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Review of heat exposure equipment and \textit{in-situ} characterisation techniques for intumescent coatings

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Abstract

The performance of commercial intumescent coatings is assessed by industrial norms and standards with clearly defined experimental conditions. In contrast, academic research on intumescent coatings is much more diverse and there are no clear guidelines on how such coatings should be characterised. Some researchers transfer the conditions defined in the industrial standards to laboratory-scale setups while others rely on cone calorimeters or Bunsen burners. This might not be an issue when comparing different coating formulations within one study. However, it significantly complicates the comparison of coatings characterised with different experimental approaches and usually provides little insight into the coating performance under industrial fire test conditions.

This review article gives an overview over different experimental approaches reported in the academic literature for the performance evaluation of intumescent coatings. The heating conditions in these different groups of setups, ranging from furnaces and ovens over radiative heaters to impinging flames, are elaborated in a tutorial style fashion. Besides the sample heating, in-situ characterisation techniques, such as measurements of char expansion, temperature, and mechanical strength will be discussed. The aim is to aid researchers in evaluating literature reports as well as stimulate the development of new and the optimisation of existing experimental approaches.

Keywords: Intumescence; Coating; Fire protective coatings; Thermal Insulation; Heating conditions; Heating rates; Thermal resistance; Fire protection

1 Introduction

Modern architecture heavily relies on steel as a building material. Even though steel is non-combustible and has a high melting temperature (approx. 1500 °C), increasing the steel temperature during a fire can have severe consequences [1]. Creep effects become significant at temperatures as low as 400 °C [2, 3]. In case of constraint steel structures, thermal expansion leads to stress buildup at rates of 2.5 MPa °C−1 [1]. Besides, the yield strength and modulus of elasticity both drop substantially between 200-600 °C [4]. For load-bearing steel members (e.g., beams, columns, struts, bars, etc.), this can, in the worst case, result in a collapse of the steel structure during a fire, with the associated loss of human lives and assets. During a fire, it is therefore crucial to extend the time before the steel structure reaches a critical temperature, enabling building evacuation and the initiation of fire fighting. This is commonly
achieved by passive fire protection materials that thermally insulate the steel.

Among the available options for the passive fire protection of structural steel, such as rock wool, gypsum boards, or concrete [5], intumescent coatings are nowadays amongst the most popular choices [6]. Such coatings are only a few millimetres thick and offer good thermal insulation of the substrate without impairing the aesthetic aspects of the steel structure. The basic working principle of intumescent coatings is that they swell at elevated temperatures (typically around 200-300 °C), leaving behind a highly porous multi-cellular char with a low thermal conductivity [7, 8]. More specifically, traditional intumescent coatings consist of three main components: an acid source, carbon source (often the coating binder), and blowing agent. When the coating is heated, an acid is released that esterifies the carbon source [7, 9]. At similar temperatures, the binder softens and the blowing agent thermally decomposes. The gases released by the decomposition of the blowing agent cause the expansion and swelling characteristic for intumescent coatings. Subsequently, dehydration of the previously formed ester occurs, leaving behind a solid multi-cellular structure composed of carbonaceous char and inorganic residues [7, 9]. In the past decades, a large number of intumescent coating ingredients were studied, including acrylic [10, 11] and epoxy based binders [12, 13], different blowing agents [14, 15] and functional additives such as clay [16, 17], TiO₂ [18–20], graphite [16, 21], or basalt fibres [15, 22]. Details of the roles of the different components as well as summaries of the developed coating formulations can be found in a number of recent reviews [6–8, 23–25]. Given the extensive literature on intumescent coating formulations and working principles, these aspects will not be repeated here.

The certification of commercial intumescent coatings is regulated by a number of regional and international fire safety standards and guidelines [26–29]. However, the cubic meter sized industrial furnaces and large steel samples required for such tests are seldomly used in academia or during the research and development phase. Here, a much more diverse range of testing equipment and conditions have been developed and used. This diversity is desirable because it enables the fast screening of novel coating formulations [30–32], the testing under non-standard fire conditions [33, 34], and the measurement of additional parameters [35, 36] that help to generate new knowledge on different aspects of intumescent coatings. However, it also makes the comparison of different coating formulations across different research groups and published literature difficult. Similarly, not all testing equipment is suited equally well for all purposes. For example, an impinging flame [37] might be the cheapest and easiest method to get a first impression regarding the coating performance. However, more sophisticated furnaces or radiative heaters with
better defined boundary conditions might be required if the experimental results will be compared to numerical models [34, 38] or if the thermal conductivity of the intumescent char is the sought quantity.

No in-depth review regarding testing methods and equipment for the characterisation of intumescent coatings during their expansion is currently available. The necessity for characterising the coatings while they are being exposed to heat originates from the fact that their properties change dramatically not just with temperature but also depending on the time-temperature history they experienced. The aim of this review is therefore to summarise in a tutorial-style fashion testing equipment reported in the academic literature and to critically discuss their advantages and drawbacks. The focus is hereby on the exposure of the intumescent coatings to various heat sources as well as measurements that can be conducted while heating the coating. In order to bring the academic literature concerned with a potentially commercialisable coating into perspective, key aspects of industrial standards and guidelines will briefly be summarised first.

2 Industrial standards for fire testing

Intumescent coatings are commercial products and as such, they must comply with certain national and/or international standards. If a coating formulation performs well in laboratory tests but fails the standards to fulfil fire regulations, the benefit of the research and development work is limited to the gained knowledge. However, if the gained knowledge is not applicable to realistic fire scenarios, it is of little use. Applying industrial standards directly in academic research is not feasible because of the necessary large-scale facilities and the amount of time and resources required for each experiment. This is particularly true when areas such as the weathering of the intumescent coatings are the research focus. However, some researchers do apply parts of industrial standards, such as nominal temperature-time curves. In any case, it is worth being aware of the experimental conditions defined in industrial standards and ideally apply similar conditions in lab-scale experiments whenever feasible.

This section will summarise key experimental conditions defined in industrial standards. It does not aim at being an exhaustive compilation of all standards. Neither will all details defined in the standards be mentioned. Rather, the section aims at giving a brief overview over parameters that might be of interest for the industrial or academic researcher working on laboratory scale characterisation of intumescent coatings. In particular, most fire safety standards provide guidelines to assess the fire resistance of components or assemblies and are not intended to
quantify material properties or the performance of a single component (i.e., the intumescent coating). However, parts of them (mainly the temperature-time curves) are applied in laboratory scale testing and during the development of coatings, which is the focus of this review. It is worth noting that criticism was raised in literature because the fire scenarios represented by the standard temperature-time curves are somewhat outdated and exhibit an unrealistically rapid fire growth phase. These concerns and alternative, more characteristic fire curves will be discussed at the end of this section.

2.1 Standards for cellulosic fires

Standards for cellulosic fires are applicable where the main fuel source is composed of cellulose materials, such as paper or wood. These were traditionally compartments such as residential buildings, offices, or warehouses. In the decades since the standards were introduced, the fuel sources in such buildings changed, however, and synthetic plastics and fibres became more popular. The fire load and heat release rate of such synthetic materials might be very different to cellulose. Thus the actual fire scenario in a modern building might differ substantially from the nominal temperature-time curves defined in industrial standards [39]. Nevertheless, they remain to be the main reference for building fires.

A global standard for fire tests is ISO 834 [29]. Given that ISO standards are defined by committees consisting of national standard bodies, it is not surprising that many parameters of ISO 834 can also be found in other regional and national standards. For example, the ISO 834 standard heating curve is identical to the British Standard BS 476 [40] (note that BS 476 also defines a hydrocarbon fire curve in Appendix D) and is also applied in the Eurocodes [41], EN 1363 [28], and the Chinese fire standards (e.g., CECS200 [42]). ISO 834 defines experimental conditions to evaluate the fire resistance of building construction elements. Part 1 specifies general test equipment and calibration procedures while part 10 focuses on fire protection materials for structural steel. The temperature $T_f$ of the furnace fired with liquid or gaseous fuels is given by [29]:

$$T_f = 345\log_{10}(8t + 1) + 20,$$

(1)

where $T_f$ is the furnace temperature in °C and $t$ is time in minutes. Tolerances between Eq. 1 and the actual furnace temperature are given in terms of the percentage difference of the areas below the temperature-time curve. The furnace temperature
is measured by plate thermometers [43]. These consist of sheathed K-type thermocouples mounted on nickel alloy sheets and enclosed by thermal insulation material. The main advantage of plate thermometers over regular thermocouples is that they measure temperatures more representative of the actual thermal conditions experienced by the sample [43]. The specimen temperature is measured either by plate, roving, or internal thermocouples. The former two options consist of K-type thermocouples mounted to a copper disk to assure good thermal contact between the probe and the substrate. Also the oxygen content and flow velocity inside the furnace is mentioned in the calibration procedure for ISO 834, however, without providing quantitative limits. Additional details that are provided are, for example, the pressure inside the furnace, mounting of the samples, mechanical loading, or sample deformation. However, these guidelines are usually not followed in laboratory scale testing and will therefore not be discussed here.

The ten Eurocodes (EN 1990-1999) define standards for the structural design of buildings. The scope is therefore rather broad but also temperature-time curves for fire testing are defined. Eurocode 1 (EN 1991-1-2) [41] specifies the same standard temperature-time curve as ISO 834 (Eq. 1) with the slight difference that $T_f$ is replaced by the gas temperature $T_g$ with a convective heat transfer coefficient of $25 \text{ W m}^{-2} \text{ K}^{-1}$. Also EN 1363 [28, 44], the European standard for fire resistance tests, uses the ISO 834 [29] cellulosic (Eq. 1) and hydrocarbon fire curves (Eq. 2). Identical to ISO 834, the furnace temperature is measured with plate thermometers while the unexposed sample surface is probed with K-type thermocouples mounted to a copper disk. The atmosphere inside the test furnace ought to contain $>4\%$ (presumably vol.%) of oxygen but no upper limit is given [28]. Another European standard relevant to intumescent coatings is EN 13381-8 [45] where reactive protections to steel members are described. This standard can, for example, be used to calculate an effective thermal conductivity of the intumescent coating [46].

A US fire safety standard for construction components is ASTM E119 [27]. It defines testing conditions for a wide range of building members (roofs, floors, walls, columns, beams) and criteria they should meet under the fire scenario. ASTM E119 defines a tabulated temperature-time curve for a severe building fire with an initial rapid temperature rise followed by a continues, more gradual increase (Fig. 1). Heat flux or oxygen concentration measurements are not mentioned.

### 2.2 Standards for hydrocarbon fires

If the main fuel source is based on hydrocarbons, the rate of heat release is much higher than for cellulosic fuels. This means that the temperature rise in the initial
Figure 1. (a) National and international standard temperature-time curves for fire testing. Also shown are two alternatives to the commonly used nominal temperature-time curves. (b) Corresponding temperature gradients within the first 36 min for the curves shown in panel (a). For clarity, the legend is only shown in panel (b).

phase is more rapid and that a higher temperature can be reached. Possible scenarios for hydrocarbon fires are petrochemical plants or offshore oil platforms.

The Eurocodes [41] define a temperature-time curve that takes into account the more severe heat release during a hydrocarbon fire:

\[
T_g = 1080(1 - 0.325e^{-0.167t} - 0.675e^{-2.5t}) + 20, \tag{2}
\]

with \( T_g \) in °C and time \( t \) in minutes. In addition, a convective heat transfer coefficient of 50 W m\(^{-2}\) K\(^{-1}\) is specified. The Eurocode hydrocarbon fire curve defined by Eq. 2 is very similar to the BS 476, part 20 [40]. Only the starting temperature (0 °C in BS 476 and 20 °C in Eq. 2) and initial temperature ramp differ marginally (Fig. 1).

The US standard for assessing intumescent coatings under hydrocarbon fire conditions is UL 1709 [26]. This standard aims specifically at protective materials for structural steel. The sample is exposed to a sharp temperature increase from room temperature to 1093±56 °C within 5 min, where it remains for the duration of the test (Fig. 1). Simultaneously, the heat flux to the sample is supposed to reach 204±16 kW m\(^{-2}\) within these 5 min. The exact curve shape within the first 5 min is not defined and a linear rise to 1093 °C is used in Fig. 1. The furnace tempera-
The temperature is monitored with K-type thermocouples with welded junctions protruding into the furnace chamber. The furnace is calibrated using the average reading of such thermocouples, as well as a water-cooled calorimeter to record the heat flux. During the calibration, gas samples from the furnace are taken to measure oxygen concentrations. Limits for the oxygen concentrations are not specified but they can be expected to be below atmospheric (>21vol.%) given that industrial furnaces are usually fired by gaseous or liquid hydrocarbons. The temperature of the coated/covered steel member is measured with a number of K-type thermocouples and averaged, as well as maximum temperatures, are evaluated. The protective material passes the test if the average or peak steel temperature does not exceed 538 °C or 649 °C, respectively, within 50-90 min. If this criterion is not met, the thickness of the protective material may be changed. The exact time when either of the temperature limits is reached is referred to as time-to-failure. It is also worth noting that a range of exposure conditions are defined to simulate ageing of the samples in real applications.
Table 1. List of the industrial standards that define temperature-time curves that might be used to assess the performance of intumescent coatings. Note that this is not an exhaustive list and that other standards exist. Besides, the table intends to give an overview only and temperature-time curves are just one element of these industrial standards. Please refer to the listed references for a detailed description of all the procedures that have to be followed in order to comply with the industrial standard.

<table>
<thead>
<tr>
<th>Standard name and reference</th>
<th>Temperature-time curve(^{a})</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 834-1: Fire-resistance tests – Elements of building construction – Part 1: General requirements [29]</td>
<td>(T_t = 345\log_{10}(8t + 1) + 20)</td>
<td>Cellulosic fire. (T_t) is measured with plate thermometers.</td>
</tr>
<tr>
<td>EN 1363-1: Fire resistance tests – Part 1: General requirements [28]</td>
<td>(T_t = 345\log_{10}(8t + 1) + 20)</td>
<td>Cellulosic fire. (T_t) is measured with plate thermometers. Oxygen concentration of (&gt;4%) (presumably vol.%).</td>
</tr>
<tr>
<td>EN 1363-2: Fire resistance tests – Part 2: Alternative and additional procedures [44]</td>
<td>(T_t = 1080(1 - 0.325e^{-0.167t} - 0.675e^{-2.5t}) + 20) (T_t = 660(1 - 0.687e^{-0.32t} - 0.313e^{-3.8t}) + 20) (T_t = \begin{cases} 154t^{0.25} + 20 \text{ for } 0 &lt; t \leq 21 \ 345\log_{10}(8(t - 20) + 1) + 20 \text{ for } t &gt; 21 \end{cases})</td>
<td>Hydrocarbon, external fire exposure, and slow heating curves.</td>
</tr>
<tr>
<td>BS 476-20: Fire tests on building materials and structures – Part 20: Method for determination of the fire resistance of elements of construction (general principles) [40]</td>
<td>(T_t = 345\log_{10}(8t + 1) + 20) (b^{b}T_t = 1100(1 - 0.325e^{-0.1667t} - 0.204e^{-1.417t} - 0.471e^{-15.833t}))</td>
<td>Cellulosic and hydrocarbon fire. (T_t) is measured by bare wire or stainless steal sheathed thermocouples. Oxygen concentration not specified but recommended to be between 5-10 % (presumably vol.%).</td>
</tr>
<tr>
<td>Eurocode 1 EN 1991-1-2: Actions on structures – Part 1-2: General actions – Actions on structures exposed to fire [41]</td>
<td>(T_g = 345\log_{10}(8t + 1) + 20) (T_g = 660(1 - 0.687e^{-0.32t} - 0.313e^{-3.8t}) + 20) (T_g = 1080(1 - 0.325e^{-0.167t} - 0.675e^{-2.5t}) + 20)</td>
<td>Cellulosic, external, and hydrocarbon curve. In addition, to the temperatures, convective heat transfer coefficients of 25, 25 and 50 W m(^{-2}) K(^{-1}), respectively, are defined. The standard also describes a procedure to calculate parametric temperature-time curves.</td>
</tr>
<tr>
<td>ASTM E119-18(^{c}): Standard test methods for fire tests of building construction and materials [27]</td>
<td>Defined by tabulated temperature-time values. See Fig. 1 for plot of these values.</td>
<td>Cellulosic fire. Furnace temperature measured with thermocouple enclosed by an Inconel 600 pipe.</td>
</tr>
<tr>
<td>UL 1709: Rapid rise fire tests of protection materials for structural steel [26]</td>
<td>Heat flux of (204\pm16) kW m(^{-2}) and temperature of (1093\pm56) °C within 5 min, afterwards constant for the duration of the test</td>
<td>Rapid-temperature-rise fire (e.g., hydrocarbon fire). Furnace temperature is measured by bear wire thermocouple protruding from a pipe. No oxygen concentration is specified but gas samples are taken during the furnace calibration.</td>
</tr>
</tbody>
</table>

\(a^{a}\)Temperatures \(T_t\) and \(T_g\) are given in °C, time \(t\) is given in minutes.  
\(b^{b}\)Specified in Appendix D. Hydrocarbon curve.
2.3 Standards for other fire scenarios

There are a number of additional national and international standards for fire scenarios that differ from cellulosic or hydrocarbon fires. For example, the Eurocodes [41] also define an external fire curve. However, such fire scenarios find currently little application in the academic literature for intumescent coating testing and are therefore only mentioned here for completeness.

EN1363-2 [44] defines a slow heating curve characteristic for smouldering or slow growing fires. This temperature-time curve shows a very low heating rate (Fig. 1b) within the first 21 min of testing, followed by a temperature rise similar to the cellulosic standard temperature-time curve. This heating curve might be of interest for testing of intumescent coatings because a number of studies showed that too slow heating can have a deteriorating effect on the coating performance.

Jet fires can occur if hydrocarbons leak from pressurised tanks or vessels, inflame, and impinge onto a surface. Such fires are even more severe than hydrocarbon pool fires because the turbulent mixing between the hydrocarbon and the fuel increase the flame temperature and the high flow velocities can cause erosion of the surface. ISO 22899 [47] defines conditions of how samples can be exposed to such a fire scenario. Due to furnaces not being able to simulate the severe conditions of a jet fire, ISO 22899 [47] defines conditions for tests with an impinging flame jet. Specifically, 0.3 kg s$^{-1}$ of propane vapour are ejected from a nozzle with a diameter of 17.8 mm and impinge onto a surface 1 m away. Propane is used rather than methane to increase the amount of soot inside the flame and thus the luminosity and radiative heat transfer to the substrate [47].

Other standards define conditions as they occur in tunnel fires. Examples are the German Richtlinien für die Ausstattung und den Betrieb von Straßenstunneln (RABT) or the Rijkswaterstaat (RWS) developed by the Ministry of Transport in the Netherlands. The time temperature curves defined in these standards are similar to the hydrocarbon curves in the sense that there is an initial rapid temperature rise to above 1000 °C within the first 5 min. However, tunnel fire curves reach even higher temperatures than the hydrocarbon curves, 1200 °C for the RABT and 1350 °C for the RWS curves.

2.4 Alternatives to nominal temperature-time curves

All of the fire scenarios discussed in the previous section, with the exception of jet fires, are nominal temperature-time curves. They can easily be adapted by different laboratories to assure that similar boundary conditions are employed and they
can also be used to imitate some fundamentally different cases, such as cellulosic or hydrocarbon fires. However, they are not based on parameters governing a specific fire case, for example, building size, fire load, or air ventilation. Some researchers raised additional concerns because nominal fire curves barely changed in the last 100 years even though the interior of buildings did (i.e., increasing amounts of synthetic materials) [39] and because their generally rapid initial temperature rise implies multiple ignition sources (see below). Alternative temperature-time curves were reported that are based on more recent fire tests and therefore mirror more closely the heating rates, maximum temperatures, and subsequent temperature decay observed in modern building fires. Even though the majority of research on intumescent coatings still relies on nominal temperature-time curves, a brief summary of these alternative curves will be given below. It should be kept in mind that no two fires are identical and there is no "perfect" temperature-time curve that captures all possible fire scenarios. Rather, the aim is to find heating rates and temperatures that are characteristic for the most typical fires encountered in real life.

Alternatives to nominal temperature-time curves are parametric fire curves that enable modifications of the fire load and ventilation conditions. The Eurocode 1 (EN 1991-1-2) [41] defines such a parametric temperature-time curve:

\[
T_g = 1325(1 - 0.324e^{-0.2t\Gamma} - 0.204e^{-1.7t\Gamma} - 0.472e^{-19t\Gamma}) + 20, \tag{3}
\]

The unitless constant \(\Gamma\) depends on the building type and size, as well as the window size and location and fire load. Details on how \(\Gamma\) is calculated can be found in Eurocode 1. Fig. 1 shows an example of the parametric Eurocode 1 temperature-time curve applying parameters reported in the literature [48]. Notably, the parametric curve also includes a cooling phase. The initial temperature rise and the time when the maximum temperature is reached depends on the severity of the fire and if it is fuel or ventilation controlled. Many more details are provided in Eurocode 1 [41], such as guidelines for the fire load and heat release rate calculations. More complex, advanced fire models are also discussed. These are however beyond the scope of this review.

An example for an empirical fire curve that is oriented on actual fire tests is the BFD curve developed by Barnett [48, 49]:

\[
T = T_m e^{-z} + T_a \tag{4}
\]

with the ambient temperature \(T_a\) and the maximum temperature above \(T_a, T_m\), both in °C. The parameter \(z\) is given by [48, 49]:

\[
12
\[ z = \frac{(\log(t) - \log(t_m))^2}{s_c} \]  

(5)

Here, \( t_m \) is the time in minutes until \( T_m \) is reached and \( s_c \) is a shape factor. The curve described by Eq. 4 was shown to fit temperature-time profiles from fire experiments exceptionally well. It relies on only three parameters, includes a cooling phase, and exhibits a more realistic heating phase (i.e., single rather than multiple ignition sources). Notably, it was argued that nominal temperature-time curves are based on research fires that were ignited with multiple sources. This causes a more rapid heat release and more rapid temperature rise in the initial phases than for natural fires that are generally induced by a single ignition source (e.g., faulty electronic device or cable, overheated cooking equipment, tipped candle, etc.). Arson (i.e., deliberately setting fire) is one of the few situations where one might encounter multiple ignition sources [48, 49].

The parameters required for the BFD curve can also be predicted from the type of building (size, ventilation, wall materials, etc.) and fire load. The equations and methodology were summarised in literature and can be applied to calculate a realistic temperature-time curve for modern buildings [39]. Fig. 1 shows the BDF curve reported by Ariyanayagam and Mahendran [39] for compartment A with a opening factor of 0.08 m\(^{-0.5}\). Further details about the calculations and bases for the employed parameters can be found in [39] and references therein. Key differences of this BFD curve to the nominal temperature-time curves are the presence of a pre-flashover and a less rapid temperature rise, a higher peak temperature, as well as the inclusion of cooling phase.

3 Heat source

A wide range of heating devices was used in the literature to test the performance of intumescent coatings. They differ by parameters such as the main mechanism of heat transfer (convective or radiative), achievable heating rates, conformity with nominal or parametric temperature-time curves, and others. The choice of heat source also determines which other experimental instrumentation can be used, such as infrared sensors or thermocouples for temperature measurements or cameras or endoscopes to monitor char expansion. The following section gives an overview over the most commonly applied heating methods (furnaces, radiative heaters, impinging flames) and discusses their key characteristics.
Generally speaking, the net heat flux to a specimen, \( \dot{q}''_{\text{net}} \), is the balance between the radiative (\( \dot{q}''_{\text{rad}} \)), convective (\( \dot{q}''_{\text{conv}} \)), and conductive heat fluxes (\( \dot{q}''_{\text{cond}} \)):

\[
\dot{q}''_{\text{net}} = \dot{q}''_{\text{rad}} + \dot{q}''_{\text{conv}} + \dot{q}''_{\text{cond}}
\]  

This net heat flux to the sample is arguably the key determining factor when characterising the thermal conditions the sample is exposed to. The contributions of the different types of heat flow as well as their directions (i.e., if they contribute to heating or cooling of the sample) depend on the type of heat source and geometric arrangements. Ultimately, the conditions the sample experiences (at least right below its surface) do not depend on the source of the heat fluxes. Nevertheless, one should keep in mind that, for example, knowing the incident radiative heat flux to the sample surface is not the same as knowing the overall net heat flux to the sample. This will be further discussed in the following sections. Note that temperature variations within the steel can generally be neglected due to its high thermal conductivity and low thickness.

### 3.1 Ovens/furnaces

#### 3.1.1 General considerations

![Figure 2](image)

**Figure 2.** Conceptual drawing of the modes and directions of the heat fluxes to and from a sample in (a) a furnace and (b) under a radiative heater. \( T_s, T_f \) and \( T_g \) are the temperature of the sample, furnace and gases, respectively. The heat fluxes caused by radiation, convection and conduction are \( \dot{q}''_{\text{rad}}, \dot{q}''_{\text{conv}} \) and \( \dot{q}''_{\text{cond}} \). The heat flux emitted from the radiative heater is \( \dot{q}''_{\text{irr}} \).

Before summarising studies that applied ovens or furnaces to evaluate the performance of intumescent coatings, it is worth to consider how they heat a sample. In
the most simple scenario, heat conduction away from the sample is neglected while the heating occurs through convection and radiation (Fig. 2a). For unprotected steel samples, heat conduction within the steel can generally be neglected and the change of steel temperature, $T_s$, is given by [50, 51]:

$$\frac{dT_s}{dt} = \frac{\chi}{c_p \rho} \left[ \alpha_c (T_g - T_s) + \epsilon_{\text{eff}} \sigma (T_f^4 - T_s^4) \right]$$

Here, $c_p$ is the heat capacity, $\rho$ is the density, $\alpha_c$ is the convective heat transfer coefficient, $\epsilon_{\text{eff}}$ is the effective emissivity, $\sigma$ is the Stefan–Boltzmann constant, $T_g$ is the gas temperature, and $T_f$ is the temperature of the furnace lining. The section factor $\chi$ in $m^{-1}$ is defined as the exposed surface area $A_m$ divided by the sample volume $V$. Note that in Eq. 7, heat conduction away from the sample is neglected, which is only valid if the back side of the steel sample is well insulated (see below). Values for $T_f$ and $T_g$ are usually not measured directly but assumed to be equal to the temperature measured by a thermocouple or plate thermometer inside the furnace chamber. However, Eq. 7 also applies to the temperature probe and thus does generally not measure the actual gas temperature directly. In Eq. 7, the contributions to the net radiative heat flux $\dot{q}_{\text{rad}}''$ are lumped into an effective emissivity $\epsilon_{\text{eff}}$. This value accounts for heat radiation from the sample to the surroundings, radiative heating of the sample by the surrounding gases and potential soot particles, radiative heating of the sample from the furnace walls/lining, and a configuration factor accounting for the sample/furnace geometries (view factor). It should be noted that Eq. 7 is not directly applicable to steel substrates covered with intumescent coatings because one would have to take into account the heat conduction through the intumescent char, which evolves and expands during heating. This area is beyond the scope of this review but there are a number of studies dedicated to heat transfer in intumescent coatings [38, 52–57].

Even though Eq. 7 applies only to a simplified system with unprotected steel, some important characteristics of heating inside a furnace can be seen. For example, the radiative heat flux scales with the fourth power. Consequently, radiative heating becomes significant at higher absolute temperatures while convective heating dominates at lower temperatures. Besides, two furnaces with identical $T_g$ and $T_f$ might heat a sample differently if the furnace and sample geometries or the furnace lining materials differ. In case of flame-fired furnace, also the fuel type (e.g., oil, propane, butane, or natural gas) and furnace aeration has an influence on the radiative heating because incandescent carbonaceous particles significantly contribute to the radiative heat fluxes [51]. Further complications arise if the emissivity of
the surface changes during the experiment, as might be the case for an intumescent coating. For \( \alpha_c \), a value of 25 W m\(^{-2}\) K\(^{-1}\) is recommended in Eurocode 1 [41], which might not be accurate for every furnace. For example, a value of 28.1 W m\(^{-2}\) K\(^{-1}\) was reported for a 1 m\(^3\) natural gas fired furnace [50]. In the same study, Staggs and Phylaktou [50] report a methodology to determine \( \epsilon_{\text{eff}} \) based on exposing a sample coated with a low and high emissivity paint to identical heating conditions. An even larger \( \alpha_c \) was reported by Nørgaard et al. [52] (34 W m\(^{-2}\) K\(^{-1}\)), however radiative heating was neglected when calculating this value.

Eq. 7 also indicates the importance of sample geometry and mounting of the sample. If the sample is not well insulated on its back, conduction would have to be included in Eq. 7 and the sample temperature would be decreased. Similarly, a thicker steel substrate would lead to a smaller section factor \( \chi \) and thus a slower temperature rise of the steel temperature. Another issue that becomes of particular importance when testing smaller samples in laboratory scale setups are edge effects [58, 59]. These include, for example, the heat transfer through the sample edges and thus around the coated surface that is being tested. In case of well insulated sample edges, the coating expansion might be physically constrained and due to the limited sample size, the coating expansion throughout the sample can be reduced.

### 3.1.2 Examples of hydrocarbon-fired furnace setups

![Figure 3. (a) A 1.5x1.5x1.5 m\(^3\) gas fired furnace to expose samples to the ISO 834 cellulosic fire curve [34]. (b) Scheme of the 26 dm\(^3\) propane fired furnace used to expose coated panels to the UL 1709 hydrocarbon fire curve [14].](image)

Most of the industrial standards, such as BS 476 [40] or EN 1363 [28, 44], specify hydrocarbon-fired furnaces as testing equipment for fire testing in general or intumescent coatings in particular. They are thus likely amongst the most common
Table 2. Overview of academic literature using furnaces to test the performance of intumescent coatings. The key experimental parameters are also provided. Note that only furnace with a volume below 1 m$^3$ were included.

<table>
<thead>
<tr>
<th>Furnace type</th>
<th>Temperature-time profile</th>
<th>Sample size [mm$^2$]</th>
<th>Notes</th>
<th>Year of publication and References</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Propane fired</strong></td>
<td>UL 1709 hydrocarbon fire</td>
<td>100x100</td>
<td>Quartz window for optical excess and air-jet to test mechanical stability of char. Furnace temperature measured with K-type thermocouple of unspecified dimension. Sample back side not insulated.</td>
<td>2019 [14, 60], 2016 [16, 61], 2013 [17, 62, 63]</td>
</tr>
<tr>
<td><strong>Propane-butane fired</strong></td>
<td>EN 1991-1-2 cellulose fire$^a$</td>
<td>100x100</td>
<td>Furnace temperature measured with K-type thermocouple of unspecified dimension.</td>
<td>2019 [64], 2018 [65]</td>
</tr>
<tr>
<td><strong>natural gas fired</strong></td>
<td>ISO834 cellulose fire$^a$</td>
<td>200x300</td>
<td>Laminar gas flow over sample surface. Furnace temperature measured with K-type thermocouple of unspecified dimension.</td>
<td>2016 [52], 2014 [66]</td>
</tr>
<tr>
<td><strong>Electric</strong></td>
<td>EN 1363-1 cellulose fire$^a$ as well as two self-defined curves (BAM1 and BAM2).</td>
<td>75x75</td>
<td>High-temperature endoscope enables optical observation of sample. Furnace temperature measured 1 mm sheathed K-type thermocouples.</td>
<td>2020 [67], 2017 [31, 33, 68]</td>
</tr>
<tr>
<td><strong>Electric</strong></td>
<td>UL 1709 hydrocarbon fire</td>
<td>75x75</td>
<td>Furnace temperature measured with B-type thermocouple with ceramic sheath</td>
<td>2020 [59, 69], 2019 [32, 70]</td>
</tr>
<tr>
<td><strong>Electric</strong></td>
<td>ISO834 cellulose fire$^a$</td>
<td>360x360</td>
<td>Furnace temperature measured with K-type thermocouple of unspecified dimension.</td>
<td>2019 [71], 2017 [20]</td>
</tr>
</tbody>
</table>

$^a$Note that ISO834, EN 1363-1, and EN 1991-1-2 all refer to identical cellulose fire curves.

testing equipment for intumescent coatings even though they appear less often in the academic literature [33, 72]. Some exceptions will be summarised below as well as in Table 2.

Bourbigot and co-workers developed a propane fed laboratory scale furnace specifically intended to imitate the conditions in large scale industrial furnaces (Fig. 3b). The furnace was mostly used for hydrocarbon fires according to UL 1709 [26] but is mentioned to be also suitable for cellulose fire tests [61, 62]. The
furnace chamber has a volume of 26 dm³ and is lined with refractory fibers [14, 17]. In its initial design, a single 35 kW propane burner was used for the heat generation [63], which was replaced by two 20 kW propane burners shortly after [16, 62]. The flow to the burners is regulated to adjust the temperature inside the chamber. The chamber temperature is measured using K-type thermocouples but no details regarding thermocouple shape or location are given [17, 62]. The furnace door can accommodate 10x10 cm² large coated samples (typically steel) [60, 61] and the sample backside is open to ambient air to enable optical access for the temperature measurements.

A very similar furnace design was used by Tomczak et al. [64] and Kazarinov et al. [65]. They used an automatically regulated propane-butane gas burner to follow the Eurocode 1 (EN 1991-1-2) [41] cellulose fire curve. The furnace temperature was monitored using a K-type thermocouple and the 10x10 cm² coated steel panels were mounted into the furnace wall [64, 65]. One difference to the furnace developed in Bourbigot’s group [17, 61–63] is that the steel substrate temperature was measured by K-type thermocouples rather than an IR pyrometer. This enabled the thermal insulation of the steel backside [64, 65] because no optical access was required.

Another medium-scale gas-fired furnace was used by Nørgaard et al. [52, 66]. The 20x30 cm⁻² sample was mounted vertically into the vent wall. The sample back sides were thermally insulated with 8 cm mineral wool. The furnace was fired with a 10:1 volumetric ratio of natural gas and air, which would translate to a theoretical oxygen concentration inside the furnace of 1%. Even though the authors note that this value might not be accurate, it gives a valuable indication what order of magnitude O₂ levels might reach in fired furnaces. The furnace design caused a continuous laminar flow of hot gases parallel to the sample surface. The advantage of such a configuration is that it allowed for the estimation of the flow velocity (0.6 m s⁻¹) [52], potentially facilitating the estimation of convective heat transfer coefficients. However, it differs to conditions in industrial furnaces with a generally random convective or turbulent flow.

### 3.1.3 Examples of electric furnace setups

The main advantages of electric ovens or furnaces are that they can be easily controlled to follow a predefined temperature-time profile and that they can be purchased "off the shelf" for comparably little capital costs. They can be used directly or after modifications to optimise them for the testing of intumescent coatings. An example of a bench-scale electric furnace that was used to mimic standard fire curves is the standard time temperature oven (STT Mufu⁺; see Fig. 4a) [31, 35,
It consists of an electric 5.78 dm³ muffle oven that was modified such that coated samples can be tested according to the standard temperature-time curve in EN 1363–1 [28] (Fig. 1a). Specifically, the oven door was altered to accommodate 7.5x7.5 cm² coated steel substrate and a shutter was installed to facilitate the initial rapid heating required by EN 1363 (Fig. 1b). Hydrocarbon fire curves could not be realised with the STT Mufu⁺ due to power limitations [67]. The sample back side was thermally insulated but no further details were provided. During the experiments, the oven is pre-heated to 500 °C before the shutter is removed to initiate heating of the sample [68]. The oven temperature is measured with two sheathed K-type thermocouples [68] having a diameter of 1 mm [67]. One of the mentioned advantages over burner fired furnaces is that the char structures are not damaged by flow disturbances [35], making the STT Mufu⁺ especially attractive for subsequent offline analysis of the chars [67]. However, it might also imply that the modes of heating are different to industrial furnaces because the convective heat transfer coefficient, \( \alpha_c \), (see Eq. 7) would likely be different. Accordingly, the authors suspect the mode of heating to be mainly radiative, also because the oven uses four radiative heaters as heat source [68]. As discussed in section 3, it should not matter how a sample is heated as long as the overall net heat flux to the sample is the same. However, it would be interesting to see how the heat flux to the sample differs from an industrial furnace if different thermocouples are used or if identical temperatures but different heat transfer coefficient are applied. Nevertheless, the STT Mufu⁺ is able to generate reproducible heating conditions in accordance with an established temperature-time curve, making it one of the most advanced laboratory scale setups for testing intumescent coatings.

**Figure 4.** (a) The Mufu⁺, an electric furnace modified for the testing of coated steel panels [68]. (b) A large-scale electric oven used to test intumescent coatings under non-standard heating conditions [33].
The rapid initial heating required for many standard temperature-time curves (Fig. 1) was achieved by the STT Mufu+ by exposing the sample to a preheating oven chamber when removing the shutter. A somewhat similar approach was used by Nørgaard et al. [73] who inserted samples into a horizontal tube furnace preheated to 1100 °C. This extremely rapid heating was intended to mimic potential damaging of the coating during a fire and the accompanied removal of the top char layer. Experiments were compared to more gentle heating rates of 10 °C min\(^{-1}\). The low heating rates led to negligible expansion of the intumescent coating [73]. This finding highlights that for intumescent coatings, the worst case scenario might not always be the most rapid heating. The tube furnace design is also one of the few that enabled the adjustment of the gas atmosphere from air to pure nitrogen. It was shown that low oxygen concentrations led to a higher mass loss and increased char expansion. The same furnace was later used to expose primers for intumescent coatings to 500 °C with a temperature ramp of 10 °C min\(^{-1}\) [66]. It was shown that the primer was less likely to detach from the substrate under N\(_2\) than under air atmosphere.

Another modified electric furnace was recently introduced by the Coatings Science and Technology Centre (CoaST) at DTU, Denmark [32, 59, 69] (Fig. 5). Compared to the STT Mufu+, the CoaST furnace is smaller (1.58 dm\(^3\)) and more powerful, facilitating experiments according to the UL 1709 [26] hydrocarbon curve (see Fig. 1a). A 6x6 cm\(^2\) large sample is mounted into the modified furnace door and its sides and back are thermally insulated. The furnace temperature is monitored and controlled with the provided furnace temperature control system, a B-type thermocouple sheathed with a ceramic tube. A lever to adjust the airflow gives some control over convection and oxygen concentration in the furnace. After the experiments, it was possible to recover the char samples without breakage, facilitating subsequent offline analyses. Furthermore, the electric control and well-defined boundary conditions led to standard deviations in the time until the coated substrate reached 400 or 550 °C of <1% [32]. Comparisons with an industrial furnace showed identical trends in terms of coating performance but a slightly lower char expansion was observed in the laboratory-scale furnace due to edge effects [59]. In explicit, the expansion close to the edges was physically restrained, leading to an arc shaped char [59]. However, the good test reproducibility of this setup is encouraging. Similar to the STT Mufu+, it would be interesting to compare the \(\alpha_c\) and \(\epsilon_{\text{eff}}\) of the CoaST furnace [32] to other experimental setups to truly evaluate the net heat flux to the sample rather than furnace temperatures.

Mariappan et al. [20, 71] used an in-house constructed electric furnace for the
characterisation of waterborne intumescent coatings. The furnace temperature followed the ISO 834 cellulosic fire curve and was monitored using a K-type thermocouple. Details such as thermocouple size or sheathing were not provided. The steel substrate size was $360 \times 360 \times 5$ mm$^3$ with the intumescent coating being applied to the central area of $250 \times 250$ mm$^2$. It is reported that the sides and edges of the steel substrate where thermally insulated, however the provided scheme indicates that no insulation was applied to the steel backside [20].

![Customised electric oven developed at DTU CoaST, Denmark. The coated steel panel is mounted into the furnace door. The steel backside is thermally insulated while its temperature is measured with a disc thermocouple.](image)

**Figure 5.** Customised electric oven developed at DTU CoaST, Denmark. The coated steel panel is mounted into the furnace door. The steel backside is thermally insulated while its temperature is measured with a disc thermocouple.

Lucherini et al. [33] compared the performance of intumescent coatings in electric ovens with a medium-scale gas fired furnaces and radiative heaters. Four non-standard heating curves rated as very slow, slow, medium and fast were tested in the electric oven with a chamber volume of $572.69$ dm$^3$ (Fig. 4b). However, all of them were slower than the heating ISO 834 standard curve tested with the gas fired furnace. Nevertheless, similar trends were observed in both setups. Notably, some of the coating formulations performed better when heated fast while others favoured slow heating [33].
3.2 Radiative heater

3.2.1 General considerations

Radiative heaters and especially cone calorimeters are widely used in the field of fire science and safety. Cone calorimeters are commonly used to measure heat release rates, likely the most important parameter to assess a fire hazard \[74\]. Standards specifying the experimental procedures to measure heat release rates and smoke evolution are, for example, ISO 5660-1 \[75\] or ASTM E1354 \[76\]. Because radiative heaters are so well established in fire research, they are used extensively to characterise intumescent coatings \[77–80\].

Analogue to Eq. 7, the transient temperature response of a steel sample heated by a radiative heater is given by \[50\] (Fig. 2b):

\[
\frac{dT_s}{dt} = \frac{1}{\delta c_p \rho} \left[ \epsilon q_{irr}'' + \alpha_c (T_g - T_s) + \epsilon \sigma (T_g^4 - T_s^4) \right]
\]

(8)

where \(T_g\) is the ambient gas temperature, \(\epsilon\) is the emissivity of the sample surface, and \(\delta\) is the sample thickness. The radiative heat flux emitted from the heater (\(q_{irr}''\)) is usually obtained with a calibration measurement and set during the experiment. This radiative heat flux is what heats the sample while the other two terms on the right hand side of Eq. 8 contribute to sample cooling. The latter is due to the ambient gas temperature \(T_g\) being below the sample temperature \(T_s\).

Even though the \(q_{irr}''\) is usually known, knowledge about \(\epsilon\) is required to estimate the actual heat flux transferred to the sample. The reason is that not all of the incident radiative heat flux is actually absorbed by the sample surface. In most cases concerning intumescent coatings, \(\epsilon\) is however not known. Furthermore, the chemical reactions in the coating and the char formation during its decomposing can be accompanied by a change in \(\epsilon\) with time. It was also noted that the expansion of the intumescent coating changes the distance between the sample surface and the heater, as well as the geometric view factor \[81\]. The latter is hereby the fraction of radiation emitted by one surface and received by another. Given that \(q_{irr}''\) is calibrated for a fixed heater-surface distance, the expansion of the intumescent coating can led to an increase in \(q_{irr}''\). Further uncertainties arise by a usually unknown convective heat transfer coefficient \(\alpha_c\). Staggs and Phylaktou \[50\] showed that convective cooling during cone calorimeter experiments was previously underestimated. The reason was that values for \(\alpha_c\) were previously based on free convection for hot horizontal plates (10-15 W m\(^{-2}\) K\(^{-1}\)) while measured values for \(\alpha_c\) were closer to 28 W m\(^{-2}\) K\(^{-1}\) \[50\]. It should also be noted that estimating the convective and radiative heat loss
from the sample requires knowledge of the sample surface temperature $T_s$ while the backside steel temperature is commonly measured when characterising intumescent coatings.

### 3.2.2 Examples of radiative heater setups

Compared to furnaces, radiative heaters are generally not suitable to follow standard temperature-time curves (Fig. 1). One of the exceptions is the Heat-Transfer Rate Inducing System (H-TRIS), a vertically oriented and propane or natural-gas fired radiant panel that is mounted on a linear motion system [79, 84–86] (Fig. 6c). The distance between the sample and the radiative heater can be continuously changed to follow a predefined time-incident heat flux profile. This enabled the authors to replicate the conditions in EN 1363 [28, 44] cellulosic, hydrocarbon, and smouldering fire curve [79]. In case of cellulosic and hydrocarbon fire curves, the H-TRIS used at the time was not powerful enough to reach the required heat fluxes after 30 and 10 min, respectively. One reason is probably that samples are typically not enclosed into a thermally insulated chamber when tested with radiative heaters and the accompanied high heat losses from the sample reduce the net heat flux into the sample. However, even for a perfectly insulated sample incident heat fluxes of 204 kW m$^{-2}$ as defined in UL 1709 [26] will be difficult to reach with radiative heaters. It was, however, argued that it would be adventurous to follow a predefined time-heat flux profile rather than a temperature-time curve as for common furnace experiments [84]. For example, defining a heat-flux would simplify and better define thermal boundary conditions, reduce experimental uncertainties, and enhance the reproducibility [84]. However, as seen in Eq. 8, parameters such as sample emissivity $\epsilon$, convective heat transfer coefficient $\alpha_c$ (which can also change with temperature [78]), or sample surface temperature still need to be determined to fully define the thermal boundary conditions. Such parameters were in fact measured to facilitate the modelling of heat and energy fluxes during intumescent coating testing using the H-TRIS [86].

While the H-TRIS makes use of a variable sample-heater distance to modify the temporal incident heat flux, it is also possible to directly tune the radiant heater output power. This approach was used to replicate the heating conditions of a cellulosic fire curve and good agreement was achieved within the first 40 min [78]. The authors note, however, that the cone calorimeter used for the experiments would not be able to follow the heating conditions of a hydrocarbon fire curve beyond 10-15 min. In the same study [78], the coating emissivity and convective heat transfer coefficient were identified as crucial factors, both of which are usually unknown.
Additional issues might be different gas atmospheres and sample orientations com-

Figure 6. (a) A modified cone calorimeter heater which is moved away from the expanding sample to keep the heat-sample distance and thus heat flux constant [82]. (b) A modified cone calorimeter to test samples under well-defined gas atmospheres [83]. (c) The H-TRIS, a radiative heater panel that is moved towards the sample to expose it to a variable heat flux [84].
Table 3. Overview of literature using radiative heaters to test the performance of intumescent coatings. The key experimental parameters are also provided.

<table>
<thead>
<tr>
<th>Incident Heat flux [kW m(^{-2})]</th>
<th>Sample-heater distance [mm]</th>
<th>Sample size [mm(^2)]</th>
<th>Notes</th>
<th>Year of publication and References</th>
</tr>
</thead>
<tbody>
<tr>
<td>5-130</td>
<td>Variable</td>
<td>200x200 and 300x300</td>
<td>H-TRIS: Vertical radiant heaters on linear motion system. Time dependent heat flux profiles can be followed.</td>
<td>2020 [85], 2019 [84, 86], 2014 [79]</td>
</tr>
<tr>
<td>up to ~100</td>
<td>25</td>
<td>100x100</td>
<td>Temperature of cone heating elements is varied with time to induce a time dependent heat flux.</td>
<td>2011 [78]</td>
</tr>
<tr>
<td>30</td>
<td>40</td>
<td>50x50</td>
<td>-</td>
<td>2013 [87], 2006 [30]</td>
</tr>
<tr>
<td>20, 40 and 60</td>
<td>60</td>
<td>100x100</td>
<td>Comparison of cone calorimeter with electric and gas fired furnace experiments.</td>
<td>2018 [33]</td>
</tr>
<tr>
<td>up to 100</td>
<td>Typically 40</td>
<td>Discs with 30-70 mm diameter</td>
<td>CAPA II: Gas atmosphere can be controlled. Thermal boundary conditions were evaluated in detail.</td>
<td>2017 [77], 2019 [83, 88]</td>
</tr>
<tr>
<td>50 and 65</td>
<td>50</td>
<td>100x100</td>
<td>Heat flux at different heat distances is measured to compensate for sample expansion.</td>
<td>2012 [38]</td>
</tr>
<tr>
<td>5–56</td>
<td>40–60</td>
<td>50x50 and 100x100</td>
<td>-</td>
<td>2010 [58]</td>
</tr>
<tr>
<td>25, 50, 75</td>
<td>25</td>
<td>100x100 or 100 mm discs</td>
<td>Position of heater is automatically adjusted to keep the sample-heater distance and thus incident heat flux constant during the char expansion.</td>
<td>2019 [82], 2018 [89]</td>
</tr>
<tr>
<td>35, 50, 65</td>
<td>25</td>
<td>70x70</td>
<td>-</td>
<td>2019 [90]</td>
</tr>
<tr>
<td>30, 45, 60, 75, and 90</td>
<td>Not specified</td>
<td>100x100</td>
<td>Experiments can be conducted in air or under reduced O(_2) concentrations (8-10%)</td>
<td>2003 [91]</td>
</tr>
<tr>
<td>90</td>
<td>Not specified</td>
<td>100x100</td>
<td>Coating oriented vertically. A 25 m s(^{-1}) airflow jet was introduced after 5 min to evaluate the mechanical char properties.</td>
<td>2013 [17, 93]</td>
</tr>
<tr>
<td>35</td>
<td>Not specified</td>
<td>100x100</td>
<td>Coating surface temperature is measured using laser-induced phosphorescence.</td>
<td>2007 [36]</td>
</tr>
</tbody>
</table>

pared to furnace tests and the movement of the sample surface towards the heater
during expansion. Nevertheless, the cone heater led to similar trends and can thus be seen as a rapid and economic screening method prior furnace testing.

The potential issue of a non-constant heat flux during char expansion and thus variable heater-sample distance was addressed by Kang et al. [82, 89]. They modified a conical radiant heater such that its position is continuously adjusted based on the detected sample surface (Fig. 6a). This way, the heater-sample distance and thus incident heat flux remained constant throughout their experiments.

The influence of the O$_2$ concentration on the performance of intumescent coatings was studied by Griffin et al. [92]. The modified cone calorimeter allowed experiments in air or reduced O$_2$ (8-10%) atmospheres. The key findings were that the char expansion and the intumescent process are barely influenced by presence of O$_2$ while char degradation started at lower temperatures in air. Besides, a flame might develop when the coating ignites during experiments in air, leading to a higher heat release rate and elevated substrate temperatures [92].

Another modified cone calorimeter that facilitates experiments under modified gas atmospheres is the Controlled Atmosphere Pyrolysis Apparatus II (CAPA II, Fig. 6b) [77, 83, 88]. Besides the possibility to test samples under reduced oxygen atmospheres, a major advantage of this setup is that the heating conditions were characterised in depth. For example, the convective flow conditions were evaluated using CFD simulations and heat fluxes to the samples were estimated at different sample-heater distances and sample slopes [77]. The latter is important because intumescent coatings tend to form uneven rather than flat surfaces. Given the well defined heating conditions, the CAPA II is particularly useful for the development of pyrolysis and charring models [83, 88].

3.3 Impinging flame

3.3.1 General considerations

Flames are readily available in most fire safety laboratories because they are required for standard tests such as the Limiting Oxygen Index according to ISO 4589-2 [94] or the polymer flammability tests according to UL-94 [95]. Besides, the capital and operating costs of a Bunsen burner are significantly lower than for a cone calorimeter or furnace. It is therefore not surprising that impinging flames are amongst the most common heat source to test the performance of intumescent coatings.

The heat transfer from an impinging flame to a substrate is largely dominated by convection [96]. The reason is that in the case of flames, the forced convection induced by the impinging gas stream increases the convective heat transfer coeffi-
cient, $\alpha_c$. The scale of $\alpha_c$ is difficult to predict as it is influenced by a number of parameters, such as the level of turbulence, burner nozzle geometry, burner nozzle to substrate distance, and the actual flame temperature [96]. The latter hereby itself is dependant on the employed fuel, the fuel to air (or oxygen) ratio, the entrainment of the surrounding gases, and again turbulence and the accompanied fuel/oxygen mixing [97]. It should also be noted that measuring flame temperatures is not a trivial task and generally requires correcting the recorded temperature by radiative and conductive heat losses from the thermocouple junction [98]. Furthermore, $\alpha_c$ also changes in radial direction, further complicating the assessment of the heating conditions the substrate experiences. As the intumescent coating expands, the distance to the burner nozzle does not just decrease but the substrate might become curved, which would also affect $\alpha_c$ [96]. Given the above, it is clear that defining the thermal boundary conditions for impinging flames is very challenging. It is therefore also difficult if not impossible to compare such experiments unless all of the key experimental parameters are provided. Impinging flames might be a very rapid and economic approach to screen different coating formulations and to get a first impression regarding their behaviour under heat exposure. Whenever possible however, more advanced setups with better defined and more homogeneous thermal boundary conditions should be used. One exception of course are tests under jet fire conditions.

### 3.3.2 Examples of impinging flame setups

![Diagram of impinging flame setup](image)

**Figure 7.** Scheme of a typical impinging flame experiment used to test intumescent coatings [22].

A burner that was specifically developed to assess intumescent coatings under extreme conditions is the high-performance burner [99]. It is fueled with an oxygen-propane mixture, enabling experiments at up to 1800 °C. Such extreme temperature
conditions can occur during metal fires or re-entry of space vessels into the earth’s atmosphere.

More commonly used flames for assessing the performance of intumescent coatings are commercially available Bunsen burners. A summary of reported flame configurations is given in Table 4. Main differences are the type of employed fuel and the reported flame temperature while the sample-burner distance is typically 70 mm. Unfortunately, the air supply to the Bunsen burner or the degree air/fuel pre-mixing is typically not reported even though it significantly impacts the flame temperature and thus experimental reproducibility. It is also clear that not only the flame temperature but also its size influences the heat transfer to the substrates. The amount of heat generated by the flame might be estimated by the fuel flow rate, but it is typically not reported either. Impinging flames are therefore mainly applied to assess the relative performance of different coating formulations within one laboratory. It should also be noted that in many studies, little consideration is given to sample mounting or thermal insulation. This further complicates matters and might reduce the reproducibility of the results.

4 Parameters measured during heat exposure

4.1 Temperature measurements

When testing intumescent coatings, temperatures at different locations within the set-up can be measured. The most commonly reported one is the steel substrate temperature. However, also temperatures within the expanding char layer or on the coating surface can be measured and used as input to analytical heat transfer models or numerical simulations. The temperature around the sample, i.e., the flame or furnace temperature are also important in order to evaluate how well the intumescent coating insulates the substrate. Unfortunately, details of how flame and furnace temperatures are measured are seldomly reported even though parameters such as the thermocouple size and sheathing will influence the obtained temperature reading. This is because the thermocouple temperature is governed, just as the sample itself, by the balance of convective, radiative, and convective heat transfer to and from the thermocouple bead and thus the wire diameter, bead size, and bead emissivity all contribute. Industrial standards therefore specify how furnace temperatures should be measured. For example, UL 1709 [26] requires No. 14 B&S gauge K-type thermocouples with wires inside a porcelain insulator and with the junction protruding from an iron, steel, or inconel pipe while ISO 834 [29] uses plate
Table 4. Overview of literature using impinging flames to test the performance of intumescent coatings. The key experimental parameters are also provided.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Fuel/oxidiser mixture</th>
<th>Flame temperature [°C]</th>
<th>Sample-heater distance [mm]</th>
<th>Flow rate</th>
<th>Year of publication and References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Butane</td>
<td>Premixed but no details given</td>
<td>1350</td>
<td>70</td>
<td>Not specified</td>
<td>2018 [100]</td>
</tr>
<tr>
<td>Methane</td>
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<td>1100</td>
<td>Not specified</td>
<td>Not specified</td>
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</tr>
<tr>
<td>Propane</td>
<td>Premixed; Bullfinch No. 1270</td>
<td>1000</td>
<td>350</td>
<td>Not specified but adjusted to achieve heat flux of 100 kW m⁻²</td>
<td>2018 [101]</td>
</tr>
<tr>
<td>Butane</td>
<td>Premixed; Dremel VersaFlame 2200</td>
<td>1150</td>
<td>30</td>
<td>Not specified</td>
<td>2016 [102], 2017 [103]</td>
</tr>
<tr>
<td>Methane</td>
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<td>954</td>
<td>70</td>
<td>Not specified</td>
<td>2013 [104], 2017 [105]</td>
</tr>
<tr>
<td>Liquefied petroleum gas</td>
<td>Bunsen burner with unspecified air supply</td>
<td>950</td>
<td>70</td>
<td>Not specified</td>
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<td>80</td>
<td>Not specified</td>
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</tr>
<tr>
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<td>20</td>
<td>160 g h⁻¹</td>
<td>2015 [19]</td>
</tr>
<tr>
<td>Butane</td>
<td>Bunsen burner with unspecified air supply</td>
<td>100-1250⁰</td>
<td>70</td>
<td>130 g h⁻¹</td>
<td>2018 [22], 2019 [15]</td>
</tr>
</tbody>
</table>

*Range in which the flame temperature was estimated [22] or controlled [15].

thermometers instead. Given that literature on intumescent coatings generally do not discuss furnace and flame temperature measurements, they will not be discussed here but further information can be found in the literature from other academic fields [43, 98, 108–110].

4.1.1 Substrate temperature

The substrate temperature is the parameter that is reported in virtually all publications that assess the performance of intumescent coatings. There are broadly two methods to measure this temperature: thermocouples or infra-red sensors/cameras.
Measuring the steel temperature with thermocouples is comparably simple. The thermocouple is in contact with the hot steel and is thus heated by conduction. It is therefore important to assure a good thermal contact between the steel sample and thermocouple. One option is the use of disc thermocouples [32, 70]. Here, a thermocouple is attached to a copper disc to extend the contact area between the thermocouple and the steel surface. This method is described in the European standards for measuring unexposed surface temperatures [28, 29]. Another option is to directly weld the thermocouple onto the back side of the steel substrate [31, 35, 36]. Also embedding the thermocouple into a hole drilled into the steel substrate was shown to give reliable temperature readings [50, 52, 78, 111]. Such thermocouples are described in ISO 834 [29] to measure internal steel temperatures. Han et al. [58] compared internal and plate thermocouples for measuring the steel substrate temperature in radiative heater experiments and found no significant difference between the two. Besides the thermal contact, other parameters that should be taken into account when using thermocouples are heat loss by conduction through the thermocouple wires and the thermocouple time response.

Compared to thermocouples, infrared (IR) sensors (camera or pyrometer) for temperature measurements have the advantage that temperatures are recorded contactless. This means that no probes with wires have to be attached to the steel, making IR sensors especially attractive when samples are replaced frequently to char-

![Figure 8](image.png)

**Figure 8.** (a) Scheme of the arrangement of thermocouples and heat transducers before the sample was exposed to high temperature [89]. The top two thermocouples extrude from the virgin coating and are embedded during char expansion to measure the internal char temperature. (b) Image recorded with an infra-red camera of the surface of an intumescent coating while being exposed to a radiative heater [86]. If the emissivity of the surface is known (or set to assumed value), the char surface temperature can be calculated.
acterise a large number of coatings. The drawback is that the steel backside has to be optically accessible and therefore thermal insulation is usually neglected [16, 83]. Furthermore, this technique requires a known and ideally high specimen emissivity. This can be achieved by coating the steel backside with a high temperature and high emissivity coating [14, 30, 63]. Alternatively, a copper foil with high emissivity coating can be mounted on the sample backside [77, 88].

4.1.2 Internal char temperature

The internal coating or char temperature can be measured by positioning a number of thermocouples in front of the virgin coating such that they become embedded into the char during the intumescent process (Fig. 8a). The obtained data is of particular interest for the development of mathematical or numerical models for the intumescent process and the thermal conductivity of the char layer [52, 89, 112, 113].

Nørgaard et al. [52] placed five thermocouples at intervals of 1 cm in front of the coated steel substrate. A significant deviation from the measured temperature evolution was taken as indication for embedding of the thermocouple by the expanding char layer. In addition, the internal as well as steel substrate and gas temperatures were used to fit a simple engineering model to the experiments. This approach enabled the authors to derive a temperature-dependant effective thermal conductivity of their coating system.

Kang et al. [89] used protruding thermocouples to measure two internal as well as the surface temperature of a commercial intumescent coating. An additional transducer was used to measure the heat flux through the sample and, combined with the internal temperature measurements, enabled the effective thermal conductivities to be obtained at different locations within the char. The heat flux emitted from the cone heater was also varied to investigate the effect of heating rate on the effective thermal conductivity of the chars. Bozzoli et al. [113] and Lucherini et al. [85] also measured the internal char temperature with initially protruding thermocouples and used a radiative heater as heat source. Bozzoli et al. [113] additionally calculated the apparent thermal conductivity from the experimental results based on model fitting and finite element modelling [113].

Instead of having the thermocouples protrude through the steel substrate and virgin coating [52, 89], it is also possible to place the thermocouples in front of the coating surface [10]. Han et al. [10] used this approach to measure internal char temperatures to elucidate the stages involved in the intumescent process.

Temperature measurements at known spatial locations inside the char can also
be used to estimate the char surface temperature. This approach was reported by Gibson et al. [101] who embedded two thermocouples inside the coating to extrapolate the hot surface temperature. The surface temperature was used as input to a two-parameter thermal model. As noted by the authors [101], extrapolating the surface temperature led to lower temperatures than the temperature of the impinging propane flame [101], thus avoiding overestimation of the thermal boundary condition.

### 4.1.3 Char surface temperature

The coating or char surface temperature is seldomly measured even though it would provide useful inputs to the modelling of heat transfer through the char and help characterising the thermal boundary conditions inside a given heating environment. The reason is likely that surface temperatures are not easily measured. The surface is moving during the expansion, which makes the positioning of thermocouples challenging. The coating emissivity if usually not known and changes during the char formation and expansion, making optical temperature measurements difficult. Consequently, the coating surface temperature is often set equal to the surrounding gas temperature, which might over or under estimate the surface temperature depending on the thermal boundary conditions [101].

If the surface temperature of the coating is measured by infra-red techniques, the emissivity of the surface has to be known or alternatively, a value has to be assumed. Lucherini & Maluk [86] assumed an emissivity of 0.92 and measured the coating surface temperature with an infra-red camera (Fig. 8b). The coating was hereby heated with the H-TRIS (see section 3.2.2 and Fig. 6c). Also de Sá et al. [103] used an infrared camera to obtain char surface temperatures, however, without providing details on the assumed surface emissivity.

Two examples where embedded thermocouples were used to estimate the char surface temperature were already discussed in the previous section (see section 4.1.2). One is Kang et al. [89] where one thermocouple was positioned in such a way that it’s tip is within 2 mm of the fully expended char layer. Advantage is that the surface temperature is measured directly but multiple experiments might be necessary until a suitable thermocouple position prior expansion is found. The other example is Gibson et al. [101] where the internal temperatures are used to extrapolate to the surface temperature.

A novel method to measure the char surface temperature optically is based on seeding the surface with thermographic particles. This approach was described by Omrane et al. [36] to measure intumescent coating surface temperature inside a cone.
The surface was seeded with phosphor particles (Mg$_3$FGeO$_4$:Mn) and excited with a pulsed Nd:YAG laser during the experiments. Unfortunately, the sophisticated equipment required is not widely available in the area of intumescent coating science.

### 4.2 Coating expansion and char formation

![Figure 9](image)

**Figure 9.** (a) Image taken from within the electric furnace STT Mufu+ using a high temperature endoscope [31]. (b) Scheme of a setup in which a laser diode and sensor are used to measure the char expansion [89].

Intumescent coatings insulate the underlying material by swelling during heat exposure. Therefore, data on the char expansion during heating is crucial to understand how the coatings work under different heating scenarios. This enables the researcher to link char expansion to thermal insulation and substrate temperature, which might provide new insights for future coating formulations.

In the simplest case, the coating surface is optically accessible and the char expansion can be directly observed. This is often the case in cone calorimeter experiments [38, 114], such as in the CAPA II [77] (see section 3.2.2). Here, a camera positioned perpendicular to the coating surface was used to measure the surface profile as a function of time [77, 83].

In case of setups where the sample holder is moved during radiative heating to keep the expanding surface at a constant position, this movement can be recorded to obtain the char expansion. For example, Elliott et al. [79] manually moved the sample holder in the H-TRIS setup (see section 3.2.2 and Fig. 6c) such that the surface position of the reactive coating remained unchanged during the experiment. The movement of the sample holder was recorded and taken as coating expansion over time [79]. The same approach was used by Kang et al. [89], however using an
optical surface detection and automated motion system (Fig. 9b).

An example where the coating expansion was measured inside a furnace is the STT Mufu+ (see section 3.1.3). Here, a high temperature endoscope was added to a commercial electric oven to observe the expansion process [31, 35, 68] (Fig. 9a). Also this approach provides surface profiles and the expansion at different locations can be used to evaluate sliding of the vertically oriented coating due to gravity [68].

The char expansion can also be assessed with the aid of thermocouples protruding known distances from the virgin coating. Once the expanding char covers the thermocouple, a significant drop in the measured temperature is detected, which provides the current location of the coating surface [52].

Another approach is the use of parallel-plate rheometers to measure char expansion [30, 32, 115]. Here, a free-standing intumescent sample is placed between two plates and heated up. The two plates are pressed together with a small constant force while the gap between them is recorded. However, the employed heating rates (10-50 °C min\(^{-1}\)) and peak temperatures (500-600 °C) that can be reached with rheometers [30, 32, 115] are typically lower than in fires.

Other researchers measured the char expansion after completion of the experiment [116], usually in cases where no in-situ method for measuring expansion is available. Such an approach can give an impression of how different coating formulations or heat treatments influence the final char. However, no information regarding expansion rate, swelling onset temperature, or char oxidation can be gained. Given that the focus of this review is on in-situ characterisation techniques, these studies will not further be discussed here.

### 4.3 Resistance of char against mechanical impact

In the event of a fire, convective gas flows, dropping debris, or explosions might damage expanded intumescent coatings. This would impair their thermal insulation properties and reduce the protection they offer against the fire [117]. It is therefore worthwhile to test not only the thermal insulation of a coating under ideal, unperturbed conditions but also assess the resistance of the char to mechanical damages. As noted by Reshetnikov et al. [118], no universal definition of char strength exists and different criteria might be applied to assess the resistance of a char to mechanical impact. Some of them will be discussed in the following.

Testing of the mechanical properties of char during the heat exposure is challenging because of spatial constrains in the experimental setup and the inhomogeneous structure of the formed chars. Due to the former, testing is often conducted at room temperature after the heat treatment was completed. Some examples for such an
approach are the dropping a testing weight onto the char from a fixed height and measuring the penetration depth [68], measuring the force of total char destruction normalised by the char gap height [120], or measuring force-displacement curves while pressing a piston into the char [116, 121]. However, the mechanical properties of a char at room temperature might be different to the ones at elevated temperatures. Muller et al. [122] compared different protocols for testing the mechanical properties of char and showed that the temperature at which the mechanical strength is measured influences the outcome. Specifically, an intumescent coating was heated to 500 °C and compressed at the same temperature or after cooling it to room temperature. The char tested at 500 °C showed a higher mechanical strength, which was explained by the dynamic processes (char morphology, composition, and rheology) that depend on the time-temperature history of the coating [122]. Whenever possible, one should therefore measure mechanical properties at elevated temperatures close to what is expected in the event of a fire.

Some of the pioneering work on the mechanical testing of intumescent chars was done by Reshetnikov et al. [118, 120], who compared different setups and protocols for assessing mechanical strength. One example is the heating of the coating with a oxygen-acetylene burner and measuring the force required to press a rod into the

![Figure 10](image_url)

**Figure 10.** (a) Scheme of the procedure to assess the mechanical strength of an expanding intumescent coating in a rheometer [119]. (b) Scheme of a setup used to impinge an air-jet onto the surface of a intumescent coating to test its mechanical properties [16].
char [118]. Another setup used was a revolving table containing the intumescent coating as well as a convective gas heater. The intumescent coating was heated while the table rotated, eventually breaking off the char cap due to the centrifugal force [118]. Both approaches measure char strength at elevated temperatures even though the heating rate and actual char temperature during the mechanical testing might differ from nominal fires (Fig. 1). Also, both approaches measure different properties of the char, one being the resistance against compression while the other is related to the pull-off force required to break the weak spots.

An approach that is often used is based on high-temperature rheometer (Fig. 10a). A free-standing coating film is placed between the two rheometer plates and is allowed to expand freely during heating. Afterwards, the gaps between the two plates is reduced continuously while recording the force. This procedure was used by Jimenez et al. [13, 123] to assess how different coating ingredients alter the mechanical strength of the char. The same approach was also adapted by other authors. For example, Bodzay et al. [119] investigated how different clays influence the char strength. Muller et al. [122] used the plate-plate rheometer setup to test the mechanical properties of chars formed from intumescent coatings exposed to different thermal conditions: a mass loss calorimeter, a tubular oven, or directly in the rheometer furnace. They showed that the temperature at which the mechanical tests are conducted, as well as the heating rate and final temperature during the char formation influence the mechanical properties [122]. The mechanisms responsible for the observed trends were not further discussed.

The plate-plate rheometer methodology has the advantage that chars can be tested at elevated temperature, however at significantly lower temperatures than what is encountered during fires (typically up to 500 °C). Also the heating rates achievable with rheometer furnaces are much lower than what is required in typical nominal temperature-time curves. One should keep in mind however that fire curves define surface temperatures while the interior of an intumescent coating might heat up much slower. More realistic thermal conditions during testing can be achieved by using impinging air-jets [16, 17, 61, 93]. Gardelle et al. [17, 93] exposed their samples to a 35 kw m$^{-2}$ heat flux using a cone heater. Once the maximum char expansion was reached, a 25 m s$^{-1}$ air-jet was introduced and impinged onto the sample surface. Assessment of the mechanical properties was done by visual observation of the damage caused by the air-jet.

A further advancement in the mechanical testing of intumescent coatings under realistic fire conditions was introduced by Naik et al. [16] and later adapted by others [61]. Here, an air-jet was introduced into a gas-fired furnace (Fig. 10b) rather
than a radiative heater [17, 93]. The samples are exposed to the UL 1709 [26] hydrocarbon temperature-time curve and the air-jet is introduced once the steel substrate reached 350 °C [16]. The aim was to simulate wind perturbation during a fire and to evaluate the char destruction. The effect of the air-jet was quantitatively assessed by comparing the times until the steel temperature increased to 500 °C.

5 Complementary experimental techniques at elevated temperatures

The above sections summarise equipment to expose intumescent coatings to high temperatures and highlight what parameters can be measured while the sample is being heated. However, some parameters, such as the viscoelastic behaviour or chemical decomposition kinetics, can only be measured in dedicated instruments. These will be briefly explained in this section for completeness. There are of course a wide range of additional experimental techniques that can be used to characterise intumescent chars, such as Fourier-transform infrared spectroscopy, X-ray diffraction, or scanning electron microscopy just to name a few. These are however outside the scope of this review because they measure chars ex-situ at room temperature after the heat exposure experiment was completed.

5.1 Thermogravimetric analysis

Thermogravimetric analysis (TGA) is widely used to characterise intumescent coating systems or its constituent parts [12, 20, 65, 80, 111, 124, 125] even though it is not always clear how results are transferable to full-scale fire tests. In a typical TGA experiment, a few milligrams of sample are placed in an inert crucible and heated with a constant rate (typically 5-50 °C min⁻¹) while recording the sample mass [18, 100, 104]. The gradient of the sample mass as function of temperature provides the mass loss rate (referred to as derivative thermogravimetry, DTG [64, 100]) and can be used as input or reference for numerical models. It is also possible to combine TGA measurements with other techniques, such as a gas analysis system to characterise volatile decomposition products [124], or differential scanning calorimeter (DSC) to investigate the endo- or exothermic nature of the reactions.

Amongst the most common applications of TGA in intumescent coating research is the determination of residual char weight as a function of the coating formulation [12, 18, 22, 104]. For example, Wang & Yang [12] varied the molecular weight of the epoxy resin in their coating formulation and conducted TGA experiments with
20 °C min⁻¹ in air. A higher molecular weight binder was shown to lead to a higher residual mass, which was explained by an improved oxidation resistance of the coating. Similarly, Gillani et al. [100] used TGA to show an increase in residual char mass when boric acid is replaced by zinc borate. The authors also studied the DTG curves to show a shift of the first decomposition step towards higher temperatures as zinc borate is introduced [100]. The effect of melamine and boric acid addition on the residual weight was studied by Ullah et al. [104]. Furthermore, the authors used DTG to show the number and sequence of reactions leading to the final char [104].

In order to investigate the coating decomposition pathways in more detail, Kunze et al. [124] coupled TGA with mass and Fourier transform infrared spectroscopy. TGA results were linked to detected gas-phase species to show the initial endothermic formation of NH₃ and H₂O, followed by melamine and hydrocarbon release, and the eventual exothermic char oxidation coupled with CO₂ and H₂O formation [124].

A more detailed insight into the kinetics of the coating and char decomposition can be gained by conducting TGA experiments with different heating rates [92, 126, 127]. The obtained weight loss curves can be fitted to simplified models to obtain the kinetic parameters of the reactions. For example, Griffin et al. [92] used four parallel reactions (melting, intumescence, char formation, char degradation) in their model. Experiments under air and N₂ atmosphere showed that melting and intumescence are not influenced by the oxygen concentration. The char formation and degradation however differ under air and N₂ but trends depend on the exact coating formulation [92]. Jimenez et al. [127] also conducted TGA experiments in air and N₂ to study the degradation of boric acid and ammonium polyphosphate. The degradation of the complete coating formulation was fitted with four successive n-dimensional nucleation/nucleus growth equations [127]. The char degradation kinetics were also analysed in depth by applying the method of invariant kinetic parameters and calculating probabilities for the involvement of different kinetic equation [92, 126].

Another application of TGA is to obtain kinetic parameters for models of intumescence and thermal insulation. Given the complexity of the chemical reactions that occur during the coating degradation, the kinetic parameters are usually only extracted for very simplified model reaction mechanisms. Zhang et al. [38] proposed a three-step reaction mechanism to describe the thermal decomposition of their intumescent coating and fitted this model to TGA curves. The derived parameters provided the pre-exponential factors and activation energies as required for their model to describe the char expansion, oxidation, and thermal insulation of a steel substrate [34, 38].

A potential issue of TGA studies is that only small fragments of the coating
can be tested. Cirpici et al. [55, 57] noted that gases formed during the thermal degradation of the coating are more likely to be released from such fragments than from larger samples encountered in real applications. It should also be noted that the heating rates in TGA experiments are significantly lower than defined in typical fire curves. This means that TGA experiments can not replicate conditions seen by the sample surface but are probably more representative for heating rates seen in the coating interior.

5.2 High-temperature rheology

The coating rheology plays an important role in the intumescence process. Only with the right viscosity can the coating expand during heating to form the thermally insulating multicellular char [80]. If the coating becomes too soft during heating (i.e., viscosity too low), the gases released by the blowing agent might simply diffuse through the coating and escape [30]. Also dripping of the coating might become an issue for too low viscosities. If the coating viscosity is too high however, the resistance against expansion is too high and cracks might form. It is therefore crucial to formulate a coating that exhibits a suitable viscosity in the temperature range where intumescence occurs.

The most common method used to measure viscosity of intumescent materials at elevated temperatures are plate-plate (or parallel-plate) oscillation rheometers [30, 32, 115, 125]. The setup can be used to measure the complex viscosity of the system as a function of temperature, as well as the storage and loss moduli.

Duquesne et al. [115] used a parallel-plate rheometer to measure the dynamic viscosity depending on the utilised binder system and as a function of temperature. They showed that an increased dynamic viscosity around 320-350 °C is beneficial for the char expansion. Similarly, Zeng et al. [32] studied the influence of zinc borate on the dynamic viscosity using a parallel-plate rheometer. A viscosity minimum at temperatures between the melting and charring of the coatings (350-375 °C) was observed and linked to the coating expansion.

Jimenez et al. [30] also used a parallel-plate rheometer to characterise their intumescent coatings but reported the complex instead of the dynamic viscosity. The complex viscosity is a combination of the dynamic viscosity and elasticity of a material, i.e., the in- and out-of-phase part of the strain response to an induced stress. Nevertheless, the main conclusion drawn from the experiments were similar to Zeng et al. [32] and Duquesne et al. [115]: the viscosity around 330 °C is a determining factor for the intumescent process [30].

Anna et al. [125] studied the viscoelastic properties of a polypropylene based
inducement system in more detail, reporting not just the complex viscosity but also loss tangent (i.e., tangent of the phase angle). This enabled the authors to investigate the effect of boroxo siloxane elastomer on the elasticity and plasticity of the intumescent material as a function of temperature [125].

A less common alternative to measure rheological properties of intumescent coatings are capillary rheometers. The basic principle of this technique is to press a molten sample through a capillary with the aid of a piston while measuring the required pressure. This technique was used by Fan et al. [128] to investigate the influence of inorganic fillers on the coating viscosity at 200 °C. As opposed to plate-to-plate rheometers, this technique can only be used at temperatures below the swelling onset temperature of the intumescent coating.

6 Summary and outlook

In the last two decades, significant advances were made in the area of intumescent coatings. This includes the development of new and improved coating formulations as well as testing equipment to assess the performance of them.

In terms of the heat source, impinging flames are by far the most economic and rapid testing method. However, it is not advisable to use impinging flames when testing intumescent coatings intended for cellulosic or hydrocarbon pool fires. The reason is that these flames are typically not well characterised and the heat input in radial direction can be very inhomogeneous. Other issues of flames used for the characterisation of intumescent coatings, such as unknown heat losses from the backside of the coated substrate, could be resolved quite easily. Nevertheless, the use of impinging flames for the testing of intumescent coatings should be limited to an initial screen or when evaluating coatings intended for jet fires.

Experimental results from radiative heaters are often used to develop numerical models of intumescent coatings. This is partially because they are readily available in many fire safety laboratories and also because the incident heat flux can be directly set during the experiments. At the same time, their operation allows for fast changing of samples and rapid screening of different coating formulations. The sample is optically accessible during the experiments, facilitating the simultaneous measurement of char expansion and surface temperature over time. Besides, significant improvements have been made in recent years in order to better define the thermal boundary conditions during the experiments and to allow for additional parameters to be measured. Some examples are the adjustment of the heater-sample distance during the experiments to adjust for the char expansion [82, 89], adjusting
the gas atmosphere [77, 83, 88], or inducing a time dependent incident heat flux by adjusting the radiator power [78] or the radiator-sample distance [79, 84, 86]. However, there are also some areas that need further development. This includes everything that might help estimating the true net heat flux to the sample, i.e., the convective heat transfer coefficient, heat losses from the sample back side in case no thermal insulation is used, radiative heat loss from the sample surface, or sample surface emissivity.

The conditions in hydrocarbon fired furnaces are likely closest to a real fire, involving a combination of radiative and convective heat transfer to the sample, a reduced oxygen atmosphere, and turbulent convective flow that might damage the char. However, their use in academia is rather limited. Here, modified commercial electric furnaces are more common. Besides the combination of the two modes of heat transfer, advantages of furnaces are the very high heating rates that can be achieved (incl. hydrocarbon fire conditions) and that temperature-time profiles can be directly set during the experiments. Another advantage is that char expansion is rather homogeneous and that the chars can be recovered intact, facilitating its studies on char morphology. One shortcoming of most reports using furnaces is that the exact boundary conditions are seldomly determined or discussed. For example, in gas fired furnaces the forced convection will increase the convective heat transfer coefficient compared to most electric furnaces. Also, the furnace temperature measured with a thermocouple does not equal the gas temperature but depends on the thermocouple geometry and heat transfer to and from the bead to the surrounding. The use of plate thermometers [43, 108] rather than thermocouples to measure furnace temperatures could be an attractive approach because the measured temperature is more representative to what the sample experiences. This would also be in line with ISO 834 [29] and the European standards. The plate thermometer results can be used to calculate incident heat fluxes, which would further aid in the characterisation and comparison of different experimental setups. A similar approach was reported by Staggs & Phylaktou [50] to quantify radiative and convective heat transfer contributions.

In terms of in-situ characterisation techniques, impinging flames and radiative heaters usually have an advantage over furnaces because the sample is easily accessible in the former two setups. This makes the acquisition of additional parameters, such as char expansion, much easier. There were however a number of encouraging reports in recent years of modified furnaces. Some examples are high-temperature endoscopes to observe the char expansion and colour change [31, 35, 68] or impinging air-jets to assess the mechanical char strength [16, 61].
Amongst the in-situ parameters that were measured and reported in the academic literature, the substrate temperature is by far the most common and important one. This parameter ultimately determines if an intumescent coating performs well or not. One issue with this parameter is that it does not allow an easy comparison between different studies. The reason is that it depends on the thermal conditions the sample was exposed to (incl. insulation of the substrate back side) and the thickness of the virgin coating. Therefore, the effective thermal conductivity of the intumescent char might be a more useful measure. Some excellent work was done in this area in the last decade or so [33, 55, 67, 87, 112, 129, 130] and a more widespread use of similar approaches would be extremely helpful.

A wide range of additional in-situ parameters can be measured and can help to elucidate how intumescent coatings work or identify how they might be improved. Some examples are the char expansion, internal and surface temperature of the char, resistance to mechanical impact, thermal degradation kinetics, or rheological properties. Especially the mechanical testing and acquisition of internal and surface temperatures hereby require further development.

There are also other in-situ parameters that would be useful but were only reported in very few studies, such as char surface temperature [36]. Another valuable parameter that could be measured is the mass loss rate as a function of temperature for a complete substrate-coating system. Such experiments could be conducted with equipment such as the CAPA II [77, 83, 88]. Such experiments could help to resolve the issue raised by Cirpici et al. [55, 57] regarding the discrepancy between gases released by the actual coating and small amounts of samples analysed by thermogravimetric analysis.

7 Conclusions

Research and development of intumescent coatings requires reliable and reproducible characterisation tools. Ideally, these tools should be well defined such that researchers can easily compare the performance of two coatings reported in different scientific studies. However, this is currently not the case. The diversity of experimental methods and, in some cases, lack of provided information or insufficient characterisation of experimental conditions, makes comparisons between research groups difficult.

The ideal experimental setup should be able to reproduce realistic fire conditions while facilitating the measurement of a wide range of parameters. Note that ”realistic fire” hereby means that the heating rates and peak temperatures are similar to
a typical natural fire the test is trying to mimic. However, no such all-round setup exists and the most suitable characterisation method depends on the type of sought information. A simple impinging flame might be sufficient to compare different coating formulations within one project but will generally not allow a comparison to other studies. For this, a better definition or characterisation of the thermal boundary conditions would be required. Radiative heaters provide better defined heating conditions, making them especially useful for the evaluation of numerical models. Other advantages are that additional parameters are more easily recorded. However, the mode of heating, heating rate, and peak temperature are generally different to natural fires. Furnaces can reproduce more realistic fire conditions but are also comparably expensive, especially when custom-made modifications are required to accommodate the sample or to measure additional parameters.

All of the experimental techniques discussed in this review have their place, be it for rapid screening of samples or the detailed investigation of intumescent and heat transfer. A general recommendation however is to provide as much experimental detail as possible and whenever feasible, improve the characterisation of the thermal boundary conditions. For example, a flame temperature alone is insufficient to assess the heat flux to the sample. Similarly, two furnace temperatures can only be compared when also the thermocouple geometries and sheaths are identical. If more such details are provided, comparison between studies will simplify and researchers might converge towards more similar experimental conditions.

8 Acknowledgement

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