

Computational study of how inert additives affect the flammability of a polymer

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Abstract

All polymers are flammable to some degree. For safety, polymer flammability is most commonly reduced through flame retardants that are designed to primarily act chemically as opposed to physically. Here, we investigate computationally using the code Gpyro how inert additives such as hollow glass spheres (HGS) and boron nitride platelets (BNP) alter the flammability properties of glass fibre reinforced polybutylene terephthalate (PBT-GF), in a cone heater and UL94 setup. The Gpyro model is first validated against experiments and another code, both from the literature, for pure PBT-GF. According to the predictions, HGS leads to higher surface temperatures but lower temperatures in-depth, whereas adding BNP yields the opposite effect. Modelling numerically the cone heater setup shows that at 50% HGS loading, the time to ignition is reduced to a quarter while the semi-steady state mass loss rate is reduced to a third; at 50% BNP loading, the time to ignition is doubled while the peak mass loss rate is approximately doubled. In the UL94 setup, where the sample is smaller than cone heater, the effects are similar although less pronounced. A sensitivity study of the thermophysical properties shows that time to ignition is primarily controlled by emissivity, density and specific heat capacity, while peak mass loss rate is controlled by thermal conductivity and specific heat capacity. This work shows how heat transfer within a thermoplastic polymer can be utilised to improve its flammability characteristics through inert additives as well as the limitations of this retardancy approach.

KEYWORDS:

modelling; heat transfer; ignition; PBT

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Nomenclature Listing

A	Pre-exponential factor (s^{-1})	Greek	
c	Specific heat capacity ($J\ kg^{-1}\ K^{-1}$)	ε	Emissivity (-)
E	Activation energy ($J\ mol^{-1}$)	ν	Yield (-)
h	Convective heat transfer coefficient ($W\ m^{-2}\ K^{-1}$)	ρ	Density ($kg\ m^{-3}$)
H	Enthalpy ($J\ kg^{-1}$)	σ	Stefan–Boltzmann constant ($Wm^{-2}\ K^{-4}$)
k	Thermal conductivity ($W\ m^{-1}\ K^{-1}$)	$\dot{\omega}'''$	Reaction rate (kg/m^3s^{-1})
\dot{q}''	Heat flux (Wm^{-2})	κ	Effective radiative absorption coefficient (m^{-1})
R	Universal gas constant ($J\ mol^{-1}\ K^{-1}$)	δ	Length of the sample
t	Time (s)	Subscripts	
T	Temperature (K)	∞	Free stream
m''	Mass per unit area	g	Gas
		m	Melt
		p	Pyrolysis
		0	Initial
		ig	Ignition
		r	Radiative
		s	Surface

1. INTRODUCTION

Polymer flammability is a problem which is increasing in importance as the amount of polymers produced worldwide and utilised in everyday products increases steadily. To address this problem, flame retardants acting chemically are most commonly used [1]. This chemical action can be designed in several ways. The most common ones react at elevated temperatures to form organic or inorganic layers on the material surface, decompose endothermically, reduce the energy release of the flame via radical scavenging, or simply dilute the fuel in either the solid or the gas phase [1]. The effects of additives on the heat transfer within the polymer have received relatively little attention in the field of flammability.

By flammability, we refer to the ease of fire to ignite and spread through a system. When the fuel is in the gaseous phase, flammability refers to the range of mixture compositions with air that can ignite and sustain burning. But for a solid fuel, flammability is a much more complex term and includes pyrolysis, ignition of the pyrolyzed mixture above the free surface, and sustained burning (including flame spread). For ignition calculations a critical temperature of ignition or a critical mass loss rate are the most commonly used criteria to estimate the point of ignition for a material as they provide reasonable estimates [2, 3].

Modifying material properties through inert fillers is commonly used for applications below pyrolysis temperatures to aid manufacturing, thermal management, or mechanical properties [4]. The changes to the heat transfer induced by these additives are now investigated for their effect on flammability. There are some studies which investigated experimentally and numerically the effect of increasing the thermal diffusivity in epoxy through nano-silica or expanded graphite [5, 6]. The effect of a reduction of the thermal diffusivity through inert additives on flammability has not yet been studied to the best of the authors knowledge.

If the flammability can be reduced using inert additives, this can lead to a reduction in chemically active flame retardants. Some of which can reduce the mechanical performance of the polymer significantly [7]. Some inert additives, such as nano-silica, can be used to boost the mechanical performance in certain polymers [5]. Hence a combination of chemically active and inert additives could allow for flame retardant polymer formulations with improved mechanical properties.

To understand the influence of additives with significantly changed thermophysical properties relative to the base polymer, numerical simulations of surface and in-depth temperature are performed in addition to the calculation of overall mass loss rate in two commonly used flammability tests. This allows for the desirable aspects of the modifications of the thermophysical properties of the bulk material to be evaluated as well as potential drawbacks which can guide future design decisions on how to utilise heat transfer within a polymer for improved flame retardant performance.

2. EFFECT OF MATERIAL PROPERTIES ON FLAMMABILITY BEHAVIOUR

Transient heat conduction through a material is affected by its thermophysical properties. When studying transient heating scenarios, each of these properties play different roles in the temperature distribution and evolution of a sample[8].

Dimensional analysis of transient heat transfer yields two dimensionless parameters, *Fourier* number ($\alpha t/\delta^2$) (relating to the governing equation) and *Biot* number ($h\delta/k$) (relating to boundary condition) [8]. For materials with same size (δ) and a convective boundary condition (h), the *Fourier* number and *Biot* number (Bi) can only be changed by thermal diffusivity (α) and thermal conductivity (k) of the material. Thermal diffusivity is defined as $k/c\rho$ where k is the thermal conductivity, density is ρ , and specific heat capacity is c . it characterizes the speed of heat transfer through a material, with a high thermal diffusivity relating to a fast heat transfer throughout the sample. In addition to the effect of the thermal diffusivity, the thermal conductivity also characterizes the influence of boundary condition on temperature gradient, with a high thermal conductivity relating to a faster heat transfer rate entering through the boundary.

$$\frac{\partial T}{\partial t} = \frac{k}{c\rho} \frac{\partial^2 T}{\partial y^2} \tag{1}$$

The illustration in Fig 1 visualises the heat spread and temperature distribution for two materials with high and low values of thermal diffusivity, heated from the top and insulated at the bottom. The sample with high thermal diffusivity exhibits a lesser temperature gradient with a faster temperature rise in depth. The lower thermal diffusivity material increases more quickly its surface temperature but is cooler in depth with a large gradient across the material.

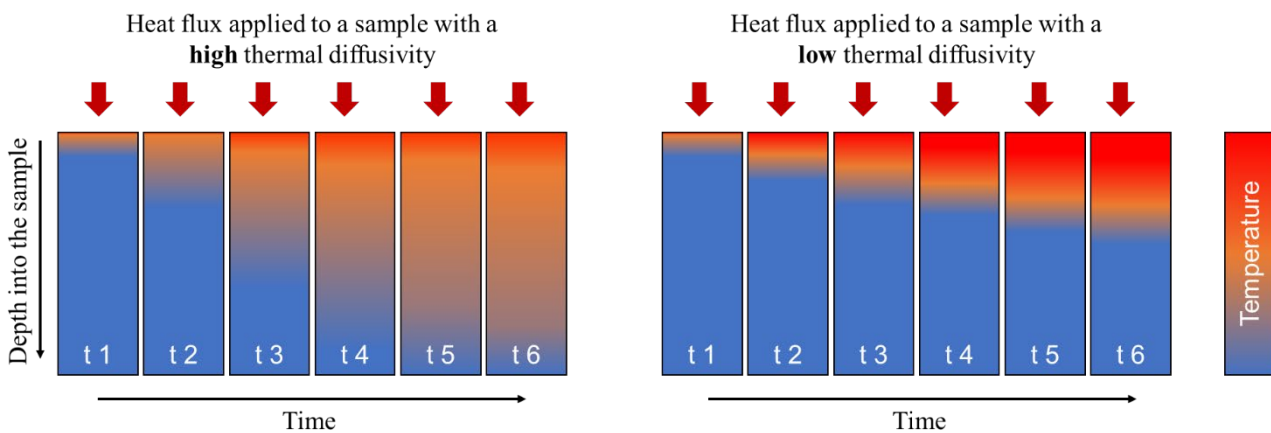


Fig. 1 Representation of heat transfer in a thermally thick sample with added BNP (left) or HGS (right), resulting in high or low thermal diffusivity when exposed to the same heat flux.

The non-dimensional analysis shows the influence of k, c, ρ on sample heating but by itself does not give direct guidance on the two criteria used to define flammability, namely time to ignition and mass loss rate.

Time to ignition as defined by a critical surface temperature cannot be easily solved without making some assumptions. When estimating the time to ignition for a thermally thick sample ($Bi > 0.1$), the same thermal properties as in the thermal diffusivity appear but arranged as $k c \rho$ as shown in Eq 2 and are referred to as thermal inertia [9]. As such they directly define the time a material takes until reaching a critical ignition temperature in the thermally thick case and is hence a solution to a particular scenario and is not universally applicable.

$$t_{ig} = \frac{2}{3} (k\rho c) \frac{(T_{ig}-T_0)^2}{\dot{q}''} \tag{2}$$

With regards to mass loss rate as a critical parameter to determine ignition and flame spread during the burning process, the situation is even more complex. The chemical kinetics of pyrolysis link with the heat transfer in the material and can hence not easily be solved analytically.

As can be seen, a lot of information can be inferred from basic heat transfer as well as analytical solutions derived for particular scenarios. However, in real flammability experiments more factors play a role requiring numerical modelling to assess. The accuracy and limitations of these theoretical predictions are revisited at the end of this work and compared against the findings.

Additives such as hollow glass spheres (HGS) and boron nitride platelets (BNP) change the thermal behaviour by modifying the bulk materials thermophysical properties [4, 10]. The additives shape and relative size are shown representatively in Fig. 2. These two additives are currently used to modify the heat transfer polymers for manufacturing, thermal management, or similar purposes.

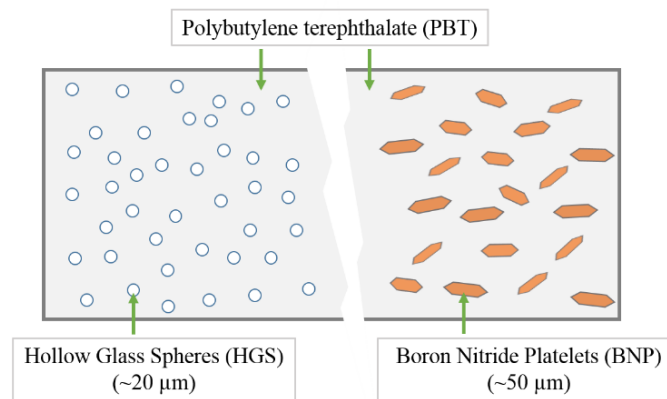


Fig. 2 Schematic of the additives dispersed in the polymer showing their approximate shapes and sizes.

3. MODELLING

Computational modelling was performed using Gpyro, an open source code [11] capable of modelling heat and mass transfer (Eq. 3) combined with pyrolysis chemistry (Eq. 4). It is one of the most commonly used numerical codes for pyrolysis modelling, next to ThermaKin [12], and FDS [13].

$$\frac{\partial(\bar{\rho}H)}{\partial t} = \frac{\partial}{\partial y} \left(\bar{k} \frac{\partial T}{\partial y} \right) - \omega_d''' (\Delta H_p + \Delta H_m) - \bar{k} \dot{q}_r'', \quad T > T_m \tag{3.a}$$

$$\frac{\partial(\bar{\rho}H)}{\partial t} = \frac{\partial}{\partial y} \left(\bar{k} \frac{\partial T}{\partial y} \right) - \omega_d''' \Delta H_p - \bar{k} \dot{q}_r'' \quad , \quad T < T_m \tag{3.b}$$

$$\dot{\omega} = \frac{\partial m''}{\partial t} = m_0'' A e^{-\frac{E}{RT}} \left(\frac{m''}{m_0''} \right) \tag{4}$$

The Gpyro model created is based on the work of Kempel, et al. [14]. Using the ThermaKin input parameters for a PBT-GF model as a starting point, an equivalent model was created. The material properties at room temperature and reaction kinetics are shown in Table 1. For the mixture of PBT-GT and additives, the properties are the mass-weighted values of the mixture, which are noted by $\bar{\quad}$ as shown in Eqs.(3) and (4). The properties of HGS and BNP are taken as representative values obtained from the literature [4, 10]. As BNP and HGS come in different shapes and sizes, average values of their properties relating to the k , c , and ρ in polymers had to be extracted. Furthermore, a linear rule of mixing with regards to the thermophysical properties of the polymer additive blend is assumed by Gpyro. As the main interest of this study is the general

response and not the modelling of any specific experiments performed in the lab, this simplification is considered adequate. Modifying properties relating to parameters other than the three named were neglected for the purposes of this study. The reaction scheme is a single step shown in Eq. 5.



To take into account the large changes in specific heat capacity in PBT-GF with respect to temperature, Eq. 6 is used. The power-like function is commonly used to describe the temperature dependence of parameters of solid properties [11, 14]. Approximating the measurement of specific heat capacity by Kempel et al. [14], the parameters fitted are $c_0 = 800 \text{ J kg}^{-1}\text{K}^{-1}$, $T_0 = 300 \text{ K}$, and $p = 2.924$. This fit is used up to 400 K after which the specific heat capacity stays constant at $1860 \text{ J kg}^{-1}\text{K}^{-1}$ (c_{max}) [14]. The comparison of fitting curve and experimental data is presented in Fig. 3. The conductivity of additives is modelled by a constant value, as the improvement of introducing a temperature dependency was minimal.

$$c(T) = \begin{cases} c_0 \left(\frac{T}{T_0}\right)^p, & T < 400\text{K} \\ c_{max}, & T \geq 400\text{K} \end{cases} \quad (6)$$

where T_{ref} the reference temperature, and p the specific heat capacity temperature dependency exponent.

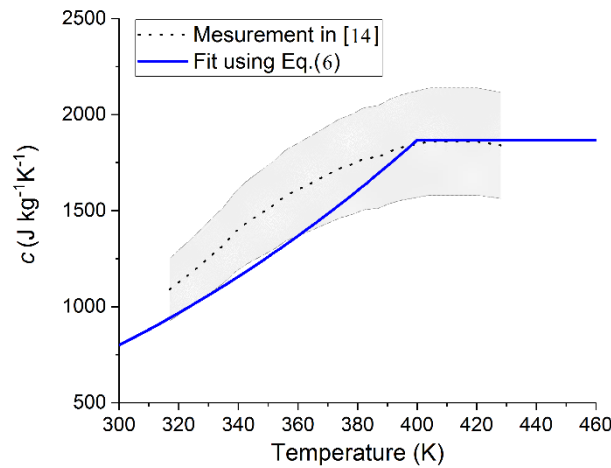


Fig. 3 Validation of the temperature dependence of specific heat capacity of PBT-GF; Dotted line represents experimental measurement and shaded area shows $\pm 15\%$ uncertainty range; solid line represents numerical fit

Table 1. Material properties at room temperature [4, 10, 14]

Parameter	Symbol	Unit	PBT-GF	Residue	HGS	BNP
Density	ρ	kg m^{-3}	1520	451	460	1900
Thermal conductivity	k	$\text{W m}^{-1}\text{K}^{-1}$	0.35	0.0705	0.024	1.56
Specific heat capacity	c	$\text{J kg}^{-1} \text{K}^{-1}$	800	850	1005	1601
Emissivity	ε	-	0.87	10 000	0.87	0.87
Radiative absorption coefficient	κ	m^{-1}	2901	-	2901	2901
Melting enthalpy	ΔH_m	J kg^{-1}	32 000	-	-	-
Melting temperature	T_m	K	493.15	-	-	-
Heat of Pyrolysis	ΔH_p	J kg^{-1}	355 000	-	-	-
Activation Energy	E	J mol^{-1}	389 731	-	-	-
Pre-exponential factor	A	s^{-1}	$2.27\text{e}20$	-	-	-
Yield	v	-	0.3	-	-	-

Two 1D domains were chosen, representing two common fire test methods. The first one represents the cone heater. In this bench scale test a square plate, with side length in the order of 10 cm, is exposed to a constant

irradiation via a hot conically shaped coil [15]. It is a comparatively simple test to model as the boundary conditions are constant and due to the aspect ratio of the sample 1D conditions are a reasonable assumption.

The second test is the UL94 test. It is a quick and simple test to perform, but more difficult to analyse and model scientifically. In this test, a specified 50W methane flame is applied to a vertically suspended strip. The strip is typically 13 x 125 mm² with a user specified thickness, usually in the order of 1 mm. The flame is applied twice for 10 s, allowing the sample to self-extinguish in between the flame applications. The test ends when the sample no longer burns self-sustained after the second application. The sample is then rated on a scale defined by the standard to classify the performance [16].

Apart from being two commonly used experiments, they were also chosen to represent thermally thick and thin behaviour as well as the behaviour when transitioning between the two as the heat transfer properties are changed by the addition of HGS or BNP.

The domain shown in Fig. 4A represents a cone heater experiment. The boundary condition at $y = \delta$ is an adiabatic condition as per Eq. 7. The heated surface ($y = 0$) is treated as a BC with radiative heating and convective cooling to lab ambient temperatures, shown by Eq. 8.

Fig. 4B shows the 1D UL94 domain used. The domain devised has been shown to be suitable for approximating the thermophysical response during the first flame application despite the simplification made [5]. Modelling of the full UL94 test including melting and dripping is currently still being researched, although some attempts have been made with varying degrees of simplification [17, 18]. The boundary conditions used for the work presented in this paper utilise a symmetry plane (Eq. 7) at half of the sample thickness. Consequently, the numerical result obtained from the simulations for the mass loss rate has been doubled for the results shown in the results section. The exposed sample surface assumes a constant convective-irradiative boundary condition (Eq. 8). The convective heat transfer coefficient and ambient gas temperatures used are in the case of the cone heater type flammability experiment 10 W/m²K and 300K respectively. In the UL94 scenario these constants rise to 54 W/m²K and 2026K [19].

$$-\bar{k} \frac{\partial T}{\partial y} \Big|_{y=\sigma} = 0 \tag{7}$$

$$-\bar{k} \frac{\partial T}{\partial y} \Big|_{y=0} = \bar{\epsilon} \dot{q}_r'' + h(T_\infty - T_s) + \bar{\epsilon} \sigma (T_\infty^4 - T_s^4) \tag{8}$$

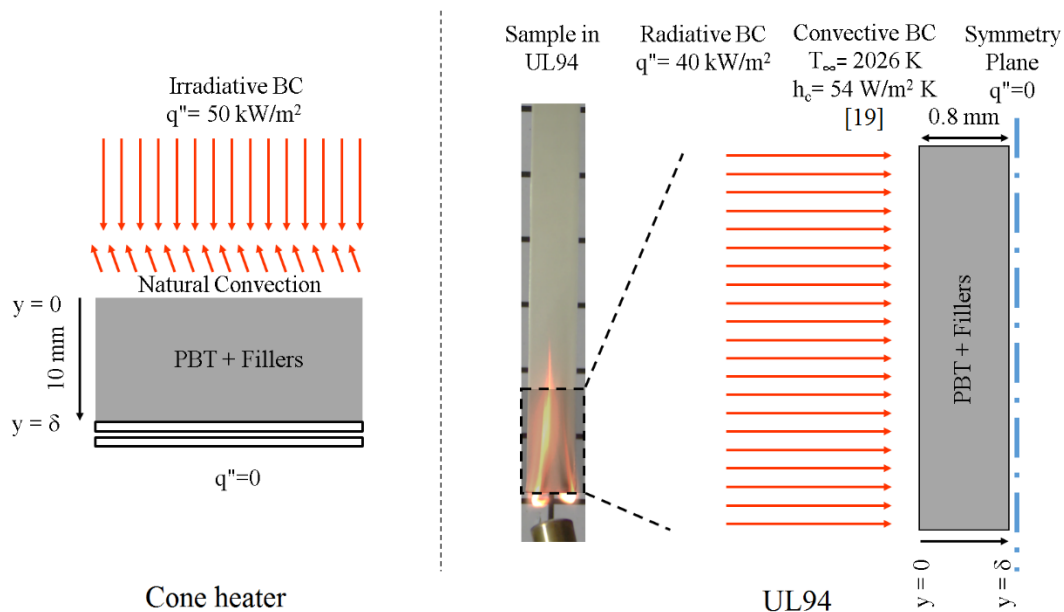


Fig. 4 1D domains used to model a cone heater type flammability experiment (A) and a UL94 experiment (B).

4. RESULTS AND DISCUSSION

4.1 Validation against experiments

The model is first validated against the experiment conducted by Kempel et al. [14] as well as the simulations using ThermaKin as extracted from the literature [12]. To verify that the model is capable of simulating experimental data as well as the literature simulations performed using ThermaKin, the same domain as used in the literature is employed for a validation simulation. Kempel et al. [14] modelled a 4 mm thick PBT-GF slab with the properties in Table 1 on top of a near perfect insulation material with an assumed near zero thermal conductivity of $1 \times 10^{-5} \text{ W m}^{-1} \text{ K}^{-1}$, density of 250 kg m^{-3} , and specific heat capacity of $25 \text{ J kg}^{-1} \text{ K}^{-1}$. As it can be seen in Fig. 5, Gpyro is able to closely reproduce the experiment and the ThermaKin model with only small deviations. This shows that using the Gpyro model developed on the basis of the ThermaKin model is valid.

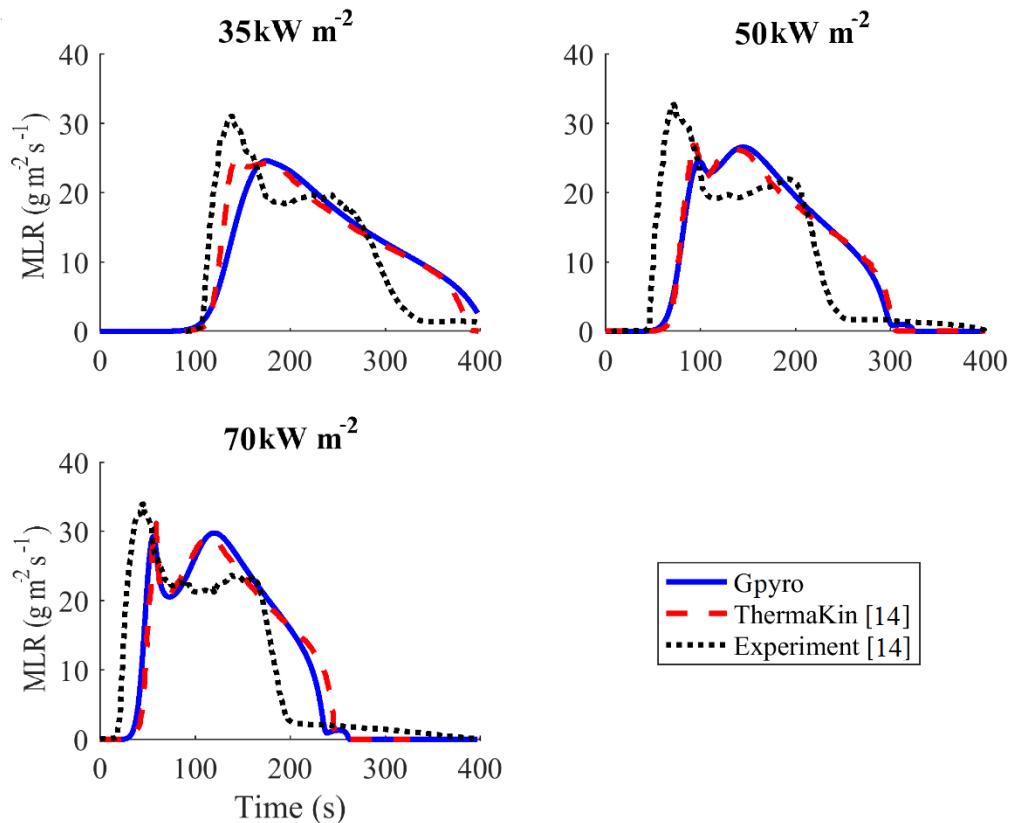


Fig. 5 Validation of Gpyro model against experimental data and numerical simulation of Kempel et al. [14]

4.2 The influence of additives

The results obtained from the Gpyro model are shown in Fig. 6 for the case of the cone heater, and Fig. 7 for the UL94 scenario. The cone heater case shows that as the hollow glass spheres are added, the time to ignition is reduced from approximately 100 s to about a quarter at 50% HGS loading. Time to ignition is estimated by critical mass loss rate (MLR), ($3.4 \text{ g m}^{-2} \text{ s}^{-1}$ [3]) and critical ignition temperature ($382 \text{ }^\circ\text{C}$ [3]). This reduction in time to ignition is not desirable as a flammability property. However, the semi-steady-state mass loss rate post ignition is reduced to about a third of the pure PBT-GF one. This translates to a smaller fire post-ignition, a desirable property.

The addition of BNP has the opposite effect. The gradient in temperature across the sample is reduced, and as the surface is cooler for longer, the time to ignition is approximately doubled. However, once the sample is heated through, the low thermal gradient means that there is a significant spike in MLR shortly before burnout. This would equate to a much shorter, but more intense fire with a longer time to ignition. The general shape of the mass loss rate shown in Fig. 6B matches the one from the literature when expanded graphite, a substance with a high thermal diffusivity, was added to epoxy [6]. An increase of time to ignition was also noted when

nano-silica was added to epoxy [5]. This observation gives confidence in the accuracy of the blind predictions performed.

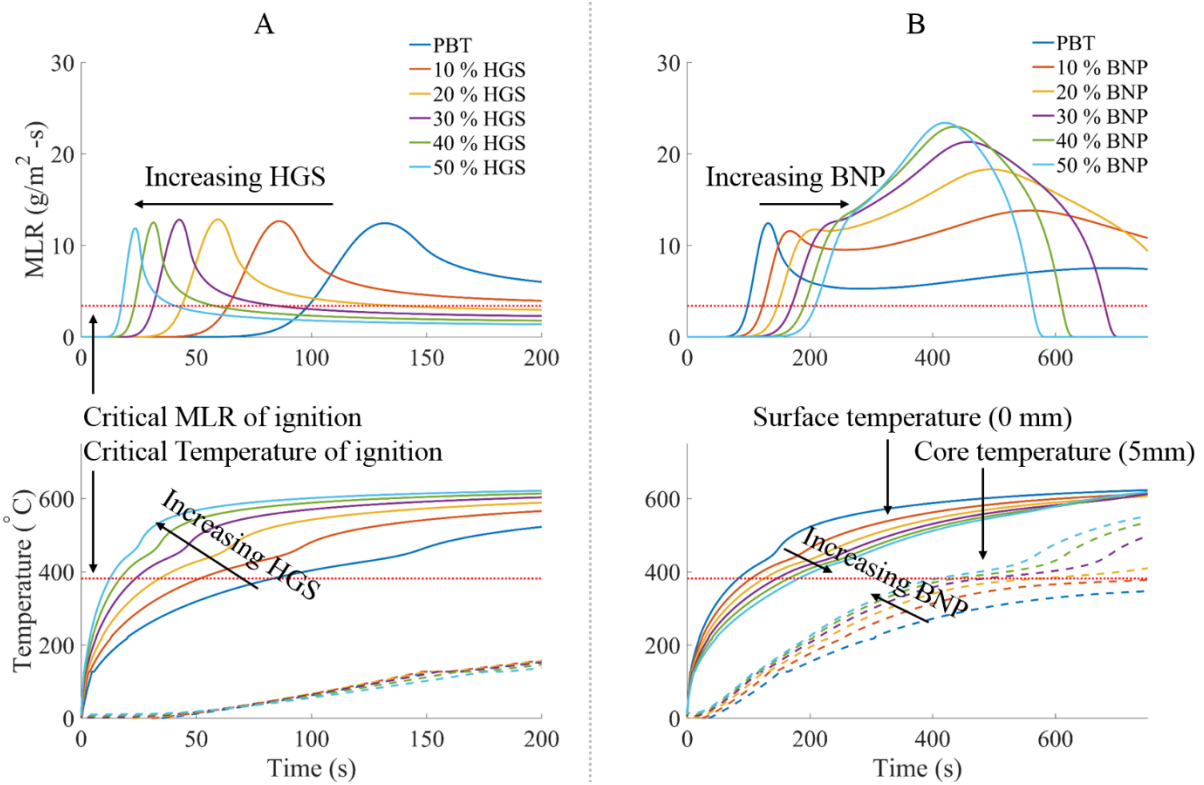


Fig. 6 Mass loss rate and temperature evolution for a PBT sample with increasing concentration of HGS (A) and BNP (B) (cone heater setup).

When considering a thinner sample under combined convective and radiative heating the general behaviour stays the same although it is less pronounced as shown in Fig. 7. Again, when adding HGS the time to ignition is reduced but also the mass loss rate. BNP acts again in the opposite way although with the thinner material, the effects are less significant as there is less depth for the heat to spread through. Nonetheless a significant change in behaviour can be observed numerically as has also been observed experimentally in a similar configuration [5].

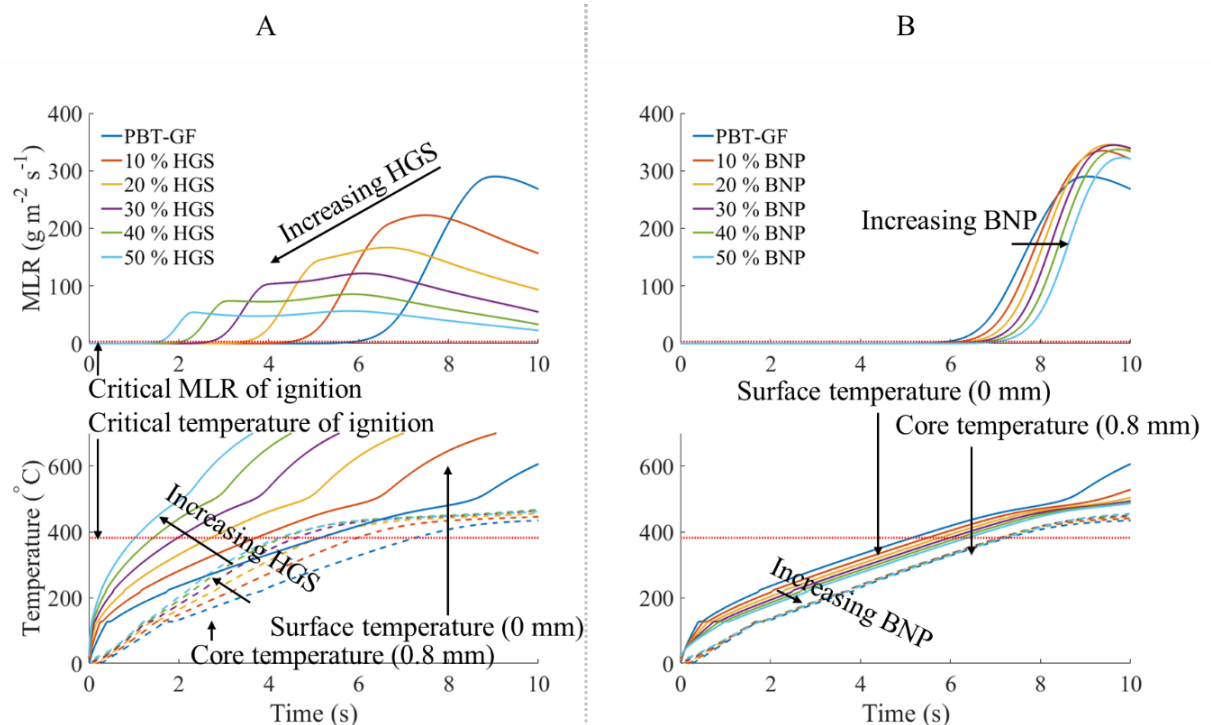


Fig. 7 Mass loss rate and temperature evolution for a PBT sample with increasing concentration of HGS (A) and BNP (B) (UL94 setup).

4.3 Sensitivity analysis of thermo-physical parameters

A parametric sensitivity study is used to assess the impact on the output Y of a model when a variation is applied to a single input parameter X . It is a commonly used analysis method used in fire science [20-22]. In this work, the sensitivity study is conducted to study the influence of different thermo-physical parameters on the time to ignition and peak MLR in both cone heater and UL94 test.

Two different methods are used in the sensitivity analysis: scatter-plot analysis [23] and One-at-a-time (OAT) analysis [23]: A scatter plot is a graphical sensitivity analysis approach, which can demonstrate how the output changes with the parameter of interest while the other parameters stay fixed at their base values. For the convenience of comparison, the variation of different parameters is normalized by their base values (i.e the values shown in Table. 1).

OAT analysis is used to quantify the sensitivity level of parameters using sensitivity coefficient s_i , which can be regarded as the local derivative of output with respect to the parameter of interest (X_i). Since the parameters compared here have different units, the dimensionless sensitivity coefficient \bar{s} is used. It can be calculated by Eq. 9.

$$s = \frac{Y(X_0 + \Delta X) - Y(X_0)}{\Delta X} \frac{X_0}{Y(X_0)} \tag{9}$$

In this study, the time to ignition (t_{ig} , using temperature as the ignition criterion) or peak mass loss rate is taken as Y and the 5 thermo-physical parameters (density, thermal conductivity, specific heat capacity, absorptivity, and emissivity) listed in Table 1 are treated as X_i . The absolute value of \bar{s} is given here for the convenience of comparison. The pure PBT-GF cases simulated in Fig. 6 and Fig. 7 are used as base cases for sensitivity analysis.

4.3.1 Cone heater setup

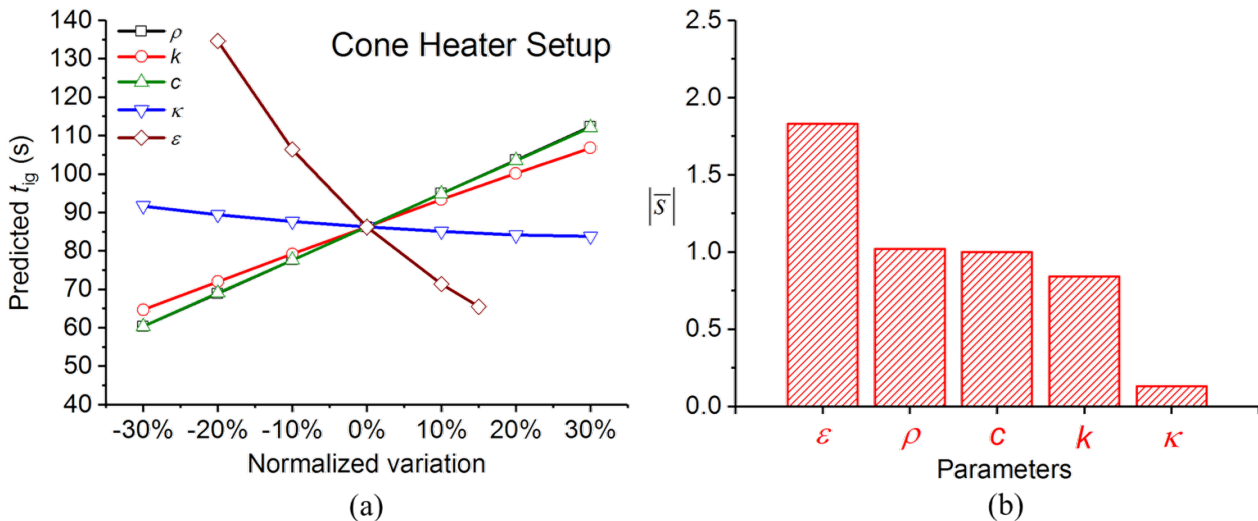


Fig. 8 Sensitivity analysis on t_{ig} for cone heater setup; (a) Scatter-plot analysis results (the lines of ρ and c overlap). Legends refer to different parameters; (b) OAT analysis results.

Fig. 8 compares the sensitivity level of five parameters on t_{ig} (using temperature as the ignition criterion) for the cone heater setup. In Fig. 8 (a) every single line displays how t_{ig} changes with the variation of a single parameter while the other parameters fixed at their base values (i.e the values in Table.1). All the parameters are varying from -30% to +30%, except for ϵ , for which around 20% variation is used to avoid the unphysical value (i.e $\epsilon > 1$). ϵ has the largest sensitivity level and sensitivity coefficient is 1.8. Reducing it by 20%, the onset of ignition can be largely delayed from 85 s to 135 s. The influence of κ is the lowest with a sensitivity coefficient is 0.13. 30% variation of it can only lead to 5 s change of t_{ig} . ρ , c and k have nearly equal effect on the time to ignition. Their sensitivity coefficients are all around 1, which means that the relationship between t_{ig} and these three

parameters is almost linear. 30% increase of them can lead to 30% increase of t_{ig} (~25 s). The same sensitivity level of these three parameters can also explain how t_{ig} behaves with different additives as shown in Fig. 6. HGS has a significantly lower density (~1/3 of PBT-GF) and thermal conductivity (~1/15 of PBT-GF) than PBT-GF and a slightly larger specific heat capacity (1.25 of PBT-GF). Thus, adding HGS into a pure PBT-GF material largely reduce the bulk values of ρ and k without increasing too much of c . As discussed before, t_{ig} is nearly proportional to these three quantities. Adding HGS can therefore lead to an earlier ignition. In terms of BNP, its ρ , k , and c are all larger than the PBT-GT. Using BNP as additive can therefore delay the onset of ignition, as t_{ig} are positively correlated to these three parameters.

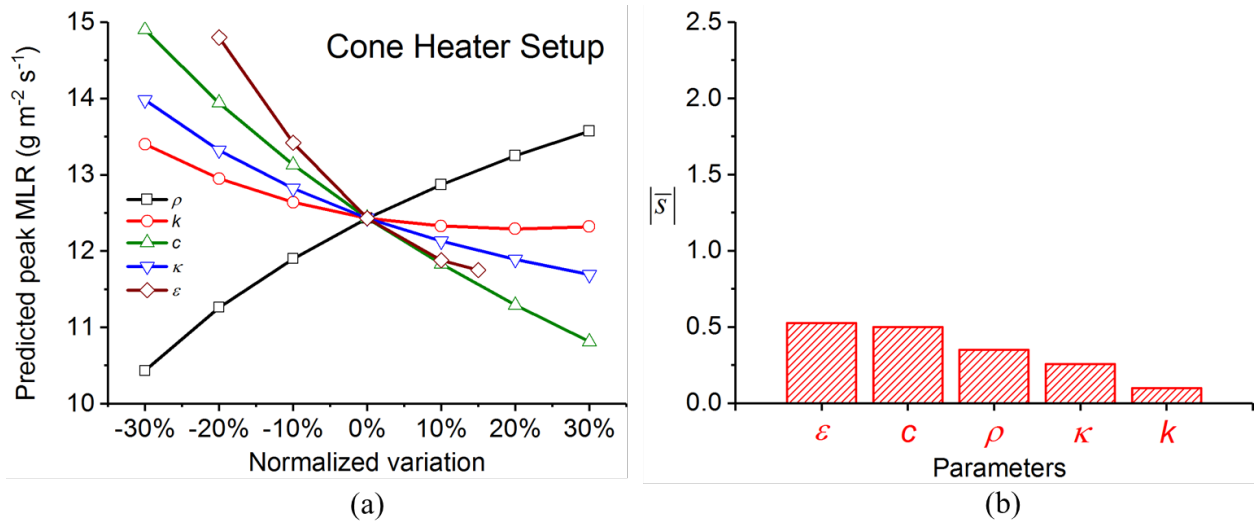


Fig. 9 Sensitivity analysis on the peak MLR for cone heater setup; (a) Scatter-plot analysis results. Legends refer to different parameters; (b) OAT analysis results.

Fig. 9 compares the sensitivity level of five parameters on peak MLR for the cone heater setup. The sensitivity level of the five parameters are comparable to each other. ε still has the highest sensitivity coefficient (0.5). 15% increase of ε can lead to 1 g m⁻² s⁻¹ decrease of peak MLR. c , ρ , and κ play a secondary role. Varying them by 30%, the peak MLR can change by 1.5-2.5 g m⁻² s⁻¹. k has smallest influence on the peak MLR and its sensitivity coefficient is only 0.1. The sensitivity analysis result can also be used to explain the variation of peak MLR with the additive of HGS as shown in Fig. 7. HGS has a smaller density and thermal conductivity than PBT-GF. In this case, the decreasing trend of peak MLR induced by a smaller ρ is compensated by the increasing trend induced by a smaller k . Therefore, mixing PBT-GF with HGS doesn't affect the peak MLR much. In terms of BNP, as shown in Fig. 7 adding it to PBT would result in a formation of second peak in MLR. On the other hand, the sensitivity analysis approach used here focuses on the local variation of parameter and therefore is not suitable to provide the explanation for the variation of the second peak.

From the sensitivity analysis, it is interesting to note that the increase of c has a double positive effect: delaying the time to ignition (increase of t_{ig}) and decreasing the fire intensity (decrease of peak MLR). Thus, an additive targeting primarily the specific heat capacity is most well suited to decreasing the flammability of polymers.

4.3.2 UL94 setup

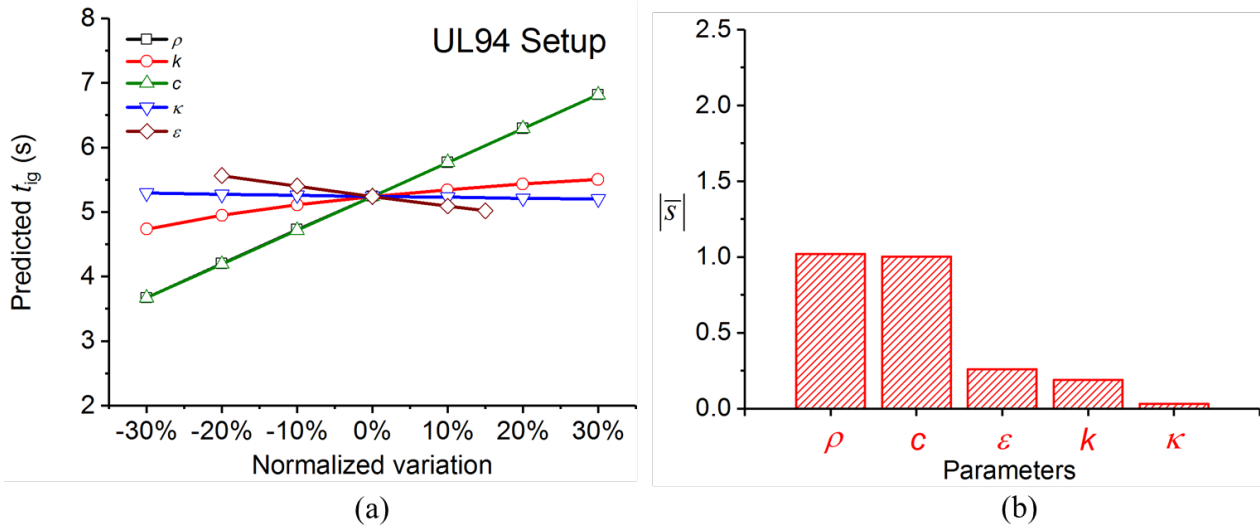


Fig. 10 Sensitivity analysis on t_{ig} for UL94 setup; (a) Scatter-plot analysis results. Legends refer to different parameters (the lines of ρ and c overlap); (b) OAT analysis results.

Fig. 10 compares the sensitivity level of five parameters on t_{ig} in UL94 setup. ρ and c have the dominant influence and the sensitivity coefficient of them is 1. 30% increase of ρ and c can lead to 1.8s delay of ignition in UL94 setup. The effect of ϵ , k are secondary. Their sensitivity coefficients are less than 0.25. 30% variation of them can only lead to 0.5s change of t_{ig} . The effect of κ is negligible for the range of changes evaluated. t_{ig} almost does not change with κ . Likewise, the sensitivity analysis can be also used to explain how additives affect t_{ig} in UL94 setup as shown in Fig. 7. As stated in the discussion of Fig. 8 before, HGS has a significantly lower ρ and k than PBT-GF and a slightly larger c . Therefore, the decrease of ρ and k is the dominant change for the material. Fig. 10(a). In terms of BNP, its c , k , and ρ are all higher than PBT and therefore adding it to the base PBT material can delay the onset of ignition, which can be easily deduced from the Fig. 10(a).

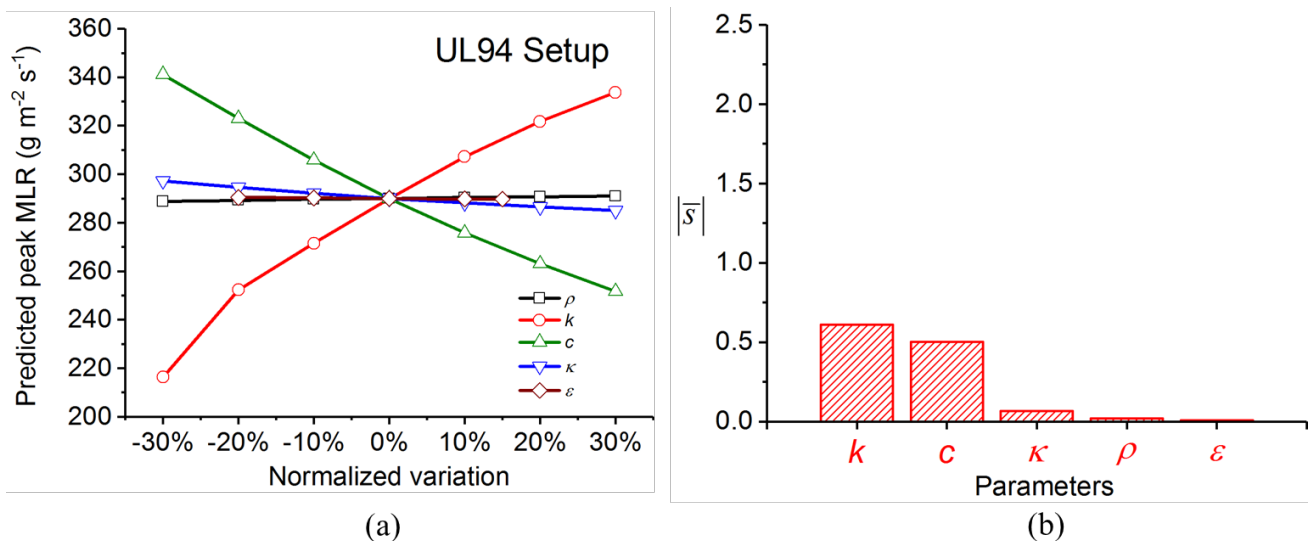


Fig. 11 Sensitivity analysis on peak MLR for UL94 setup; (a) Scatter-plot analysis results. Legends refer to different parameters; (b) OAT analysis results.

Fig. 11 demonstrates the sensitivity level of five parameters on peak MLR for UL94 setup. k and c have dominant influence on peak MLR. The sensitivity coefficients of them are 0.55 and 0.52 respectively. 30% variation of k and c can lead to approximately $20 \text{ g m}^{-2} \text{ s}^{-1}$ change of peak MLR. The influences of κ , ρ , and ϵ are negligible in the range of variation studied. The peak MLR hardly changes with these three parameters. Similarly, the

sensitivity analysis can help to interpret the effect of additives on peak MLR. Adding HGS to the material leads to significant increase of c and decrease of k . Both contribute to the decline of peak MLR as seen from Fig. 11(a). In terms of BNP, it has 3.5 times larger k than PBT and 1 times larger c . The increase of these two parameters have an opposite effect on peak MLR. However, since the increase of k is much more than c , the former has dominant influence. Thus, in general, adding BNP can increase the peak MLR as shown.

The double positive effect of increasing c still exists in UL94 test: it can still delay the time to ignition and decrease the fire intensity. Thus, an additive targeting primarily the specific heat capacity is most well suited to decreasing the flammability of polymers.

What is not studied by this sensitivity analysis is the range of normalised variation achievable using various additives. A range of 30% in the positive and negative direction was chosen to give representative results, however some additive may be able to change some parameters by higher magnitudes which is not captured here. Therefore, the insensitive parameters identified should not be ignored on this basis alone, although the biggest impact can of course be achieved by additives utilising the parameters of a very high sensitivity.

The results from the sensitivity study, combined with the numerical modelling of the cone heater and UL94 with varying amounts of additives allow a comparison of the predictions of heat transfer in the material, time to ignition, and mass loss rate based on theoretical considerations of heat transfer based on Fourier number, Biot number, and thermal inertia.

Thermal diffusivity as resulting from the analysis of Fourier number predicted higher in-depth heating for samples with a higher thermal diffusivity. This was found to be accurate as could be seen in Fig 6 and 7 as BNP and HGS were added to base polymer.

The predictions of boundary condition being primarily controlled by thermal conductivity as concluded from the analysis of Biot number yielded mixed results. The strong effect of ε in the purely radiatively heated cone scenario was not captured by this analysis. In the UL94 this prediction was more accurate as convection is the primary heating mode.

Time to ignition correlates positively in the cone heater and UL94 with ρ , c , and k . This is expected for the cone heater case as the sample is thick. In the UL94 case the correlation is less strong but still exists indicating that the sample still acts thermally thick. Indeed, calculating the Biot number for the sample based on the domain and material properties of PBT-GF yields a Biot number of 0.123 slightly above the critical threshold of 0.1 for thermally thick samples. Studying a third case with a Biot number below 0.1 would be interesting in the future to analyse the limitations of thermal inertia considerations more deeply.

Mass loss rate could not be predicted easily using a theoretical analysis of heat transfer. However, interpretations of the findings based on a fundamental understanding can be made. c correlated strongly negatively in both cone heater and UL94 with peak MLR. This is most likely due to c effectively increasing the amount of energy needed to raise the temperature of the material and pyrolyse it further. This slows the degradation process and hence mass loss rate. ρ correlated strongly positively with MLR in the cone heater but only weakly in the UL94. This is most likely due to ρ being directly linked to mass which itself is a direct positive factor in the calculation of mass loss (Eq. 4).

5. CONCLUSIONS

Hollow glass spheres or boron nitride platelets can be used to significantly alter the flammability of a polymer by modifying its thermophysical properties. By either increasing or decreasing the heat transfer rate and thermal gradients at the boundaries, the time to ignition can increase or decrease and the mass loss rate post ignition can increase or decrease as well.

Altering flammability solely by thermal behaviour is likely not enough to pass flammability standards. Either the time to ignition can be increased at the expense of a subsequent high mass loss rate. Alternatively, the time to ignition can be shortened with the benefit of a lower mass loss rate post-ignition.

The sensitivity study conducted shows that next to the emissivity in the case of the cone heater, the density and specific heat capacity are the most significant parameters to influence the peak mass loss rate and time to ignition. Increasing the specific heat capacity can delay the time to ignition and reduce heat release rate. Thus, an additive targeting solely the specific heat capacity is therefore well suited to decreasing the overall flammability of polymers.

This work shows that using thermal management techniques to influence the flammability behaviour of polymers offers a route which should be investigated in more detail. As the effects seen in this study are likely not enough to pass flammability standards, a combination with chemically active flame retardants, tailoring the effects to each other, is a promising route for flame retardancy. Combining the synergies of both approaches could pass the flammability requirements at a lower overall additive loading, reducing cost, and improving mechanical as well as manufacturing behaviour.

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