

QUANTIFYING THE COMBUSTION BEHAVIOR OF POLYMERS BY THE COMBUSTION EFFICIENCY WITH REGARD TO THE WEIGHTING OF FIRE LOADS

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Research article

Abstract: For assessing fire loads in industrial buildings it is essential to quantify the burning behavior of materials as accurate as adequate. There for the combustion efficiency is used. To determine the combustion efficiency required energies and energy rates can be measured via Cone Calorimeter. Exemplified by two polymers, polyethylene and polymethylmethacrylate, these parameters are determined and analyzed with regard to the calculation of the combustion efficiency.

Keywords: Combustion efficiency, heat release rate, Cone Calorimeter, fire load, polymers.

Introduction

For quantifying the burning behavior of materials the combustion efficiency is used. It is a dimensionless factor that describes the relation between the inherent energy of a material to the energy which is really set free from it in case of a fire. Consequently, the combustion efficiency varies from 0 (no combustion) to 1 (complete combustion).

Reckoning this factor is practically important for weighting fire loads in the context of preventive fire protection: especially in industrial buildings huge amounts of different materials are handled respectively stored which leads to accordingly high requests for preventive fire protection measures. The precise estimation of the measures required, and therefore the extent of energy really set free from the goods in stock in case of burning, is quite essential. Otherwise unnecessary expense might follow: for disproportionately high fire protection measures on the one hand and for the company's risk of a fire and its consequences on the other.

Materials and methods

The combustion efficiency can be determined via Cone Calorimeter by different methods. The following variants are distinguished (Hahn et al., 2013):

χ_{EHC}	combustion efficiency based on the effective heat of combustion (EHC) $\Delta h_{c,eff}$;
χ_{FL}	combustion efficiency based on the fuel load (FL) q ;
$\chi_{HRR,mean}$	combustion efficiency based on the average heat release rate (HRR) from ignition until the end of the test (for criteria see (ISO5660-1:2002)) \dot{Q}''_{mean} ;
$\chi_{HRR,180s}$	combustion efficiency based on the average heat release rate from ignition until three minutes after ignition \dot{Q}''_{180s} .

The combustion efficiencies are determined by combining the energy yields (EHC, FL) with the lower heating value (LHV) respectively by combining the heat release rates with the LHV and the average specific mass loss rate (ASMLR). The formulas for calculating the mentioned variants as well as a detailed survey of the necessary values for determining the combustion efficiencies are described in (Hahn et al., 2013). Beside the designated properties, many other values were determined via Cone Calorimeter, for example further mass loss properties or parameters concerning smoke and soot.

More information about the applied apparatus, its functionality and its capabilities is provided by (ISO5660-1:2002; Babrauskas, 2002). Here, it just should be noted that with the Cone Calorimeter, the most precise method to determine the HRR, the oxygen consumption calorimetry (Grellmann and Seidler, 2011), is used. It refers to the fact that in the

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burning process of organic materials the consume of 1 kg of oxygen typically results in almost the same amount of energy (13,1 MJ) which is set free (Thornton, 1917; Huggett 1980). Moreover, by referring to the HRR, the most important parameter for quantifying a fire (Babrauskas, 1992) is implemented.

In this case, polyethylene (PE) and polymethylmethacrylate (PMMA) were tested. Before commenting on the results, the main aspects concerning the combustion of melting polymers are considered below. From the physical point of view, the decomposition of melting materials is a phase change from solid via liquid to gaseous. In contrast to thermal stable liquids which “only” evaporate, i.e. whose molecules sustain and just a phase change takes place, polymers usually show an additional chemical deformation: long-chained molecules are divided into (miscellaneous) smaller molecules (Beyler and Hirschler, 2002). The chemical mechanism of decomposition for thermoplastics like PE and PMMA can be described as follows:

- decomposition of the main polymer chain, resulting in a decreasing molecular weight and formation of volatiles,
- differentiation between:
 - decomposition at the end of the chains, resulting in the formation of monomers (PMMA) and
 - decomposition at randomly selected points of the chain, resulting in the formation of monomers and oligomers (Beyler and Hirschler, 2002) as well as various other molecules (PE).

The melting temperature of polymers is, beside the molecular weight, affected by the sort and interaction of the chains. Concerning other factors influencing the melting point (Beyler and Hirschler, 2002) can be consulted. The same is true for the necessary activation energy. The effect of the humidity for both materials can be neglected as their hygroscopicity is marginal (Auer, 2013; Lehmann, 2001).

Using the Cone Calorimeter, polyethylene was tested in the form of granulate with a layer height of 20 and 40 mm as well as in the form of thin foil which was pressed and fixed by wire to a height of 21 mm. Further tests were conducted with blackened polymethylmethacrylate in the form of 18 mm thick plates. The surface area of each specimen was 10 cm to 10 cm. Beside the height and the sort of preparation of the material, the heat flux (HFX) with which the specimens were penetrated was varied (20, 35, 50 and 70 kW/m²). Each test has been repeated at least three times which led to a total amount of over 30 tests for melting plastics (for

further experiments see (Hahn et al., 2013)). In the following, the results of PE are analyzed. They are succeeded by the collected data and appraisal for PMMA.

Results and discussion

Factors of the combustion efficiency for polyethylene

The results measured for PE are presented in Tab. 1. Figure 1 illustrates two specimens before, while and after the penetration with 35 kW/m².



PE granulate, 20 mm, 35 kW/m²

PE foil, 21 mm, 35 kW/m²

Fig. 1 Polyethylene granulate and foil before, during and after the penetration via Cone Calorimeter (35 kW/m²)

Regarding the heat release rate, its maximum value \dot{Q}''_{peak} and the time of this maximum t_{peak} are specified in addition to the values already mentioned. Further on, the time to ignition is given with t_{ign} . It has to be noted that, due to the vast ignition time, the values measured at 20 kW/m² are not representative.

Tab. 1 Test results for polyethylene via Cone Calorimeter

Test	HFX	$\Delta h_{c,eff}$	q	\dot{Q}''_{180s}	\dot{Q}''_{mean}	\dot{Q}''_{peak}	t _{peak}	t _{ign}
	[kW/m ²]	[kJ/g]	[kJ/g]	[kW/m ²]	[kW/m ²]	[kW/m ²]	[s]	[s]
Specimen height 40 mm (except other mentioned)								
Granulate	20	43,0	27,9	134,7	251,1	335,3	1077	194
Granulate	35	42,3	41,7	200,9	427,8	692,4	1377	43
Granulate	50	42,3	41,7	272,9	587,3	1062,9	1013	21
Granulate	70	42,5	42,2	397,3	790,8	1300,0	785	10
Granulate, 20 mm	35	42,4	42,0	204,5	443,4	1071,1	620	40
Foil, 21 mm (4 tests)	35	43,0	42,2	147,9	624,8	1373,6	1115	73

From the energetic point of view, the nearly residual-free burning PE shows almost the same amounts for the effective heat of combustion and the fuel load. The slight difference of these values rises from the varying reference mass (mass before starting the test respectively burnt mass). Both determined energies are a little bit smaller than the LHV of PE (43,90 kJ/g (DIN18230-3:2002)). With regard to the preparation of the material the energy yields ($\Delta h_{c,eff}$ q) are similar.

As expected, the heat release rates increase with the HFX. For the first three minutes after ignition the HRR is lower than the mean value. This rises from the fact that in the beginning of the combustion more energy is spent for melting, until a steady state of the two phases is reached. The influence of the necessary energy for decomposition also can be seen regarding the HRR curve. The heat release rate rises first, then remains at a high level and finally has its maximum in the end of the burning period before steeply decreasing (see Fig. 2).

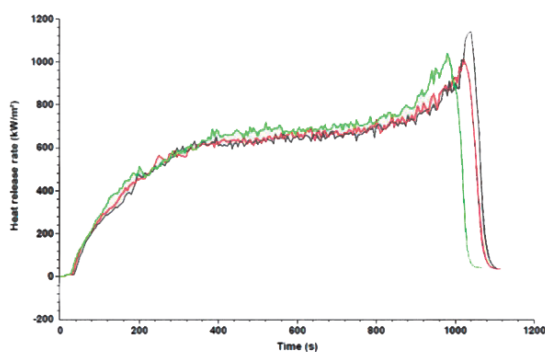


Fig. 2 Heat release rate of polyethylene granulate (Cone Calorimeter, 50 kW/m², 40 mm, 3 tests)

Comparing the measured heat release rates of 20 and 40 mm high specimens a further factor of influence becomes clear: the distance between the specimen's surface and the conical heater of the Cone Calorimeter (25 mm at the start of the test) increases with the combustion progressing. While

at an initially identical and then similar interval the time to ignition and the HRR \dot{Q}''_{180s} are almost the same, the mean heat release rate and its maximum are higher for the 20 mm specimens. Due to the melting and burning progress and the subsequent "slumping down" of the specimen the distance from the combustion zone to the heater for the 40 mm specimens is extensive in the end and causes a lower mean HRR (and ASMLR).

Qualitatively, the burning process of foil equals the one of the 40 mm granulate. The energy yields are comparable, too. The time to ignition instead is later and the HRR for the first three minutes is lower. This can result from the higher thermal inertia of the foil (especially higher density). Further on, the mean HRR and its peak are significantly greater than for granulate (at the same heat flux). Furthermore, the HRR is larger than for 20 mm granulate; a possible purpose are material-dependent modifications. It can be stated that for all PE specimens particularly the time for the energy transformation, i.e. the burning process, varies while the energy yields are equivalent.

To determine the combustion efficiency the measured energies and heat release rates are divided by the lower heating value respectively by the lower heating value and the ASMLR. Using formulas (5) to (8) (Hahn et al., 2013) the combustion efficiencies shown in Tab. 2 result. The literature gives values from 0,799 to 0,885 (Schneider and Schjerve, 2011). Due to the reasons already mentioned (insufficient specimen height/heat flux), the following analysis focusses on the tests conducted for 40 mm specimens and heat fluxes of minimum 35 kW/m².

Tab. 2 Combustion efficiencies for polyethylene

Test	HFX	χ_{EHC}	χ_{FL}	$\chi_{HRR,mean}$	$\chi_{HRR,180s}$
	[kW/m ²]	[-]	[-]	[-]	[-]
Specimen height 40 mm (except other mentioned)					
Granulate	20	0,98	0,64	0,91	0,49
Granulate	35	0,96	0,95	0,85	0,40
Granulate	50	0,96	0,95	0,84	0,39
Granulate	70	0,97	0,95	0,83	0,42
Granulate, 20 mm	35	0,97	0,96	0,68	0,31
Foil, 21 mm (4 tests)	35	0,98	0,96	0,76	0,18
Average granulate (35, 50, 70 kW/m ²)		0,96 (± 0,01)	0,95 (± 0,00)	0,84 (± 0,01)	0,40 (± 0,02)

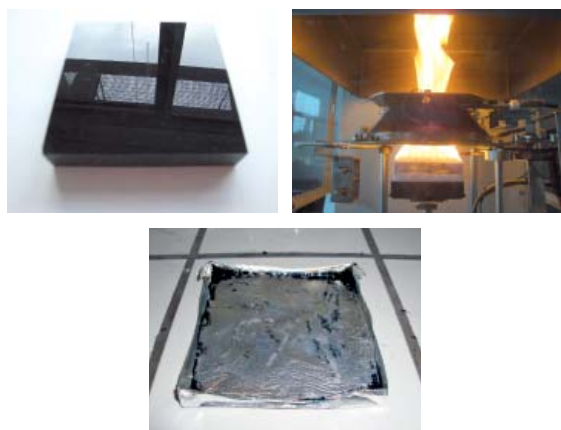
The combustion efficiencies based on the fuel load are a little bit lower than the ones based on the EHC, resulting from the different referencing mass, as already mentioned. As the combustion is almost residual-free they are still very similar. Due to the influence of the mass loss weighted ASMLR

(referring to the main burning period) the combustion efficiencies based on the mean HRR are smaller than the ones based on the energetic values. Caused by the high energy needed for the phase change especially in the beginning of the test, the HRR referring to the first three minutes after ignition and therefore the corresponding combustion efficiencies are lower.

Finally, it is apparent that each of the different methods of determining the combustion efficiency shows just small deviations. Especially comparing to tests with timber (Hahn et al., 2013) this becomes evident. It results from the fact that polyethylene, in contrast to timber which is built of various molecules, has a considerably homogenous composition and due to this a consistent burning behavior.

Factors of the combustion efficiency for polymethylmethacrylate

For further investigation, in the following the test results for polymethylmethacrylate are illustrated and analyzed. A specimen of PMMA before, during and after testing is shown in Fig. 3.



PMMA plate, 18 mm, 70 kW/m²

Fig. 3 Plate of polymethylmethacrylate (blackened) before, during and after the penetration via Cone Calorimeter (70 kW/m²)

Tab. 3 gives the results for plates of blackened PMMA conducted at varying heat fluxes. Again it has to be said that the tests at 20 kW/m² aren't characteristic due to the mentioned reasons.

From the energetic point of view the results are analogous to PE: for the practically residual-free burning polymer PMMA the fuel load equals the effective heat of combustion which is slightly smaller than the lower heating value (24,88 kJ/g (DiNenno, 2002)). As expected, the HRR rises with increasing HFX, too. Moreover, the HRR referring to the first three minutes after ignition again is less than the

mean value. The development of the HRR is similar to the one of PE but the plateau is more distinctive. It is related to a stronger rise in the beginning of the combustion and a slight slope (see Fig. 4).

Tab. 3 Test results for polymethylmethacrylate (blackened) via Cone Calorimeter

Test	HFX	$\Delta h_{c,eff}$	q	\dot{Q}''_{180s}	\dot{Q}''_{mean}	\dot{Q}''_{peak}	t _{peak}	t _{ign}
	[kW/m ²]	[kJ/g]	[kJ/g]	[kW/m ²]	[kW/m ²]	[kW/m ²]	[s]	[s]
Specimen height 18 mm								
Plate	20	25,2	25,2	242,3	379,0	497,9	1388	165
Plate	35	24,7	24,7	420,2	514,9	626,0	893	42
Plate	50	24,7	24,7	570,0	669,3	813,9	630	21
Plate	70	25,3	25,3	797,7	822,2	1067,1	427	12

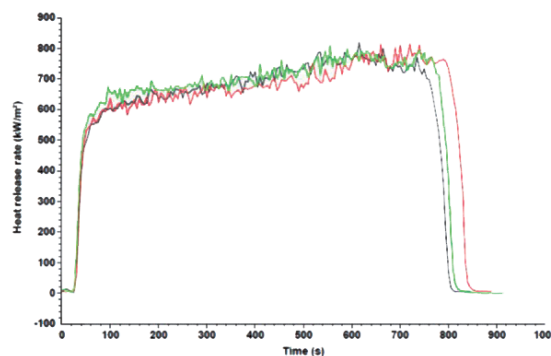


Fig. 4 Heat release rate of blackened polymethylmethacrylate plate (Cone Calorimeter, 50 kW/m², 18 mm, 3 tests)

The considerably more uniform combustion of PMMA results from its mechanism of decomposition: the monomer yield for the decomposition is amounted to 91 - 98 % (Beyler and Hirschler, 2002). Thus, PMMA burns steadier and it reaches earlier an equilibrium regarding the phase changes. In contrast, the monomer yield of PE is 0,03 % (Beyler and Hirschler, 2002); here, in consequence of the random chain scission up to 70 different molecules (mainly hydrogen carbonates) are built (Beyler and Hirschler, 2002). Accordingly for PMMA the HRR \dot{Q}''_{180s} is higher, the maximum HRR conspicuously lower and the mean HRR a bit greater than for PE. The times to ignition of the polymers are almost identical. Indeed PMMA has a higher density but its influence on the thermal inertia is compensated by lower values of the heat conductivity and the specific heat capacity. Again, with the heat flux mainly the HRR varies while the energetic values are equivalent.

For determining the combustion efficiency the measured energies and heat release rates are divided by the lower heating value respectively by the lower heating value and the ASMLR, too. Using

the formulas already mentioned, the combustion efficiencies shown in Tab. 4 result. Partly yields > 1 are calculated which can be explained by usually existing uncertainties. Stated for the reasons before, the average values again are determined for heat fluxes from 35 to 70 kW/m². The literature gives a combustion efficiency of 0,96 for PMMA (Schneider and Schjerve, 2011).

Tab. 4 Combustion efficiencies for polymethylmethacrylate (blackened)

Test	HFX [kW/m ²]	χ_{EHC} [-]	χ_{FL} [-]	$\chi_{HRR,mean}$ [-]	$\chi_{HRR,180s}$ [-]
Specimen height 18 mm					
Plate	20	±0±	±0±	0,94	0,60
Plate	35	0,99	0,99	0,94	0,77
Plate	50	0,99	0,99	0,94	0,80
Plate	70	±0±	±0±	0,89	0,86
Average plates (35, 50, 70 kW/m ²)		1,00 (± 0,02)	1,00 (± 0,01)	0,92 (± 0,03)	0,81 (± 0,05)

Due to the already stated residual-free combustion, the combustion efficiencies based on the energy yields (EHC, FL) are again identical and in this case lead to 1. Regarding the combustion efficiencies based on the HRR, similar to PE the one for the first three minutes after ignition is lower than the combustion efficiency $\chi_{HRR,mean}$. Besides, once more the combustion efficiency based on the mean HRR is lower than the ones related to the energy yields as it refers to the mass loss weighted ASMLR. Furthermore, the measured combustion efficiencies are higher than the referring yields for PE at all. Concerning the ones based on the energetic values this is affected by the thoroughly complete combustion. Using the HRR as a basis the considerably lower LHV of PMMA shows a greater impact than the higher values for the ASMLR and the HRR. The deviations of the variants are again smaller than the ones for wood.

Conclusion

It can be stated that the burning behavior of the two tested polymers is really similar. Due to their main property of melting and the resulting liquid like combustion this meets the expectations. As a criterion to differentiate and somehow to predict the development of the combustion respectively the heat release rate the monomer yield of the decomposition can be consulted. A high monomer yield thus leads to:

- a strong rise of the HRR in the beginning of the combustion until reaching a plateau, i.e. achieving the plateau quickly,

- a distinct plateau,
- a slight maximum in the end of the combustion and accordingly
- yields of \dot{Q}''_{180s} and \dot{Q}''_{peak} which are comparable to the mean HRR.

Of course, for assuring the conclusions further investigations have to be carried out.

Moreover, the results discussed approve the considerations for wood concerning (Hahn et al., 2013). Hence, the time to ignition has to be contemplated and its influence to be minimized by choosing the appropriate specimen height and heat flux. With regard to the heat flux tests with a penetration of more than 20 kW/m² have been proved as convenient. Again, it can be stated that the combustion efficiency referring to the average HRR of the first three minutes after ignition is less adequate for rating a fire. Nevertheless, this value can be helpful to give additional information about the beginning of the combustion process. Concerning the energy based combustion efficiency it can be reassured that the one based on the fuel load is more meaningful for weighting fire loads as it refers to the initial mass. Unburnt parts of a material are consequently incorporated and taken into account “positively”. The EHC-based combustion efficiency instead is related to the mass burnt and therefore gives rather information about the completeness of a combustion regarding the generated combustion products.

After having introduced the potential of the Cone Calorimeter for determining factors of the combustion efficiency, a comparison with tests on a larger scale has to be done. For this purpose a modified Single Burning Item test (EN13823:2010) is used. Furthermore, a comparison with tests conducted in real-scale (e.g. by Room Corner Test (ISO9705:1993)) is reasonable. As a result, dependencies, similarities and differences can be revealed and explained so that ideally the burning behavior of materials can be predicted from small-scale tests adequately accurate for the weighting of fire loads in industrial buildings.

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