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Effect of flow velocity, atmosphere and sample thickness on the mass loss rate of PMMA in the tube furnace

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Abstract. The experiments in this contribution have been conducted in an adapted tube furnace, a new gram scale experiment, based on the ISO 19700, in which an online mass loss measurement has been installed. The benefit of this set-up is that it allows to conduct gram-scale pyrolysis experiments under well-defined boundary conditions. In this set-up, samples with a length up to 50 cm can be investigated under different atmospheres and flow rates. In this contribution, the effect of several experiment parameters on the mass loss rate is studied. For this purpose, black cast PMMA samples were heated at a constant heating rate of 5 K/min. The atmosphere as well as the flow rate through the tube furnace were varied. Additionally, samples with different thicknesses were tested. It was observed that unless the sample auto-ignites, different flow rates do not result in differences in the mass loss rate. Nitrogen versus air atmosphere does make a significant difference on the mass loss rate. Under air atmosphere the PMMA reacts at lower temperature than under nitrogen atmosphere. The thicker the sample, the more the peak mass loss rate shifts to higher temperature and the lower the normalised peak mass loss rate.

1. Introduction

The ISO 19700 [1] describes the tube furnace, which is used for toxicity analysis. The general procedure is to insert a sample into a tubular oven at a continuous rate to reach a steady state burning condition. Previous work has described how a tube furnace, based on the ISO 19700, has been modified to accommodate for online mass loss measurements [2]. This adaptation offers the benefit of conducting gram-scale pyrolysis or burning tests under precisely defined boundary conditions. In contrast to other gram-scale experiments, such as the cone calorimeter [3], where factors like the flow field around the sample driven by uncontrolled natural convection are not accurately characterised or controlled. In the tube furnace, it is possible to vary both the atmosphere and the flow. The set-up is especially considered for studying electrical cables. The dimensions of the furnace allow conducting experiments on representative cable samples. Contrary to, for example, the thermogravimetric analyser (TGA), where mg-samples need to be taken from a cable.

In this contribution, the effect of different experiment parameters, like sample thickness, flow rate and atmosphere in the furnace, are examined. The results are compared to similar studies that have been performed in other milligram- and gram-scale experiment set-ups. For example, it has been demonstrated that in the cone calorimeter, a thicker sample results in a longer time to reach the peak heat release rate (HRR), a lower peak HRR value and a longer steady burning

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phase [4, 5]. From TGA data, it is known that the rate of thermal decomposition of PMMA is different under air than under nitrogen atmosphere. The onset of the main reaction peak as well as the maximum mass loss rate (MLR) is earlier under air atmosphere. While the main peak has a steeper fuel production rate under nitrogen atmosphere [6, 7]. Additionally, it has been shown that in the TGA, the flow rate of the carrier gas does not have a significant effect on the measured MLR [6, 7].

2. Material

For the tube furnace experiments, PMMA plates with a length of 50 cm and a width of 2 cm were used. Four different thicknesses of cast black PMMA (9H10 by Evonik) were purchased: 6 mm, 10 mm, 15 mm and 20 mm. TGA experiments were performed to ensure the similarity in thermal decomposition of all four samples. A Jupiter F3 TGA by Netzsch was used for the thermal analysis. From the plates, small discs with a diameter of 5 mm were manufactured. 8.5 mg of sample was tested at a heating rate of 5 K/min and 10 K/min. The results of the TGA tests are shown in figure 1.

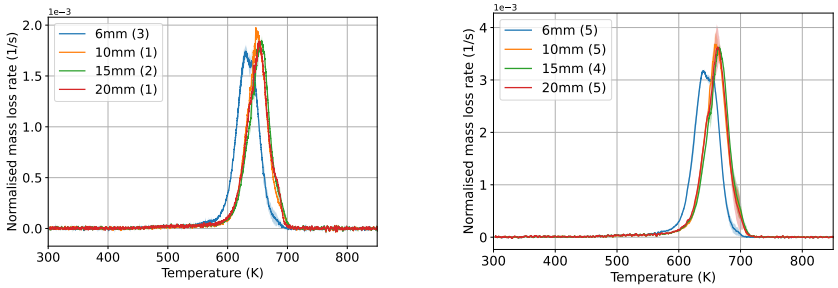

Figure 1: TGA results for the different samples at 5 K/min and 10 K/min, results are averaged, the amount of repetition experiments is shown in brackets. Shaded areas indicate two standard deviations.

It can be seen that discs prepared from 10 mm, 15 mm and 20 mm are in good agreement with each other, while the MLR of samples made out of 6 mm thick plates seem to deviate from the other. This could be due to a difference in composition of the material. This should be taken into account when comparing the different thicknesses in the tube furnace.

3. Experiment set-up

A more complete description of the adapted tube furnace can be found in [2]. A schematic image of the experiment set-up is shown in figure 2. The main part of the set-up consists of a tubular oven surrounding a quartz glass tube. The inner diameter of the tube is 90 mm and the length of the oven that is heated is 51 cm. For experiments at a constant heating rate, the sample is placed in a glass boat (a half tube with a diameter of 44 mm), which is positioned in the oven. To avoid the sample reacting with the quartz glass boat, the specimen boat is coated in a thin layer of boron-nitride spray. The glass boat is lying on a balance beam, which is used as a cantilever. The other side of the balance beam is resting on a Sartorius load cell (resolution: 1 mg). A counterweight is located on the balance beam above the load cell, to ensure contact between the load cell and the balance beam. The mass loss of the sample is determined by equating the momentum on both sides of the cantilever:

$$\Delta m_s g d_s = \Delta m_l c g d_{lc}, \tag{1}$$

where Δm_s is the mass loss of the sample, $\Delta m_l c$ is the mass loss measured by the load cell and d_s and d_{lc} are the distance between the sample respectively the load cell and the cantilever. Previous work [2], has validated the balance by comparing the mass loss rate of the balance with the CO_2 production rate, for $CaCO_3$ samples.

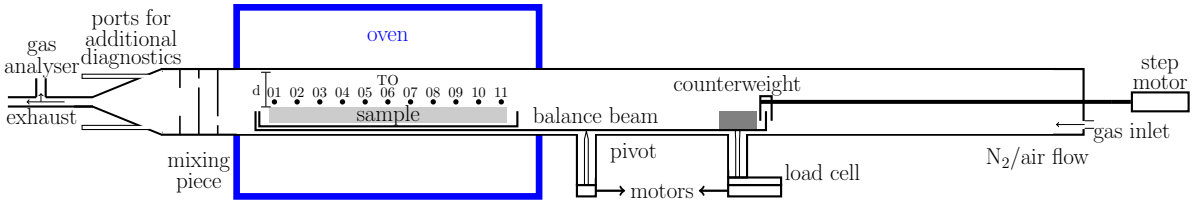

Figure 2: Schematic view of the experiment set-up, the numbered dots on the oven tube indicate the locations of the thermocouples on the outside of the glass tube, used to regulate the heating rate.

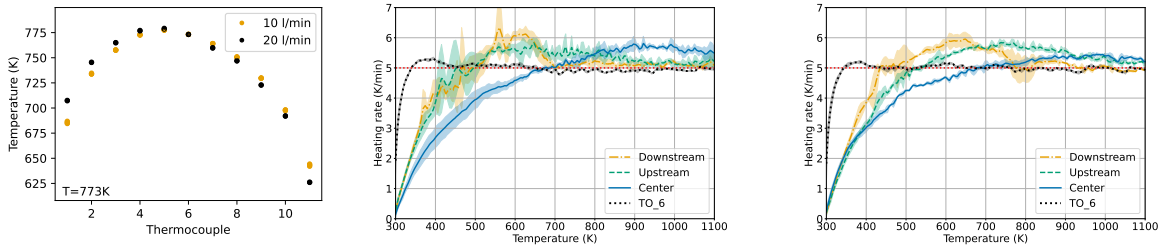

Figure 3: Left: Temperature distribution, measured at the outside of the tube, when the middle has reached 773K for 10 l/min and 20 l/min. Middle and right: heating rate at 1/4, 1/2 and 3/4 of the sample length for 10 l/min and 20 l/min.

In order to compensate for buoyancy effect in the oven upon heating, empty runs are conducted with the same flow rates as used during the experiments. The average mass loss of at least four empty runs are used to correct the experimental data. The composition and flow rates of the gasses injected into the tube (far upstream end of the tube) are controlled using mass flow controllers. This allows to inject mixtures of different gasses at different rates. In this contribution, pure nitrogen or pure air experiments are presented. Flow rates of 10 l/min and 20 l/min are tested.

Temperature measurements are done at several locations. For all experiments, 11 thermocouples are installed at the outside of the glass tube (at locations indicated with the dots in figure 2), measuring the outer surface temperature of the glass tube. A temperature gradient is present between the outer edges of the furnace, as can be seen in figure 3. For 10 l/min, the maximal temperature difference that is reached during heating is around 145 K, while for 20 l/min it is 165 K. The temperature gradient indicates that thermal equilibrium is not reached over the length of the furnace. The tube furnace power is controlled to achieve a heating rate of 5 K/min. The power versus time curve is manually optimised, based on the thermocouple in the middle at the outside of the oven (TO_06), to achieve the desired heating rate. A different power versus temperature curve has to be used for 10 l/min than for 20 l/min to ensure a heating rate of 5 K/min. Temperature measurements have also been conducted inside the oven, without sample, to characterise the heating rate inside the oven. Thermocouples are installed at the mid of the sample location and at a quarter both in the upstream and downstream direction. In figure 3, the heating rate as function of the temperature is displayed both for TO_06 and for the thermocouples installed inside the furnace. The result is the average of four (10 l/min), respectively three (20 l/min) different repetition experiments, an uncertainty of one standard deviation is indicated in the shaded area.

The heating rate at the inside of the tube needs longer before it reaches a stable value than the heating rate measured by the thermocouples on the outside. Nevertheless, PMMA does not react before 600 K, therefore this initial deviation can be neglected. The heating rate inside the tube furnace fluctuates more than on the outside and is very sensitive to the exact placement of the thermocouple. Therefore, the outer thermocouples are chosen to regulate the heating rate as those results are more reproducible. Nevertheless, there are no big deviations in heating rate

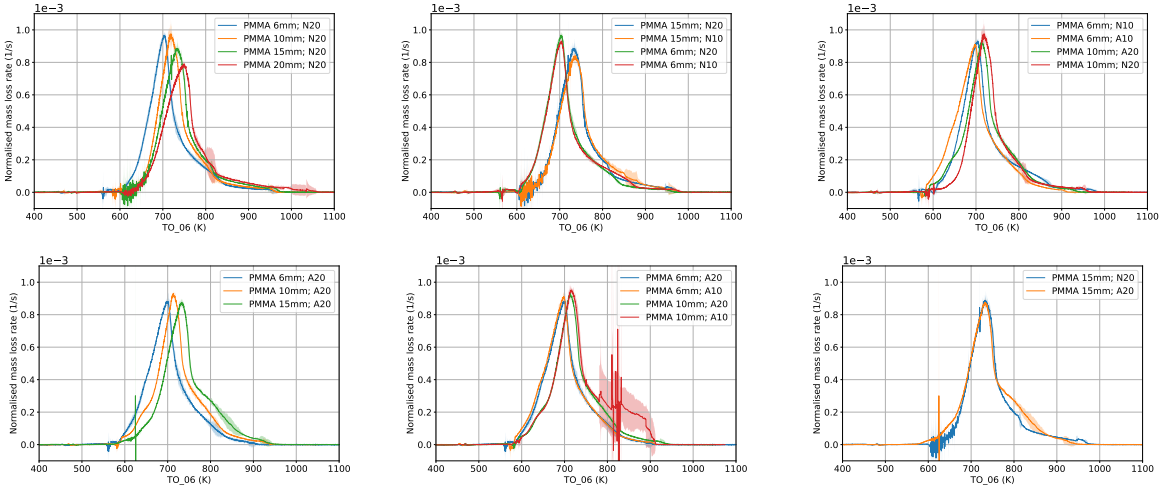

Figure 4: Normalised MLR as function of temperature. Left: for different sample thicknesses (top: nitrogen, bottom: air). Middle: for different flow rates of carrier gas, (top: nitrogen, bottom: air). Right: for different atmospheres (N-nitrogen, A-air), top: 6 mm and 10 mm thick, bottom: 15 mm thick.

between 10 l/min and 20 l/min.

4. Results

In table 1, an overview of the conducted experiments is shown with the number of repetitions for each experiment. Under air atmosphere, some of the experiments auto-ignite, which is also indicated in the table. At a flow rate of 10 l/min, the 10 mm, 15 mm and 20 mm thick plates ignite. The 10 mm thick samples only ignite near the end of the experiment, while the 15 mm and 20 mm samples ignite before the main MLR peak. After ignition, all the available oxygen is consumed. At a flow rate of 20 l/min, only the 20 mm thick plates ignite. The focus of this contribution is on pyrolysis. Therefore, the data obtained after ignition will not be studied in detail.

Table 1: The number of repetition experiments

Thickness/ Condition	6 mm	10 mm	15 mm	20 mm
Air (10 l/min), A10	3	5 (Ignition)	2 (Ignition)	1 (Ignition)
Air (20 l/min), A20	2	3	4	1 (Ignition)
Nitrogen (10 l/min), N10	2	3	2	3
Nitrogen (20 l/min), N20	4	2	2	2

None of the experiments left any residue in the sample boat.Figure 4 shows the normalised MLR of the PMMA samples for the different conditions. Normalisation was done using the total mass of the sample. The plots are smoothed with a 11-point running mean. All results are averaged over the repetitions of the experiments. The shaded area shows an uncertainty of two standard deviations, based on averaging.

At the start of the mass loss, all samples show a significant amount of noise in the MLR. It is observed that at this point, the sample starts reacting while making popping sounds. It is assumed that the popping sounds are small gas bubbles at the sample surface bursting, resulting in a short and sudden momentum on the scale. The mass loss rates of the samples that ignited are not included in the plots, except for the 10 mm thick samples as these only ignite after the main peak and therefore do not disturb the peak MLR readings. For the 10 mm thick plates, not all repetition experiments ignite at the same time.

Table 2 gives an overview of the onset temperature for the different experiment conditions. A mass loss of 1% of the total mass is taken as criteria for the onset temperature. Table 3 gives

an overview of the peak normalised MLR and the corresponding temperature. For the samples that ignited before the maximum MLR is reached, the peak values were not calculated. For both tables the results are averaged over the repetition experiments.

Table 2: Onset temperature (K)

Thickness/ Condition	6 mm	10 mm	15 mm	20 mm
Air (10 l/min)	597 ± 1	607 ± 2	607 ± 3	620 ± 0
Air (20 l/min)	599 ± 1	605 ± 3	606 ± 11	-
Nitrogen (10 l/min)	608 ± 9	631 ± 4	650 ± 2	653 ± 1
Nitrogen (20 l/min)	615 ± 1	625 ± 8	647 ± 0	651 ± 2

Table 3: Peak temperature (K) and peak normalised MLR (10^{-3} 1/s), separated by |

Sample	6 mm	10 mm	15 mm	20 mm
Air (10 l/min)	698±1|0.92±0.00	716±1|0.96±0.01	-	-
Air (20 l/min)	700±1|0.89±0.01	713±0|0.93±0.01	728±9|0.83±0.10	-
N2 (10 l/min)	704±1|0.93±0.00	720±2|0.96±0.02	730±6|0.85±0.01	750±2|0.76±0.01
N2 (20 l/min)	704±1|0.97±0.00	718±1|0.98±0.01	727±7|0.92±0.01	749±0|0.80±0.00

Since the width and length of the samples, remains the same, thicker samples are also heavier. As revealed by TGA data (see section 2), when comparing the effect of thickness, care should be taken with using the 6 mm samples. Therefore, only the 10 mm, 15 mm and 20 mm thick samples are taken into account, for studying the effect of varying sample thickness. Thicker samples have a lower maximal normalised MLR. The peak temperature and the onset temperature shifts to higher temperatures. For thicker samples two main effects might play a role. On one hand, thicker samples have a bigger thermal inertia, which would result in a less steep normalised MLR. On the other hand, the distance between the sample and the glass tube (d, see figure 2) is smaller for thicker samples, which would result in more radiation arriving at the sample surface. This would result in a steeper normalised MLR. Based on the normalised MLR shown in figure 4, the thermal inertia seems to play a much larger role than the increased radiation.

In order for the PMMA to ignite, a flammable mixture of pyrolysis products and oxygen is needed. This mixture depends on the flow rate and on the fuel mass flux of volatiles (i.e. the mass loss rate of the solid). In order to ignite, the flammable mixture needs to absorb sufficient energy. For thicker and therefore heavier samples, the absolute amount of volatiles released is larger. For smaller flow rates, more fuel gas accumulates above the sample, resulting in a higher chance for spontaneous ignition. Depending on the concentrations in the flammable mixture more energy is needed to ignite the mixture, this explains why the 10 mm thick plates only ignite at higher temperatures than the 15 mm and 20 mm thick plates. Many conditions influencing the ignition (like oxygen concentration, amount of volatiles gas (by changing sample size) and flow of the carrier gas) can be varied in the tube furnace. More experiments should be conducted to study the effect of the different parameters on ignition.

Under nitrogen atmosphere, a change in flow rate does not influence the MLR, taking into account the uncertainty. Under air atmosphere, the flow rate influences whether the sample ignites. However, for samples that do not ignite, the flow rate does not have a significant effect. These results are in line with the expectations based on flow rate studies in the TGA. Together with the flow rate, the heating power of the furnace is adapted to maintain the same heating rate. Therefore, different flow rates lead to similar heating conditions in the furnace, explaining the similarity in mass loss rates for different flow rates.

Under air atmosphere, PMMA has a lower onset and a slightly lower peak temperature than under nitrogen atmosphere. The normalised MLR is steeper under nitrogen atmosphere,

the peak MLR is similar under both atmospheres. These results are also in the same line as previous TGA results. The difference in MLR for different atmospheres seems to become smaller for thicker samples. However, since only a comparison between 10 mm and 15 mm can be made, the dataset is too limited to draw any conclusions.

5. Conclusion & outlook

In this paper, the influence of several experimental parameters on the MLR of PMMA in an adapted tube furnace was studied. The following points summarise the main conclusions.

- Thicker samples have a lower peak normalised MLR and higher onset and peak temperature. This indicates that the thermal inertia of the samples plays an important role on predicting pyrolysis parameters like maximum MLR or onset temperature.
- The flow rate of air influences whether the sample ignites or not. For non-igniting samples, the flow rate does not have a significant effect.
- When comparing experiments under nitrogen or under air atmosphere, similar effects as in the TGA were found. PMMA starts reacting sooner under air atmosphere than under nitrogen atmosphere.

Further experiments should be considered addressing the effect of different geometries for samples with a constant mass. As well as experiments to further characterise the effect of the convective versus the radiative heating in the tube furnace. As a next step, a methodology should be developed to determine fire spread relevant parameters from the tube furnace data. This would allow to estimate whether the studied experimental parameters have an effect on the relevant parameters for fire spread modelling.

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