the mass loss and the melt-drip behaviour of some of the commercially important chain-growth polymers have been accomplished.^[21,22]

Cone calorimetry

Whilst the LOI test is a valuable laboratory tool for highlighting and ranking the flame retardance of polymeric materials, the results give very little information as to how a material will behave in a real fire scenario. For this, the method of choice at present is the cone calorimeter. The cone calorimeter is a bench-scale instrument that was developed by

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3 the National Institute of Standards and Technology (NIST, formerly the National Bureau
4 of Standards, NBS) in 1982.^[23] The instrument measures a number of important fire
5 parameters under fully ventilated radiant heating conditions that include: time to ignition,
6 mass loss rate, heat release rates (peak and average), total heat released, effectiveness of
7 combustion (through CO/CO₂ ratios), smoke obscuration, etc.

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11 The rate of heat release of a material during combustion is considered to be one of the
12 most important parameters in determining how a material will contribute to fire growth,
13 and is calculated by the oxygen consumption principle.^[24,25] The oxygen consumption
14 principle is based on work carried out by Thornton in 1917, which showed that organic
15 fuels released an approximately constant amount of heat for each gram of oxygen
16 consumed during complete combustion.^[26] Huggett extended this work in 1980 by
17 obtaining an average value of 13.1 kJ for heat released for each gram of oxygen consumed
18 during combustion.^[25] Furthermore, he showed that this value was not significantly
19 affected by incomplete combustion. Huggett concluded that the heat released for *most*
20 organic materials could be calculated from the consumption of oxygen to within an
21 accuracy of $\pm 5\%$.
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30 A cone calorimeter simultaneously measures the consumption of oxygen and the mass loss
31 rate of a material and can, therefore, be used to calculate the effective heat of combustion.
32 In addition to this, the CO and CO₂ yields in the exhaust gases are also determined which
33 provides information on the efficiency of combustion, and hence on the likely toxicity of
34 that material should it be involved in a fire. Two standard test methods for using the cone
35 calorimeter are reported in the literature.^[27,28]
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40 Essentially, a sample measuring 100 mm x 100 mm and of specified thickness (*ca.* 6 mm)
41 is exposed to a pre-determined irradiance from the conical-shaped heater. Subsequent
42 degradation of the sample occurs resulting in the evolution of flammable species. The
43 volatile flammable gases diffuse with the air to form a flammable mixture, which is
44 ignited by the ignition source. The time to sustained ignition, which is defined as the
45 presence of a flame for longer than 10 seconds is then recorded. The exhaust gases are
46 separated in to two lines. The first line goes directly to the CO, CO₂ analyzer, whilst the
47 second line of gases is passed through soda lime and silica gel before reaching the
48 paramagnetic oxygen analyzer. The data is recorded every five seconds by an online
49 computer which automatically processes the data to calculate the rate of heat release, etc.
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58 During the tests, the mass loss and its rate of the specimen is monitored, through a load
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3 cell, and the smoke density by means of laser scattering technique. For better reliability,
4 usually, the runs are repeated in triplicate for a given radiance (say for example at: 35, 50
5 and 75 kW/m²).
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8 9 10 **Pyrolysis Combustion Flow Calorimetry (PCFC)**

11 Pyrolysis Combustion Flow Calorimetry (PCFC), also known as micro-scale combustion
12 calorimetry, was shown to be a very valuable small-scale technique for screening
13 flammability of different materials in recent years.^[29] PCFC is a very useful and rapid
14 screening technique as it only requires a few milligrams of a polymer for testing, and often
15 provides a wealth of combustion-related data. PCFC works on a principle of oxygen
16 depletion calorimetry, thus relating to Hugget's principle.^[25] At first, a polymeric sample
17 is rapidly heated to a state of controlled pyrolysis in an inert atmosphere of nitrogen
18 (method A: anaerobic conditions) or in a mixture of nitrogen and oxygen (method B:
19 aerobic conditions), followed by a rapid oxidation at high temperatures (i.e. combustion)
20 of the pyrolysate in an excess of oxygen.^[30] Generally, the former test method is widely
21 used in the case of polymeric materials. This method also is an established ASTM
22 standard for testing flammability characteristics of solid materials.^[29] PCFC is capable to
23 measure the following parameters: peak to heat release rate (PHRR); temperature at peak
24 heat release rate (TPHRR); total heat release (THR); heat release capacity (HRC) and a
25 percentage of the char residues. The values of HRC (i.e. maximum amount of heat
26 released per unit mass per degree temperature) can serve as a reliable indicator of a
27 polymer's flammability.^[30]
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43 **Large-scale tests**

44 There is a wide range of large-scale flammability tests, often prescriptive, and also varies
45 amongst different types of materials tested, for example for building materials, cables,
46 electrical appliances, upholstered furniture, clothing materials, mattresses, etc.^[31] In
47 addition, there are often other customized flammability tests, or tests which are popular in
48 certain countries (Forced Ignition Spread Test-FIST; Steiner Tunnel Test; etc.). The
49 former also encompasses special tests for materials that are used in aircrafts, railway
50 passenger cars, ships and submarines, etc. Quite often, large scale tests are difficult to
51 perform, and are costly and time consuming- the results so obtained can also generally be
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3 patchy with poor reproducibility, and can often do not have any significant correlations
4 amongst the various tests. Nonetheless, some of these tests are frequently needed to be
5 carried out, primarily, owing mandatory requirements. These include: road and railway
6 tunnel tests; flammability tests in the mining sector; flammability tests in the
7 transportation sector; proprietary furnace tests for large-scale construction structures like,
8 walls, roofs, ceilings, facades; etc.

9
10 Most construction products sold in Europe are needed to be tested and classified using a
11 relatively new test method called the Single Burning Item (SBI) EN 13823 test.^[32] The
12 Single Burning Item test is a method for determining the reaction to fire of building
13 products (excluding floorings) when exposed to the thermal attack by a single burning
14 item (a sand-box burner supplied with propane). The specimen is mounted on a trolley that
15 is positioned in a frame beneath an exhaust system. The reaction of the specimen to the
16 burner is monitored instrumentally and also visually. Heat and smoke release rates are
17 mainly measured instrumentally and physical characteristics are assessed predominantly by
18 observation. SBI has also defined the criteria for assessing building products into classes
19 A-F. Although other test methods are also required, the SBI is needed to classify all non-
20 flooring products into the classes A2, B, C and D, which are the major classes inhabited by
21 most products other than those that are principally inorganic and thus classified as non-
22 combustibles.

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24 One other large-scale test commonly used is the room-corner test where the specimen is
25 mounted on the walls as well as on the ceiling of a proprietary built enclosure.^[33]
26 According to Nordtest Fire 025, the ignition source, a propane gas burner, is operated at
27 two levels: 100 kW for the first 10 min and then 300 kW if flashover has not taken place
28 after 10 min. Flashover occurs when the total heat release reaches 1000 kW, which is
29 roughly when flames emerge from the doorway. The two burner output levels are
30 introduced to allow for discriminating between products of a wide range of flammability
31 properties. Products with good fire properties will not spread the fire beyond the
32 vicinity of the burner for an exposure of 100 kW, but may do so for 300 kW. The
33 lower output level is high enough to cause flashover of some products used in practice
34 while still being a relevant fire scenario, simulating, for example, a burning piece of
35 furniture or a waste paper basket.

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Measurements of smoke and toxic gases

The formation as well as the evolution of smoke from fires in enclosures is an important aspect of the fire safety design in built environments, as inhalation of smoke toxic gases, mainly CO, could account for the majority of fire fatalities. Therefore, analyses of the gaseous effluents from burning materials are of utmost importance. Whilst the propensity of a material to produce smoke and the extent of combustion reactions, measured in terms of the CO/CO₂ ratios, can be obtained through cone measurements, there are more specific and dedicated test methods to gauge these. One of the most readily available and widely used techniques involves the measurements using the National Bureau of Standards (NBS) smoke chamber.^[34] This instrument has been established for many years and is used widely in all industrial sectors for the determination of smoke generated by solid materials and assemblies mounted in the vertical position within a closed chamber. This widely-used test instrument measures the specific optical density of smoke generated by materials when an essentially flat specimen, up to 25 mm thick, is exposed vertically to a radiant heat source of 25 kW/m², in a closed chamber, with or without the use of a pilot flame.^[35]

A better understanding into physio-chemical degradation, and thereby the production of the volatile toxic products from polymeric materials, can be obtained through a steady state tube furnace (Purser furnace: ISO 19700).^[36] The apparatus consists of a tube furnace with a moving test specimen, controlled temperature and air flow. The apparatus has been used very successfully as a research tool, establishing a correlation between CO yields (the most toxic component in most fire gases) and the equivalence ratio (actual to stoichiometric fuel/air ratio). The technique allows for steady combustion conditions to be established. In addition to continuous monitoring of the key components of the fire gas, other volatile species may be analysed from grab-sampling by Gas Chromatography/Mass Spectrometric (GC/MS) and other techniques.

Coupling of condensed-phase to gaseous-phase: the 'hyphenated' techniques

The real time quantitative analyses of, at least, the major components emanating from materials undergoing pyrolysis are extremely crucial in unravelling the kinetics of gas-phase reactions, and thereby formulating appropriate mechanisms for the flammability and the flame retardation, if applicable, in these systems. Ideally, one should be able to

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3 quantify all major volatile species from solid fuels by appropriately chosen method(s) that
4 give reliable and reproducible results. Quantitative and real time analyses of the gaseous
5 species have been attempted in the past by employing various types of hyphenated
6 techniques such as TGA or Simultaneous Thermal Analysis (STA) coupled either to
7 Fourier Transform Infrared Spectroscopy (FTIR) or to Gas Chromatography/Mass
8 spectrometry.^[37,38] In spite of the vast amount of procedures cited in the literature and the
9 enormous advances in instrumentation techniques and associated software, there are still a
10 lot of issues that need be resolved before the best quantitative information can be
11 deduced.^[39-41] For example, the TGA/FTIR method of analysing the gaseous species often
12 face problems such as low concentrations of species of interest and/or their inadequate IR
13 response, condensation at the inter-phasing junctions, secondary undesirable chemical
14 reactions along transfer lines that are generally kept at elevated temperatures, etc. Whilst
15 mass spectrometry is highly sensitive for gaseous species analyses, for acquiring
16 quantitative results it often needs to be pre-phased with some sort of gas chromatographic
17 provision. This not only introduces a time delay into the analyses but also associated
18 problems of an off-line sampling and constraints on the availability of proper columns
19 and/or the corresponding calibration standards.

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32 Laser pyrolysis/time-of-flight mass spectrometry (LP/TOF-MS) has been applied to study
33 the pyrolysis reactions analogous to those that occur in the condensed phase-flame
34 interface of a burning polymer.^[42-44] Essentially, a sample is located just below the
35 ionisation chamber of the TOF-MS and the polymer surface is exposed to a 500 μs wide
36 neodymium-glass laser pulse at 1.06 μm . The temperature increase of the sample during
37 heating is estimated to be in the range of 650-1000 $^{\circ}\text{C}$. The volatiles escape from the
38 reaction zone and are quenched due to a rapid drop in pressure as they enter the pulsed
39 electron beam ionisation chamber. The fragments are then analysed by the TOFMS at 25
40 μs intervals. The data collected can then be downloaded on to computer for manipulation
41 and subsequent analyses.

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49 Curie point, or a high frequency pyrolyzer, eliminates some of the problems associated
50 with filament pyrolyzers.^[45,46] Essentially, a polymer film is coated on a thin,
51 ferromagnetic filament that is then placed in a quartz tube. The filament is rapidly heated
52 by the absorption of energy from an oscillator high frequency field until the spontaneous
53 magnetic polarisation decreases to zero (i.e. the Curie-point temperature is reached). For
54 example, a pyrolysis temperature of 590 $^{\circ}\text{C}$ was achieved using a Curie-point filament of
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3 composition: 60% nickel/ 40% iron. The volatiles emanating from material is fed into a
4 gas chromatograph equipped with an appropriate column, using helium as the carrier gas.
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6 An online quadrupole mass spectrometer with electron impact source was used to identify
7 the volatile species.
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10 11 **Char residue analyses**

12 Char is a complex material, both chemically and structurally. It is also difficult to prepare
13 it in a reproducible way, or to obtain in a homogeneous state. Therefore, relatively little
14 information is available on the chemical compositions and structures of chars.
15 Nevertheless, structural morphology and chemical nature of char residues from burning
16 polymers can lead to a valuable information about the mechanistic aspects of flame
17 retardants.^[47,48] Elemental composition, especially, with respect to hetero-elements, like P,
18 Si, B, etc., can be obtained through digesting the char samples with mixtures of
19 concentrated acid oxidants, and then analysing the aqueous extracts, either through
20 conventional techniques, or by employing inductively-coupled plasma/optical emission
21 spectroscopy.^[45,49] X-ray photoelectron spectroscopy (XPS) has been also extensively used
22 to study chemical bonding, elemental composition and depth profiles of the surfaces of
23 some intumescent flame retardant systems.^[50-53] FTIR and solid-state multi-nuclear
24 Nuclear Magnetic Resonance (NMR) spectroscopies are rapidly emerging as useful tools
25 in the characterization of solid residues from burning polymers.^[45] Scanning electron
26 microscopy (SEM) has been explored as an essential tool to study the surface morphology
27 of complex char structures.^[49,54]
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43 **Correlation among various test methods**

44 The relatively high concentrations of oxygen involved in the use of LOI technique are
45 unrepresentative of a real fire, and generally there is a lack of correlation between this test
46 method and others. However, limited but significant correlations were obtained between
47 the oxygen indices and char yields (both from the TGA experiments and from the amount
48 of char residues obtained through actual burning of specimens) in case of predominantly
49 char forming polymers. Of particular importance in this area is the work of van Krevelen
50 on the linear correlation between char and LOI, and it suggested that, in general, the LOI
51 of a polymer is proportional to the amount of residue formed on combustion.^[55] Although
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3 such correlations were not found in halogen-containing polymers, there were other
4 instances where this was found to be true, especially, in the cases of some phosphorus-
5 modified chain growth polymers that showed relatively high char forming tendencies.^[47,56]
6 Here, linear correlations were also obtained between the reductions in the heats of
7 combustion of the modified polymers, measured through oxygen bomb calorimetry, and
8 the weight percentages of phosphorus in the polymers. This affirms the fact that generally
9 phosphorus-containing flame retardants are predominantly active in the condensed phase
10 in polymers with noticeable char forming tendency. Furthermore, as heat of combustion is
11 closely correlated to the oxygen demand during combustion, it could be also assumed to be
12 related to LOI. There were also several successful attempts to estimate the values of LOI
13 from elemental composition of polymers.^[57]

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15 A review of literature on LOI methodology shows that, although there is abundant
16 information on the test, it is not clear that its results correlate well with those of any other
17 test, or indeed with those of real fires.^[58] Theoretical considerations indicate that the test
18 could be improved by using it with bottom ignition rather than with the standard top
19 ignition. A number of materials were tested in the cone calorimeter and their LOI values
20 generally show inverse correlations with those properties measured in the cone. These
21 correlations were not sufficiently sensitive, even when investigating small effects on a
22 single base polymer system to justify using LOI technique as a proxy for the cone
23 calorimetric test in any way. However, the LOI is likely to be continued as a quick,
24 reproducible laboratory scale test to rank the relative propensity of a material to undergo
25 piloted ignition.

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27 In the case of some thermoplastics, correlations were found to exist between UL-94 ratings
28 and some cone calorimetric measurements (for example, peak heat release rate and
29 average heat release rate).^[59] However, no relationship was found in the case of other
30 measurements like the time to ignition and total heat release. Therefore, a broad
31 quantitative relationship between UL-94 and cone calorimeter still remains elusive;
32 however, cone measurements can be useful to understand why a material passes or fails a
33 particular UL-94 rating. In the case of fire retardancy of polymer nano-composites, owing
34 to the formation of a barrier and the enhanced viscosity effects on combustion, would exert
35 specific impacts on their fire properties that consequently cause varying flame retardant
36 efficiency in different fire tests.^[60] The barrier formation retards mainly the flame spread
37 (thus affecting the heat release rate) in developing fires, but does not reduce the fire load
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3 (i.e. the total heat evolved), ignitability or the flammability (do not increase LOI values or
4 improve the UL-94 rating). Furthermore, the flame retardancy effect increases with the
5 increasing levels of irradiance in the cone calorimeter.
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8 The increased melt viscosity generally prevents dripping, which is beneficial or
9 disadvantages depending on the fire test used (i.e. UL-94 *versus* cone calorimetric test). In
10 some tests (for instance in LOI measurements), it can become a dominant factor
11 transforming self-extinguishing samples into flammable materials, or can cause the
12 wicking effect. It should be noted here that the barrier formation and changes in the melt
13 viscosity attributes in the case of nano-composites alone are not sufficient for them to be
14 classified as fire safe materials, especially, when it comes to large-scale test, or in real fire
15 scenarios. Recently, more comprehensive and quantitative approaches to closely gauge the
16 melt-dripping behaviours of polymeric materials have been reported.^[21,22]
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19 There is little doubt, when it comes to assessing the flammability attributes of a polymeric
20 material on a laboratory scale, that cone calorimetry is instrument of choice as it provides,
21 overall, a better combustion profile of the material under question. Furthermore, the
22 maximum rate of heat release is understood to be the most important measurable
23 parameter, from the cone calorimetric measurements, concerned with fire hazard and fire
24 scenarios, as it controls the rate of burning, the rate of mass loss and the probability of
25 secondary ignition of the surrounding environment. Therefore, attempts to reduce the rate
26 of heat release are now being to dominate research into flame retardants and fire
27 behaviour. While there is an increasing need to screen the flammability of the newly
28 modified materials for their flammability using a cone calorimeter, there is still a lack of
29 strong consensus within the fire science community on the interpretation of the cone
30 data.^[61] There are several important experimental variables that need close scrutiny before
31 any meaningful results and correlations can be derived from the cone data. These include:
32 applied heat flux and the distance of the cone heater from the sample surface; orientation
33 of the sample with respect to applied heat flux; length scale, sample
34 morphology/thickness; sample holder material/dimensions/configurations; temperature;
35 ventilation; role of anaerobic pyrolysis; melt-flow/wicking effects; etc. Simple empirical
36 approaches to correlate cone results with other fire tests have not met with much success,
37 and are usually limited to certain classes of materials.
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40 However, in the case of a limited number of materials, better correlations between cone
41 calorimeter and other tests was reported.^[62] In addition, the correlations with test results of
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3 other bench-scale tests are significantly improved, if the comparison is limited to those
4 tests which represent similar fire scenarios to the cone calorimeter, like the Swedish Forest
5 Product Research Laboratory (STFI) open-test arrangement, Ohio State University (OSU)
6 Calorimeter, Factory Mutual Research Corporation (FMRC) flammability apparatus, and
7 the flame height apparatus.^[63-65] Here again, the correlations are further improved when
8 adequate compensation is made for the differences between operating parameters of the
9 methods. Although the cone calorimeter targets fire properties of materials during the
10 developing phase of a fire, direct predictions of flame spread or heat release rates in
11 established large-scale tests, such as SBI test or the room-corner test, are not easy.
12 However, the recent developments in software tools have enabled the use of cone
13 calorimeter data to make reasonable predictions of the results of other tests. Furthermore,
14 specialized approaches based on empirical flame spread modelling have shown
15 increasingly satisfactory correlations, particularly for the SBI, the room-corner test, as well
16 as for other fire growth tests.^[66-69]

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27 Conventional methods of assessing the flammability attributes of a polymeric material,
28 through LOI, or by UL-94, or by employing cone calorimetric technique, requires tens to
29 hundreds of grams of material, and are not well suited to automation. In order to
30 circumvent some of these experimental constraints, Pyrolysis Combustion Flow
31 calorimetry (PCFC) has been developed in recent years as a potentially useful small-scale
32 screening technique that only uses milligrams of a test material. In addition, owing to the
33 small sample size required and the ability to provide fundamental flammability data,
34 PCFC is well suited to high throughput research.^[70] In a recent reports, some correlations
35 between PCFC and conventional flammability tests in the case of several polymeric
36 materials were also presented.^[29,71] However, the PCFC like any milligram-scale test
37 method fails to account for the physical effects that typically occur on larger length or
38 mass scales, such as dripping or intumescence. Since the length scale of the
39 component/sample plays a large role in the fire behaviour, there are in principle strong
40 limitations for correlating micro-scale with real-scale fire tests. Combining results from
41 PCFC with those from oxygen bomb or cone calorimeter tests might yield an additional
42 understanding of fire behaviour.^[56]

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Concluding remarks

As can be seen from the above sections that, whilst there are a wide variety of analytical techniques and test methods to assess the flammability attributes and combustion characteristics of polymeric materials, most of the test methods are prescriptive in nature and do not necessarily reflect on the actual behaviour of the materials in a real fire scenario. In addition, the various small-, medium- and large-scale methods generally tend to concentrate on some specific aspects of the flammability of the material in question and often lack meaningful correlations. Therefore, the results from a particular test are strongly biased to a particular fire risk, or fire hazard, involving a particular specimen in a particular fire scenario. Ideally, one should be able to predict the behaviours of the various solid materials in real scale fire scenarios by looking into the intrinsic properties of the materials (such as its density, thermal conductivity, heat capacity, thermal diffusivity, etc.) and from other related empirical parameters without having to resort to actually carrying out expensive, and often time consuming, large-scale tests. However, this task is rather difficult owing to the complex nature of the combustion processes of solid polymeric materials and to the poor reproducibility of fires themselves. This necessitates a more concerted effort from the scientific community, involved in fire safety research, to try to formulate methodologies that would harmonize the various test regimes, and the ensuing results, performed at different scales. In doing so it might become possible, in the near future, to predict the realistic behaviours of various materials in real fire scenarios, from the empirical parametric evaluations obtained through scientifically-sound and economically-viable small- to medium-scale laboratory experiments.

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