

Central Lancashire Online Knowledge (CLOK)

Title	Investigation of the thermal decomposition and flammability of PEEK and its carbon and glass-fibre composites
Type	Article
URL	https://clock.uclan.ac.uk/id/eprint/1917/
DOI	https://doi.org/10.1016/j.polymdegradstab.2010.11.009
Date	2011
Citation	Patel, Parina, Hull, T Richard, Lyon, Richard E., Stoliarov, Stanislav I., Walters, Richard N., Crowley, Sean and Safronava, Natallia (2011) Investigation of the thermal decomposition and flammability of PEEK and its carbon and glass-fibre composites. Polymer Degradation and Stability, 96 (1). pp. 12-22. ISSN 01413910
Creators	Patel, Parina, Hull, T Richard, Lyon, Richard E., Stoliarov, Stanislav I., Walters, Richard N., Crowley, Sean and Safronava, Natallia

It is advisable to refer to the publisher's version if you intend to cite from the work.
<https://doi.org/10.1016/j.polymdegradstab.2010.11.009>

For information about Research at UCLan please go to <http://www.uclan.ac.uk/research/>

All outputs in CLOK are protected by Intellectual Property Rights law, including Copyright law. Copyright, IPR and Moral Rights for the works on this site are retained by the individual authors and/or other copyright owners. Terms and conditions for use of this material are defined in the <http://clock.uclan.ac.uk/policies/>

Investigation of the Thermal Decomposition and Flammability of PEEK and its Carbon and Glass-Fibre Composites

Parina Patel^a, T. Richard Hull^{a*1}, Richard E. Lyon^b, Stanislav I. Stoliarov^c, Richard N. Walters^b, Sean Crowley^b and Natallia Safronava^d

^a Centre for Fire and Hazards Science, School of Forensic and Investigative Science, University Of Central Lancashire, Preston, PR1 2HE, UK

^b Fire Safety Branch, Federal Aviation Administration, William J. Hughes Technical Centre, Atlantic City International Airport, NJ 08405, USA

^c Department of Fire Protection Engineering, University of Maryland, MD 2042, USA

^d SRA International, Inc., 1201 New Road, Linwood NJ 08211, USA

Abstract

Conventional thermally durable materials such as metals are being replaced with heat resistant engineering polymers and their composites in applications where burn-through resistance and structural integrity after exposure to fire are required. Poly aryl ether ether ketone (PEEK) is one such engineering polymer. Little work has been published with regards to the flammability of PEEK and its filled composites. The current study aims to assess the flammability and fire behaviour of PEEK and its composites using thermogravimetric analysis, pyrolysis combustion flow calorimetry, limiting oxygen index, a vertical flame resistance test, and fire (cone) calorimetry.

1. Introduction

Applications in which polymers are replacing traditional materials are on the increase. In many cases, polymers and their composites are now being used where the fire risk scenario is dissimilar to any encountered previously. In addition to ignition resistance and low heat release rate, engineering polymers may now be required to resist burn-through and maintain structural integrity whilst continuing to provide fire protection when exposed to fire or heat.

Aryl poly ether ether ketone (PEEK) is an engineering thermoplastic first introduced by Imperial Chemical Industries (ICI) in 1978 [1]. Its excellent thermal, chemical and mechanical properties have allowed for its use in a variety of high performance applications: the polymer has recently been adopted in the aviation and automotive industries where conventional thermally durable materials, such as metals, are being replaced by lighter weight, high thermal stability polymers [2] [3] [4]. To date, little work has been published on the flammability of poly(aryletherketones) with more attention assigned to the material's thermal [5] [6] [7] [8] [9] [10] [11] and thermo-kinetic properties [12] [13] [14] [15] [16] [17] [18] [19]. As a result of the increased interest in engineered polymers such as PEEK and its composites, robust flammability data is necessary for applications requiring lightweight fire performance.

* Corresponding author. Tel: +44 (0)1772 893543. Fax: +44 (0)1772 894981
E-mail: trhull@uclan.ac.uk

PEEK's excellent thermal properties are attributed to the stability of the aromatic backbone comprising the bulk of the monomer unit, shown in Figure 1.

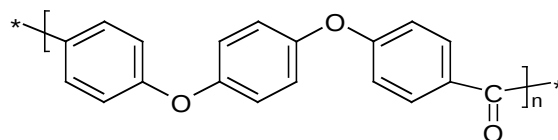


Figure 1. Repeat Unit of Poly(oxy-1,4-phenyleneoxy-1,4-phenylenecarbonyl-1,4-phenylene) (PEEK)

Semi-crystalline PEEK has a glass transition temperature (T_g) of 143°C, a continuous use temperature of 260°C, a melting point (T_m) of 343°C and an onset of decomposition temperature between 575 and 580°C [20] and thus, is one of the most thermally stable thermoplastic polymers available.

Techniques employed for measuring the ignition and burning behaviour of a polymer are numerous. Fire tests in common use aim to determine the following properties of materials [21]:

- Ease of ignition
- Rate of flame spread
- Rate of heat release
- Ease of extinction
- Smoke/Toxic gas evolution

Of those listed, many authors argue that the single most important parameter for determining a materials' fire hazard is its heat release rate (HRR) [22] [23] as this, together with the rate of surface flame spread will determine the fire growth rate. As direct determination of heat release rate is practically problematic, this parameter is typically determined on an oxygen consumption calorimetry basis: the approximation that 13.1 kJ of energy is produced per gram of oxygen consumed [24]. Two methods for measuring heat release rate effectively are the Cone Calorimeter and Pyrolysis Combustion Flow Calorimeter (PCFC). Developed in 1982, [25] the Cone Calorimeter has become one of the most important and widely used instruments for the research and development of fire retardant polymeric materials. The PCFC was developed in 1999 [22] [26] by researchers of the Federal Aviation Administration (FAA) as a tool to assist in the flammability assessment of milligram-sized samples. Recent correlations between the two methods have been established [27] [28]. Heat release rates determined by the PCFC and cone calorimeter provide information on oxygen consumption at micro and bench scales, respectively.

Other parameters such as flame spread and ease of extinction are commonly determined in small-flame flammability tests such as the UL-94 and Limiting Oxygen Index (LOI), respectively. In addition, thermogravimetric analysis (TGA) can provide information on the thermal stability of a material in both oxidative and inert atmospheres. Mass loss in air primarily reflects the thermal-oxidative decomposition processes occurring at the surface prior to ignition whereas an inert atmosphere, such as nitrogen, is representative of the fuel gas production below the surface and after ignition, as the concentration of oxygen under a flame is close to zero [29].

This study assesses the flammability behaviour of PEEK and two composites containing carbon and glass fibre in order to characterise their fire behaviour.

2. Experimental

2.1 Materials

The samples of PEEK used in this study were supplied by Victrex plc and were semi-crystalline (~35% crystallinity as measured by Differential Scanning Calorimetry (DSC)) Victrex PEEK™ grades 450G, 450CA30 and 450GL30. The unfilled 450G polymer has a molecular weight of approximately 100 000 g mol⁻¹. The 450CA30 and 450GL30 are reinforced grades of the 450G PEEK containing 30 percent (%) carbon and glass fibre by weight, respectively. 450CA30 contains carbon fibres derived from polyacrylonitrile (PAN) with a length of ~200 µm and diameter of 7 µm. 450GL30 contains glass fibres with a length of ~200 µm and diameter of 10 µm. Both carbon and glass fibres are incorporated for added strength, stiffness and dimensional stability. All materials are available commercially.

2.2 Thermogravimetric Analysis

Thermal decomposition was investigated by thermogravimetric analysis (TGA) in an inert atmosphere using a Mettler Toledo TGA/SDTA 851. Measurements were performed on samples of 10 mg (±0.5 mg) under a nitrogen atmosphere with a heating rate of 10°C min⁻¹ and flow rate of 35 ml min⁻¹. Thermal analysis in air was undertaken using a TA Instruments Q500 TGA. Sample weight was 10 mg (±5 mg) with a heating rate of 10°C min⁻¹ and an air flow rate of 35 ml min⁻¹.

2.3 Pyrolysis Combustion Flow Calorimeter

Small-scale flammability tests were carried out on the Federal Aviation Administration's Pyrolysis Combustion Flow Calorimeter and samples were tested in triplicate according to ASTM D7309-07 [30]. Samples were 5 mg (±0.5mg) in weight and were obtained from the centre of the cone calorimeter plaques detailed below. The heating rate was 60°C min⁻¹ in an 80 cm³ min⁻¹ stream of nitrogen; the maximum pyrolysis temperature was 900°C. The anaerobic thermal degradation products in the nitrogen gas stream were mixed with a 20 cm³ min⁻¹ stream of oxygen prior to entering the combustion furnace at 900°C. The heat release was determined by oxygen consumption calorimetry.

2.4 Limiting Oxygen Index

The flammability, characterised by the ability of a material to sustain candle-like burning, was determined using the FTT Limiting Oxygen Index apparatus according to ISO 4589-2 [31], using injection moulded samples with the following dimensions: 125 x 10 x 4 mm.

2.5 Underwriters Laboratory Vertical Test for Flammability of Plastics UL-94 V

The ignitability and flame spread were determined using the standard UL-94 vertical burn test according to BS 60695-11-10 [32]. Injection moulded samples were 125 x 13 x 3 mm. As a UL-94 V-0 rating for 450G, 450CA30 and 450GL30 has already been obtained, the results were recorded to compare the burn lengths and times for each material. Ten samples of each material were examined.

2.6 Fire (Cone) Calorimetry

A Fire Testing Technology (FTT) Cone Calorimeter was utilised to characterise forced flaming behaviour following the procedure outlined in ASTM D1354-04a. [33]. Sample dimensions were 100 x 100 x 2.5 mm and all materials were tested in triplicate in the horizontal orientation. An irradiance of 50 kW m⁻² was used.

3. Results and Discussion

3.1 Thermogravimetric Analysis

Anaerobic Thermal Decomposition in Nitrogen

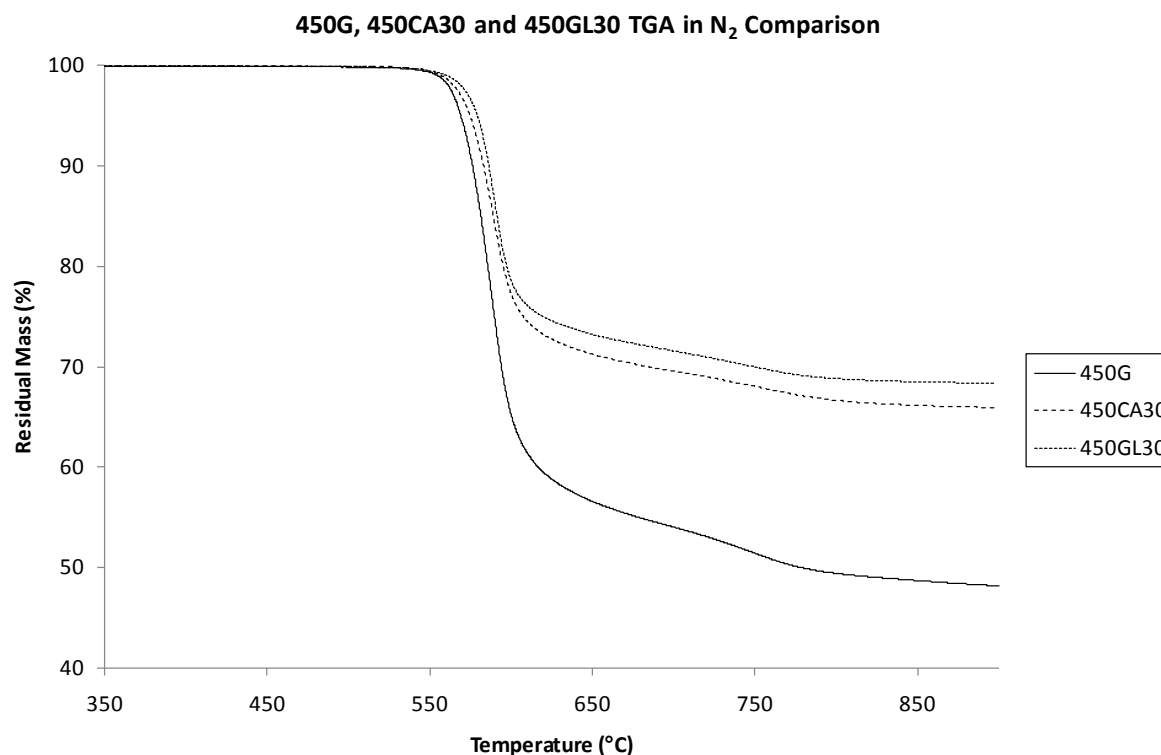


Figure 2. TGA in N₂ Data for 450G, 450CA30 and 450GL30

Samples of 450G, 450CA30 and 450GL30 were analysed in an inert atmosphere in the TGA and averaged data for the triplicate analyses are shown in Figure 2. Thermal decomposition of PEEK begins at around 555°C which is much higher than for most polymers. Thermal decomposition is a two-step process, with the first step of thermal decomposition centred at 585 °C and attributed to the random chain scission of the ether and ketone bonds [18] [34] [35]. The second decomposition step occurs above 600°C, and is attributed to the cracking and dehydrogenation of the crosslinked residue produced in the first stage of decomposition and results in a thermally stable carbonaceous char [20]. The 10% mass loss temperature of 450G occurs between 570 and 580°C. Interestingly, 30% of the loss in the first stage of decomposition occurs within a 30°C window, and is complete after a 40% mass loss. There is no obvious component within PEEK's structure which corresponds to a 40% mass loss. The second stage only loses 10% of the original mass up to 900°C, giving a 50% char yield. There is little further loss after 800°C; and at 900°C the material appears stable. Scission and release of both the ether and ketone groups would result in 21% weight loss, based on the repeat unit of PEEK. 40% weight loss indicates that some aromatic compounds are also being released as products – possibly in the form of phenol, observed in pyrolysis gas chromatography-mass spectrometry (pyGC-MS) as a major decomposition product of PEEK [9].

For the filled materials, 450GL30 has a slightly higher onset of decomposition temperature than 450CA30; both have a higher onset temperature than 450G. 450CA30 and 450GL30 show a similar

first stage of decomposition resulting in around 23% weight loss. It may be assumed that a process occurs at 600°C which either delays 450GL30 decomposition or accelerates 450CA30 decomposition. After 600°C, both materials enter the second stage of decomposition with 450CA30 continuing to decompose at a faster rate than 450GL30. After 800°C, little weight loss is observed and the final mass of material remaining for 450CA30 and 450GL30 is 65% and 68%, respectively, which is slightly higher than the sum of the mass fractions of the inert filler and the char fraction of the PEEK matrix. In an inert atmosphere, the presence of filler increases the thermal stability of pure PEEK and 450GL30 appears to be the more thermally stable of the fibre-filled materials.

Thermal Oxidative Decomposition in Air

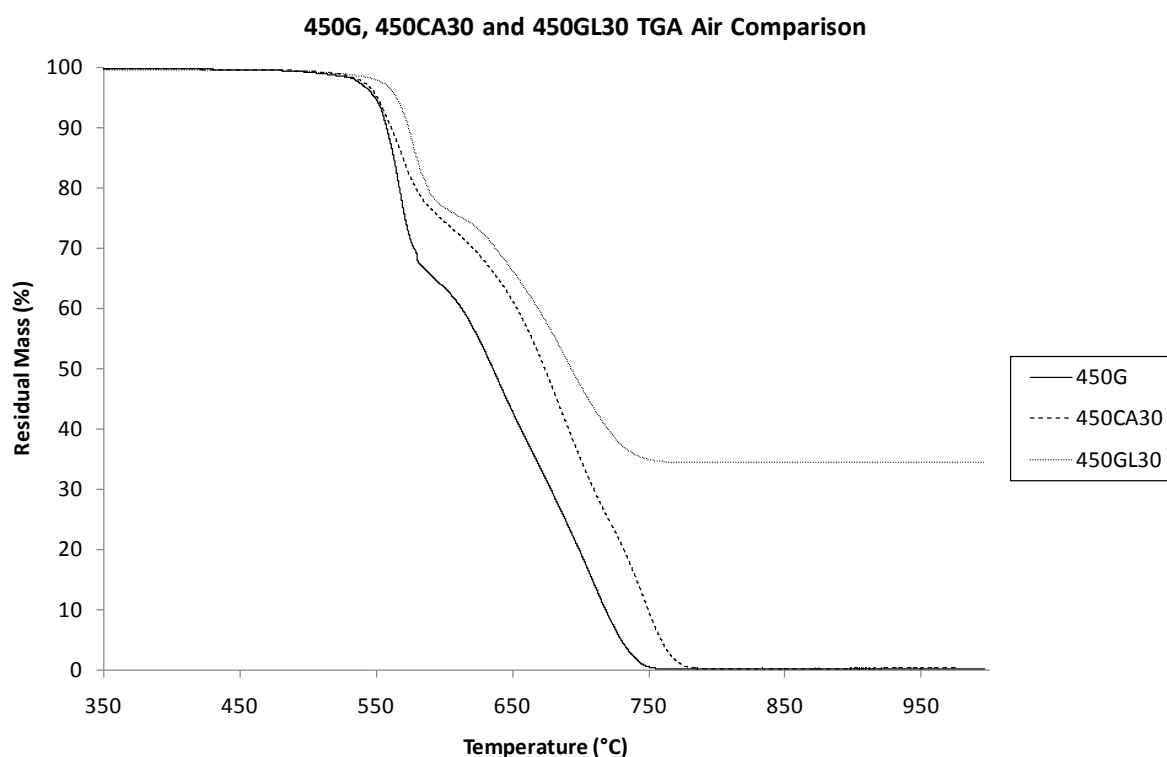


Figure 3. TGA in Air Data for 450G, 450CA30 and 450GL30

Similarly, in an oxidative environment, decomposition of PEEK occurs by a two-step process as shown in Figure 3. The onset of thermal oxidative decomposition for 450G and 450CA30 is between 520°C and 530°C. The onset of thermal oxidative decomposition for 450GL30 is slightly higher at ~560°C. The difference in stability between the carbon and glass-filled polymers may be due to the oxidation of the carbon fibres resulting in the material losing more weight at an earlier stage. However, the carbon fibre appears slightly more thermally stable than the carbonaceous PEEK residue. 450G loses 35% weight in the first stage of thermal oxidative decomposition with 30% weight loss occurring within a 30°C window. This corresponds to the thermal decomposition in an inert atmosphere, indicating that scission of the ether and ketone bonds do not require, or are not enhanced by an oxidative environment. For 450G, the remaining mass is lost in the second decomposition stage where all the carbonaceous material is thermally oxidised by 750°C. Although 450CA30 has a similar onset of thermal oxidative decomposition temperature as 450G, it loses mass at a steadier rate. At around 650°C, there is a 3% difference in weight loss between 450CA30 and

450GL30 with a loss of 25% and 22% weight loss attributed to the first decomposition stage, respectively. In the second stage of thermal oxidative decomposition, 450CA30 continues to lose 75% weight at a similar rate to 450G and the carbonaceous char and carbon fibres are completely oxidised by 775°C. Weight loss associated with thermal oxidation of the PEEK char continues in the second stage of decomposition with a loss of around 43% at 800°C, when the material remains at around 35% weight up to 1000°C.

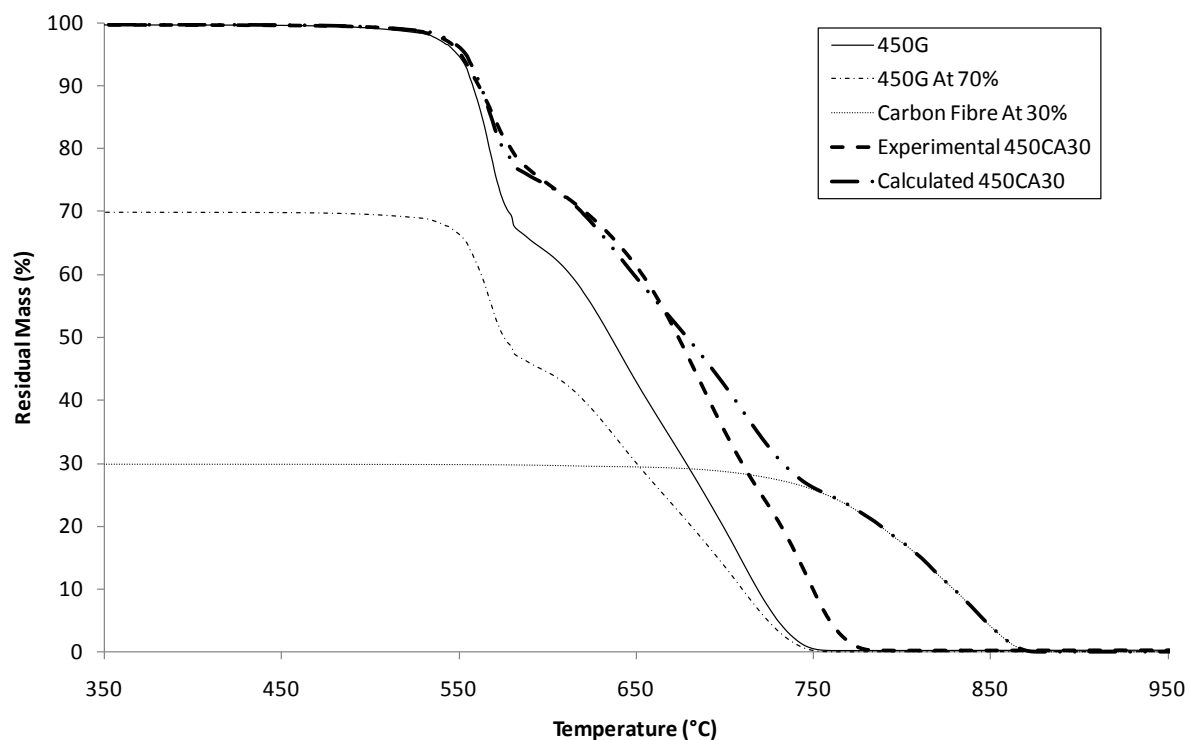


Figure 4. 450G and 450CA30 – Experimental and Calculated TGA in Air

To investigate the affect of carbon fibre on the decomposition of PEEK, a TGA curve has been calculated by proportional addition of the TGAs of the individual components, 450G and carbon fibre as shown in Figure 4. Interestingly, the experimental and calculated TGA curves for 450CA30 show two slight delays in the actual onset of decomposition to mass losses around 30% and 50% followed by significant differences in the second stage of decomposition whereby the calculated 450CA30 is more stable, with total mass loss occurring at 870°C compared to 780°C. The calculated 450CA30 also shows a distinct third stage of decomposition that is not present in the experimental curve, indicating that this slower oxidation process of carbon fibre is eliminated in the presence of PEEK. This suggests that the PEEK residue enhances the oxidation of carbon fibre.

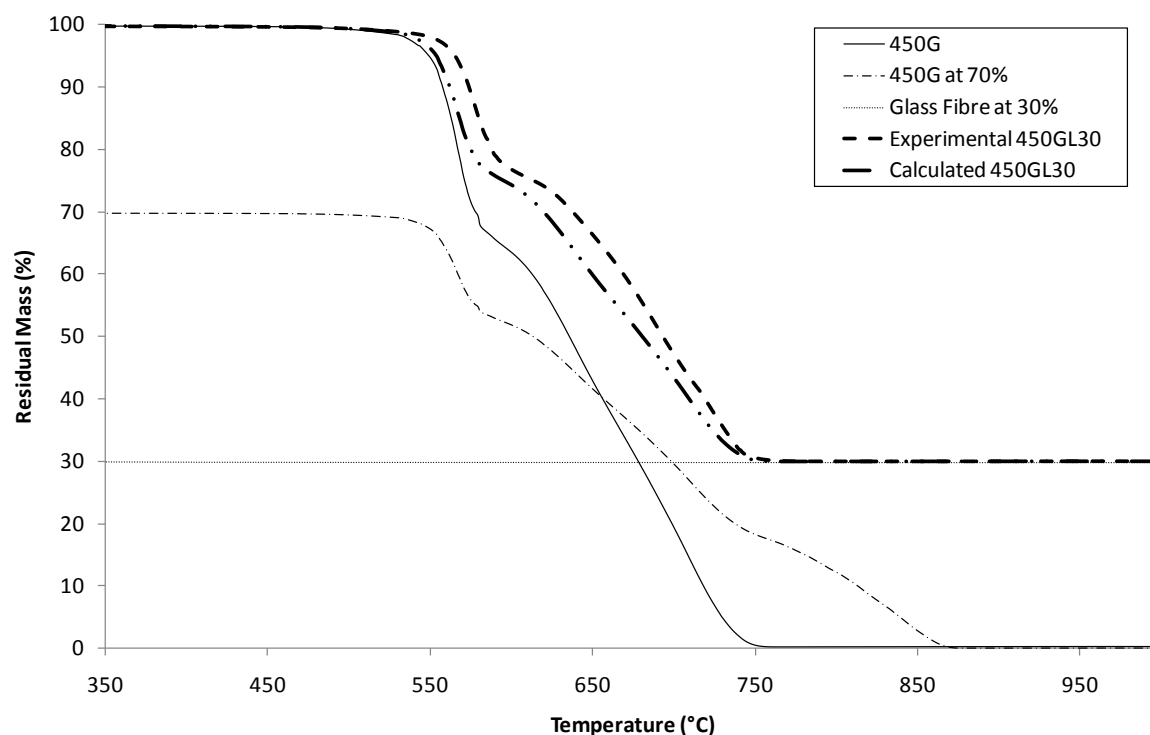


Figure 5. 450G and 450GL30 – Experimental and Calculated TGA in Air

Similarly, a calculated curve has been compared to the actual decomposition of 450GL30 as shown in Figure 5. Here similarities exist between the two curves – to a greater extent than the 450CA30 calculated curve. The presence of glass fibre appears to enhance the onset of decomposition to a greater extent than that seen in the calculated curve. Moreover, no enhancement is evident in the earlier stages of the decomposition of PEEK (equivalent to 30% and 50% mass loss) for glass fibre-filled composite. This difference in behaviour between both fibre-filled composites indicates that the modest enhancement in the thermal stability is a chemical effect of carbon fibre rather than the effect of physical blocking by any fibre.

3.2 Pyrolysis Combustion Flow Calorimeter

Samples of 450G, 450CA30 and 450GL30 were tested in the PCFC. The results are shown in Figure 6 and a summary of the data is presented in Table 1. The unfilled polymer begins releasing heat prior to the filled polymers; this is expected as 450G thermally decomposes earlier than the filled polymers as seen in the anaerobic TGA experiments. The average peak heat release rate of the unfilled samples is 302 W g^{-1} and therefore higher than the filled samples. Again there are differences between the filled materials. 450GL30 gives a higher average peak heat release rate (232 W g^{-1}) than 450CA30 (195 W g^{-1}). However, both reduce the peak heat release rate when compared to the unfilled material with a 35% reduction for 450CA30 and a 23% reduction for 450GL30. Interestingly, the presence of 30% filler does not reduce the peak heat release rate uniformly. In the glass fibre-filled composite a more rapid pyrolysis rate, and hence the release of flammable material occurs compared to the carbon-fibre composite. The temperature at incipient heat release rate

(onset temperature) corresponds to the transient ignition temperature (flashpoint) of PEEK, while the temperature at peak heat release rate in the PCFC corresponds to the sustained ignition (steady burning) temperature [35]. The average peak heat release rate temperature for 450G is 618°C, for 450CA30 is 621°C and for 450GL30 is 623°C. It has been argued that around 10% mass loss in the TGA in air corresponds to the piloted ignition temperature [29]. In an inert atmosphere in the TGA, 450G reaches 10% mass loss at 576°C, 450CA30 at 583°C and 450GL30 at 586°C. These temperatures are similar to the onset heat release rate temperatures determined from the PCFC data. The differences are due to the higher heating rate ($60^{\circ}\text{C min}^{-1}$) in the PCFC. The anaerobic pyrolysis residues/char yields (Y_c) in the TGA and PCFC show good agreement. The sample heat release (HR) of the 450G in the PCFC is reduced by the inert fraction of glass/carbon fibre (30%) for the 450GL30 and 450CA30 composites. However, the average heat of combustion of the pyrolysis gases, $H_c = \text{HR}/(1-Y_c) \approx 22 \text{ kJ/g-gas}$ is independent of the presence or absence of reinforcing fibre, as would be expected for inert filler.

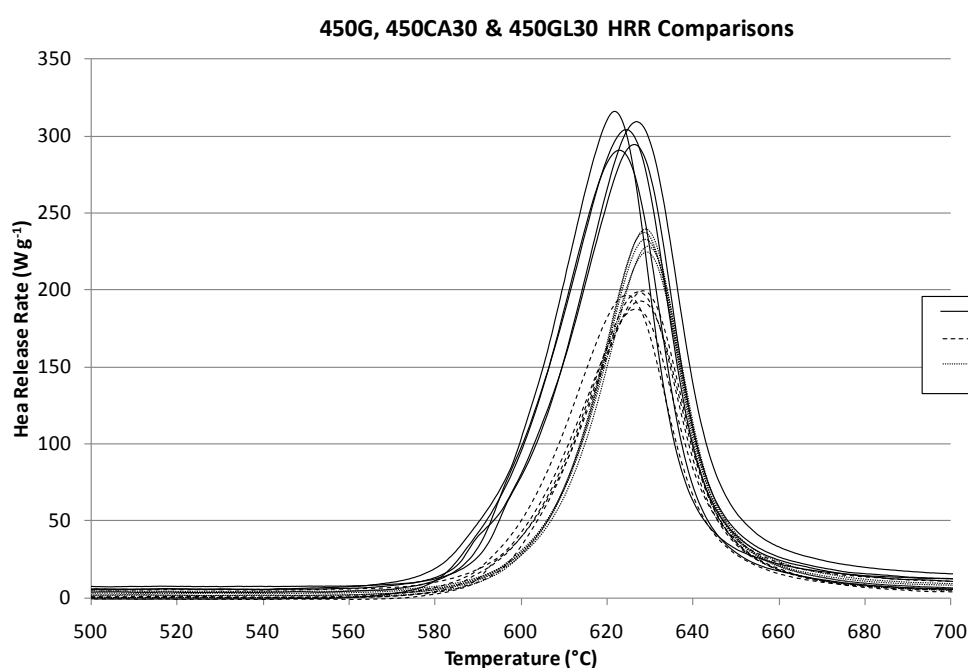


Figure 6. PCFC Heat Release Curves for PEEK 450G, 450CA30 and 450GL30

	Onset Heat Release Rate Temperature	Peak Heat Release Rate Temperature	Peak Heat Release Rate	Char	Heat Release	Heat of Combustion Gases (H_c)
	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	(W g^{-1})	(%)	(kJ g^{-1})	(kJ g^{-1})
450G	594 ± 1.8	611.2 ± 2.2	302.8 ± 10.3	51.6 ± 2.6	10.7 ± 0.3	22.1
450CA30	596.4 ± 0.9	613.6 ± 1.5	194.9 ± 4.8	68.5 ± 3.8	7.0 ± 0.2	22.2
450GL30	605.6 ± 0.5	615.7 ± 0.3	232.5 ± 6.1	65.9 ± 1.5	7.2 ± 0.1	21.1

Table 1. Summary of PCFC Data for PEEK and Composites

3.3 Limiting Oxygen Index

Samples of 450G, 450CA30 and 450GL30 were tested in the LOI and results are shown in Table 2. 450G exhibited a lower LOI value than both filled materials as expected from the TGA and PCFC data whereby filled composites have a greater thermal stability than unfilled samples. Again there were differences between the filled materials – 450CA30 had a higher LOI than 450GL30 albeit by 0.8%. There were also differences in the ways the materials behaved during the tests. 450CA30 samples would curl in on themselves – thus enclosing the flame and causing the sample to extinguish (see Figure 7). Similarly, 450GL30 samples twist round themselves and enclose the flame (see Figure 8) – although this occurred to a lesser extent than with the carbon fibre-filled samples. A possible reason for this effect is the residual stress present from injection moulding the polymer samples and exists to a greater extent in the fibre-filled samples. These differences in physical behaviour may account for the differences in the LOI values of the fibre-filled composites; the ‘curling’ seems to be quite effective at enclosing a flame and promoting self extinguishing behaviour, however should be seen as an artefact of the LOI test in terms of quantifying flammability.

Material	LOI	Comments
PEEK 450G	37.3%	n/a
PEEK 450CA30	45.5%	Samples curl in on themselves
PEEK 450GL30	44.7%	Samples twist around themselves

Table 2. LOI Data for 450G, 450CA30 and 450GL30

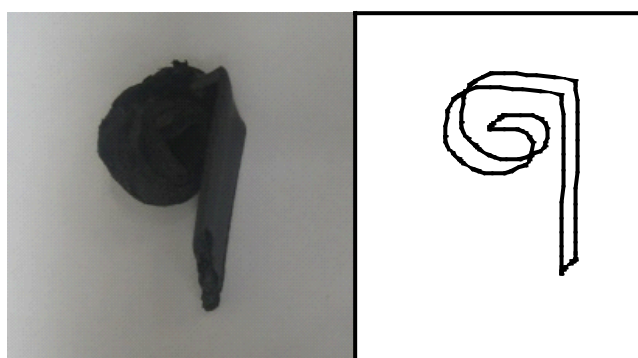


Figure 7. 450CA30 LOI Sample 'Curling'

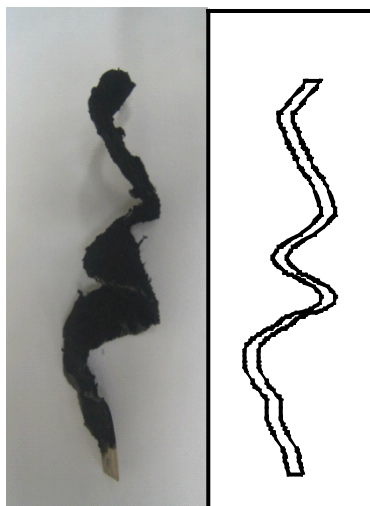


Figure 8. 450GL30 LOI Sample 'Twisting'

3.4 Underwriters Laboratory Vertical Test for Flammability of Plastics (UL94-V)

All materials tested were classified as achieving the optimum UL-94 rating (V-0). Differences exist in the burn times t_1 and t_2 of the filled and unfilled polymers as shown in Table 3. t_1 refers to the time a flame is sustained after the primary 10 second flame application and t_2 refers to the time a flame is sustained after the secondary 10 second flame application. For 450G, t_1 is on average greater than t_2 ; for both 450CA30 and 450GL30, the opposite is true. Once ignited, the unfilled polymer char is less easy to reignite while the filled polymer char is easier to reignite. There also appears to be a greater burn length and a shorter total burn time (the sum of t_1 and t_2) for the filled samples— although there is uncertainty due to the scatter present in the data. It is interesting that although there are clear differences between the filled and unfilled polymer in terms of burning behaviour, these differences are not evident within the V-0 UL-94 test criterion. Correlations have been found between cone calorimeter peak heat release rate data and UL-94 V-ratings although the closest correlations were observed at low heat fluxes (30 kW m^{-2}), close to the ignitability limits for many materials [36]. The critical heat flux (CHF) for ignition of PEEK is calculated as the sum of the radiative and convective heat losses at incipient ignition:

$$\text{CHF} = \alpha\sigma(T_{\text{ign}}^4 - T_0^4) + h(T_{\text{ign}} - T_0) \approx 24 \text{ kW m}^{-2} \quad (1)$$

In Equation 1, the surface absorptivity is $\alpha = 0.8$, the ignition temperature is assumed to be equal to the onset thermal (oxidative) decomposition temperature $T_{\text{ign}} = 808\text{K}$ (535°C), the ambient temperature is $T_0 = 298\text{K}$ (25°C), the convective heat transfer coefficient in the cone calorimeter is $h = 10 \text{ W/m}^2\text{-K}$, and σ is the Stefan-Boltzmann constant ($5.67 \times 10^{-8} \text{ W m}^{-2} \text{ K}^4$). The calculated CHF is in reasonable agreement with experimental values between 30 and 40 kW m^{-2} [37]

	t_1	t_2	Total Time	Burn Length
Sample	(s)	(s)	(s)	(mm)
450G	3.7 ± 1.0	2.7 ± 1.1	6.5 ± 1.1	30.9 ± 7.9
450CA30	1.9 ± 1.3	4.1 ± 1.5	6.0 ± 1.9	34.0 ± 17.5
450GL30	2.2 ± 0.8	3.5 ± 0.9	5.7 ± 1.5	39.4 ± 26.1

Table 3. UL-94 Average Data for 450G, 450CA30 and 450GL30

3.5 Fire (Cone) Calorimetry

Samples of PEEK 450G, 450CA30 and 450GL30 were tested in the cone calorimeter in triplicate at 50 kW m⁻². In these and other studies, we have observed inconsistencies in the burning behaviour of PEEK compared to other materials. The individual heat release rates are shown in Figure 9, Figure 10 and Figure 11 respectively, together with their average data summarised in Table 4. For the unfilled polymer (450G), all three samples ignited within a 15 second window – the average time to ignition was 110 seconds. In terms of burning behaviour, all three samples ignited, reached a shoulder at around 140 seconds and 200 kW m⁻², and then continued to burn to reach an average peak heat release rate of 415 kW m⁻². An average char yield of 50.6% was obtained with an average of 36.2 MJ m⁻² heat released in total. After the flame extinguishes, the heat release rate does not return to zero as the char continues to oxidise (smoulder) without flaming as evident in all three heat release curves. The effective heat of flaming combustion per unit mass of volatiles up to the point of flame extinction is reported as EHOC in Table 4. Dividing the effective heat of combustion of the volatiles EHOC by the heat of complete combustion of the volatiles H_c from Table 1 gives the flaming combustion efficiency in the cone calorimeter, $\chi = \text{EHOC}/H_c$ listed in Table 4. It is seen that the combustion efficiency is approximately 90% for PEEK burning in the well-ventilated cone calorimeter, independent of the presence or absence of reinforcing fibre as would be expected for gas phase combustion chemistry.

For the carbon fibre-filled samples (450CA30), the average time to ignition was 156 seconds and samples burned with an average peak heat release rate of 147 kW m⁻². An average char yield of 66.4% was obtained with an average of 26.9 MJ m⁻² of total heat released. Similarly to the 450G samples, the heat release rate does not return to zero.

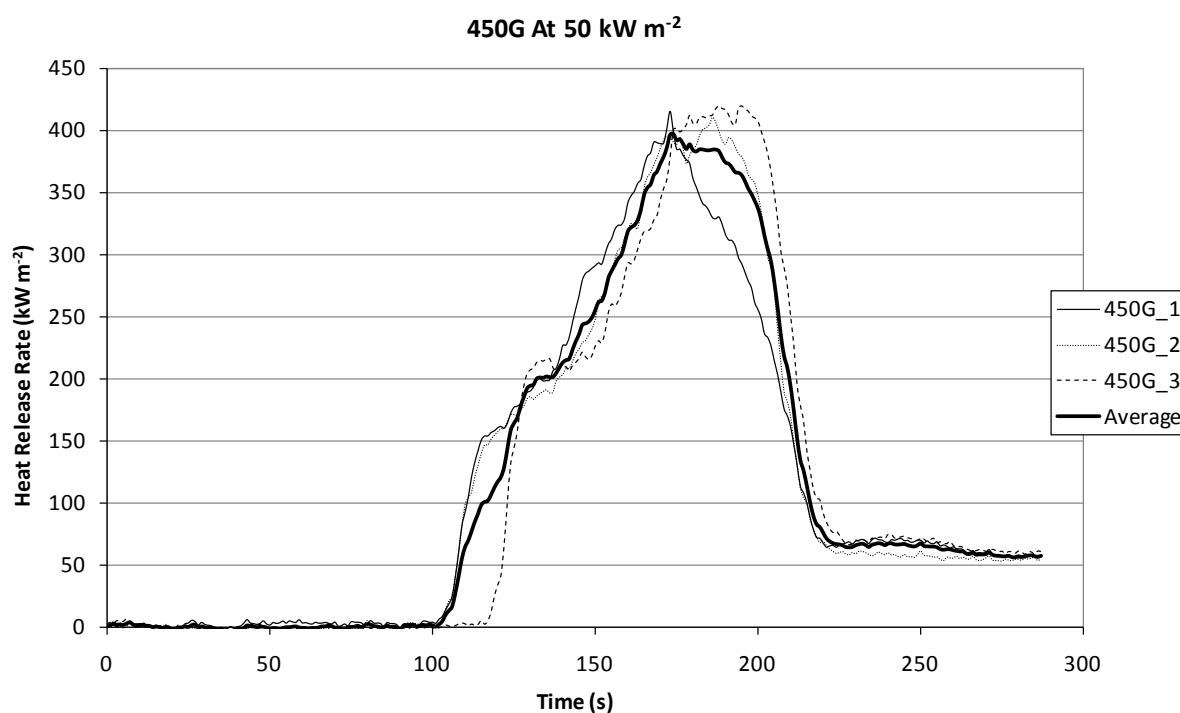


Figure 9. Cone Calorimeter Data for HRR of PEEK 450G. Triplicates and Average

	Time to Ignition	PHRR	tPHRR	Char Yield	EHOC	THR	χ
	(s)	(kW m ⁻²)	(s)	(%)	(J/kg)	(kW m ⁻²)	
450G	110 ± 8	415.2 ± 4.9	182 ± 8	50.6 ± 1.6	1.999 × 10 ⁷	36.2 ± 1.1	90%
450CA30	156 ± 13	146.7 ± 5.8	279 ± 20	66.4 ± 2.9	1.022 × 10 ⁷	26.9 ± 2.6	87%
450GL30	115 ± 15	120.5 ± 13	278 ± 5	71.8 ± 0.3	7.552 × 10 ⁶	23.3 ± 1.9	88%

Table 4. PEEK and Composites at 50 kW m⁻² – Summary: Time to Ignition, Peak Heat Release Rate (PHRR), Time to Peak Heat Release Rate (tPHRR), Char Yield, Effective Heat of Combustion (EHOC), Total Heat Released (THR) and Flaming Combustion Efficiency (χ)

For the glass fibre-filled samples (450GL30) the average time to ignition was 115 seconds and samples burned with an average peak heat release rate of 121 kW m⁻². An average char yield of 71.8% was obtained with an average of 23.3 MJ m⁻² total heat released. Again, like the 450G and 450CA30 samples, the 450GL30 heat release curves do not return to zero.

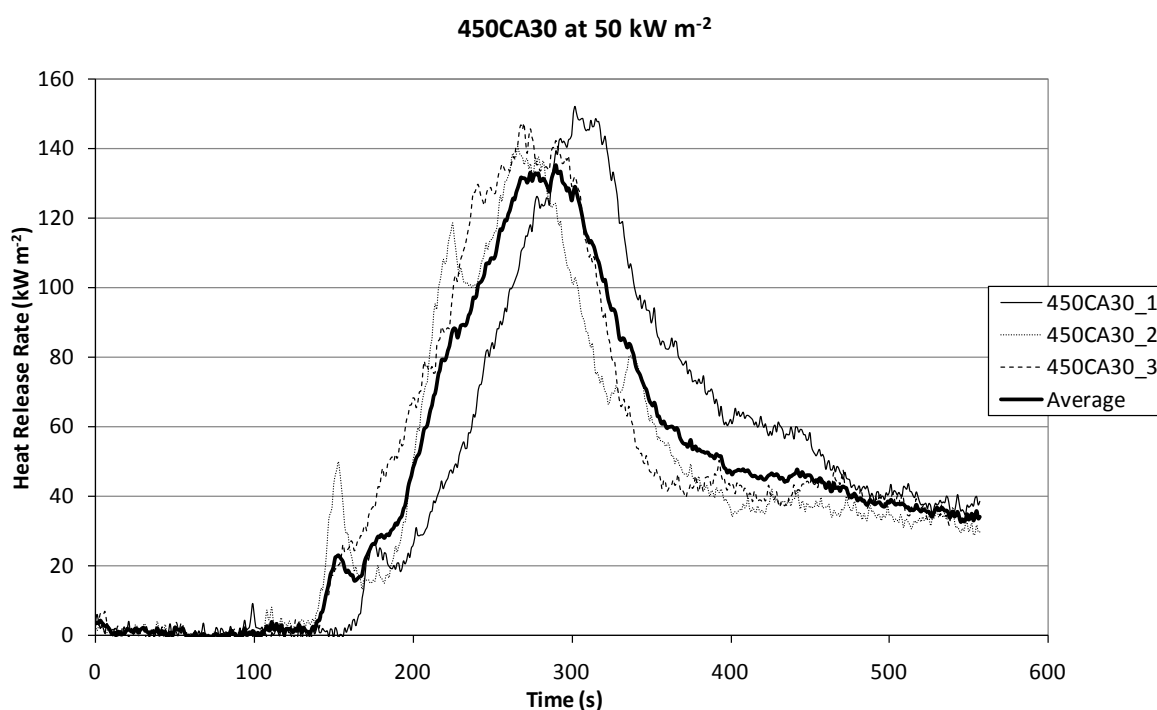


Figure 10. Cone Calorimeter Data for HRR of PEEK 450CA30. Triplicates and Average

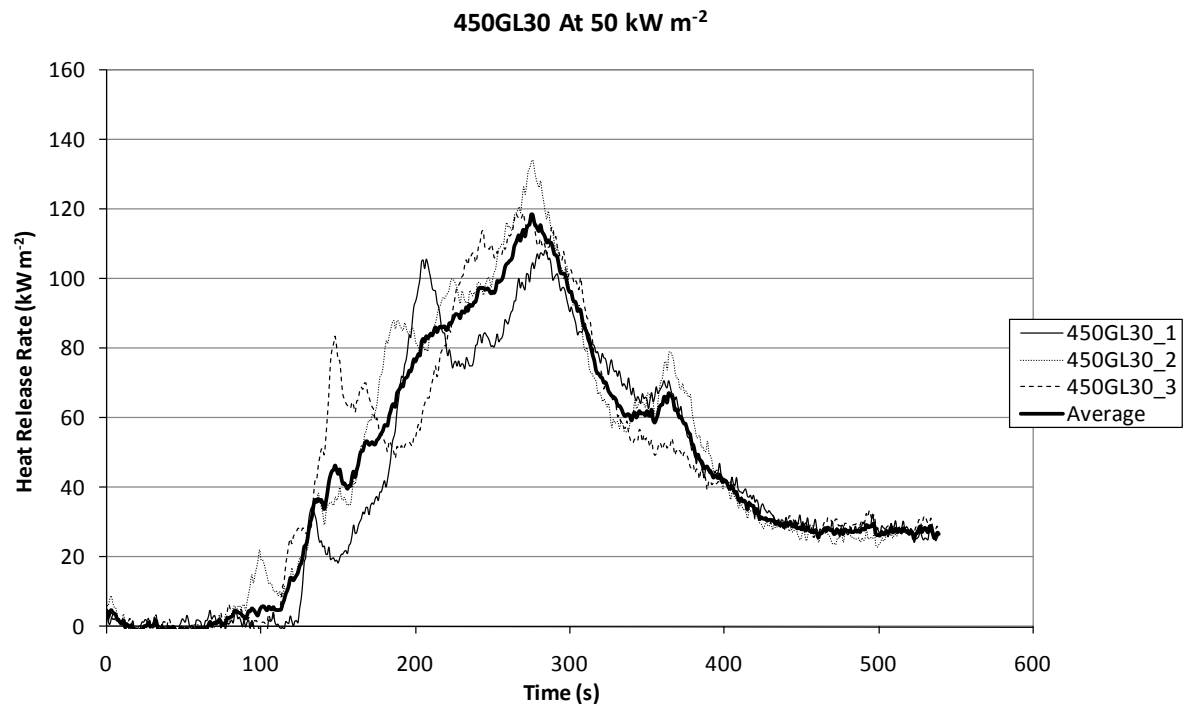


Figure 11. Cone Calorimeter Data for HRR of PEEK 450GL30. Triplicates and Average

Ignition Behaviour of 450G, 450CA30 and 450GL30

Piloted ignition is sustained when the heat released from the combustion of volatilised fuel is sufficient to vaporise its replacement from the condensed phase. For the horizontal sample configuration of the cone calorimeter, only a small portion of the radiant heat will be transmitted back to the condensed phase fuel and therefore, only a portion of this heat will result in fuel volatilisation. For thermally thick solids (typically thicknesses above 1.5 mm [38]) the thermal inertia, $k\rho c$, which is the product of thermal conductivity (k), density (ρ), and specific heat (c), governs the material's ignition and flame spread properties for a given set of conditions. It is the rate at which the surface reaches the thermal (oxidative) decomposition temperature and generates gaseous fuel, that controls the time to ignition [37] – [39]. The time to ignition (t_{ig}) of a thermally thick solid exposed to a constant net heat flux, $Q_R = Q_{ext} - CHF$ is obtained from unsteady heat conduction as:

$$t_{ig} = \frac{\pi}{4} k\rho c \frac{(T_{ig} - T_0)^2}{\dot{Q}_R^2} \quad (2)$$

The material properties $k\rho c$ are presumed to be known, at least under ambient conditions; and an estimate for the temperature at ignition is the onset thermal oxidation decomposition temperature in the TGA, $T_{ign} = 808\text{K}$. The samples tested in the cone calorimeter for this study were 2.5 mm in thickness and as a result, the thermally thin scenario may be more appropriate. The time to ignition of a thermally thin solid exposed to a constant net heat flux has been expressed through the following:

$$t_{ig} = \rho c \tau \frac{(T_{ig} - T_0)}{\dot{Q}_R} \quad (3)$$

Where $\tau = 0.0025$ m is the thickness of the cone calorimeter samples. The values for k , ρ and c listed in Table 5 (obtained from Victrex plc - Technical Data Sheets) were used to calculate the time to ignition for PEEK and its composites using $T_{ign} = 808$ K and $Q_R = Q_{ext} - CHF = 50 \text{ kW/m}^2 - 24 \text{ kW/m}^2 = 26 \text{ kW/m}^2$ for both the thermally-thin and thermally-thick cases. The results of these calculations are shown in Table 5.

Where $\tau = 0.0025$ m is the thickness of the cone calorimeter samples. The values for k , ρ and c listed in Table 5 (obtained from Victrex plc - Technical Data Sheets) were used to calculate the time to ignition for PEEK and its composites using $T_{ign} = 808$ K and $Q_R = Q_{ext} - CHF = 50 \text{ kW/m}^2 - 24 \text{ kW/m}^2 = 26 \text{ kW/m}^2$ for both the thermally-thin and thermally-thick cases. The results of these calculations are shown in Table 5.

Input Data							
	k	ρ	c	T_{ig}	Predicted Thermally Thin t_{ig}	Predicted Thermally Thick t_{ig}	Actual Cone t_{ig}
	$\text{W m}^{-1} \text{K}^{-1}$	Kg m^{-3}	$\text{J Kg}^{-1} \text{K}^{-1}$	K	s	s	s
450G	0.25	1300	2160	808	138	212	110 ± 8
450CA30	0.92	1410	1850	808	128	725	156 ± 13
450GL30	0.43	1510	1710	808	127	336	115 ± 15

Table 5. Time to Ignition Parameters, Prediction and Comparison with Actual Data

The time for the surface temperature to reach the ignition temperature following an instantaneously applied and constant net heat flux (time to ignition) calculated for the thermally-thin case correlates more closely to the experimental values for PEEK and its composites than does the thermally-thick case. However, calculations of this nature rely on the concept of an ignition temperature, which is only one of several criteria proposed for ignition of combustible solids [35]. The calculated time to ignition for the fibre-filled composites is slightly lower, possibly due to a lower specific heat.

Comparison of Burning Behaviour

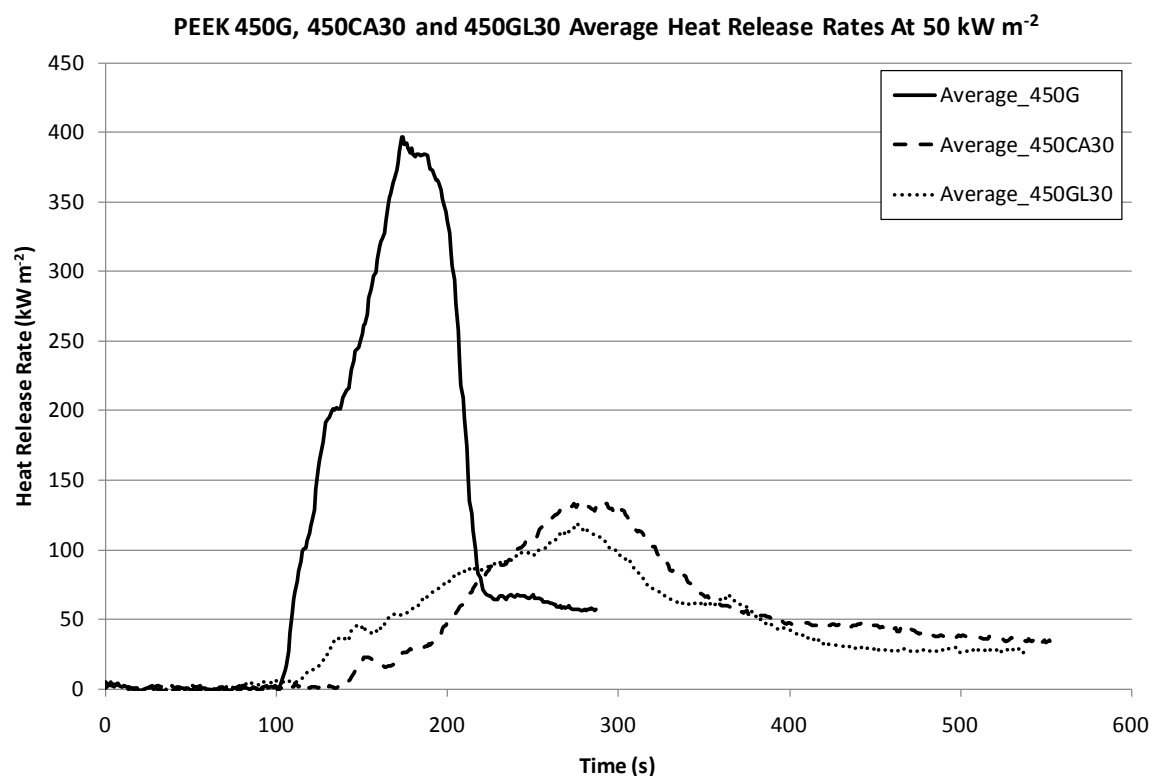


Figure 12. Cone Calorimeter Data for Average HRR of PEEK 450G, 450CA30 and 450GL30

The average heat release rate curves of PEEK and its carbon and glass fibre composites are shown in Figure 12. The shapes of cone calorimeter heat release rate curves have been discussed previously [40] [41]. The virgin polymer (450G) initially exhibits 'intermediate thick non-charring' behaviour showing a short period of steady heat release rate marked by a shoulder within the curve. As the remaining material becomes thinner, all of the applied heat flux is concentrated on a small amount of fuel, which as a result, burns quicker. Both the filled samples behave in a similar manner but may be characterised as 'thick charring' depicted by an initial increase in heat release rate until an effective char layer has been formed. As this layer continues to thicken, the heat release rate decreases until the polymer extinguishes.

The unfilled polymer exhibits a much higher peak of heat release rate than the filled polymers. A similar but smaller effect is seen in the PCFC data. There are also differences between the carbon and glass fibre-filled composites in terms of burning behaviour. The presence of fillers reduces the peak heat release rate by 64% for 450CA30 and 71% for 450GL30 in the cone calorimeter: 450CA30 exhibits a higher peak of heat release, approximately 25 kW m⁻² higher than 450GL30. The reduction in heat release rate due to the presence of filler is observed to a lesser extent in the PCFC. Additionally, in the PCFC, 450CA30 shows a greater reduction in heat release rate than 450GL30, the opposite of that observed in the cone calorimeter. These differences could be accounted for by the differences in the nature of each experiment. In the PCFC, and similarly in the TGA samples are heated from numerous directions from the furnace. In the cone calorimeter, samples are exposed to a radiant heat source and therefore heating of the polymer occurs initially through radiative heat transfer with the presence of a (black) carbon fibre having a greater ability to absorb radiation close to the surface.

In the cone calorimeter, the total heat released is lower for the filled materials with a reduction of 26% for 450CA30 and 35% for 450GL30. In the PCFC data, both fillers reduce the total heat released

by 30% when compared to 450G, which may be expected with the absence of 30% polymer. In the cone calorimeter, the combination of oxygen and radiant heat causes some oxidation of the carbon fibre. In the PCFC, under nitrogen, the carbon fibre will remain in the condensed phase.

Comparison of Charring Behaviour

From TGA data in nitrogen, PEEK has a char yield of ~50% for the virgin polymer and ~70% for the filled composites. It is worth noting that subsequent to ignition, all samples show a significant degree of intumescence (see Figure 13 for 450G). As seen in Figure 14 the intumescent structure formed from the radiant heating of 450GL30 has greater structural integrity than the structure formed by 450CA30 (Figure 15) presumably due to fusion of the glass fibres. The very large differences in the char shape after intumescence will affect the heat release rate. As the unfilled char swells, it will become very close to the cone heater, and the applied heat flux will increase. This will have two consequences, increasing char oxidation near the heater, while protecting any unburned polymer near the base of the swollen mass. For the filled samples, the intumescence is held back by the reinforcing fibres and this effect is much less apparent. It could be argued that the heat flux on swelling was an artefact of behaviour in the cone calorimeter that would not be observed in a real fire. In addition, the one-dimensional burning of a larger bulk of material (a 2.5 mm thick cone calorimeter sample) allows the fibres to reinforce the char structure, acting as a physical and radiation barrier. In the PCFC and TGA, where no temperature gradient exists within the sample, this protective effect is not observed, hence the higher char yields in the cone calorimeter. The char yields obtained from TGA, PCFC and cone calorimetry are shown in Table 6. Similar values are attained by the TGA and PCFC, with differences attributed to the heating rate used.

	Char Yield (%)		
	TGA N ₂ (at 900°C)	PCFC	Cone
450G	49	51.6 ± 2.6	50.6 ± 1.6
450CA30	65	68.5 ± 3.8	66.4 ± 2.9
450GL30	68	65.9 ± 1.5	71.8 ± 1.9

Table 6. Char Yield Comparison of 450G, 450CA30 and 450GL30



Figure 13. 450G Cone Calorimeter Sample Intumescence



Figure 14. 450GL30 Cone Calorimeter Sample Intumescence



Figure 15. 450CA30 Cone Calorimeter Sample Intumescence

3 Conclusions

PEEK is very heat resistant, with negligible thermal decomposition below 550°C. PEEK thermal decomposition occurs via a two-step process. In the virgin polymer, 30% of the PEEK is decomposed to gaseous fuel within a 30°C window in the first stage of decomposition in both anaerobic and oxidative atmospheres, indicating that the process of volatile fuel generation does not require, or is not enhanced by oxygen in the environment. The rapid mass loss has been attributed to random chain scission with the loss of ether and carbonyl groups leaving most of the aromatic residue to crosslink and further decompose to carbonaceous char. The presence of filler increases the thermal stability of pure PEEK with the glass-fibre filled composite being the more thermo-oxidatively stable of the fibre-filled materials.

The presence of filler has a significant influence on the flammability of the materials; however the burning behaviour of PEEK and these two fibre-filled composites is very scenario dependent. This has been observed using a number of techniques and as a result, more is understood about the effects attributed to the presence of fillers. The PCFC shows differences in the ignition temperature between glass and carbon filled materials - 450GL30 has a slightly higher ignition temperature. However, in the cone calorimeter where heat transfer through the bulk of the solid is also important, 450GL30 ignites earlier than 450CA30. This is reversed in the PCFC where it is observed that 450CA30 ignites and begins losing weight at a lower temperature. The average heat release rate in the PCFC is 302 W g⁻¹ for the virgin polymer, 195 W g⁻¹ for the carbon fibre-filled composite and 232 W g⁻¹ for the glass fibre-filled composite. The ignition temperature of all three polymers is between 611°C and 616°C – being slightly lower for the unfilled material.

The burning behaviour of the fibre-filled composites also shows differences in the LOI tests. The carbon fibre-filled composites curl in on themselves whilst glass-fibre filled composites twist round themselves – the former being a more effective method for enclosing a flame and resulting in self-extinguishing behaviour, although may have no effect in real fire behaviour.

Differences are noted between the filled and unfilled samples in the UL-94 tests, which are not noted when simply observing the V-ratings of the materials. The main difference is that for the unfilled polymer, the first flame application time (t_1) is greater than the second (t_2) – this is reversed for the filled polymers. This shows that unfilled PEEK forms a better protective layer on first ignition, where as the fibre-filled samples are easier to ignite after first ignition.

In both the cone calorimeter and the PCFC, the total heat released is reduced by the inert fraction of the fibre-filled composites. In the cone calorimeter, the glass fibre-filled composite has a lower average peak heat release rate than the carbon fibre-filled composite. Possible reasons for this are the enhanced structural integrity of the glass fibre char which forms a mechanically stable thermal radiation shield for the underlying composite. The combustion efficiency of the fuel gases in the flame for PEEK and its composites are similar and in the order of 90%.

Conversely, the higher thermal conductivity of the carbon fibre-filled composite increases the materials' time to ignition giving, an average ignition delay time of 46 seconds when compared to the virgin polymer and 41 seconds compared to the glass fibre-filled composite.

Acknowledgements

The authors would like to thank the Engineering and Physical Science Research Council (EPSRC) for the award of a CASE PhD Studentship (No. 07001444). Additional gratitude is expressed to Victrex plc for technical support.

References

¹ Rose, J. B., and Staniland, P.A., Thermoplastic Aromatic Polyketones. European Patent 0001879B2, August 22 (1978).

² Hergenrother, P. M., Thompson, C. M., Smith Jr, J. G., Connell, J. W., Hinkley, J. A., Lyon, R. E., and Moulton, R., (2005), Flame Retardant Aircraft Epoxy Resins Containing Phosphorus. *Polymer*, **46**(14), Pages 5012-5024.

³ Morgan, A. B., Gagliardi, N. A., Price, W.A., and Galaska, M. L., (2009), Cone Calorimeter Testing of S2 Glass Reinforced Polymer Composites. *Fire and Materials*, **33**(7), Pages 323-344.

⁴ Matsui, J., (1995), Polymer Matrix Composites (PMC) In Aerospace. *Advanced Composite Materials*, **4**(3), Pages 197-208.

⁵ Day, M., Cooney, J. D., and Wiles D. M., (1989), "The Thermal Stability of Poly(Aryl Ether Ether Ketone) As Assessed By Thermogravimetry", *Journal of Applied Polymer Science*, **38**(2), 323-337.

⁶ Cole, K. C., and Casella, I. G., (1992), "Fourier Transform Infrared Spectroscopic Study of Thermal Degradation in Films of Poly(Ether Ether Ketone)", *Thermochimica Acta*, **211**, 209-228.

⁷ Cole, K. C., and Casella, I. G., (1993), "Fourier Transform Infrared Spectroscopic Study of Thermal Degradation in Poly(Ether Ether Ketone) – Carbon Composites", *Polymer*, **34**(4), 740-745.

⁸ Hay, J. N., and Kemmish, D. J., (1987), "Thermal Decomposition of Poly(Aryl Ether Ketones)", *Polymer*, **28**, 2047-2051.

-
- ⁹ Tsai, C. J., Perng, L. H., and Ling, Y. C., (1997), "A Study of Thermal Degradation of Poly(Aryl-Ether-Ether-Ketone) using Stepwise Pyrolysis/Gas Chromatography/Mass Spectrometry", *Rapid Communications in Mass Spectrometry*, **11**, 1987-1995.
- ¹⁰ Naffakh, M., Ellis, G., Gomez, M., and Marco, C., (1999), "Thermal Decomposition of Technological Polymer Blends. 1. Poly(Aryl Ether Ether Ketone) with a Thermotropic Liquid Crystalline Polymer", *Polymer Degradation And Stability*, **66(3)**, 405-413.
- ¹¹ Nandan, B., Kandpal, L., and Mathur, G. N., (2002), "Poly(Ether Ether Ketone)/Poly(Aryl Ether Sulphone) Blends: Thermal Degradation Behaviour", *European Polymer Journal*, **39(1)**, 193-198.
- ¹² Huo, R., Luo, Y., Liang, L., Jin, X., and Karasz, F. E., (1990), "Kinetic Studies on Thermal Degradation of Poly(Aryl Ether Ether Ketone) and Sulphonated Poly(Aryl Ether Ether Ketone) by Thermogravimetry", *Journal Of Functional Polymers*, **4**, 426-433
- ¹³ Nam, J. D., and Seferis, J. C., (1992), "Generalised Composite Degradation Kinetics for Polymeric Systems under Isothermal and Nonisothermal Conditions", *Journal of Polymer Science*, **30(5)**, 455-463.
- ¹⁴ Day, M., Cooney, J. D., and Wiles, D. M., (1989), "The Kinetics of the Oxidative Degradation of Poly(Aryl-Ether-Ether-Ketone) (PEEK)", *Thermochimica Acta*, **147(1)**, 189-197.
- ¹⁵ Day, M., Sally, D., and Wiles, D. M., (1990), "Thermal Degradation of Poly(Aryl-Ether-Ether-Ketone): Experimental Evaluation of Crosslinking Reactions", *Journal of Applied Polymer Science*, **40**, 1615-1620.
- ¹⁶ Day, M., Cooney, J. D., and Wiles D. M., (1990), "The Thermal Degradation of Poly(Aryl Ether Ether Ketone) (PEEK) as Monitored by Pyrolysis-GC/MS and TG/MS", *Journal of Analytical and Applied Pyrolysis*, **18**, 163-173.
- ¹⁷ He, J., Duan, X., and Wang, Z.-X., (1997), "Study on the Kinetics And Mechanism of Thermal Degradation of PEEK by Temperature Programmed Decomposition", *Acta Chimica Sinica*, **55(12)**, 1152-1157.
- ¹⁸ Perng, L. H., Tsai, C. J., and Ling, Y. C., (1999), "Mechanism and Kinetic Modelling of PEEK Pyrolysis by TG/MS", *Polymer*, **40**, 7321-7329.
- ¹⁹ Yao, F., Zheng, J., Qi, M., Wang, W., and Qi, Z., (1991), "The Thermal Decomposition Kinetics of Poly(Ether-Ether-Ketone) (PEEK) and its Carbon Fibre Composite", *Thermochimica Acta*, **183**, 91-97.
- ²⁰ Zhang, H., (2004), Fire-Safe Polymers and Polymer Composites. US Department Of Transport. Report Number: DOT/FAA/AR-04/11. Federal Aviation Administration.
- ²¹ Friedman, R., Friedman, J., and Linville, L., (2003) *Principles of Fire Protection Chemistry and Physics: Part II – Fire Protection Chemistry and Physics*. Chapter 10 – Fire Characteristics: Solid Combustibles. 3rd Edition. Jones and Bartlett Publishers, London, UK.
- ²² Lyon, R. E., and Walters, R., (2002), *A Microscale Combustion Calorimeter*. US Department of Transport. Report Number: DOT/FAA/AR-01/117. Federal Aviation Administration.
- ²³ Babrauskas, V., and Peacock, R. D., (1992), Heat Release Rate: The Single Most Important Variable in Fire Hazard. *Fire Safety Journal*. **18(3)**, Pages 255-272.
- ²⁴ Hugget, C., (1980), Estimation of the Rate of Heat Release by Means of Oxygen Consumption Measurements. *Fire and Materials*. **4(2)**, Pages 61-65.
- ²⁵ Babrauskas, V., (1982), Development of the Cone Calorimeter. A Bench-Scale Heat Release Rate Apparatus Based on Oxygen Consumption (NBSIR 82-2611). US National Bureau of Standards.

-
- ²⁶ Lyon, R.E., and Walters, R. N., Microscale Combustion Calorimeter, US Patent 5,981,290, November 9 (1999).
- ²⁷ Schartel, B., Pawlowski, K. H., and Lyon, R. E., (2007), Pyrolysis Combustion Flow Calorimeter: A Tool to Assess Flame Retarded PC/ABS Materials? *Thermochimica Acta*. **462(1-2)**, pages 1-14.
- ²⁸ Lu, H., and Wilkie, C. A., (2010), Synergistic Effect of Carbon Nanotubes and Decabromodiphenyl Oxide/Sb₂O₃ in Improving the Flame Retardancy of Polystyrene. *Polymer Degradation and Stability*. **95(5)**, pages 564-571.
- ²⁹ Hull, T. R., and Stec, A. A., (2009), *Polymers and Fire*. Chapter 1. In Hull, T. R., and Kandola, B., K., (editors) *Fire Retardancy of Polymers: New Strategies and Mechanisms*. Royal Society of Chemistry, UK.
- ³⁰ ASTM D7309: 2007. Determining Flammability Characteristics of Plastics and Other Solid Materials Using Microscale Combustion Calorimetry.
- ³¹ ISO 4589: 1996. Plastics – Determination of Burning Behaviour by Oxygen Index. Part 2: Ambient-Temperature Test.
- ³² BS 60695: 1999. Fire Hazard Testing. Part 11-10 Test Flames – 50 W Horizontal and Vertical Flame Test Methods.
- ³³ ASTM Standard E 1354-04a. Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products Using an Oxygen Consumption Calorimeter, ASTM International, West Conshohocken, PA, 2007.
- ³⁴ Patel, P., Hull, T. R., McCabe, R. W., Flath, D., Grasmeder, J., and Percy, M., (2010), Mechanism of Thermal Decomposition of Poly(Ether Ether Ketone) (PEEK) From a Review of Decomposition Studies. *Polymer Degradation and Stability*. **95(5)**, pages 709-718.
- ³⁵ Lyon, R. E., and Janssens, M. L., (2005), *Polymer Flammability*. US Department Of Transport. Report Number: DOT/FAA/AR-05/14.
- ³⁶ Morgan, A.B., and Bundy, M., (2007), Cone Calorimeter Analysis of UL-94 V-Rated Plastics. *Fire and Materials*. **31**, pages 257-283
- ³⁷ Lyon, R. E., and Quintiere, J. G., (2007), Criteria for Piloted Ignition of Combustible Solids. *Combustion and Flame*. **151**, pages 551-559.
- ³⁸ Quintiere, J. G., (1997), *Principles of Fire Behaviour*. Delmar. Albany, NY.
- ³⁹ Drysdale, D., (1999), *An Introduction to Fire Dynamics*. 2nd Edition. John Wiley & Sons, Chichester.
- ⁴⁰ Lyon, R. E., (2002), Ignition Resistance of Plastics. Lewin, M., (editor) *Recent Advances in Flame Retardancy of Polymers*. Volume 13. Business Communications Co. Inc. Norwalk. 14-25.
- ⁴¹ Schartel, B., and Hull, T.R., (2007), Application of Cone Calorimetry to the Development of Materials with Improved Fire Performance. *Fire and Materials*. **31**, pages 327-354