Pyrolysis combustion flow calorimeter: A tool to assess flame retarded PC/ABS materials?

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Abstract

The pyrolysis combustion flow calorimeter (PCFC) as a tool for assessing the flammability of a polycarbonate (bisphenol A)/acrylonitrile–butadiene–styrene (PC/ABS) blend containing different flame retardants and additives was investigated. Strategies are proposed for analysing multi-step decomposition. The heat release capacity (HRC) and total heat release (HR), obtained by PCFC, are related to the char yield and the heat of complete combustion of the volatiles. Physical affects such as dripping, wicking, and sample thickness are not described, nor are chemical effects such as flame inhibition because pyrolysis and combustion are forced to completion on a small (milligram) sample. Varying the combustion temperature or oxygen concentration results in incomplete combustion as occuring in real fires. The correlations with flammability (UL 94, LOI) and forced flaming combustion in a cone calorimeter are discussed. The best correlation is found between HR and LOI. Reasonable correlation exists between HRC and char residue with the LOI and for HRC and HR with peak heat release rate (pHRR) in the cone calorimeter. Combining results from PCFC with those from oxygen bomb or cone calorimeter tests yields an additional understanding of fire behaviour.
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1. Introduction

The pyrolysis combustion flow calorimeter (PCFC) or microscale combustion calorimeter (MCC) has been proposed as a tool to assess the fire behaviour of mg-sized samples [1–5]. However, the PCFC like any mg-scale test method fails to account for physical effects that typically occur on larger length or mass scales, such as dripping or intumescence. Since the length scale of the component/sample plays a large role in the fire behaviour, there are in principle strong limitations for correlating microscale with real-scale fire tests. However, there is increasing demand for using at least some small-scale or mg-scale methods to screen new materials and for high-throughput methods of materials synthesis and development [6]. Indeed, reasonable correlation has been observed between fire properties and material properties that can be determined with mg-sized sample, such as van Krevelen's correlation of flame resistance with the anaerobic char yield of halogen-free polymers determined in thermogravimetric (TG) measurements [7,8]. In the last decade, this concept was extended by Lyon et al. [9–11] to include measurements of the rate and total amount of heat released by combustion of fuel gases generated during thermal decomposition in the PCFC.

The experimental principle of the PCFC has been reported previously in detail [3,4]. Fig. 1 shows a schematic view of the PCFC accompanied by a graphic of a burning polymer. The PCFC simulates the burning of a polymer solid since it uses anaerobic pyrolysis and a subsequent reaction of the volatile pyrolysis products with oxygen under high temperatures in a combustion zone to simulate surface gasification and flaming combustion, respectively. The PCFC methodology combines the constant heating rate and flow characteristics of thermal analysis methods such as thermogravimetry (TG) with the capability to determine a heat of combustion typical of oxygen bomb calorimetry. However, the PCFC determines the heat release and heat release rate using the oxygen consumption method, so that it corresponds to a fire calorimeter rather than to thermal analysis. The total heat released per unit initial mass (HR), the heat

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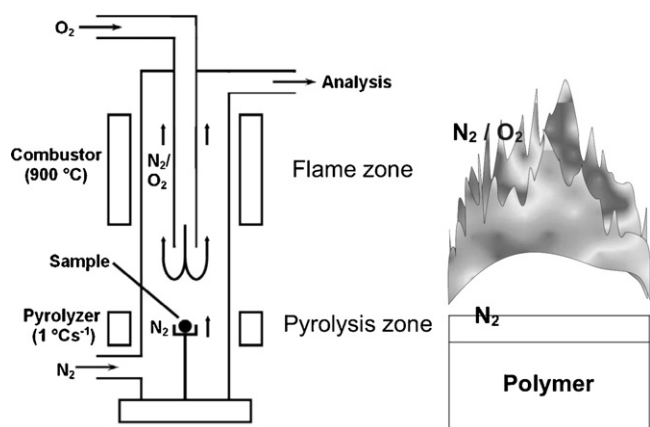 *E-mail address:* bernhard.schartel@bam.de (B. Schartel).

Fig. 1. Experimental set-up of the PCFC (left) in comparison to flaming combustion of a polymer (right).

release capacity (HRC), defined as the maximum heat release rate divided by the constant heating rate in the test, and the temperature at the maximum heat release rate (T_{max}), are the principle results obtained from the PCFC. Of these three parameters, the HRC has been proposed as the single best measure of the fire hazard of a material [1,3].

Initially PCFC was developed by the Federal Aviation Administration in the United States to identify inherently fire resistant polymers for use in commercial aviation. Inherently fire resistant polymers are often characterized by high heat resistance/thermal stability and/or a high mass fraction of char remaining after pyrolysis and/or the release of incombustible pyrolysis products. Early PCFC results compared polymers having widely differing flammability such as poly(ethylene), poly(propylene), poly(styrene), poly(methyl methacrylate), poly(ethylene terephthalate), poly(ether ether ketone), and poly(benzimidazole). Most of these materials thermally decompose in a single step and reasonable correlations between HRC and fire calorimetry were observed, so the method was adopted by the FAA to screen new polymers for heat release rate in flaming combustion [1–4,9,10]. Recently, the PCFC has been used to assess the conditions for flame extinction (flame resistance) of polymers containing additive [12,13] or reactive [14] flame retardant chemicals. Correlation between PCFC data and flame resistance is not straightforward because flame extinction is characterized by incomplete combustion in contrast to forced combustion (i.e., PCFC and cone calorimeter).

So far, there are several gaps in understanding the potential of the PCFC with respect to flame retarded polymers. Consequently, it is necessary to develop the relationships between PCFC data and the flame resistance of polymers containing flame retardant additives. Flame retardant additives function in the condensed phase by char promotion, fuel replacement, endothermal effects, and as barriers to mass and heat transfer. Flame retardant chemicals act in the gas phase through flame poisoning, lowering flame temperature, and fuel dilution. Further, several flame retarded materials and polymer blends show a multi-step decomposition which is not accounted for in the simple theory currently used to interpret PCFC data [1,3]. To be a practical tool for investigating fire behaviour in general,

and flame resistance in particular, the elementary theory used to interpret PCFC data must be extended to account for the effect of flame retardant chemicals on the flammability of polymers.

This study was performed to evaluate the potential of PCFC to determine the flame resistance and fire behaviour of polymers containing flame retardant additives. To this end a polymer blend exhibiting two, well resolved thermal decomposition peaks, was mixed with several flame retardant additives representing typical formulations. The base polymer was a particular blend of bisphenol A polycarbonate (PC) with acrylonitrile–butadiene–styrene (ABS). Consequently, this paper represents a limited, albeit practical, test of the PCFC to discriminate between flame resistance of a particular PC/ABS containing different types and levels of flame retardants and additives. The analysis of multi-step decomposition is discussed and the influence of the residue on flammability is investigated. Correlations between PCFC data and results in established fire tests are examined and the ability of PCFC to screen for flammability of flame retarded polymers is evaluated. Further, PCFC data are combined with results from oxygen bomb calorimetry and cone calorimetry to provide new insights on fire behaviour. Finally, the standard PCFC experimental protocol is modified to allow incomplete oxidation in the PCFC in an attempt to approximate flaming combustion.

2. Experimental part

2.1. Samples

Seventeen different materials consisting of a polycarbonate (bisphenol A)/acrylonitrile–butadiene–styrene (PC/ABS) blend and different additives were investigated: PC/ABS with and without poly(tetrafluoroethylene) (PTFE), PC/ABS with bisphenol A bis(diphenyl phosphate) (BDP), PC/ABS + PTFE with resorcinol bis(diphenyl phosphate) (RDP) and BDP, PC/ABS + PTFE + 10 wt.% talc, PC/ABS + PTFE + BDP with several percentages of talc (2.5, 5, 10, 15, and 20 wt.%), PC/ABS + PTFE + RDP + 1 wt.% boehmite (AlO(OH)), PC/ABS + PTFE + BDP with 1 and 5 wt.% AlO(OH), PC/ABS + PTFE + 5 wt.% zinc borate, and PC/ABS + PTFE + BDP with 5 wt.% zinc borate. Aryl phosphates with 12.5 wt.% were added to each material. A PC:ABS ratio of 4.7:1 was maintained at all times. The samples were provided by Bayer Material Science AG (Dormagen, Germany). For polyamide 6 (PA 6), polyamide 66 (PA 66), 30 wt.% glass fibre reinforced PA 66 (PA 66-GF) and poly(vinyl chloride) (PVC) commercial products were used. Data for various polymers were taken from the literature [1,9].

2.2. Methods

A PCFC apparatus constructed by, and located at, the Federal Aviation Administration (FAA, USA) was used to investigate the multi-step decomposition, the influence of the residue, the propensity for screening and flammability assessment, and the combination of PCFC results with those from the bomb calorimeter and cone calorimeter. For the simulation of real fire scenarios a PCFC apparatus from FTT, UK was used at the

Federal Institute for Materials Research and Testing (BAM, Germany). The heating rate was $1\,^{\circ}\mathrm{C}\,\mathrm{s}^{-1}$, the maximum pyrolysis temperature was $750\,^{\circ}\mathrm{C}$ and the combustion temperature $900\,^{\circ}\mathrm{C}$. The flow was a mixture of O_2/N_2 $20/80\,\mathrm{cm}^3\,\mathrm{min}^{-1}$ and the sample weight was 5 ± 0.5 mg. In order to simulate real fire scenarios characterized by incomplete combustion, the combustion temperature was varied between 650 and $900\,^{\circ}\mathrm{C}$ and the oxygen concentration between 0.5% and 20%. Each measurement was performed at least twice and the results were averaged.

The thermal decomposition was investigated with thermogravimetry (TG) using a TGA/SDTA 851 (Mettler Toledo, Germany). All measurements were performed under nitrogen with a heating rate of $10\,^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$. The sample weight was 10 ± 0.5 mg. The standard deviation for the TG results was about 1 wt.% (including the contribution of bouyant forces).

A cone calorimeter (FTT, UK) was used to characterize the forced flaming behaviour according to ISO 5660. Different heat fluxes were used (35, 50, and $70\,\mathrm{kW/m}^2$) and the samples ($100\,\mathrm{m} \times 100\,\mathrm{m} \times 3\,\mathrm{m}$) were measured horizontally in a frame. All measurements were repeated and the results averaged. The flammability of the samples was determined by limiting oxygen index (LOI) measurements according to the International Standards Organization ISO 4589 (sample size: $80\,\mathrm{mm} \times 10\,\mathrm{mm} \times 4\,\mathrm{mm}$) and by the Underwriters Laboratory test for flammability of plastics (UL 94) according to IEC 60695-11-10. UL 94 classification for each material was measured for two thicknesses; the specimen sizes were $125\,\mathrm{mm} \times 13\,\mathrm{mm} \times 3\,\mathrm{mm}$ and $125\,\mathrm{m} \times 13\,\mathrm{m} \times 1.5\,\mathrm{m}$.

For bomb calorimeter measurements a C 5000 Control Calorimetry System (IKA, Germany) was used. The calorific values were determined according to DIN 51900-3 under adiabatic conditions.

Correlations were determined using the Pearson product moment correlation coefficient (PEARSON) [15]. PEARSON is used to measure the linear relationship between variables and is described in any introductory statistics text. It can range from -1 to $+1$. The value of PEARSON, either positive or negative, indicates the strength of the relationship between two variables.

3. Results and discussion

3.1. Multi-step decomposition

The major influence limiting the rate of heat release in the PCFC or in a fire is the thermal decomposition of the polymer, which releases volatile fuels, thus feeding the flame zone. The specific heat release rate, $q(\mathrm{W/g}) = h_c^0\,\mathrm{d}m/\mathrm{d}t$, depends on the mass loss rate $\mathrm{d}m/\mathrm{d}t$ (g/s), the effective heat of combustion of the volatiles $h_c^0(\mathrm{J/g})$, and the flaming combustion efficiency χ (dimensionless). In the PCFC the residence time, the oxygen concentration and combustion temperature in the combustion zone are chosen to ensure complete combustion ($\chi = 1$). The heat release capacity (HRC) is defined for a single-step thermal decomposition process [2]:

$$\mathrm{HRC} \equiv \frac{q_{\max}}{\beta} = \frac{(1-\mu)h_c^0}{eRT_{\max}^2/E_a} = \frac{\mathrm{HR}}{\Delta T_p} \qquad (1)$$

with β is the heating rate, μ the char yield, E_a the global activation energy for pyrolysis, $T_{\max}$ the sample temperature at maximum heat release rate $q_{\max}$, and ΔT_p is the pyrolysis temperature interval. Using HRC as the measure of fire risk is based on the reasonable assumption that the maximum specific heat release rate at the decomposition temperature reached at a constant heating rate correlates more or less directly with the mass loss rate during pyrolysis in a fire characterized by a transient temperature gradient.

Since constant heating rates are used in both the PCFC and TG methods, the heat release rate of the PCFC is related to the mass loss rate observed in TG measurements by the instantaneous heat of complete combustion of the pyrolysis products, $h_c^0 = \mathrm{HR}/(1-\mu)$. Fig. 2 shows four examples comparing the heat release rate measured in the PCFC with the mass loss rate measured by TG. Fig. 2a is the result for PA 6 for which both the mass loss rate in TG and the heat release rate in PCFC are similar and show a single-step thermal decomposition [16,17]. The temperature at the maximum heat release rate was shifted to higher temperatures because of the higher heating rate ($1\,^{\circ}\mathrm{C}\,\mathrm{s}^{-1}$ for PCFC versus $10\,^{\circ}\mathrm{C}\,\mathrm{min}^{-1}$ for TG). Even though the h_c^0 may be different for the individual pyrolysis products a rather constant characteristic value for the decomposition step was observed; thus PCFC delivered more or less the same information as the TG, but in the form of the heat release rate, which is the accepted measure for fire risks [18]. For systems having multiple decomposition steps, significant different characteristic h_c^0 values may be observed for the different decomposition steps. For poly(vinyl chloride) (PVC) the first peak of mass loss rate is much higher than the second peak, but for the heat release rate it is the other way round (Fig. 2b). This is because in the first decomposition step of PVC mainly HCl is released [19–22], providing a significant mass loss but no heat release due to oxidation. It should be noted that the comparison of mass loss rate and heat release rate for PVC especially illustrates the principle and advantage of the PCFC. For PC/ABS blends the mass loss rate and the heat release rate were characterized by two decomposition steps (Fig. 2c and d). A small, low temperature peak at 420–$440\,^{\circ}\mathrm{C}$ (TG) corresponds to the minor (ABS) component, while the larger high temperature peak at 500–$530\,^{\circ}\mathrm{C}$ (TG) corresponds to the major (PC) component of the investigated materials [23–25]. Both the TG mass loss rates and the heat release rates of the PC and ABS components overlapped but were well resolved, with peak separation that was even independent of the heating rate for part of the investigated materials (Fig. 2d)—suggesting that the PC and ABS components thermally decompose with similar kinetics and with limited interaction. Further, the similar ratios between the mass and heat release maxima for TG and PCFC data, respectively, indicates also similar h_c^0 for both decomposition processes.

For polymers that decompose in a single step such as PA 6 in Fig. 2a, the HRC is calculated according to Eq. (1), by simply dividing the peak heat release rate $q_{\max}$ by the heating rate. For multiple decomposition steps having q_1, q_2, etc., (Fig. 2b–d), it is not clear whether the largest peak/global maximum ($q_{\max}$) adequately describes the burning propensity of a material in terms of HRC. If the surface burning temperature
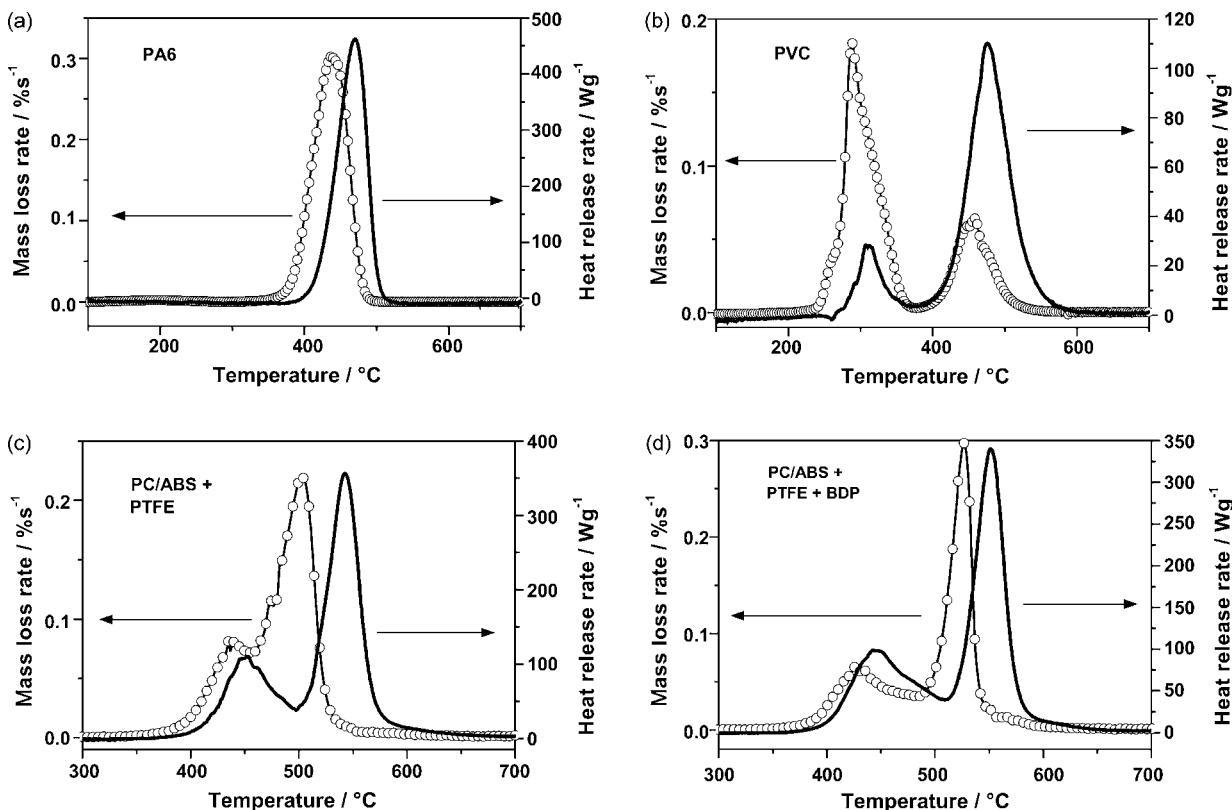
Fig. 2. Comparison between heat release rate and mass loss rate monitored with PCFC (thick line) and TG (open circles + thin line), respectively, for (a) PA 6, (b) PVC, (c) PC/ABS + PTFE, and (d) PC/ABS + PTFE + BDP.

corresponds to the highest pyrolysis temperature then the ABS and PC components decompose simultaneously in the pyrolysis zone, and some weighted average of q_i should be used to compute HRC for the multi-peak data rather than simply using the global maximum q_{max}. In the case of PC/ABS, where the pyrolysis products of both components have high fuel value, are probably evolved at the same time during burning, and are non-interacting, the HRC should correspond to a linear combination of the individual HRCs weighted for their mass fraction. If, m_i is the mass of component i in a sample of initial mass m_0, Q_i is its heat release rate (W), and $\phi_i = m_i/m_0$, is its mass fraction, then for a non-interacting two component mixture, e.g., PC/ABS, the mass-fraction–weighted-average HRC is obtained by summation:

$$\text{sumHRC} = \frac{\phi_1}{\beta}\frac{Q_1}{m_1} + \frac{\phi_2}{\beta}\frac{Q_2}{m_2} = \text{HRC}_1 + \text{HRC}_2 \qquad (2)$$

In the following, sumHRC is computed adding together the individual peak heights for PC and ABS according to Eq. (2). Recently, Lyon et al. proposed an alternative approach using a moment-averaged HRC (avgHRC) for multi-component and complex structured HRR curves. The avgHRC is defined as [26]:

$$\text{avgHRC} = \frac{\text{THR}}{\Delta T_p} = \frac{\text{THR}}{2\delta T} \qquad (3)$$

where δT is the standard deviation of T about the mean temperature in the test. Eq. (3) calculates a lower HRC than Eq. (2) but

it is less ambiguous because it is independent of the number of peaks selected for analysis.

It should be noted, that all three approaches, using the maximum HRC, the sumHRC, and the avgHRC, represent reasonable models depending on whether a particular performance of the material is controlled by the largest, a sum of, or the average of the individual contributions.

3.2. Screening PC/ABS materials based on PCFC

Table 1 lists PCFC results HRC_i, HR_i and sumHRC for the investigated PC/ABS materials. Fig. 3 illustrates the measures HR and HRC at the same time and the relationship between HR and HRC for the PC/ABS blends as well as various polymers. The difference between the homologous series of PC/ABS, for which similar material characteristics determine the data, and various polymers becomes obvious. For the homologous series with two decomposition steps, $\text{HR} = \text{HR}_1 + \text{HR}_2$, and together with Eqs. (1) and (2):

$$\text{sumHRC} = \text{HRC}_1 + \text{HRC}_2 = \frac{\text{HR}_1}{\Delta T_1} + \frac{\text{HR}_2}{\Delta T_2} = \frac{\text{HR}}{\Delta T_1}$$
$$-\text{HR}_2\left(\frac{1}{\Delta T_1} - \frac{1}{\Delta T_2}\right) \qquad (4)$$

Rearranging Eq. (4) gives the equation similar as for a line with intercept $\text{HRC}_2(\Delta T_2 - \Delta T_1)$ and slope ΔT_1:

$$\text{HR} = \text{HRC}_2(\Delta T_2 - \Delta T_1) + (\text{sumHRC})(\Delta T_1) \qquad (5)$$
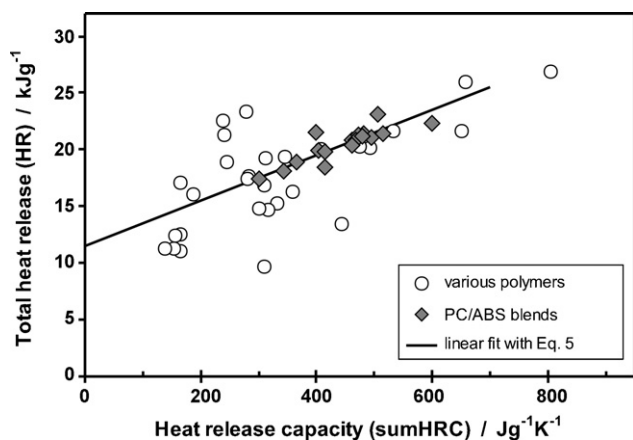
Fig. 3. Assessing materials using PCFC: total heat release (HR) plotted vs. heat release capacity (sumHRC). The line through PC/ABS data is Eq. (5) assuming constant values for HRC_2, ΔT_2, and ΔT_1.

Approximating HRC_2, ΔT_2, and ΔT_1 to be constant for the homologous series of PC/ABS, Eq. (5) becomes a linear equation and is plotted in Fig. 3 with $\Delta T_1 = 20$ K, $\Delta T_2 = 53.1$ K, $HRC_2 = 348.6$ J/(g K) determined through fitting Eq. (5) to the 17 PC/ABS samples in Table 1. Although HRC_2 obtained by the fitting procedure is close to the average value in Table 1 for this parameter, $HRC_2 = 326 \pm 67$ J/(g K), the pyrolysis temperature intervals differ somewhat from the average values calculated from the data in Table 1, $\Delta T_1 = HR_1/HRC_1 = 68 \pm 67$ K and $\Delta T_2 = HR_2/HRC_2 = 41 \pm 6$ K. For the various other polymers in Fig. 3 having single-step decomposition, $\Delta T_1 = 0$, and $sumHRC = HR_2/\Delta T_2 = HRC$.

The UL 94 results are shown in Fig. 4 plotted as the UL rating versus sumHRC and avgHRC. For all materials the UL 94 results for 3 and 1.5 mm thick samples were the same with

the exception of the PC/ABS + PTFE + RDP + 1 wt.% AlO(OH). For the latter material the thinner specimen showed a V-1 classification, whereas the thicker specimen a V-0, and thus PC/ABS + PTFE + RDP + 1 wt.% AlO(OH) is represented in Fig. 4 by two different points. The UL 94 was used since this flame test has probably been the most important and widely used measure for screening the flammability of polymeric materials. It is obvious from Fig. 4 that the UL 94 flame resistance is determined not only by the thermal combustion properties measured in the PCFC but also by factors such as the viscosity of the melt which determines dripping behaviour, thermal conductivity, specific heat and the specimen geometry. The UL 94 measures the resistance to sustained ignition by a small flame in a specific, well-defined scenario rather than measuring a material property. Despite this principle difference, in earlier studies Lyon et al. observed that HRC values between 200 and 400 J/(g K) correspond to the changeover from HB to V-0 results for polymers that thermally decompose in single-step [11]. Four empirical regimes were proposed [3]:

- HRC ≥ 400 J/(g K); no vertical rating in UL 94 vertical burn test and LOI < 25.
- HRC = 200–400 J/(g K); self-extinguishing in UL 94 test (V-2/V-1) and LOI = 25–30.
- HRC = 100–200 J/(g K); self-extinguishing in UL 94 test (V-0/5V) and LOI = 30–40.
- HRC ≤ 100 J/(g K); no ignition in UL 94 and LOI > 40.

Most recently Lyon reported two different empirical critical values for reaching flame extinction [12]:

- HRC < 250 J/(g K) for polymers and filled polymers.
- HRC < 480 J/(g K) for flame retarded polymers.

Table 1
PCFC results of the investigated PC/ABS materials with different additives (% = weight percent)

Compound	PCFC[a]							
	HRC_1 (J/(g K))	HR_1 (kJ/g)	HRC_2 (J/(g K))	HR_2 (kJ/g)	sumHRC (J/(g K))	avgHRC (J/(g K))	HR (kJ/g)	μ (g/g)
PC/ABS+								
–	113.5	7.8	381	15.3	507	249	23.1	0.188
PTFE	119.5	7.0	465.5	15.4	599	234	22.4	0.183
BDP	122.5	7.8	338	13.5	473	216	21.3	0.211
PTFE + BDP	119.5	7.9	397	13.7	516	195	21.4	0.206
PTFE + RDP	103.5	7.0	347	13.9	462.5	179	20.9	0.202
PTFE + BDP + 1% AlO(OH)	103.5	8.4	367	13.0	482	196	21.4	0.21
PTFE + RDP + 1% AlO(OH)	110.5	7.6	373	13.5	495	180	21.1	0.196
PTFE + BDP + 5% AlO(OH)	122.5	8.2	267	13.2	398.5	206	21.5	0.206
PTFE + 10% talc	134	7.9	324.5	12.9	468.5	264	20.8	0.249
PTFE + 2.5% talc + BDP	116	7.6	334.5	12.9	461	193	20.4	0.241
PTFE + 5% talc + BDP	108.5	7.7	285.5	12.2	403	191	19.9	0.259
PTFE + 10% talc + BDP	103	6.5	254	12.3	365.5	187	18.9	0.3
PTFE + 15% talc + BDP	113	6.8	222	11.3	343	188	18.1	0.340
PTFE + 20% talc + BDP	96	7.0	198.5	10.5	301.5	177	17.5	0.364
PTFE + 5% zinc borate	106	6.7	362.5	14.6	479.5	206	21.2	0.224
PTFE + BDP + 5% zinc borate	90.5	6.8	314.5	13.1	415.5	178	19.9	0.253
PTFE + BDP + 10% talc 5% zinc borate	91.5	7.5	314	10.9	415.5	159	18.4	0.317

The results for the two decomposition steps (HR_1, HR_2, HRC_1, and HRC_2) are added to obtain sumHRC and HR; avgHRC is calculated according Eq. (3).

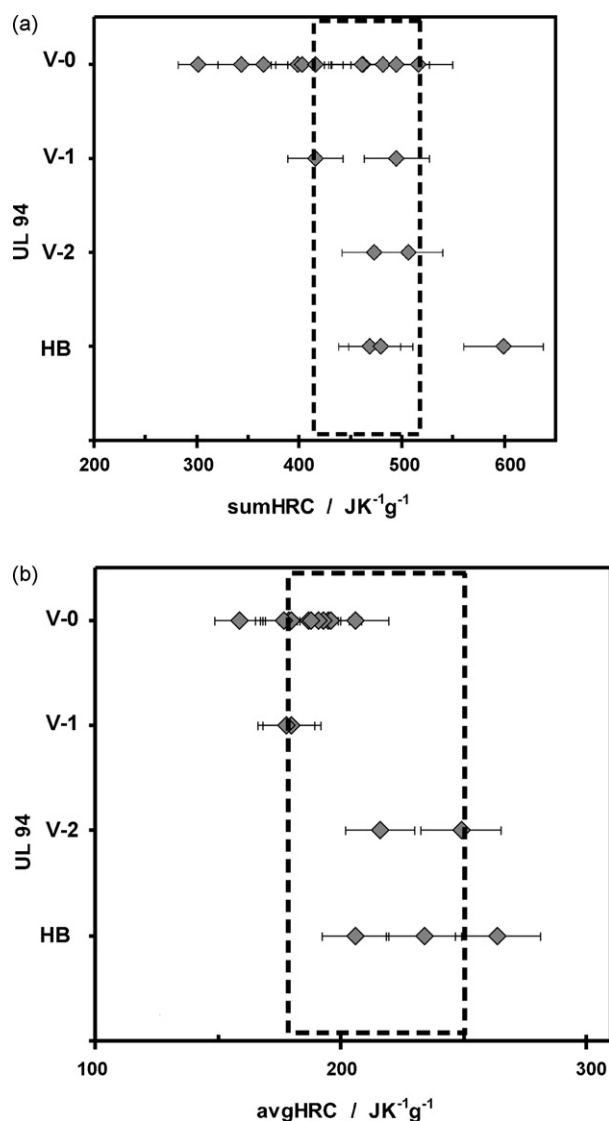[a] sumHRC shows errors of 3–10%; HR of 1–5%; μ of 1–10%.

Fig. 4. UL 94 classification for 1.5 and 3 mm thick specimen of the 17 materials plotted against (a) the sumHRC and (b) the avgHRC. The same mean error (6.5%) for all HRC data was indicated, even though the real deviations were between 3% and 10%. Apart from PC/ABS + PTFE + RDP + 1wt.%AlO(OH), the materials showed the same UL 94 classification for both thicknesses represented by one point. The dashed rectangle indicates the transition region between HB and V-0.

The broad range of HRC at extinction of FR polymers is due to the wide range of burning efficiency or incomplete pyrolysis/combustion resulting from extrinsic factors such as gas phase inhibition and condensed phase mass/heat transfer that are not measured in the PCFC. The need to account for the burning behaviour of polymers containing flame retardant additives *a priori* in order to correlate PCFC results with flame tests certainly reduces the utility of the PCFC as a screening device. In this study it was observed that:

- sumHRC(PC/ABS) $\geq$ 468 J/(g K); no vertical rating in UL 94 and LOI < 24.
- sumHRC(PC/ABS) = 473–507 J/(g K); V-2 self-extinguishing in UL 94 and LOI = 23–26.

- sumHRC(PC/ABS) = 415–495 J/(g K); V-1 self-extinguishing in UL 94 and LOI = 30–33.
- sumHRC(PC/ABS) = 301–516 J/(g K); V-0 self-extinguishing in UL 94 and LOI = 28–43.

The HRC regions corresponding to UL 94 results for the PC/ABS materials are in reasonable agreement with the results reported previously for a variety of polymers. A transition region between 415 and 516 J/(g K) was observed over which the materials changed from HB to V-0 classification (Fig. 4), which corresponds to the proposed value of 480 J/(g K) for flame retarded polymers. Analogous conclusions hold also for using the avgHRC in principle. However, especially with the avgHRC, for a crucial part of the investigated materials no unambiguous estimation of the UL 94 is possible. It is clear that sumHRC and avgHRC alone cannot predict flame extinction in the UL test scenario for this series of material behaviour.

Although the PCFC can measure equilibrium thermal combustion properties, the UL flame test is a scenario that is far from equilibrium and incomplete by nature, so only approximate agreement with PCFC test data is expected in the absence of more detailed analysis of the impact of physical and chemical phenomena on the critical condition at extinction. More than the half of the investigated materials were in the HRC region and it is not clear from the HRC results alone if the materials will get a V-0 or a HB classification. Indeed, the concept of describing a non-equilibrium process at criticality, such as flame extinction, using a single, equilibrium, thermal combustion property (e.g., char yield) has never been generally useful. This is particularly true in the present case where flame inhibition, dripping behaviour and/or barrier formation during a fire dramatically effect the results. Further, they were all near the transition between HB and V-0 and the deviations of and between those HRC results were in the same order of magnitude as the inaccuracy typical for the correlation between HRC and UL 94 classification. Thus for this set of materials no satisfactory assessment of the UL 94 performance is possible. It is concluded that for materials that are close to extinction, the PCFC data alone cannot distinguish between HB and V-0 rated materials with a high degree of certainty. Hence, the use of PCFC for predicting self-extinguishing behaviour of flame retarded materials requires an extremely (overly) conservative value of HRC because of the inherent uncertainty in the correlations.

3.3. Influence of residue, effective heat of combustion of the volatiles, and inert fillers

Van Krevelen described the relation between flame resistance and char yield [7,8]. He concluded that the LOI of a polymer (as an indicator of flame resistance) can be assessed on the char yield that is determined by the chemical structure of the polymer. For halogen-free polymers he proposed:

$$\text{LOI (volume percent O}_2) = 17.5 + 40\mu \qquad (6)$$

In Fig. 5 the LOI of the investigated PC/ABS materials and the correlation according to Eq. (6) is plotted against the residue.
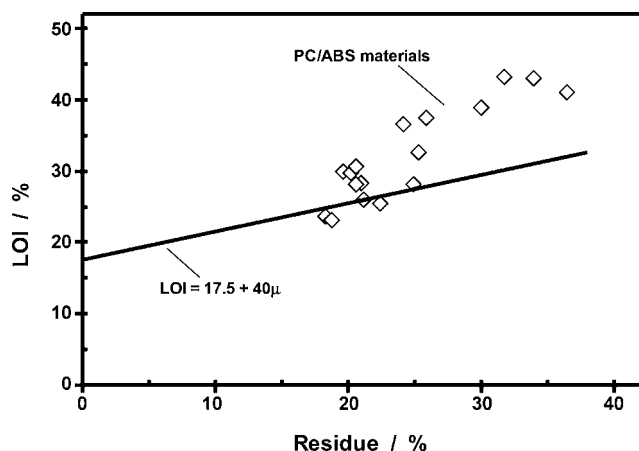
Fig. 5. Limiting oxygen index (LOI) of the investigated PC/ABS materials vs. residue (μ), compared to the relationship proposed by van Krevelen.

Fig. 6. (a) Total heat release (HR) and (b) heat release capacity (sumHRC and HRC, respectively) vs. residue (μ) for PC/ABS and various polymers. Solid lines were calculated for the PC/ABS blends using Eqs. (7) and (8) from the parameters reported in the text.

The larger the residue, the less fuel is available for burning so the higher the LOI should be is a reasonable assumption, but a significant scatter of the results and a significant deviation from the proposed linear relationship is observed. Actually, most of the PC/ABS materials, especially the blends with phosphorus containing flame retardants showed a better LOI than expected from Eq. (6). The strong influence of char is obvious but non-linear, suggesting that the LOI of the investigated PC/ABS materials is influenced by additional factors such as a gas and condensed phase burning efficiency that has been used to correlate PCFC and UL 94 results [12]. As with polymers containing halogen, the LOI of the investigated PC/ABS materials is determined at least in part by additional flame retardancy effects in the gas phase, consistent with the flame inhibition observed for these materials [23,27].

Fig. 6 shows HR and sumHRC plotted against the char fraction/residue of the investigated PC/ABS materials and various polymers. By definition HR is:

$$HR = (1 - \mu)h_c^0 = h_c^0 - \mu h_c^0 \tag{7}$$

A nearly perfect linear correlation (PEARSON = −0.96) is shown as the solid line in Fig. 6a for the PC/ABS materials which was calculated from Eq. (7) fitting an assumed constant value for h_c^0 (fitting result: $h_c^0 = 27.0$ kJ/g). The correlation between HR and μ for the other polymers in Fig. 6a (PEARSON = −0.42) is low because it depends on h_c^0 which varies widely for these polymers. A rather good linear correlation with μ is observed for sumHRC of the PC/ABS materials (PEARSON = −0.85) as expected from the rule-of-mixtures (Eq. (2)). Hence, Eq. (4) can be recast to describe the data in Fig. 6b by substituting Eq. (7) for HR:

$$sumHRC = \left\{ \frac{h_c^0}{\Delta T_1} - HR_2 \left(\frac{1}{\Delta T_1} - \frac{1}{\Delta T_2} \right) \right\} - \left\{ \frac{h_c^0}{\Delta T_1} \right\} \mu \tag{8}$$

The solid line in Fig. 6b is a plot of Eq. (8) using the previous fitting results, $h_c^0 = 27.0$ kJ/g, $\Delta T_1 = 20$ K, $\Delta T_2 = 53.1$ K, and $HRC_2 = 348.6$ J/g, for the PC/ABS blends in Table 1. Because
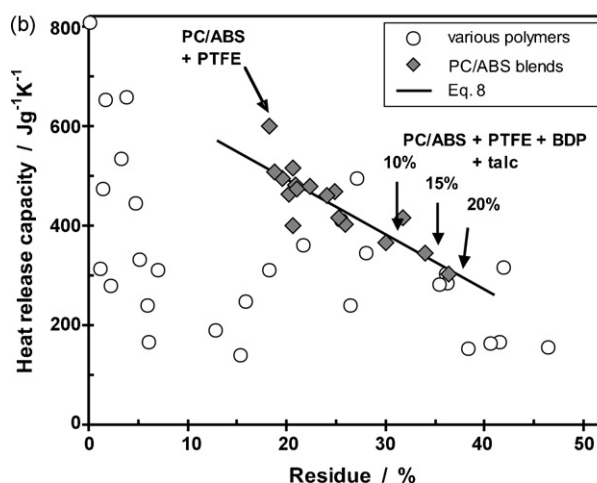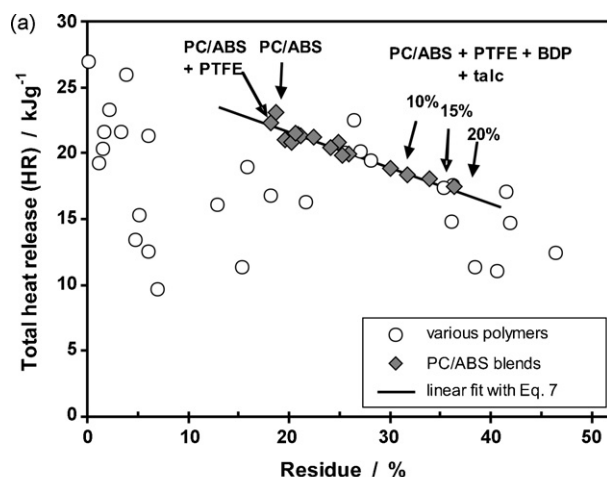
the individual h_c^0 and ΔT_i of the other polymers were not included in the PEARSON calculation there is no clear correlation using only the char yield (PEARSON = −0.51). The PCFC data are more consistent with respect to char yield for similar polymer systems that differ only in their additives and flame retardants and show rather the same effective heat of combustion of the volatiles and pyrolysis temperature intervals. A dominant influence of residue determines the PCFC results whenever it comes from charring polymer or inert filler. Effects in the gas phase such as flame inhibition and fuel dilution, which were seen clearly in the LOI results, are not measured in the PCFC.

The heat of complete combustion of the volatiles for all of the investigated PC/ABS materials is relatively constant (mean value of $h_c^0 = 27$ kJ/g, calculated using Eq. (7)) with a range of 26.1 kJ/g for PC/ABS + PTFE + RDP to 28.4 kJ/g for pure PC/ABS, amounting to only a modest deviation of < 8%. The PC/ABS materials with flame retardants containing phosphorus are between 26.1 and 27.4 kJ/g, amounting to a deviation of < 5% and indicating that h_c^0 is slightly reduced in comparison to the blends without flame retardants. As expected, flame inhi-

Table 2
Influence of glass fibre in PA 66 (HR, total heat release; HRC, heat release capacity)

Sample	Residue (%)	HR (kJ/g)	HRC (J/(g K))	LOI (%)
PA 66	0	26.4	562	23.3
PA 66-GF	29.3	18.6	372	21.5

bition due to phosphorus in the gas phase was not measured in the PCFC since h_c^0 are similar under the conditions of complete combustion in the PCFC for all materials. The minor difference in h_c^0 is probably due to fuel dilution effects by less combustible volatiles. This conclusion corresponds to the changes in pyrolysis products, especially the increase in CO_2 and decrease in C_xH_y reported for these materials [23,27]. The limited difference in h_c^0 is one reason why the PC/ABS materials are characterized by such a consistent and clear dependency on the char yield. For various polymers ranging in h_c^0 from 4 to 44 kJ/g [10,12] no clear correlation was found between μ and HR or HRC, as expected.

The PCFC does not distinguish between polymer charring and inert filler. The systematic set of PC/ABS + PTFE + BDP + talc materials with various talc contents (2.5, 5, 10, 15, and 20 wt.%) showed proportionality between μ and HR or HRC (Table 1 and Fig. 6). It seems irrelevant whether the residue consisted of carbon char or inert fillers, especially for the PCFC results. Analogous behaviour is known for another method on the mg-scale: thermogravimetry. The same influence of inert filler also exists in PCFC for well-known systems such as PA 66 and PA 66-GF. As seen in Table 2, PA 66 yields no residue, a HRC of 562 J/(g K), and a HR of 26.4 kJ/g. For PA 66 with 30% glass fibre (PA 66-GF), HR and HRC values around 30% lower are obtained. The corresponding HOC of the volatiles is unchanged. In contrast to the addition of talc in PC/ABS, which improves the PCFC results and flammability, adding glass fibre in PA 66 improves the PCFC results, but worsens flammability (LOI and UL 94). The LOI dropped from 23.3% to 21.5% for the investigated materials. This effect that in certain systems even high amounts of inert fillers such as glass fibres worsen such values as the LOI has been reported before, and is often explained by wicking effects [28,29]. In other words, LOI results are not only influenced by charring and flame inhibition as discussed before, but also by physical effects, especially changes in the melt viscosity [30]. Actual, LOI as well as UL 94 test are sensitive to reducing heat by melt flow and dripping. Isaacs [31] found that glass fibre up to a certain content increases the LOI of polycarbonate, but decreases it again at higher loadings; further, he observed that other inert fillers continually decrease the LOI of polycarbonate with increasing amount of loading. Camino and co-workers [32] showed that the addition of glass fibre to poly(butylene terephthalate) decreases the LOI and that the increase of glass fibre content approaches the value for the original polymer without glass fibre only gradually. It becomes clear that only polymer dilution by inert fillers in the condensed phase is taken into account in the PCFC, whereas in real fires physical effects such as wicking, barrier formation, and so on often exert the crucial impact of inert fillers

on fire behaviour. These physical effects are not covered by mg-scale methods such as PCFC. Thus, the realistic assessment of the fire behaviour by PCFC is strongly limited for filled polymers.

3.4. Correlation between PCFC results and other fire tests

Pearson product moment correlation coefficients (PEARSON) between PCFC results and results obtained from the cone calorimeter and LOI, respectively, are listed in Table 3. Two examples are illustrated in Fig. 7. The LOI plotted against the HR as measured by PCFC showed a good correlation (Fig. 7a). A decreased HR gives a higher LOI value and vice versa (PEARSON = −0.94). On the other hand, in Fig. 7b it is shown that the HR of the PCFC measurement was not correlated with the total heat evolved (THE) measured in the cone calorimeter at 70 kW/m^2 (PEARSON = 0.01). Correlating PCFC data with data
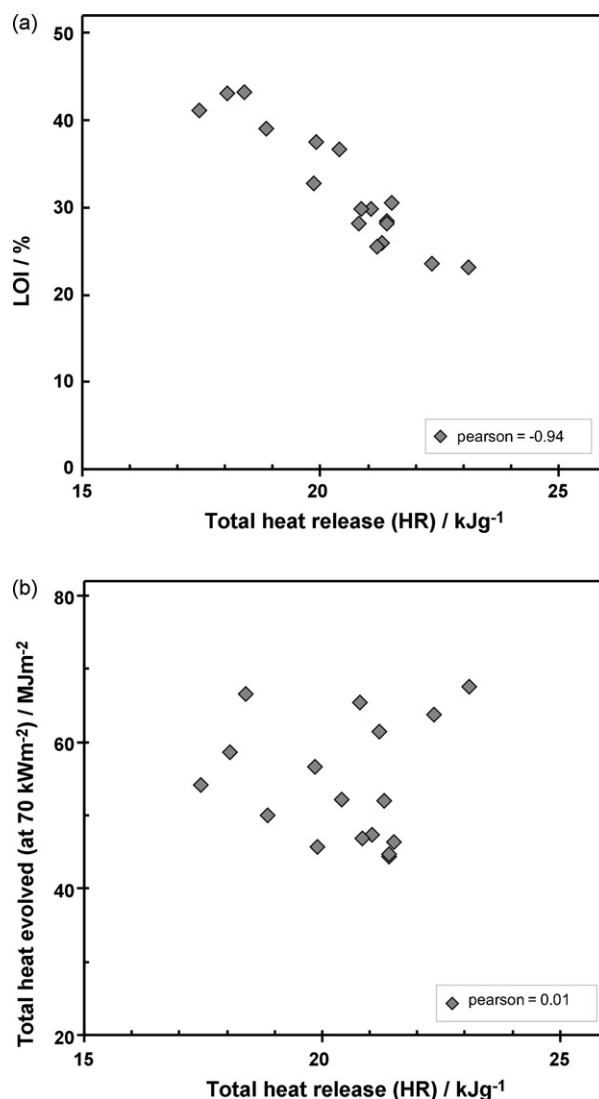

Fig. 7. Examples for (a) good correlation (PEARSON = −0.94) between total heat release HR (PCFC) and LOI and (b) no correlation (PEARSON = 0.01) between total heat release HR (PCFC) and the total heat evolved THE (cone calorimeter).

Table 3
Pearson correlations (T_d, decomposition temperature; HRC, heat release capacity; HR, total heat release; t_{ig}, time to ignition; THE, total heat evolved; pHRR, peak of heat release rate; ML, total mass loss)

Flammability		Cone calorimeter										
		t_{ig}	THE			pHRR			THE/ML			
PCFC	LOI	35 (kW/m²)	35 (kW/m²)	50 (kW/m²)	70 (kW/m²)	35 (kW/m²)	50 (kW/m²)	70 (kW/m²)	35 (kW/m²)	50 (kW/m²)	70 (kW/m²)	
T_{d1}	0.38	0.62	0.09	−0.02	0.10	−0.20	−0.18	−0.16	0.01	0.07	0.16	
T_{d2}	−0.07	−0.03	−0.37	−0.57	−0.64	0.05	−0.04	−0.24	−0.57	−0.59	−0.71	
HRC$_1$	−0.49	−0.26	0.47	0.19	0.02	0.30	0.31	0.58	−0.06	−0.06	−0.01	
HRC$_2$	−0.79	−0.28	0.11	0.15	0.13	0.61	0.69	0.64	0.22	−0.02	−0.02	
AvgHRC	−0.67	−0.34	0.69	0.47	0.44	0.64	0.60	0.84	0.37	0.32	0.44	
SumHRC	−0.82	−0.32	0.18	0.19	0.14	0.63	0.71	0.71	0.20	−0.02	0.02	
HR$_1$	−0.32	0.09	0.14	−0.06	−0.26	0.29	0.17	0.21	−0.31	−0.32	−0.35	
HR$_2$	−0.92	−0.51	0.37	0.15	0.11	0.77	0.76	0.75	0.22	−0.02	0.04	
HR	−0.94	−0.43	0.38	0.11	0.01	0.79	0.73	0.74	0.08	−0.13	−0.09	
Residue	−0.89	0.45	−0.19	0.06	0.17	−0.66	−0.62	−0.59	0.07	0.31	0.28	

from cone calorimeter and LOI, respectively, worked only for some measures. Reasonable correlations that showed PEARSON > 0.7 or < −0.7, respectively, were found for: HRC$_2$, HRC, HR$_2$, HR, and residue with the LOI; HRC, avgHRC, HR$_2$ and HR with peak HRR (pHRR) in the cone calorimeter. Comparing PCFC with cone calorimeter data at different external heat fluxes, however, resulted in rather no significant change. The absence of a correlation between HR (PCFC) and THE/ML (cone calorimeter) indicates that important fire retardancy mechanism, such as flame inhibition in the gas phase, are active in real fires but not in the complete combustion in the PCFC.

Correlations between PCFC results and LOI were always best for the added values (PEARSON = −0.49 for HRC$_1$, PEARSON = −0.79 for HRC$_2$, PEARSON = −0.67 for avgHRC and PEARSON = −0.82 for sumHRC; PERASON = −0.32 for HR$_1$, PEARSON = −0.92 for HR$_2$, and PEARSON = −0.94 for HR). Also the correlation between PCFC results and cone calorimeter seems to be better for the added values sumHRC and HR, even though the correlations between PCFC and cone calorimeter were less convincing. These results endorse the chosen approach for multi-step decomposition data.

The correlation between PCFC and LOI for the investigated PC/ABS materials increased in the sequence: avgHRC < sumHRC < residue < HR. Hence for the investigated set of materials the refined and extended HRC approach is, strictly speaking, less useful than the simple approach based on char yield. Further, just considering something like the overall fire load per mass gave the best assessment. The correlation between PCFC and pHRR in the cone calorimeter increased for the investigated PC/ABS materials in the sequence: residue < sumHRC = avgHRC < HR. As expected, the sumHRC approach is an improvement over considering only char yield. However, again the best correlation was obtained using the HR.

According to the literature [1,9], for various polymers it is possible to use the HRC determined by PCFC for an initial screening to assess fire behaviour such as the LOI (Fig. 8). The PEARSON for this data is only −0.56, but since a wide range of LOI and HRC is covered, the correlation still seems fairly reasonable. In contrast to considering various polymers, the different PC/ABS materials show a much better correlation (PEARSON = −0.82), but the HRC varied only slightly (Fig. 8). When the investigated systems are too similar (e.g., PC/ABS + PTFE + BDP compared to PC/ABS + PTFE + RDP) the differences in the results remain within the standard error. The data yielded by the PCFC provides a reasonable screening but less assistance than needed for precise prediction of the fire behaviour in a certain test. The latter limitation is highlighted by the investigated materials since rather large difference in LOI (22.7–43.2) occurred for a rather small difference in HRC (Fig. 8). Further, the data obtained for the investigated set of PC/ABS materials does not support the proposed dependency between LOI and HRC [9] elaborated for various polymers. This may be further evidence that assessing flame retarded polymers requires additional consideration in comparison to assessing pure polymers. While PCFC is a reasonable approach for measurements within the mg-scale with respect to characterizing the
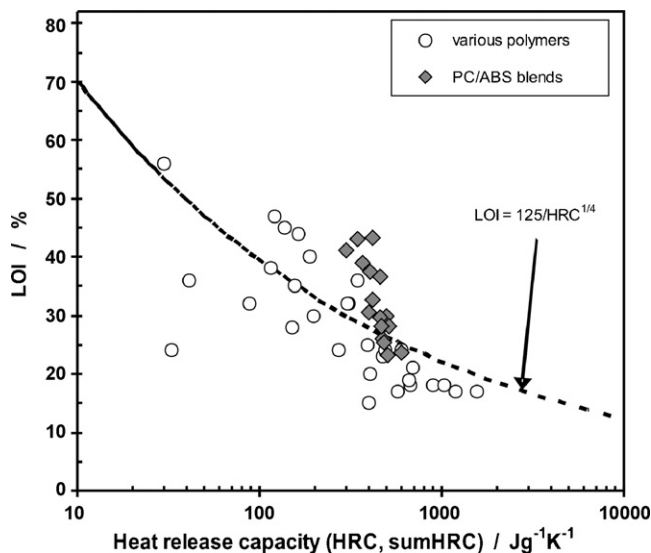
Fig. 8. Correlation between LOI and heat release capacity (sumHRC and HRC, respectively) for PC/ABS materials and various polymers. Trend for various polymers according to [1,8].

intrinsic fire hazard of a material, it cannot replace tests like LOI, UL 94 or the cone calorimeter.

3.5. Combining PCFC results with results of other methods

In Table 4 the heat of combustion determined by the bomb calorimeter (HOC_{bomb}) and HR from the PCFC are compared. Both values are normalized by the initial weight of the sample. Subtracting both values illustrated the operation principle of the PCFC. For the bomb calorimeter HOC_{bomb} is always higher than the corresponding HR in the PCFC because of the complete oxidation of the condensed phase of the polymer and the produced volatiles. Due to the experimental set-up of the PCFC, the polymer decomposition takes place under an inert atmosphere and only the volatile pyrolysis products are oxidised in the combustion zone. This simulates the burning of a polymer fairly realistically. Hence, the difference between HOC_{bomb} and HR measures the potential heat release remaining in the char/residue during a fire. This value is important in order to assess the effectiveness of a charring mechanism, but also for assessing the potential for afterglow. For the investigated PC/ABS materials it was about 10–11 kJ/g and very similar. The latter result indicates that the char yield due to the polymers did not vary much.

The data shown in Table 4 also illustrate another remarkable very important result. The char yield of these materials was between 0.183 and 0.259 (Table 1), but HOC_{bomb} − HR is around a third of HOC_{bomb}. Around 80% of the mass was released during decomposition, but HR was only around two-thirds of HOC_{bomb}. Thus, the heat of combustion of the char per unit mass of char was clearly higher than the effective heat of combustion of the volatiles. Actual, the effective heat of combustion of the chars was between 40.9 and 55.7 kJ/g. When the contribution of inert talc and zinc borate, respectively, was subtracted, the values were between 50.7 and 55.7 kJ/g. The effective heat of combustion of the volatiles was between 26.1 and 27.4 kJ/g as mentioned before. The char has a clearly higher effective heat of combustion than the neat PC/ABS material indicated by the HOC_{bomb}, the volatiles a slightly lower one. The carbon-rich or graphite-like character of the char became obvious as well as the dilution of fuel by volatiles such as CO_2. The difference between the effective heat of combustion of the volatiles and the char corresponds to the pyrolysis models for PC [23–25,27].

Real fires do not show complete combustion of the volatiles. Typically the pyrolysis products pass a fuel-rich zone above the material surface and a flame zone, where most of the oxidation occurs, towards a fuel-lean zone. The different zones are separated by the upper and lower flammability limits, respectively, and are clearly different not only with respect to fuel and oxygen concentration but also temperature. Depending on the time spent in the flame zone, different degrees of combustion are reached. The degree of combustion of a fire is characterized by the combustion efficiency χ. The combustion efficiency is always ≤ 1. A value of $\chi = 1$ means total oxidation of the volatiles. The corresponding heat release rate of steady burning is expressed analogous to Eq. (9) [9,10], which is also valid for steady burning in the cone calorimeter. Assuming that the gasification of fuel in the PCFC and in a fire occur under comparable conditions:

$$\text{HRR} = \chi \frac{h_c^0}{L_g} q_{net} = \chi \frac{h_c^0}{h_g}(q_{ext} - q_{surface} + q_{flame}) \tag{9a}$$

$$\text{HRR} = \frac{\text{HRC}}{\eta_g}(q_{ext} - q_{surface} + q_{flame}) \tag{9b}$$

with L_g is the heat (enthalpy) of gasification per unit mass of volatile fuel, h_g the $L_g (1 - \mu)$ is the heat of gasification per unit mass of solid, h_c^0 the heat of combustion of the fuel gases per unit mass of volatiles, q_{net} the net heat flux for steady flaming combustion with q_{ext} the external heat
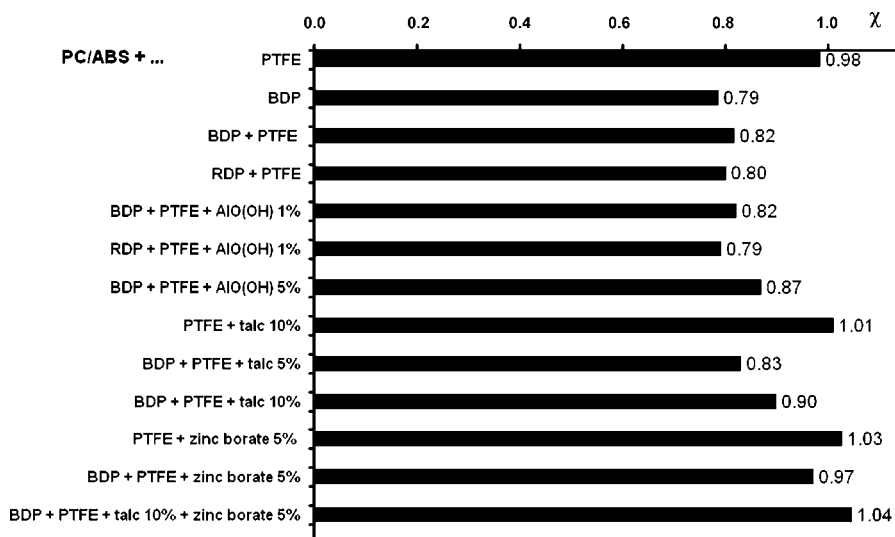
Table 4

Comparison between HR (± 0.3 kJ/g) from PCFC and HOC_{bomb} (± 0.03 kJ/g) from bomb calorimeter

PC/ABS + PTFE + $\cdots$	HOC_{bomb} (kJ/g)	HR (kJ/g)	HOC_{bomb} − HR (kJ/g)
–	32.56	22.4	10.2
RDP	31.80	20.9	10.9
BDP	32.13	21.4	10.7
BDP + talc (5%)	30.46	19.9	10.6
BDP + zinc borate (5%)	30.47	19.9	10.6

Fig. 9. Combustion efficiency (χ) of various PC/ABS materials.

flux, $q_{surface}$ the reradiation of the hot surface, and q_{flame} is the convective and radiative heat flux from the flame to the polymer surface. Eq. (9b) contains the normalizing parameter $\eta_g = h_g/\chi\Delta T_p \approx (2.5 \pm 1\,\text{kJ/g})(50 \pm 10\,\text{K})^{-1}/\chi = (50 \pm 20\,\text{J/}$ $(g\,\text{K}))/\chi$ [9] that relates HRC to HRR in flaming combustion where the flaming combustion efficiency is

$$\chi = \frac{\text{THE/ML}}{h_c^0} \tag{10}$$

The fraction of the effective heat of combustion of the volatiles (THE/ML) obtained from cone calorimeter and the heat of complete combustion of the volatiles (h_c^0) obtained from PCFC data equals the combustion efficiency χ of a specific material in the cone calorimeter. Determining χ enables a quantitative evaluation of the ventilation of a fire, but also of gas-phase mechanisms, such as flame inhibition. Values lower than one indicate a smaller flame caused, for example, by flame poisoning or cooling. A small χ is a sign for gas-phase mechanisms of flame retarding additives. For PC/ABS + PTFE $\chi = 0.98$ was obtained, meaning that almost all volatile pyrolysis products were completely oxidised in the cone calorimeter. This is in good accordance to the well-ventilated cone calorimeter fire scenario [33] and the absence of a flame inhibition effect. Similar results have been reported previously for the combustion efficiency of polymers in the cone calorimeter [34].

In Fig. 9 the combustion efficiencies of various PC/ABS materials are shown. For PC/ABS with phosphorus containing flame retardants active in the gas phase $\chi = 0.79$–0.82 was observed, confirming the described gas-phase mechanism of both organophosphates by flame poisoning [23,35]. For PC/ABS + PTFE and talc, or PC/ABS + PTFE + zinc borate, where no gas-phase mechanism occurred, values around one were found for χ. Some systems in which different additives were combined showed a significant antagonism in terms of flame inhibition and were characterized by χ between 0.8 and 1.

A condensed phase inhibition parameter θ has been proposed [12] that is analogous to the gas-phase combustion efficiency χ but accounts for the efficiency of heat transfer through the burning surface. Charring and swelling of the surface, whether intrinsic to the polymer or a consequence of flame retardant additives, reduces heat transfer and lowers θ. The product of the gas- and condensed-phase efficiencies $\chi\theta$ is the combined "burning efficiency" which, with Eq. (9b) and a critical heat release rate HRR* at flame extinction, lead to the following relationship between LOI and HR [12]:

$$\text{LOI} = \frac{h_g\text{HRR*}/b}{\chi\theta\,\text{HR}} + \frac{q_{surface}}{b} \tag{11a}$$

where b is the proportionality constant between flame heat flux and oxygen concentration. Assuming HRR* = 60 kW/m² and $b = 1.4\,\text{kW/m}^2$ [O₂], $h_g = 2\,\text{kJ/g}$, and $q_{surface} =$ critical heat flux for burning ≈ 15 kW/m² for PC/ABS [9,10,12], Eq. (11a) becomes:

$$\text{LOI}\,(\%\text{O}_2) = 11 + \frac{86\,\text{kJ} - \%\text{O}_2/\text{g}}{\chi\theta\,\text{HR}} \tag{11b}$$

Eq. (11b) can be solved for θ using HR, LOI and χ for the PC/ABS materials in Tables 4 and 5. Table 5 also contains the calculated heat transfer efficiency, that ranges from $\theta = 42\%$ to 16% over the range of LOI = 20–50.

Table 5
Flammability parameters for PC/ABS compounds

LOI (%)	HR (kJ/g)	χ	θ	$\chi\theta$
50	17	0.8	0.16	0.13
40	18	0.85	0.19	0.16
30	21	0.9	0.24	0.22
20	24	0.95	0.42	0.42

This parametric approach uses cone calorimeter data and LOI to estimate the efficacy of flame retardants in each of the gas (χ) and condensed (θ) phases. The data in Fig. 7a show good correlation (PEARSON $= -0.94$) between LOI and HR. A linear relationship between LOI and HR follows if the chain rule of calculus is applied to Eq. (11), with all other variables (x) held constant:

$$\left(\frac{\partial \, \text{LOI}}{\partial \, \text{HR}}\right)_x = \left(\frac{\partial \, \text{LOI}}{\partial \chi \theta}\right)_x \left(\frac{\partial \chi \theta}{\partial \, \text{HR}}\right)_x = \text{const.} \quad (12)$$

Linear fits of the data in Table 5 give slopes $(\partial \text{LOI}/\partial \chi \theta)_x = -99\% \, O_2$ and $(\partial \chi \theta/\partial \text{HR})_x = 0.04 \, \text{g/kJ}$, with good correlation ($R^2 = 0.96$ and 0.93, respectively). Substituting these slopes into Eq. (12), the best-fit line through the data in Fig. 7a should have a constant slope equal to $(\partial \text{LOI}/\partial \text{HR})_x = (-99)(0.04) = 4\% \, O_2/(\text{kJ/g})$, which agrees with the data.

3.6. Simulating fire scenarios

For PCFC measurements, with a definite gas flow and predetermined temperatures, a long time is spent by the pyrolysis products in a well-ventilated hot combustion zone and, similarly, the oxidizing conditions are always rather favourable. For fires and fire tests such as LOI, UL 94, and also cone calorimeter, the extension and temperature of the flame zone is dependent on the investigated polymer. The variation is observed for each polymer, even though the same external influencing variables are ensured, such as external heat flux, air flow and pilot flame. Apart from the external variables, the fire behaviour of the specimen crucially determines the fire scenario. The PCFC set-up is optimized so that complete oxidation of the pyrolysis products is always achieved, whereas for fire testing like cone calorimeter measurements more or less incomplete combustion occurs, especially in the case of flame poisoning. Therefore typical gas-phase actions are underestimated by PCFC, such as flame inhibition due to flame retardants containing halogen, but also due to the investigated organophosphates. The PCFC approach is reasonable with respect to its original task of identifying inherently flame retarded polymers, but, as discussed above, shows limitations in dealing with typically flame retardant polymers. In order to achieve incomplete oxidation in the PCFC and thus, hopefully, a more realistic assessment of fire scenarios, two approaches were performed: first, decreasing the combustion temperature and second, decreasing the oxygen concentration.

In Fig. 10a the heat release rates of PC/ABS + PTFE are shown for various combustion temperatures. With decreasing temperature, the pHRR and therefore the HRC were reduced for both decomposition steps, and HR was reduced as well. For both the decomposition of ABS and the decomposition of PC, this effect started at combustion temperatures below 750 °C and resulted from incomplete oxidation of the pyrolysis products. Nevertheless there were still two definite peaks, with maximum heat release rates at almost the same temperatures, independent of the combustion temperature. The ratio between the two maximum specific HHR values and the basic
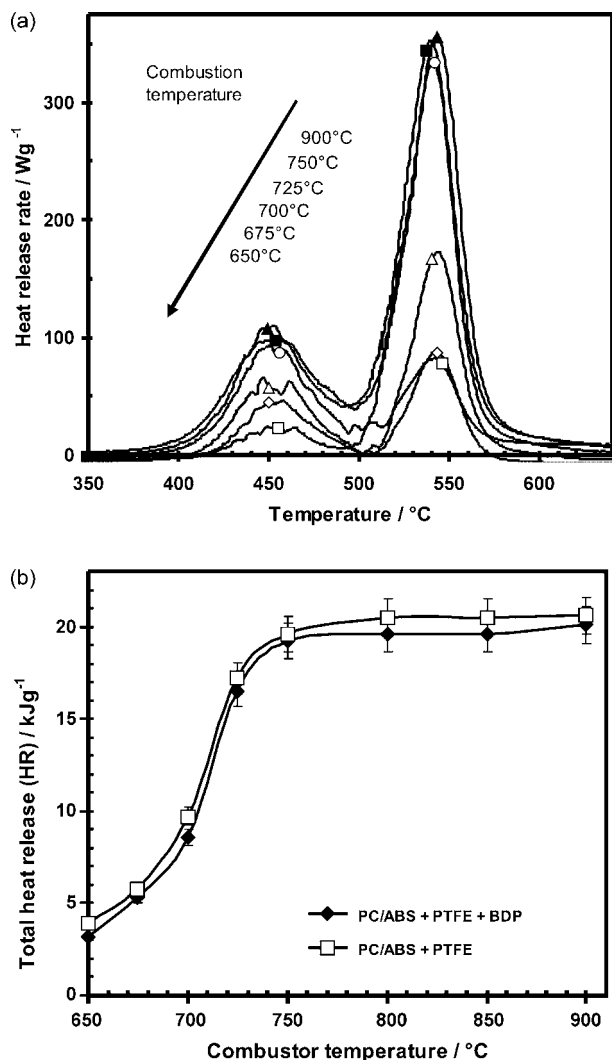

Fig. 10. (a) Heat release rate vs. temperature for PC/ABS + PTFE for various combustor temperatures (900 °C = filled triangle, 750 °C = filled squares, 725 °C = circles, 700 °C = open triangle, 675 °C = rhombi, 650 °C = open squares) and (b) total heat release (HR) vs. combustor temperature for PC/ABS + PTFE compared to PC/ABS + PTFE + BDP (average deviation of 5%).

shape remained constant. Varying the combustion temperature enables the combustion efficiency to be controlled and adjusted continuously between 1 and 0. Comparing PC/ABS + PTFE with the flame retarded system of PC/ABS + PTFE + BDP (Fig. 10b), the difference between both systems always remained equally small and within the expected variation. The gas-phase action of BDP did not become obvious for lower combustion temperatures. For the investigated materials, the combustion efficiency is still determined exclusively by the experimental set-up for each combustion temperature, not by the fire performance of the material.

In Fig. 11a the heat release rates of PC/ABS + PTFE are shown for various oxygen concentrations. With decreasing available oxygen the heat release rate and HR decreased due to incomplete combustion. The shape of the HRR curves and the ratio between the pHRR of ABS and PC was changed crucially.
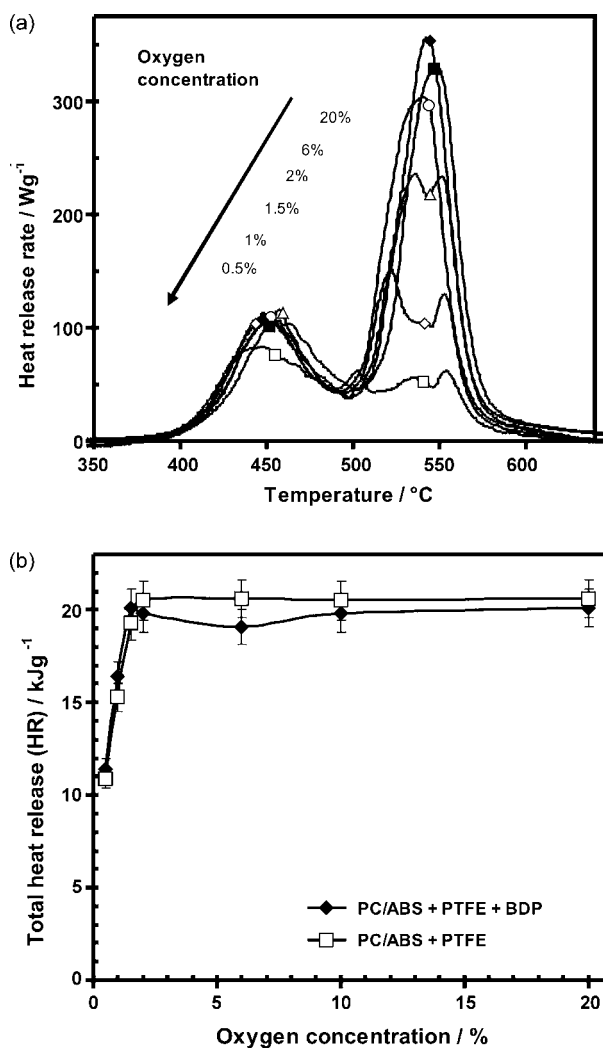
Fig. 11. (a) Heat release rate vs. temperature for PC/ABS + PTFE for various oxygen concentrations (20% = filled rhombi, 6% = filled squares, 2% = circles, 1.5% = triangle, 1% = open rhombi, 0.5% = open squares) and (b) total heat release vs. oxygen concentration for PC/ABS + PTFE compared to PC/ABS + PTFE + BDP (average deviation of 5%).

Above 1.0% oxygen, only the second decomposition step of PC was influenced. Above 1% the oxygen concentration was still high enough to oxidise all released decomposition products of ABS. For the larger mass loss rates of the pyrolysis products, incomplete oxidation occurred earlier, at about 6%, due to the decomposition of PC. For the small temperature (and therefore also time) interval of the release of PC pyrolysis products, there was not enough oxygen available for complete combustion. With decreasing oxygen concentration the maximum specific HRR was somehow cut off at a certain level determined by the oxygen concentration, and no longer by the mass loss rate. The HR decreased continuously below a threshold value. In Fig. 11b, PC/ABS + PTFE and PC/ABS + PTFE + BDP are compared again in terms of HR depending on oxygen concentration. For oxygen concentrations below 2% the HR for PC/ABS + PTFE was actually even lower than for the flame retarded blend. The gas-phase action of BDP became not observable for lower oxygen concentrations.

For each oxygen concentration, combustion efficiency is still determined crucially by the experimental set-up, not by the fire performance of the material.

Approaches that reduced the combustion temperature or the available oxygen resulted in incomplete combustion of the pyrolysis products, and thus simulate fires characterized by combustion efficiencies below one. However, a more realistic assessment of the fire behaviour was not reached for the investigated materials with respect to flame inhibition changing the combustion efficiency in real fires or fire tests. Considering the limited number of investigated materials, it remains so far unclear, if this is also a general conclusion.

4. Conclusions

The potential of PCFC as a tool to assess the fire behaviour of flame retarded PC/ABS materials was investigated. The investigated PC/ABS materials are typical flame retarded polymers, but also a specific and somehow strongly subjective one. Polymers or polymer blends with more than one decomposition step (like PC/ABS or PVC) need to be analysed with care. Actual, using the highest HRC, summing up the distinct HRC contributions as well as an averaged HRC were discussed. For the investigated PC/ABS materials that exhibit well resolved, two-step decomposition an upper bound rule-of-mixtures based on the mass fraction of the PC and ABS components was used successfully. In this approach the peak heights for both decomposition steps are simply added. Most probably, the rule-of-mixtures approach was effective because the PC and ABS components did not interact much during pyrolysis and combustion so their effects on thermal combustion properties measured in the PCFC were additive. Further, a relatively constant heat of combustion of the volatiles occurred. Hence, the results for HRC and HR are observed as consistent and simple functions of char yield for this homologous series of materials.

Of the various known effects of inert fillers, only polymer dilution in the condensed phase is considered by PCFC. The correlation of the PCFC results with data obtained for flammability and forced-flaming combustion were discussed. Reasonable correlations that showed PEARSON > 0.7 or < −0.7, respectively, were found for: HRC, HR, and residue with the LOI; sumHRC, avgHRC, and HR with pHRR in the cone calorimeter. It is concluded that sumHRC and HR values can be used for an initial screening in terms of intrinsic fire hazards of materials. Further, the performance in fire tests can be estimated, but identifying precisely the materials that pass or fail a specific test from the investigated set of materials with similar performance is clearly limited. Several effects determining the fire behaviour such as wicking, dripping, intumescence, etc. are not covered by mg-based methods such as PCFC. The PCFC screening performs better if materials that show large differences in char yield or effective heat of combustion of the pyrolysis gases are compared. The well-defined conditions of the combustion in the PCFC differ essentially from the ones of real fires and fire tests in which the fire behaviour of the specimen also crucially controls the fire scenario. The complete combustion used in the PCFC

rules out an assessment of the influence of flame inhibition in PC/ABS. Flame inhibition is not considered by PCFC. Combining the PCFC results with results from other methods enables a quantitative insight into the effectiveness of charring and flame inhibition and thus a better understanding of fire retardancy mechanisms. Attempts to simulate fire scenarios by varying the PCFC set-ups open the door to investigating incomplete combustion, and thus to simulate the characteristics of other fire tests. However, the influence of flame inhibition became not observable by these approaches.

Combining the quasi-equilibrium characteristics of thermogravimetry TG and oxygen bomb calorimetry makes PCFC a useful approach for investigating the fire behaviour of mg-samples. PCFC provides equilibrium thermal combustion properties that can be used to gain insight into forced (fire calorimetry) and unforced (flame resistance) flaming combustion. However, PCFC does not account for important physical effects occurring on larger scales, such as dripping, wicking, barrier formation, insulation and flame inhibition. Hence, neither PCFC nor any other mg-scale test method is suitable to replace flame and fire tests.

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