

# Recommendations on the scientific approach to polymer flame retardancy: Part I—Scientific terms and methods

Journal of Fire Sciences

2016, Vol. 34(6) 447–467

© The Author(s) 2016

Reprints and permissions:

sagepub.co.uk/journalsPermissions.nav

DOI: 10.1177/0734904116675881

jfs.sagepub.com



**Bernhard Schartel<sup>1</sup>, Charles A Wilkie<sup>2</sup> and  
Giovanni Camino<sup>3</sup>**

Date received: 2 September 2016; accepted: 4 October 2016

## Abstract

The correct use of scientific terms, performing experiments accurately, and discussing data using unequivocal scientific concepts constitute the basis for good scientific practice. The significance and thus the quality of scientific communication rely on the proper use of terms and methods. It is the aim of this two-part article to support the community with recommendations for discussing the flame retardancy of polymers by addressing some of the most relevant points. The first article (part one of two) clarifies some scientific terms and, in some cases, such as for “pyrolysis,” “thermal decomposition,” and “fire resistance,” critically discusses their definitions in the field of fire science. Several comments are made on proper fire testing and thermal analysis, including some thoughts on uncertainty in fire testing. The proper use of distinct concepts in flame retardancy is discussed briefly in the subsequent second article (part two). This article tries to balance imparting background on the subject with recommendations. It encourages to check scientific practice with respect to communication and applying methods.

## Keywords

Pyrolysis, fire testing, char, flame retardant, flammability, fire property

<sup>1</sup>Bundesanstalt für Materialforschung und prüfung (BAM), Berlin, Germany

<sup>2</sup>Department of Chemistry, Marquette University, Milwaukee, WI, USA

<sup>3</sup>Dipartimento di Scienza Applicata e Tecnologia and INSTM Local Unit, Politecnico di Torino, Alessandria, Italy

## Corresponding author:

Bernhard Schartel, Bundesanstalt für Materialforschung und prüfung (BAM), Unter den Eichen 87, 12205 Berlin, Germany.

Email: [bernhard.schartel@bam.de](mailto:bernhard.schartel@bam.de)

## Introduction

The essence of scientific communication is to deliver a main message, clearly describe work that has been carried out following well-defined protocols, and discuss or assess the results and phenomena observed in terms of scientific concepts. It is unfortunately true that all of us are, on occasion, guilty of failing in this regard. For instance, the concept of “synergy in flame retardancy,” methods based on milligram specimens, and the term “char,” among others, are often used according to an individual interpretation or unclear basis. The exact definitions of scientific terms seem to be bent or even ignored, as are important boundary conditions for concepts in flame retardancy, applicability of analytical methods, and quality management in fire testing. No references will be cited to illustrate the misuse of terms, because the goal is not to embarrass authors, but rather to discuss ways toward more correct usage. The aim is to offer recommendations on the use of terms in the field of flame-retardant polymers by sensitizing, reminding, and clarifying, as well as by initiating rethinking and discussion on this matter. It must not escape our notice that continuous optimization using terms, methods, and concepts in the flame retardancy of polymers is an essential part of proper quality management and a basis for competence in scientific work.

In this first article, part one of the recommendations, two points will be addressed: **first, correct wording as the basis for unambiguous description.** Methods and terms are often well described by the *International Standards Organization* (ISO) and these terms will be used throughout. It seems that the community—including the authors of this article—may not always care enough about these definitions and use their own definitions instead, or mix up terms. This misuse regularly produces misleading communication between authors and readers, or even incorrect understanding of the phenomena occurring. **In this first article, the challenges and dilemmas that accompany the use of some terms are discussed with respect to the exact meaning based on their definition,** particularly according to ISO 13943 “Fire Safety Vocabulary”:<sup>1</sup> pyrolysis, thermal decomposition/degradation, fire properties (ignition, ignitable/ignitability, flammable/flammability, combustible/combustion, etc.), particular fire resistance, toxicity/environmental friendliness, and fire/flame retardant.

**Second, methods** must be used properly to decrease uncertainty and within applicability. Performing fire tests properly demands great effort in quality management (preconditioning, regular calibration, controlling test conditions, proper mounting, etc.), and some of this is a challenge for most research studies due to a lack of time, resources, or specimens. Furthermore, the use of methods, and particularly the interpretation of the result, demands that the specific limitations of each method be taken into sufficient account. Distinct aspects are discussed in this first part: for instance, analytical methods based on mg specimens, microscale combustion calorimeter (MCC), oxygen index (OI) and UL 94 classification, and the cone calorimeter.

Several distinct topics are selected with respect to scientific terms, polymer analytical and fire testing methods in part one and with respect to concepts in flame retardancy of polymers in part two.<sup>2</sup> Together, this two-part article supports the community by offering recommendations to strengthen good scientific practice in the field of flame retardancy of polymers.

## Calling a spade a spade: correct wording as the basis for good scientific description

### General remarks

There is a common picture of two columns sustaining competence in scientific work. Each column consists of three disks. One column describes the more conceptual aspects of competence: **identify the actual tasks/questions/topics**, **describe the phenomena/mechanisms/principles**, and **use evidence to take a step ahead**. The other column summarizes the basic tools: **know-how**, **knowledge**, and **communication**. There may be no sustainable scientific excellence when any of the six aspects is weak. Using precise and correct wording is not a question of writing style, but a basis of quality in scientific work. Thus, not only choosing the most appropriate topic but also knowing the proper scientific terms and using them correctly must be a crucial part of teaching and training students. Indeed, it is an essential element of permanently improving scientific practice.

**Incorrect wording generally occurs in at least three different ways:** **first**, the incorrect use of scientific terms or incorrect wording due to a lack of knowledge or sketchy or poor communication; **second**, using distinct scientific terms and wording intentionally to upgrade results and conclusions; and **third**, the unfortunate inventing of new terms to promote personal findings. Introducing new terms ultimately misleads and confuses regarding phenomena, principles, and mechanisms for which terms already exist. Furthermore, introducing completely new terms is not recommended for phenomena so close to known behavior that the community finds it difficult to understand the difference and its importance. A proper description in good scientific practice must not use any kind of improper upgrading through wording. For instance, an improvement limited to flame spread must not be called “flame resistance,” or be sold as “general flame retardancy.” Unfortunately, the review system in use in publishing does not sufficiently curb the incorrect use of scientific terms or the use of incorrect terms. Scientific papers may not be much help, since one may not know which papers to use and which to avoid. Textbooks are a much better source for the correct use of scientific terms. However, **the best source is standards**, such as the **ISO 13943** “Fire Safety Vocabulary,”<sup>1</sup> **ASTM E176—15a** “Standard Terminology of Fire Standards,”<sup>3</sup> and the standards for specific fire tests. Standards actually summarize **the state of the art**, the essential and important basis of knowledge. It is confusing that much scientific writing is not in compliance with ISO 13943 and the more specific standards for the distinct fire tests.

### Pyrolysis

The use of wording that precisely describes the scenario defined by all the parameters affecting a phenomenon is the necessary basis scientific communication about the phenomenon itself. Understanding a fire and its interaction with materials encompasses a number of disciplines from chemistry to physics, and engineering, each of which has independently developed its own vocabulary of technical and scientific terms. The unfortunate result is that in some cases the same term may be used to designate a different scenario, depending on the disciplinary approach.

A typical example concerns the basic chemical process involved in fire, that is, the production of volatile combustible products initiated by the scission of chemical bonds of a material exposed to a heat source. In addition to the obvious dependence of the process on

the chemical nature of the material, there may also be a strong effect due to the presence of oxygen. Indeed, in the absence of oxygen, the scission of chemical bonds is exclusively due to the interaction of chemical bonds with the heat transferred to the material. In terms of kinetics, this bond scission rate is of the first order, controlled by the heat flux and activation energy for thermal bond scission. In the presence of oxygen, a reactive molecule bearing two unpaired electrons, a chemical reaction may take place between gaseous oxygen and the condensed phase of the material under investigation. The chemical process then becomes a second-order kinetic reaction, and since it occurs in a heterogeneous condensed-gaseous phase, its rate is controlled not only by the temperature and activation energy but also by the rate of oxygen diffusion and its temperature-dependent solubility. As a practical consequence, the thermo-oxidation may occur at a lower temperature than thermal decomposition, differ in number of decomposition processes, and deliver a different char and char yield. In chemistry, chemical engineering, and within the polymer degradation community, “pyrolysis” is generally accepted to mean a purely thermal process in the absence of oxygen; in the fire science ISO 13943 standard, it is defined as a heat-induced decomposition, whether based on thermo-oxidative or thermal decomposition. Furthermore, the standard reports that “pyrolysis” often refers to a stage before flaming combustion has begun, in which the material is exposed to oxygen, whereas in flaming combustion material decomposition occurs essentially in anaerobic conditions. For correct communication, it is therefore essential that in the fire literature the term “pyrolysis” be integrated with a description of the atmosphere.

### *Thermal decomposition*

Another example of possible misunderstandings connected with terms closely linked to each other concerns “thermal degradation” and “thermal decomposition,” which are mostly used synonymously. The ISO 13943 standard relates “thermal degradation” to a heat-promoted process that causes the deterioration of one or more physical properties, whereas “thermal decomposition” refers to an irreversible heat-triggered chemical modification.<sup>1</sup> By the way, in *ISO 472 Plastics—Vocabulary*,<sup>4</sup> the same differentiation between degradation and decomposition is underlined: properties degrade, whereas chemical structures decompose.

### *Fire properties*

Using the right terms without confusion is not as easy as it sounds because they are sometimes closely linked to each other. Indeed, even some of the common basic terms in fire science are hard to differentiate when no specific context, such as a certain fire test, is given. Most difficult, for instance, are the adjectives: “ignitable,” “flammable,” and “combustible.” “Capable of catching fire,” “capable of catching fire in the form of flaming combustion under specific conditions,” and “capable of catching fire and burned,” respectively,<sup>1</sup> show many more similarities than differences. In everyday life, we only know materials and components that are ignitable, flammable, and combustible all at the same time and thus use the terms as synonyms. The problem seems to be similar for the corresponding nouns: “ignitability” (“ease with which a test specimen can be ignited under specified conditions”), “flammability” (“ability to burn with a flame under specified conditions”), “burning behavior” (“response of a test specimen when it burns under specified conditions, to

examination of reaction to fire or fire resistance”), “fire behavior” (“change in, or maintenance of, the physical and/or chemical properties of an item and/or structure exposed to fire”), “fire performance” (“response of a test specimen when exposed to a fire test”), and “combustion” (“exothermic reaction of a substance with an oxidizing agent”).<sup>1</sup> Only in a specific context does exploiting the differences in the definitions become valuable, such as when describing the results in a certain fire test. The power of the strong link between fire testing and exact wording becomes most obvious, when certain fire tests give birth to certain terms like the German B1 for “schwer entflammbar” (difficult to ignite) and B2 for “normal entflammbar” (normally flammable). A correct and shared use of terms describing the behavior of a material in a fire scenario is not only a purely scientific urge, indeed it is of paramount importance in avoiding deleterious materials misuse, favored by commercial labels such as “fireproof,” understood by the end user as a material that would not burn.

A lot of common and important small-scale fire tests for polymeric materials simulate the fire scenario of ignition or, in other words, the beginning of a fire. Nevertheless, it is extremely rare that fire tests monitor whether the materials are ignitable and thus measure their ignitability. Most of the small-scale fire tests, particularly the widely used ones based on the reaction to a small flame (OI, UL 94, etc.), do not measure the ignitability of the specimen, but assess their flammability. **At the end of the day, extinction or the critical conditions for extinction are observed during the tests.** On the other end of the spectrum, the term “combustion” is generally much more suitable for all kinds of premixed flames, including the combustion of fuel in engines. A test that checks explicitly whether materials are combustible is, for instance, the non-combustible test (ISO 1182) for building products, in which the burning, temperature increase, and mass loss are observed within an oven at temperatures of up to 750°C (reminder: combustion = “exothermic reaction of a substance with an oxidizing agent”).<sup>1</sup> Certainly, there is combustion in every kind of fire test, but this is usually not the point of investigation. Even fire tests based on forced flaming combustion, such as those in the cone calorimeter, simulate developing fires and are mainly intended to observe the flammability, burning behavior, fire behavior, and fire performance of a specimen, but not its combustibility.

## Fire resistance

Apart from using exact wording to improve scientific description and to deduce correct interpretation, using wrong terms is misleading and is sometimes the starting point for confusing conclusions. A very common example of this is the use of the terms “fire-resistant” and “fire resistance” for all kinds of fire tests. **Fire resistance is the “ability to withstand fire or give protection from it for a period of time.”**<sup>1</sup> Thus, it is strongly related to fire penetration, or heat penetration and the structural integrity of components in fully developed fires simulated by standardized temperature–time curves or direct flame application. Typical criteria are fire integrity, fire stability, and thermal insulation.<sup>1</sup> **The terms “fire resistance” and “fire-resistant” must not be used in connection with fire tests simulating the beginning of a fire, which measure flammability such as reaction to small flame (OI, UL 94, etc.).** Reaction-to-fire tests such as SBI (single burning item), radiant panel, or the cone calorimeter also simulate developing fires and measure fire behavior in terms of heat release and flame spread, but not any kind of fire resistance.

### *Fire retardant and flame retardant*

Unfortunately, the most relevant definitions dealing with the capability of an additive or a treatment to provide an improved reaction to fire for a material that is “fire retardant” or “flame retardant” according to the ISO 13943 standard may seem somewhat obscure. The standard defines a “flame retardant” as “substance added or treatment applied” that suppresses/delays the appearance of a flame and/or reduces the rate of flame spread.<sup>1</sup> While the term “fire retardant,” as far as ignition is concerned, is restricted to those “substances added or treatments applied” that delay ignition, as far as combustion is concerned, it is limited to reducing the rate of combustion.<sup>1</sup> Apart from the fact that flame retardant addresses only flaming combustion, but fire retardant also smoldering combustion, the difference between reducing the rate of flame spread and the rate of combustion may not be clear. In practice, the terms “flame retardant” and “fire retardant” are widely used as synonymous. Somewhat alternatively, it has also been proposed that “flame retardant” be used for all kinds of flame retardancies acting within the beginning of fire, such as ignition, reaction to small flame/small ignition source, and reducing the rate of flame spread, whereas “fire retardant” be used with reference to developing fires and flaming combustion scenarios. No recommendation is made on this here.

### *Fire properties in different scenarios*

In the field of fire science, using the right scientific terms reaches far beyond using the correct semantics because fire properties are so far away from material properties. A fire property is the response of a defined specimen or component in a specific fire scenario and controlled by the complex interaction of a variety of different material properties such as heat of combustion, char yield, heat of gasification, decomposition temperature, heat conductivity, and viscosity of the melt. Precise description is a crucial and helpful means to communicate. It is not necessary, nor even commonly found, that important fire properties of materials will correlate with each other. The ranking of asset of materials may be different when comparing the results of different fire tests, as well as the efficiency of approaches to flame- or fire-retardant polymers. Improving the fire resistance, for instance the fire stability of a component, demands often quite different measures when compared to flame retardancy to reduce heat release rate or flame spread in reaction-to-fire tests. The same becomes obvious when comparing the performance and flame retardancy in reaction-to-fire tests with the performance and approaches in a smoldering fire. The fire scenarios are quite different as are the fire properties observed. A burn through can occur without any flame spread over the surface; efficient flame retardants in reaction-to-fire test may worsen the performance in smoldering scenarios.

### *Toxicity and environmental friendliness*

Toxicity and environmental aspects related to the use of chemicals have become emotional issues in recent decades, which in the case of fire retardants can lead to scientifically unsupported discussions and arguments.

For example, the intrinsic toxicity of some of halogen-based fire retardants and/or the decomposition products they may release have led to general requests for “halogen-free” fire retardants. This halogen-phobia is scientifically speaking somewhat grotesque, as toxicity cannot be ascribed to a single element alone. Rather, it is a biochemical characteristic of chemical compounds, involving bioaccumulation in various tissues of a living organism as

well as complex interactions with biomolecules that are dictated not only by chemical composition. A typical example is that of benzene and toluene. The first is carcinogenic and the second is not, with the only chemical difference due to a single methyl group linked. When the toxicity of benzene was discovered, had the same approach been adopted as in the case of fire retardants, all compounds bearing a benzene ring would have been banned; in actuality, whenever possible, benzene has been replaced by toluene.

The halogen-containing flame retardants, being non-selective, include inorganic, aliphatic, and aromatic chemicals. Only some of these chemicals have been shown to have major toxicity problems (polychlorinated and brominated biphenyls, poly brominated biphenyl ethers, etc.). In particular, triggered by voluntary policy instruments like eco labels and green procurement, the oversimplified technical information “halogen-free” has been widely accepted as a positive distinction. The choices dictated by generalized halogen-phobia seem to be foolishly repeated by proposing the replacement with phosphorus-based fire retardants as a general chemical class covering both rather harmless and toxic substances. This paragraph must not be misunderstood as merely listing the pro and cons for halogen-free flame retardants, but aims to point out the following: it has to be clear that toxicity must be assessed for individual compounds, dismissing any assumption based on chemical similarity.

In a similar way as toxicity, environmental friendliness also affects the development of fire retardants and is often addressed with a similar oversimplifying approach. It is common that renewable and/or recyclable is a synonym for sustainable or environmentally friendly, respectively, whereas the opposite may be true. Sometimes environmentally friendly is used as synonym for halogen-free, which is a poor definition. Indeed, it is well recognized that only a professionally applied life cycle analysis (LCA) can ensure and quantify the sustainability of comparable products and processes. Even when neglecting the source and production of a flame retardant itself, toxicity, bioaccumulation, and persistence are the main properties to check in detail when assessing the environmental friendliness.

For both topics, “toxicity” and “environmental friendliness,” it would be a tremendous help if only studies actually deliver data and results on these topics are used to formulate conclusions and statements. All common declarations, such as “sustainable,” “green,” “environmentally friendly,” and “non-toxic,” must be avoided when only based on intention, but without supporting data or referring to data on these properties. A scientifically sound discrimination of fire retardants in terms of these properties would avoid unjustified discarding of effective fire retardants.

### ***“Remarkable, excellent, outstanding”***

Last, but not least, the generous use of modifiers, such as “excellent,” “superior,” “extraordinary,” “remarkable,” and “outstanding” to underline the flame retardancy effects found is addressed in this section. These descriptors should always be supported by quantification based on a proper scale or using a proper benchmark. In general, good scientific writing is about “showing,” not “telling” results, meaning that statements should be quantified. Furthermore, any tiny reduction in a fire risk barely greater than the uncertainty must not be called “excellent.” Even quite significant reductions can be meaningless—for instance, in the rate of flame spread in UL 94 HB, or in the peak heat release rate (PHRR) in the cone calorimeter—when the absolute values indicate that the material is still burning vigorously. Particularly when discussing relative reductions, such as a reduction of 50% in the flame spread rate or in PHRR, such claims have the potential to discredit any reasonable idea of

fire performance. Indeed, a reduction of 50% can be either a rather disappointing or an impressive achievement.

## Using methods properly

### *Uncertainty in fire testing and proper fire testing*

The repeatability of fire test results is usually good within the same fire lab; the reproducibility between different labs is or is believed to be less so. Furthermore, the number of tests in fire testing is usually limited. Indeed, performing one, two, three, or six tests within a complex fire scenario is hardly enough for proper statistical determination of the uncertainty. The main reason for these problems, somewhat intrinsic to fire testing, is that three sources of uncertainty must be addressed:<sup>5,6</sup>

- Measurements quantifying fire performance;
- Material/specimen;
- Test conditions.

Application of the *Guide on Uncertainty of Measurements* (GUM) to fire tests is not trivial.<sup>7</sup> Janssens<sup>8</sup> published on this topic, discussing two examples in detail, but there is a great deal of research activity in other groups as well,<sup>9–13</sup> among others. Furthermore, several activities within ISO as well as ASTM tackle the determination of uncertainty in fire testing. However, in practice usually neither the complete set of uncertainties of the input parameters for error propagation is known or available—such as the uncertainty of the mass flow in duct, temperature, oxygen concentration, CO<sub>2</sub> concentration, E-factor (13.1 MJ/kg O<sub>2</sub>), ambient pressure, humidity, and gas expansion factor in the case of the cone calorimeter—nor is the number of tests large enough to perform proper statistical analysis. When it comes to actually calculating uncertainty, fire testing often falls short. Thus, within some of the ISO or IEC standards describing fire test methods, the community has agreed to test method-specific procedures to reasonably assess their uncertainties. The mere fact that these procedures are somehow arbitrary makes it mandatory that they be used. The lack of statistics must not be used as an excuse to skip a discussion of uncertainty or to use individual solutions.

With respect to repeatability, the operator, the quality of the specimen, and some intrinsic characteristics of the material often become the most important factors determining the uncertainty of testing. With respect to reproducibility, the test conditions may play a major role, assuming that deviations occur more from lab to lab than within the same facility. Some characteristics such as strong deformation (collapse, bending, intumescence, melt flow, etc.) may be intrinsic to a material, and it must be accepted that these lead to a deterioration in repeatability. Nevertheless, fire test results, particularly for these more difficult materials, are often extremely sensitive to test conditions such as mounting and flame application. The uncertainty due to the specific materials' behavior is amplified by improper test conditions or vice versa restricted by perfect test conditions. Representative specimens and homogeneous sets of specimens are the basis of valuable fire testing, particularly since the number of measurements is usually limited. Variations in morphology, ingredients, homogeneity, or thickness, or low numbers of specimens must be avoided. Deviations in fire test results performed by different operators are, of course, a somewhat awkward adjusting screw to turn. Simply



minimizing or ruling out the impact of the operator by partly automating the fire test is used to some extent. For instance, automated UL 94 testing, including flameout determination, has been reported.<sup>14</sup> Indeed, replacing visual observation by the operator, which is an essential part of many fire tests and interpretation of results, is not trivial. However, for the same example, UL 94 testing, another industrial study has shown that subjective visual observations, such as of ignition, flame height, and flameout, are not the actual problem.<sup>15</sup> The key parameters influencing the UL 94 result were concluded to be the heat source, that is, intensity, duration of application, and flame pull-away technique.<sup>6,15</sup> In any kind of reaction to small flame test, carefully following the instructions pertaining to the ignition source's size, location, and duration of application is essential. An analogous conclusion applies for irradiation in fire tests such as the radiant panel or the cone calorimeter. This sensitivity of fire test results on the test conditions points out that the dependence of fire test results on the operator is because of lax compliance with the test protocol, amplified by the sensitivity of the material to the testing conditions. Minimizing the impact of the operator turns out to be a task for proper training in the details and self-critical inspection of established procedures and workflows.

The reported uncertainty ranges deduced from round-robin tests are much larger than the uncertainty ranges within each lab. For instance, the literature often refers to a cone calorimeter uncertainty range of  $\pm 10\%$ , whereas cone calorimeter measurements within the same lab on well prepared, thermally thick specimens without any deformation and reasonable heat release rates can show uncertainties of below 1%–2%. The cone calorimeter is neither the only example nor the most critical one. Nevertheless, it is a good example to illustrate the challenge of ensuring proper test conditions. One challenge is the calibration of the different parts, such as the heat flux meter and the methane flux meter. Not only the daily calibration should be performed daily but also additional procedures, such as checking the heat flux meter or the methane flux meter in use with a second one, should be regularly performed. Furthermore, accurate daily use is required. Deviations in flow (pressure) measurements or leakage in the system have been identified to result in incorrect daily calibration, as well as sketchy adjustment of the irradiation deteriorating all the subsequent measurements.<sup>8</sup> Three other aspects are quite typical for fire testing: defined specimen size, correct mounting, and sufficient preconditioning. Fire tests do not measure material properties, but the reaction of a distinctly defined specimen under specified conditions. This is also true for tests such as OI, UL 94, or Bunsen burner-type test.<sup>16</sup> The results of fire tests are not independent of specimen size, and the dependency varies from material to material. The specimen size defined in the standards must not be changed. Fire test results also change when the mounting or the sample holder setup is modified.<sup>17–19</sup> Any freedom in the mounting or setup given by the corresponding standards must not be used to achieve the results desired, but only to adjust and optimize the testing toward simulating end-use conditions. In particular, piecing together specimens should be mentioned as a problematic procedure commonly done, for instance, for automotive parts which are not planar or short in size for FMVSS 302, or cone calorimeter testing under end-use conditions.<sup>6</sup> Proper preconditioning of specimens before fire testing is mandatory. It is obvious and well known that the water content of wood is one of the main parameters controlling that material's flammability. Recently, Safronava et al.<sup>20</sup> reminded us how great the difference in fire performance is for all kinds of polymers when measured in "wet" and "dry" conditions. Proper maintenance of the fire testing apparatus, including sufficient quality management but also preconditioning is part of measuring according to standards such as ISO or ASTM. The main points of the testing procedure

should be sketched to avoid misunderstandings, chosen parameters (for instance specimen thickness and irradiation or whatsoever) must be given in the description, and any deviation from the standards must be indicated.

It should be noted that these few paragraphs do not draw any complete picture of proper fire testing, but only try to draw attention to certain issues. This article cannot serve as a comprehensive manual for all kinds of fire tests, but can only sensitize the reader. Performing fire tests properly entails intensive efforts to ensure correct results with limited uncertainty. To succeed in this task, these efforts must address three independent challenges: reducing the uncertainty and ruling out systematic deviations in measurements quantifying the fire performance, selecting materials/specimens with minimized deviations, and taking care of the proper test conditions.

### *Mainly anaerobic pyrolysis with some thermo-oxidation*

After ignition, the pyrolysis of polymer products like plates and slabs is usually dominated by anaerobic decomposition when burning with a stable flame. The oxygen concentration of the gas below the flame and in contact with the specimen surface is crucially reduced. Apart from the surface layer, the oxygen absorption rate is much too low to result in noteworthy thermo-oxidative decomposition. In particular, fire residues of macroscopic specimens taken directly after flameout match the residues of thermogravimetry under N<sub>2</sub>, but not the residues obtained by thermogravimetry under air. This is one of the basics in fire science and the fire behavior of polymers, reported over and over again in common textbooks.<sup>21–23</sup> Thermo-oxidative decomposition occurs for the surface layer before ignition and for the fire residue after flameout. Phenomena such as afterglow exhibit thermo-oxidative characteristics. This is clearly illustrated by the example of burning polymer composites containing carbon fillers such as carbon black, carbon nanotubes, or graphene.<sup>24–27</sup> Carbon fillers are thermally stable and thus not consumed during burning with a stable flame, but initiate a pronounced afterglow due to their thermo-oxidative decomposition. Effective intumescent systems tend to burn without a stable flame, so that thermo-oxidative stability becomes an important property. Polymeric materials in the form of fibers, textiles, foams, and so on may also be controlled by thermo-oxidation through their high surface-to-volume ratio. Apart from these material characteristics, the testing conditions also play an important role. Two of the most popular small-scale fire tests for polymeric materials are the UL 94 and the OI. In both tests, a burner flame is applied to the specimen and extinction afterward observed. Thus, in these tests, a stable flame is applied, accompanied by anaerobic pyrolysis. On the other hand, fire tests addressing smoldering scenarios are based on thermo-oxidative decomposition. To sum up, it is advisable to reflect much more accurately about the atmosphere in which thermal analysis and preparation of residues are performed. Preparation methods and analysis based on different atmospheres must not be confused when interpreting results on fire performance and fire residues. Thermogravimetry is an extremely powerful tool to understand anaerobic pyrolysis and thermo-oxidative decomposition, but must not be misunderstood as precise or unambiguous simulation of the related phenomena occurring when a macroscopic specimen burns.

### *Analytical methods based on mg specimen: thermogravimetry as an example*

Thermogravimetry is regularly carried out by heating at 10 or 20 K/min, which provides an understanding of the intrinsic thermal decomposition behavior of the material. Pyrolysis–

gas chromatography (GC)–mass spectrometry (MS), the second most frequently proposed method to characterize pyrolysis, was originally based on jumping to a distinct temperature much higher than the typical pyrolysis temperature of a material. The information obtained must not be used as such to predict fire behavior directly, for the reasons discussed below. The decomposition may depend strongly on the actual heating rate because it often takes place through competing chemical reactions characterized by different activation energies.<sup>28–34</sup> Measurements inside the burning specimen deliver heating rates of around 60 and 130 K/min.<sup>35–37</sup> These heating rates are typical and dominant for the pyrolysis of burning polymeric samples. Due to the limited thermal conduction of polymers, only the top surface is heated at very high heating rates (>200–350 K/min), when in direct contact with a flame, for instance. Thus, the heating rates common in thermogravimetry are a little bit too low, whereas the immediate scission of all kinds of bonds in pyrolysis–GC–MS is not representative when the method is used without adjusting parameters. Oxidative decomposition is controlled by oxygen diffusion into the macroscopic specimen as the reaction rate increases. Typically, oxidative and anaerobic pyrolysis yield the same results in oxygen-sensitive polymers exposed to high heating rates, which results in an oxygen concentration too low to allow the bimolecular reaction with oxygen to compete with monomolecular pyrolysis. Actually, methods based on milligram specimens show crucial shortcomings for describing the thermo-oxidative processes of macroscopic specimens in fire tests.

Analytical methods based on milligram specimens are designed to eliminate temperature gradients within the examined sample, whereas in burning specimens distinct temperature gradients are present as an essential part of their reaction to fire. Moreover, in thermal analysis, the heating rate or pyrolysis temperature is constant, whereas in pyrolysis during fire the temperature gradient and maximum temperature are responses by the material. Indeed, pyrolysis often occurs at a rather steady state of combustion, at temperatures just above the threshold value for the production of volatiles, such that the flux of volatiles can build up a concentration above flammability limits in the gas phase. The pyrolysis of the surface may be very different from that of the bulk. Indeed, the higher heating rate, but in particular oxidative decomposition taking place, may produce not only different volatiles but also a residual surface that is thermally stable during flaming combustion pyrolysis. Typically, oxidative decomposition can result in a char which is generally resistant to anaerobic pyrolysis above 800°C.<sup>38–40</sup> Furthermore, there is no direct, straightforward link whatsoever between onset or decomposition temperature and flammability, as is often incorrectly asserted in the literature when increased thermal stability is achieved as a positive result in terms of polymer flammability. In conclusion, thermogravimetry can supply useful information on pyrolysis if it is used to simulate the thermal and atmosphere scenario to which the material is exposed during combustion.

Thermogravimetric analysis (TGA) may be used alone, simple TGA, or it may be used in combinations with evolved gas analysis (TGA-Fourier transform infrared spectroscopy (FTIR), TGA-MS, TGA-GC-MS). However it is used, it is essential for the authors to tell the readers the parameters under which the measurements were performed and the uncertainty of the results. The uncertainty due to the apparatus itself is usually quite low and close to negligible. Depending on the commercial equipment and sample holder used, it is believed that uncertainty values of below  $\pm 0.5^\circ\text{C}$ – $1.0^\circ\text{C}$  for the temperature and below  $\pm 0.1$  wt% for the mass are obtainable. Getting close to or even achieving such uncertainties requires very careful attention to a variety of details which are discussed below. In practice, this accuracy can be exploited neither for repeatability within the lab nor for reproducibility between

different labs. The TGA results are crucially dependent on all kinds of parameters such as the heating rate, the mass of the specimen, the texture of the specimen, the sample holder, the crucible used, the flow rate, and impurities within the atmosphere, as well as on the decomposition behavior of the materials investigated. The last point is of obvious importance when the sample is heterogeneous, but also applies to homogeneous materials. Variation within the parameters determines the uncertainty, so that every experiment must be repeated to gain confidence in the results. Decomposition temperatures are reported to shift by up to ca 20 K when the mass changes by a factor of 2.<sup>41,42</sup> The effect may decrease for masses >10 mg, but is a major source of uncertainty when the mass is below 10 mg. Thus, analogous to the heating rate, telling the reader the mass used in TGA is essential, as is using exactly the same mass when comparing different materials. On the other hand, one must be careful not to overstate results and recognize that small changes, particularly in temperature, may not be important. Furthermore, proper thermal contact between the specimen and the crucible is a crucial prerequisite for proper TGA. A lot of thermoplastics melt during the TGA run produce a thin film with rather perfect thermal contact to the cup. Reinforced thermoplastics, nanocomposites, and thermosets do not behave in this way. Measuring granulates for epoxy resins delivers unsatisfying TGA results with respect to both the residue and the decomposition temperature. It is recommended that all materials be measured as powder to increase repeatability. Nevertheless, there are some materials that are quite hard to measure with good repeatability because of their intrinsic properties. One group is intumescent systems. Forming a thermally insulating residue or a temperature gradient within milligram specimens is a strong violation of the measurement principle of TGA and results in much higher uncertainties in characteristic temperatures and residues, among other problems. Another group to mention is substances characterized by competing decomposition pathways. The residue yield and decomposition products of polymers such as silicone, polycarbonate, and epoxy resins become dependent on the heating rate,<sup>28–34</sup> for instance. One of the most drastic examples in the field of flame retardancy may be the flame-retardant aluminum diethylphosphinate (AlPi-Et), for which decomposition is reported to compete with vaporization in the same temperature range.<sup>43</sup> The residue amount is extremely sensitive to all kinds of parameters; for instance, it may be measured between 10 and 40 wt% when the sample amount is increased from 5 to 10 mg. Analogous rethinking is recommended for coupled evolved gas analysis. For instance, it is reported that elevated temperatures (270°C) are necessary in the transfer line and the gas cell in order to detect diethylphosphinic acid and vaporized AlPi-Et in TGA-FTIR.<sup>44</sup> Or, in other words, in evolved gas analysis, one should carefully optimize parameters for the materials under investigation. Again, this TGA discussion is incomplete. For instance, there is no mention of TGA investigations of kinetics, which usually warrant entire papers on their own.<sup>45–50</sup> Nevertheless, this paragraph underlines a crucial basis for the use of all kinds of milligram-scale methods, even though only the frequently used example of TGA is discussed. The proper use of milligram-scale methods is essential to exploit the potential for using results like the material properties in the discussion of important parameter inputs for simulations.

### *Pyrolysis combustion flow calorimeter or MCC*

The latest commercially important scientific apparatus designed to study the fire behavior of polymers is the pyrolysis combustion flow calorimeter (PCFC), also known as the MCC.<sup>51–55</sup> Volatile products from anaerobic pyrolysis produced upon heating samples 5 mg (in

principle 1–50 mg) in size, typically at 1 K/s, are conveyed by nitrogen flow to a combustion chamber kept at 900°C, where they are oxidized by mixing with oxygen. The rate of heat release is measured based on the oxygen consumption method, as a function of temperature at which volatiles are produced. The purpose of PCFC is to characterize separately the two sequential chemical processes occurring in flaming combustion, namely, the anaerobic polymer pyrolysis and oxidation of the volatiles at the same time.

PCFC is particularly useful for screening new experimental materials available in limited quantities, on the basis of their heat release capacity (maximum heat release rate (HRR)/heating rate) from the exhaustive combustion of volatile pyrolysis products generated by relatively rapid heating. Unfortunately, the benefit of PCFC for new materials also leads to the belief that PCFC can be used to assess the material's fire properties without any further fire testing. However, such an assessment implies major shortcomings and is thus rather impossible in principle because the PCFC provides data based on strict limitations and boundary conditions. PCFC simulates the chemical reactions involved in flaming combustion, which are only a portion of the combustion cycle process accomplished by the transfer of physical heat to sustain pyrolysis. Indeed, heat is a major reference driver in flammability, since the final target of any fire-retardant approach is reduction of the heat supply to the polymer below the heat flux required to sustain the flame with volatile products.

The PCFC design is not intended to take into account flame-to-polymer heat transfer, which is regulated by the characteristics of the polymer surface and may evolve during burning. Furthermore, the material's surface structure, depending on the chemistry of the material, can be strongly modified by oxidative decomposition during ignition, which is not reproduced by anaerobic pyrolysis in the PCFC. A number of other features of the PCFC apparatus limit its utility for fire behavior studies of dynamic pyrolysis conditions, because with PCFC pyrolysis occurs at almost a constant temperature in combustion, as opposed to the arbitrary temperatures in gas oxidation. Furthermore, the sample size is too small to allow physical features of the burning sample such as a residual protective layer to play their role in pyrolysis, and finally, the difference between the premixed flame produced in PCFC and a diffusion flame experienced during combustion. In fact, the residence time within the combustor is scheduled to ensure complete combustion.<sup>51,55</sup> Thus, PCFC is constructed to be blind to flame inhibition. Overall, it is concluded that PCFC is the most powerful, but also widely misused milligram-scale method for evaluating the fire behavior of materials, effective for investigating charring phenomena, fuel dilution in both the gas phase and the condensed phase, and the effective heat of combustion of the volatiles. It fails with respect to flame inhibition and the formation of any kind of protective layer including intumescence. Furthermore, it is not influenced by physical phenomena such as melt flow, dripping, or heat absorption and reflectivity. Like most historical fire testing methods, PCFC lacks a time-scale evaluation of the evolution of fire, which is of paramount importance to assess the fire hazard.

## *OI and UL 94*

Considering the efforts, time and amount of material necessary for intermediate or even full-scale fire testing investigations, which, taken together, also constitute the costs, and bench-scale methods based on small specimen sizes are required and widely used to characterize the flammability of materials. OI (ISO 4589, often called LOI) and UL 94 (IEC 60695-11-10),

but also some classifications for building products in European countries, are so common for materials that in practice their results are often communicated as the intrinsic fire properties of materials. This universal use is incorrect.<sup>56–59</sup> The length scale in small-scale fire tests is typical only for the beginning of a fire. In the common reaction-to-small-flame tests, flammability is investigated in terms of the ease of extinction of a specific specimen. The fact that these tests do not monitor any intrinsic material property becomes obvious, for instance, in the strong dependency of the results on the dimensions of the specimen.<sup>16,60,61</sup> The most common misuse is to define the properties “flammable” and “self-extinguishing” through OI values of 21 and 27 vol% (sometimes 27–30 vol%), respectively. The first interpretation is based on comparing the OI value with the oxygen content in air. This oversimplification sounds reasonable only at first glance. OI determination is based on applying a small flame to the top of a specimen and on flame spread downward. Thus, OI is a kind of a “best case” assessment and by no means a representative or worst-case consideration. Considering an OI of 21 vol% as a criterion for being flammable does not achieve any reasonable protection goal. Interpreting OI values greater than 27–30 vol% as self-extinguishing behavior is based on studies reporting a correlation between OI and self-extinguishing classification in UL 94 experiments.<sup>57</sup> Indeed, some thermoplastics do show such a correlation between OI and UL 94 classification. Nevertheless, there is no general correlation between OI and self-extinguishing in UL 94 (similar fire scenario, but upward flame spread), but often a clear lack of comparability. Indeed, polymeric materials are also reported to show a critical OI down to 23 vol% and up to 47 vol% for self-extinguishing in the UL 94 test.<sup>30,58,59,62–66</sup> Even in a set of comparable materials, the correlation can be absent when different flame retardancy mechanisms are exploited or the melt flow changes.<sup>58,67</sup> Indeed, the sense of OI as a measure of flammability is generally dubious, since its less demanding downward-burning configuration results in no or only rough correlations with other fire tests.<sup>58,59,68</sup> In this context, it should be noted that the V-1 and V-0 classifications in UL 94 are quite demanding. Usually self-extinguishing without dripping is achievable only with a substantial flame retardancy approach that usually holds as well in other different fire scenarios such as developing fires.<sup>69</sup> Nevertheless, despite all its advantages, common small-scale testing must not be used as a universal tool to assess fire response.

When polymeric materials began to be used extensively to replace traditional materials in applications involving a sizable fire risk exposure, methods such as UL 94 burning chamber and OI were developed to simulate the fire scenario of typical applications in order to assess the flammability of polymeric materials. The development of fire-retardant polymer materials driven by these tests has shown their positive contribution. However, the potential of these tests in understanding fire-retardant modes of action is far from realized. Indeed, owing to their comprehensive, balanced fire risk assessment, ranking codes do not supply detailed information on materials’ fire performance. For example, the OI by itself is rather useless for mechanistic understanding. Without experimental work in addition to that required for determining the OI, access to fire performance is gained by plotting self-quenching times as a function of oxygen concentration.<sup>60,70</sup> The transition from unstable burning to a self-sustained combustion regime is thus highlighted, yielding the parameters for OI classification, meaning the conditions for self-sustained combustion. Misleading combustion performance interpretations based solely on OI values can thus be avoided by simply examining self-quenching time as a function of oxygen concentration.<sup>71,72</sup> Information about the flame inhibition activity of fire retardants is simple to obtain by substituting nitrous oxide for oxygen in the OI apparatus (nitrous oxide index, NOI), which is a typical

experimental approach used in studies of flame chemistry.<sup>73–76</sup> If comparison of a fire retardant's dependence on the concentration of OI and NOI shows that the effectiveness of the fire retardant is affected by the nature of the oxidant oxygen or nitrous oxide, which is a much less powerful oxidizer, a gas-phase effect is likely to be relevant in the fire-retardant mechanism. A parallel trend points instead to a condensed-phase effect.

UL 94 monitors vertical upward burning, expressing fire risk by labels (V-0, V-1, V-2) that combine a number of combustion performance characteristics including burning time, dripping, and glowing. By its very purpose, the UL 94 ranking cannot be used to describe the fire behavior of a material. Indeed, the typically desired ranking of V-0, for example, is obtained whether the material burns for a limited time length without any dripping or with heavy dripping that does not ignite the cotton underneath. Furthermore, a non-ranking classification can be either due to a fast burning rate with high flames and flaming dripping or due to a very low burning rate with a small flame and no dripping, as long as the flame does not extinguish before reaching the top of the specimen. Nevertheless, vertical upward burning behavior can be described directly by quoting the relevant combustion parameters rather than condensing them in standard ranking labels like burning times, burning rate, weight burned, weight of any drops, or specimen weight as a function of burning time.<sup>77–83</sup> In conclusion, fire testing carried out to understand mechanisms of combustion and fire retardancy, which is the task of basic research, should avoid reporting only the codes and rankings that have a regulatory and/or commercial purpose, describing the fire performance instead of quoting the relevant fire properties and parameters.

### *Cone calorimeter*

The proper use of the cone calorimeter cannot be taken for granted. Intensive and accurate maintenance is necessary, for instance, with respect to daily and regular calibration as discussed above. However, even with a well-tended cone calorimeter, there is still some confusion about how to use it properly. Some of these issues are as old as the cone calorimeter itself, as they are due to the method's intrinsic limitations. First of all, the cone calorimeter simulates developing fires. Although irradiations typical for fully developed fires can be applied within the cone calorimeter, simulation of a fully developed fire is not satisfactory because of its temperature limitations. Neither the temperature–time curve nor the direct application of a flame necessary for monitoring any kind of fire resistance in fully developed fires is simulated by the cone calorimeter.<sup>84,85</sup> Indeed, it has been shown that some high-temperature mechanisms used in commercial products occur only when a standard time temperature curve is applied, but not in the cone calorimeter at 75 kW/m<sup>2</sup> irradiation.<sup>86</sup> The temperature profile and heating rates within the specimen are a response in the cone calorimeter and are less demanding. The cone calorimeter is also not capable of simulating reactions to a small-flame test, even though it measures time to ignition ( $t_{\text{ig}}$ , also sometimes written as TTI). Although low irradiations typical for ignition scenarios can be simulated by the cone calorimeter, it does not provide the combination of overall low irradiation and localized high irradiation, or the temperature of an ignition source such as a pilot flame.

The cone calorimeter performs forced flaming combustion of a specimen with the dimensions of 100 mm × 100 mm × thickness. No real flame spread is monitored, as the entire area ignites at the same time. The HRR curves over the burning time deliver information on the fire behavior of the specimen as the pyrolysis front proceeds in the  $z$  direction. The development of a fire in intermediate and full-scale fire tests is usually also strongly controlled by

flame spread/fire growth over the surface. Thus, in many fire tests, the PHRR moves along with the largest area burning, whereas in the cone calorimeter, the PHRR is associated with the thickest pyrolysis zone or the fastest velocity of the pyrolysis front in the  $z$  direction. The PHRR in the cone calorimeter is far from being a material property, but is strongly dependent on the cone calorimeter setup, material thickness, and so on, such that somewhat limited, but significant changes in HRR have been reported for poly(methyl methacrylate) (PMMA) and wood measured with and without the retainer frame.<sup>17–19</sup> However, actually both wood and PMMA are rather docile burning materials in the cone calorimeter setup. Other materials show differences in PHRR up to a factor of two<sup>87</sup> and changes in the basic shape of the HRR curve. Furthermore, PHRR in the cone calorimeter is caused by quite different phenomena for different kinds of materials. PHRR can occur after the initial increase and before the formation of a protective layer reduces HRR, toward the end of burning due to the increase of the pyrolysis zone thickness when the specimen becomes thermally thin, or toward the end of burning due to further decomposition of the interim residue, and so on.<sup>36,85</sup> In sum, even though HRR is accepted to be the most important parameter determining fire risks<sup>88</sup> and thus PHRR is usually used as a key characteristic of a cone calorimeter test, PHRR must not be used as the only important measure delivered by the cone calorimeter. Values such as total heat release (THR), time to ignition ( $t_{ig}$ ), mass loss (or residue), effective heat of combustion, and CO yield are other measures to be evaluated in a proper discussion. Furthermore, a most innovative feature of the cone calorimeter, which represented a leap forward in fire science studies compared to some other bench-scale tests, is the measurement of combustion parameters such as HRR, rate of smoke, and CO evolution as a function of time. Indeed, fire hazard is time related in principle because it is not only the absolute values of combustion parameters that matter but also whether they reach threatening values for damage to persons or property before or after evacuation time and/or the time required for fire brigade intervention. This seems to be mostly neglected in published literature, where time-related parameters such as time to PHRR, but also indices such as fire growth index (FIGRA), maximum averaged release rate of heat emission (MARHE), and so on are less often reported. Only the measure as a function of time, such as the HRR curve over time, provides comprehensive information. Synthetic simple parameters (e.g.  $t_{ig}$ /PHRR, fire performance index, FIGRA, and MARHE) should be reported to balance the fire hazard of a material between the ease of ignition and heat release rate in the cone calorimeter.

On the other hand, the discussion of peak values and indices in cone calorimeter investigations may sometimes be redundant or even ridiculous. Several data such as CO<sub>2</sub> production rate usually just follow the HRR over time and thus deliver strongly redundant information on the fire behavior. Reporting and discussing data such as the peak effective heat of combustion  $>> 50$  MJ/kg, or in other words, reporting impossible values that are artificially calculated by dividing negligibly low or uncertain mass loss rate ( $\dot{m}$ ), does not deliver insight to the fire behavior of the material. Furthermore, forced flaming combustion highlights yields, such as CO yield or smoke yield. It should be noted that apart from the yields the total CO production and the total smoke production are rather independent aspects, such that fire hazard assessment based on yields should be complemented by the HRR.

The cone calorimeter setup is not well qualified to investigate samples showing strong deformation such as collapsing foams, intumescent systems, bending or coiling plates.<sup>84,85,87,89</sup> Whatever adjustment is used to perform a reasonable cone calorimeter test, be it changing the distance between the cone heater and the surface of the specimen, or using grids or cages to suppress deformation, deteriorates the measurement principle of the



method. Thus, the maximum achievement is to minimize the artificially strong influence of specimen deformation on fire behavior during the cone calorimeter test or to replace the effect of deformation with a less dramatic effect by the effective heat flux on the specimen area or mounting.

The cone calorimeter setup is not suitable for measuring specimens of low weight or low fire load, nor specimens exhibiting short burning times, such as relatively non-combustible materials, foams, textiles, and foils. One reason for these limitations is that the relative uncertainty of the HRR increases drastically with decreasing HRR. Consequently, the uncertainty of other measures such as THR increases with decreasing value and increasing burning time. Thus, widening the application of the cone calorimeter toward non-combustible materials would entail modifications to the cone calorimeter setup, such as reducing the duct flow or increasing the size of the cone heater and the specimen.<sup>90</sup> Investigating thin specimens such as textiles, foils, or even foams clearly also approaches the limits of the method. One limitation is the balance usually used in commercial equipment. Whereas the signal-to-noise ratio in the mass loss rate is annoying for any sample, for specimens with very small masses some evaluations ultimately become irrelevant. Furthermore, when thin specimens are measured, the results interfere with the response time of the cone calorimeter, typically around 20 s for the oxygen consumption method.<sup>89,91</sup> Even though comparison within a set of samples is always possible, the question arises as to whether samples showing spontaneous ignition and burning times below 100 s should be measured in the cone calorimeter at all.

## Conclusion

In this part one of the two-part article, the meaning of scientific terms was discussed, such as “pyrolysis,” “thermal decomposition,” and “fire resistance.” Other terms were reviewed briefly, including ignitable, flammable, combustible, ignitability, flammability, burning behavior, fire behavior, and combustion. Since fire performance is not a material property, but the response of a defined specimen or component to a distinct fire scenario or fire test, communication benefits crucially from a precise use of the scientific terms within the field of flame-retardant polymers. Different fire scenarios, from smoldering, well-ventilated developing fire, to fully developed fire, were sketched as well as the corresponding different conditions controlling the pyrolysis during fire. Several useful comments were made on the proper performance of fire tests and thermal analysis based on milligram specimens. In particular, the topic of uncertainty in fire testing and the limitations of mg methods were addressed. TGA, OI, UL 94 testing, and cone calorimeter were discussed in detail in an effort to motivate scientists in the field to rethink their quality management and interpretation of results.

The main goals addressed in this set of recommendations are correct wording as the basis for good scientific description and using methods properly to decrease uncertainty and within applicability. Several recommendations are compiled here:

- Using the correct specific scientific term out of many related terms describes the fire property or phenomenon in a precise and unambiguous manner.
- The term “(thermal) degradation” applies to the loss of physical properties, while “(thermal) decomposition” designates the breaking of chemical bonds.

- Pyrolysis should always be qualified to describe whether it is anaerobic or oxidative. The results from one atmosphere must not be confused with ones in another atmosphere.
- Different fire tests yield different results. Indeed, each test reproduces a specific fire scenario to which materials are likely to be exposed, depending on application, and is intended to guide the selection of materials. A material that is excellent in one fire test may not perform well in another; one must be quite careful in describing the test and the performance and not overstate subjective performance.
- Fire resistance is linked to criteria such as fire penetration, heat penetration, and the structural integrity of components and must not be used for all kinds of fire properties.
- The use of terms such as “green” or “environmentally friendly” should be avoided unless aspects of environmental sustainability are investigated using suitable methodology in the work reported.
- Instruments should be operated according to accepted standards and reported accordingly; the limited number of tests performed within a complex fire scenario particularly demands measures to increase accuracy and reduce uncertainty.
- Each method should be applied with consideration of its applicability and limitations.

The balance of an introduction to terms and/or methods and recommendations on their utilization will, we hope, sensitize the reader and improve scientific practice.

### Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

### Funding

The author(s) received no financial support for the research, authorship, and/or publication of this article.

### References

1. ISO 13943:2008. Fire safety—vocabulary.
2. Scharrel B, Wilkie CA and Camino G. Flame retardant polymers—a guide on the use of: part II concepts. *J Fire Sci* (in press).
3. ASTM E176-15a1:2015. Standard terminology of fire standards.
4. ISO 472:2013. Plastics—vocabulary.
5. Janssens ML. Variability in oxygen consumption calorimetry test. In: Gritzo AL and Alvares NJ (eds) *The foundation of fire standards* (ASTM STP 1427). West Conshohocken, PA: American Society for Testing and Materials, 2002, pp. 147–162.
6. Janssens ML. Challenge in fire testing: a tester's viewpoint. In: Horrocks AR and Price D (eds) *Advances in fire retardant materials*. Cambridge: Woodhead Publishing Limited, 2008.
7. ISO/IEC Guide 98-3:2008. Uncertainty of measurement—Part 3: guide to the expression of uncertainty in measurement.
8. Janssens M. Uncertainty of fire test results. In: *11th international fire science and engineering conference (Interflam 2007)*, Egham, 3–5 September 2007.
9. Enright PA and Fleischmann CM. Uncertainty of heat release rate calculation of the ISO5660-1 cone calorimeter standard test method. *Fire Technol* 1999; 35: 153–169.
10. Axelsson J, Andersson P, Lönnemark A, et al. Uncertainties in measuring heat and smoke release rates in the room/corner test and the SBI. SP Report 2001:04, SP Swedish National Testing and Research Institute, Borås, April 2001.
11. Bryant RA and Mulholland GW. A guide to characterizing heat release rate measurement uncertainty for full-scale fire tests. *Fire Mater* 2008; 32: 121–139.
12. Zhao L and Dembsey NA. Measurement uncertainty analysis for calorimetry apparatuses. *Fire Mater* 2008; 32: 1–26.
13. Brohez S. Uncertainty analysis of heat release measurement from oxygen consumption calorimetry. *Fire Mater* 2005; 29: 383–394.
14. Endtner JM. Development of new halogen-free flame retardant engineering plastics by application of automated optical investigation methods. In: *10th European meeting on fire retardancy and protection of materials (FRPM'05)*, Berlin, 7–9 September 2005.

15. Blaszkiewicz M, Bowman P and Masciantonio M. Understanding the repeatability and reproducibility of UL 94 testing. In: *18th annual conference on recent advances in flame retardancy of polymeric materials*, BCC, Stamford, CT, 21–23 May 2007.
16. Schartel B. Chapter 15. Uses of fire tests in materials flammability development. In: Wilkie CA and Morgan AB (eds) *Fire retardancy of polymeric materials*. 2nd ed. Boca Raton, FL: CRC Press, 2010, pp. 387–420.
17. Kashiwagi T and Cleary TG. Effects of sample mounting on flammability properties of intumescent polymers. *Fire Safety J* 1993; 20: 203–225.
18. Babrauskas V, Twilley WH and Parker WJ. The effects of specimen edge conditions on heat release rate. *Fire Mater* 1993; 17: 51–63.
19. Tsantaris L and Östman B. Communication: retainer frame effects on cone calorimeter results for building products. *Fire Mater* 1993; 17: 43–46.
20. Safronova N, Lyon RE, Crowley SB, et al. Effect of moisture on ignition time of polymers. *Fire Technol* 2015; 51: 1093–1112.
21. Van Krevelen DW. Some basic aspects of flame resistance of polymeric materials. *Polymer* 1975; 16: 615–620.
22. Van Krevelen DW and Hoftyzer PJ. *Properties of polymers*. Amsterdam: Elsevier, 1976.
23. Lyon RE. Plastics and rubber. In: Harper CA (ed.) *Handbook of building materials for fire protection*. New York: McGraw-Hill, 2004.
24. Schartel B, Pötschke P, Knoll U, et al. Fire behaviour of polyamide 6/multiwall carbon nanotube nanocomposites. *Eur Polym J* 2005; 41: 1061–1070.
25. Dittrich B, Wartig K-A, Hofmann D, et al. Carbon black, multiwall carbon nanotubes, expanded graphite and functionalized graphene flame retarded polypropylene nanocomposites. *Polym Advan Technol* 2013; 24: 916–926.
26. Dittrich B, Wartig K-A, Hofmann D, et al. The influence of layered, spherical and tubular carbon nanomaterials' concentration on the flame retardancy of polypropylene. *Polym Composite* 2015; 36: 1230–1241.
27. Schartel B, Braun U, Knoll U, et al. Mechanical, thermal and fire behavior of bisphenol A polycarbonate/multiwall carbon nanotube nanocomposites. *Polym Eng Sci* 2008; 48: 149–158.
28. Camino G, Lomakin SM and Lagueard M. Thermal polydimethylsiloxane degradation. Part 2. The degradation mechanisms. *Polymer* 2002; 43: 2011–2015.
29. Camino G, Lomakin SM and Lazzari M. Polydimethylsiloxane thermal degradation part 1. Kinetic aspects. *Polymer* 2001; 42: 2395–2402.
30. Wang CS and Lin CH. Properties and curing kinetic of diglycidyl ether of bisphenol A cured with a phosphorus-containing diamine. *J Appl Polym Sci* 1999; 74: 1635–1645.
31. Braun U, Balabanovich AI, Schartel B, et al. Influence of the oxidation state of phosphorus on the decomposition and fire behaviour of flame-retarded epoxy resin composites. *Polymer* 2006; 47: 8495–8508.
32. Braun U, Knoll U, Schartel B, et al. Novel phosphorus-containing poly(ether sulfone)s and their blends with an epoxy resin: thermal decomposition and fire retardancy. *Macromol Chem Phys* 2006; 207: 1501–1514.
33. Liu Y-L, Hsiue G-H, Lan C-W, et al. Phosphorus-containing epoxy for flame retardance: IV. Kinetics and mechanism of thermal degradation. *Polym Degrad Stabil* 1997; 56: 291–299.
34. Müller P, Morys M, Sut A, et al. Melamine poly(zinc phosphate) as flame retardant in epoxy resin: decomposition pathways, molecular mechanisms and morphology of fire residues. *Polym Degrad Stabil* 2016; 130: 307–319.
35. Vovelle C, Delfau J-L, Reuillon M, et al. Experimental and numerical study of the thermal degradation of PMMA. *Combust Sci Technol* 1987; 53: 187–201.
36. Schartel B and Weiß A. Temperature inside burning polymer specimens: pyrolysis zone and shielding. *Fire Mater* 2010; 34: 217–235.
37. Wu GM, Schartel B, Bahr H, et al. Experimental and quantitative assessment of flame retardancy by the shielding effect in layered silicate epoxy nanocomposites. *Combust Flame* 2012; 159: 3616–3623.
38. Pastore HO, Frache A, Boccaleri E, et al. Heat induced structure modifications in polymer-layered silicate nanocomposites. *Macromol Mater Eng* 2004; 289: 783–786.
39. Zanetti M, Kashiwagi T, Falqui L, et al. Cone calorimeter combustion and gasification studies of polymer layered silicate nanocomposites. *Chem Mater* 2002; 14: 881–887.
40. Schartel B, Kunze R and Neubert D. Red phosphorus controlled decomposition for fire retardant PA 66. *J Appl Polym Sci* 2002; 83: 2060–2071.
41. Ehrenstein GW, Riedel G and Trawiel P. *Thermal analysis of plastics theory and practice*. Munich: Carl Hanser Verlag, 2004.
42. Riesen R. *Effect of sample mass on TG results* (UserCom 12, 2/2000). Schwerzenbach: Mettler Toledo, 2000, pp. 21–22.
43. Braun U and Schartel B. Flame retardancy mechanisms of aluminium phosphinate in combination with melamine cyanurate in glass-fibre-reinforced poly(1,4-butylene terephthalate). *Macromol Mater Eng* 2008; 293: 206–217.
44. Brehme S, Köppl T, Schartel B, et al. Competition in aluminium phosphinate-based halogen-free flame retardancy of poly(butylene terephthalate) and its glass-fibre composites. *E-Polymers* 2014; 14: 193–208.
45. Vyazovkin S, Chrissafis K, Di Lorenzo ML, et al. ICTAC kinetics committee recommendations for collecting experimental thermal analysis data for kinetic computations. *Thermochim Acta* 2014; 590: 1–23.
46. Vyazovkin S, Burnham AK, Criado JM, et al. ICTAC Kinetics Committee recommendations for performing kinetic computations on thermal analysis data. *Thermochim Acta* 2011; 520: 1–19.
47. Vyazovkin S and Sbirrazzuoli N. Isoconversional kinetic analysis of thermally stimulated processes in polymers. *Macromol Rapid Comm* 2006; 27: 1515–1532.
48. Chigwada G, Kandare E, Wang D, et al. Thermal stability and degradation kinetics of polystyrene/organically-modified montmorillonite nanocomposites. *J Nanosci Nanotechnol* 2008; 8: 1927–1936.
49. Bourbigot S, Gilman JW and Wilkie CA. Kinetic analysis of the thermal degradation of polystyrene-montmorillonite nanocomposite. *Polym Degrad Stabil* 2004; 84: 483–492.
50. Almeras X, Dabrowski F, Le Brasa M, et al. Using polyamide 6 as charring agent in intumescent polypropylene formulations. II. Thermal degradation. *Polym Degrad Stabil* 2002; 77: 315–323.
51. Lyon RE and Walters RN. *A microscale combustion calorimeter*. Final report, Report no. DOT/FAA/AR 01/177, January 2002. Atlantic City, NJ: Federal Aviation Administration.
52. Lyon RE and Walters RN. Pyrolysis combustion flow calorimetry. *J Anal Appl Pyrol* 2004; 71: 27–46.
53. Lyon RE, Walters RN and Stoliarov SI. Screening flame retardants for plastics using microscale combustion calorimetry. *Polym Eng Sci* 2007; 47: 1501–1510.
54. Schartel B, Pawlowski KH and Lyon RE. Pyrolysis combustion flow calorimeter: a tool to assess flame retarded PC/ABS materials? *Thermochim Acta* 2007; 462: 1–14.
55. Lyon RE, Walters RN, Stoliarov SI, et al. *RI principles and practice of microscale combustion calorimetry*. Final report,

- Report no. DOT/FAA/TC-12/53, April 2013. Atlantic City, NJ: FAA.
56. Reimschuessel HK, Shalaby SW and Pearce EM. On the oxygen index of nylon 6. *J Fire Flammability* 1973; 4: 299–308.
  57. Isaacs JL. The oxygen index flammability test. *J Fire Flammability* 1970; 1: 36–47.
  58. Weil ED, Hirschler MM, Patel NG, et al. Oxygen index: correlations to other fire tests. *Fire Mater* 1992; 16: 159–167.
  59. Wharton RK. Correlation between the critical oxygen index test and other fire tests. *Fire Mater* 1981; 5: 93–102.
  60. Camino G, Costa L, Casorati E, et al. The oxygen index method in fire retardance studies of polymeric materials. *J Appl Polym Sci* 1988; 35: 1863–1876.
  61. Wharton RK. The effect of sample size on the burning behaviour of thermoplastic materials in the critical oxygen index test. *Fire Mater* 1981; 5: 73–76.
  62. Braun U and Schartel B. Flame retardant mechanisms of red phosphorus and magnesium hydroxide in high impact polystyrene. *Macromol Chem Phys* 2004; 205: 2185–2196.
  63. Schartel B, Balabanovich AI, Braun U, et al. Pyrolysis of epoxy resins and fire behaviour of epoxy resin composites flame-retarded with 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide additives. *J Appl Polym Sci* 2007; 104: 2260–2269.
  64. Schartel B, Weiß A, Mohr F, et al. Flame retarded epoxy resins by adding layered silicate in combination with the conventional protection-layer-building flame retardants melamine borate and ammonium polyphosphate. *J Appl Polym Sci* 2010; 118: 1134–1143.
  65. Perret B, Schartel B, Stöß K, et al. A new halogen-free flame retardant based on 9,10-dihydro-9-oxa-10-phosphaphenanthrene-10-oxide for epoxy resins and their carbon fiber composites for the automotive and aviation industries. *Macromol Mater Eng* 2011; 296: 14–30.
  66. Perret B, Schartel B, Stöß K, et al. Novel DOPO-based flame retardants in high-performance carbon fibre epoxy composites for aviation. *Eur Polym J* 2011; 47: 1081–1089.
  67. Braun U, Schartel B, Fichera MA, et al. Flame retardancy mechanisms of aluminium phosphinate in combination with melamine polyphosphate and zinc borate in glass-fibre reinforced polyamide 6, 6. *Polym Degrad Stabil* 2007; 92: 1528–1545.
  68. Day AG. Oxygen index test: temperature effect and comparison with other flammability tests. *Plast Polym* 1975; 43: 64–67.
  69. Morgan AB and Bundy M. Cone calorimeter analysis of UL-94 V-rated plastics. *Fire Mater* 2007; 31: 257–283.
  70. Stuetz DE, Diedwurdo AH, Zitomer F, et al. Polymer flammability. II. *J Polym Sci Polym Chem* 1980; 18: 987–1009.
  71. Roma P, Camino G and Luda MP. Mechanistic studies on fire retardant action of fluorinated additives in ABS. *Fire Mater* 1997; 21: 199–204.
  72. Roma P, Luda MP and Camino G. Synergistic action of fluorine-containing additives in bromine/antimony fire retardant ABS. *Polym Degrad Stabil* 1999; 64: 497–500.
  73. Casu A, Camino G, De Giorgi M, et al. Fire-retardant mechanistic aspects of melamine cyanurate in polyamide copolymer. *Polym Degrad Stabil* 1997; 58: 297–302.
  74. Levchik SV, Camino G, Costa L, et al. Mechanistic study of thermal behaviour and combustion performance of carbon fibre-epoxy resin composites fire retarded with a phosphorus-based curing system. *Polym Degrad Stabil* 1996; 54: 317–322.
  75. Levchik SV, Camino G, Luda MP, et al. Epoxy resins cured with aminophenylmethylphosphine oxide 1: combustion performance. *Polym Advan Technol* 1996; 7: 823–830.
  76. Checchin M, Boscoletto AB, Camino G, et al. Mechanism of fire retardance in poly(2,6-dimethyl-1,4-phenylene ether)-high impact polystyrene. *Makromol Chem: M Symp* 1993; 74: 311–314.
  77. Kempel F, Schartel B, Marti JM, et al. Modelling the vertical UL 94 test: competition and collaboration between melt dripping, gasification and combustion. *Fire Mater* 2015; 39: 570–584.
  78. Wang Y, Zhang F, Chen X, et al. Burning and dripping behaviors of polymers under UL 94 vertical burning test conditions. *Fire Mater* 2010; 34: 203–215.
  79. Kandola BK, Price D, Milnes GJ, et al. Development of a novel experimental technique for quantitative study of melt dripping of thermoplastic polymers. *Polym Degrad Stabil* 2013; 98: 52–63.
  80. Kandola BK, Ndiaye M and Price D. Quantification of polymer degradation during melt dripping of thermoplastic polymers. *Polym Degrad Stabil* 2014; 106: 16–25.
  81. Matzen M, Kandola B, Huth C, et al. Influence of flame retardants on the melt dripping behaviour of thermoplastic polymers. *Materials* 2015; 8: 5621–5646.
  82. Wang Y, Jow J, Su K, et al. Dripping behavior of burning polymers under UL 94 vertical test conditions. *J Fire Sci* 2012; 30: 477–501.
  83. Dupretz R, Fontaine G, Duquesne S, et al. Instrumentation of UL-94 test: understanding of mechanisms involved in fire retardancy of polymers. *Polym Advan Technol* 2015; 26: 865–873.
  84. Schartel B, Bartholmai M and Knoll U. Some comments on the use of cone calorimeter data. *Polym Degrad Stabil* 2005; 88: 540–547.
  85. Schartel B and Hull TR. Development of fire-retarded materials—interpretation of cone calorimeter data. *Fire Mater* 2007; 31: 327–354.
  86. Bartholmai M and Schartel B. Assessing the performance of intumescent coatings using bench-scaled cone calorimeter and finite difference simulations. *Fire Mater* 2007; 31: 187–205.
  87. Schartel B. From know-how to challenges in bench-scale fire testing: a polymer researcher's viewpoint. In: *Workshop bench scale fire testing*, Berlin, 21 June 2015.
  88. Babrauskas V and Peacock RD. Heat release rate—the single most important variable in fire hazard. *Fire Safety J* 1992; 18: 255–272.
  89. ISO 5660-1:2015. Reaction-to-fire test—heat release, smoke production and mass loss rate—part 1: heat release rate (cone calorimeter method) and smoke production rate (dynamic measurement).
  90. ISO 5660-4:2008. Reaction-to-fire tests—heat release, smoke production and mass loss rate—part 4: measurement of heat release for determination of low levels of combustibility.
  91. Filipczak R, Crowley S and Lyon RE. Heat release rate measurements of thin samples in the OSU apparatus and the cone calorimeter. *Fire Safety J* 2005; 40: 628–645.

### Author biographies

**Bernhard Schartel** (Priv.-Doz. Dr. habil.) is head of the Technical Properties of Polymeric Materials division at the Bundesanstalt für Materialforschung und -prüfung (BAM). For over 15 years he has been quite active in the Flame Retardancy of Polymers field. His main interest is the understanding of the fire behaviour and flame-retardancy mechanisms as a basis for future development.

**Charles A. Wilkie**, PhD, hold the Pfletschinger-Habermann Professorship of Chemistry at Marquette University for a very long time, has worked for almost forty years in fire retardancy, focusing mainly on nanocomposites the last two decades. He influenced the community not only by his pioneering work, but also as chairman of important conference series and editor of several books.

**Senior Prof. Giovanni Camino**, Associated Professor for Macromolecular Chemistry (1987-2001) and since 2001 Full Professor of Industrial Chemistry and Polymer Materials at the Polytechnic of Torino, has been one of the most influencing pioneers and experts in the fields of Polymer Degradation and Stabilisation, Fire Retardance, Intumescence and Nanocomposites over the last four decades.