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Original Scientific Paper

TESTING FIRE PROPERTIES OF PMMA IN MASS LOSS CALORIMETER COUPLED WITH FTIR GAS ANALYZER

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Abstract. *In this study, PMMA samples were exposed to four irradiation levels: 20, 30, 40 and 50 kW/m^2. Experiments were performed in a custom-made installation comprising mass loss calorimeter, extraction system, and effluent analysis system with FTIR spectrometer. The aim of the study was twofold: to check the suitability of custom-made installation for testing flammability and combustion behavior characteristics of polymers and to compare the obtained results with literature findings. Measured and deducted fire properties (critical heat flux, ignition temperature, and heat of gasification), as well as effluent emissions during the combustion phase, were in good agreement with literature results.*

Key words: *PMMA, mass loss calorimeter, ISO 13927, FTIR, flammability parameters, effluents*

1. INTRODUCTION

When assessing fire hazards in enclosures, one of the very first steps is the estimation of fire load. All the combustible furnishings and content brought into the buildings, including the building construction materials, contribute to fire load and consequently alleviate the fire hazard in buildings. While combustible building construction materials are fairly well regulated, paradoxically this is not the case for items that are brought into the building (e.g. furnishings). A great deal of these brought-in goods is based on plastics. This requires a thorough investigation of the flammability and combustibility characteristics of plastic materials. While most of the plastic materials look relatively similar, the thermal decomposition of these materials doesn't follow a unique route. Generalizations are not possible and each polymer class requires separate analysis.

In this study combustibility and flammability studies of PMMA (methyl methacrylate, also known as acrylic, acrylic glass, perspex, or plexiglass) [1] samples were conducted.

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PMMA belongs to the group of most "popular" material in the fire research community. There are several reasons for this. PMMA is amorphous material without a distinct melting point and atypical thermal decomposition. Additionally, during the PMMA combustion, there is no dipping and just gas phase (monomers) evolve [2].

A number of studies in fire research were performed regarding the PMMA. Hopkins and Quintiere [3] developed a testing protocol that leads to the prediction of ignition and burning rate for thermoplastics from cone calorimeter data. The protocol was validated using the own experimental data for nylon 6/6, polyethylene, polypropylene, and black polycast PMMA. Experiments were performed in cone heater apparatus. Luche et al. [4] determined the number of thermal, flammability, and combustibility characteristics from experimental data generated during the thermal degradation of black PMMA in cone calorimeter in the air with piloted ignition. Additionally, the authors performed a thorough analysis of effluents using FTIR spectroscopy and NDIR using specially designed installation and calculated yields for dominant gases in the flue stream. Pizzo et al. [5] performed a steady and transient pyrolysis study of thick clear PMMA slabs for incident heat fluxes of 14 and 18 kW/m^2. Chen et al. [6] studied thermal degradation, kinetics, and thermodynamics characteristics of micron-sized PMMA using thermogravimetry. Similarly, Korobeinichev et al. conducted a kinetic analysis of thermal decomposition of PMMA under different heating rates [7]. Asante-Okyere et al. applied generalized regression and feed-forward back propagation neural networks in modeling flammability characteristics of PMMA [8].

The objective of this work was twofold. First to check the suitability of custom-made installation for testing flammability and combustion behavior characteristics of polymers and second to compare the obtained results with literature findings.

2. MATERIALS AND METHODS

In this study, black extruded PMMA samples were used. PMMA board with a thickness of 3 mm was procured from Tuplex [9]. Board was sawn on pieces with a dimension of 10cm x 10cm. The average initial mass of specimens was 37.4 g. Before testing, samples were wrapped with thin Al foil following the guidelines from ISO 13927 [10]. According to the retailer, the PMMA board procured didn't contain any flame retardants. Elementary analysis and size exclusion chromatography was not performed, hence PMMA elemental composition data, from the literature [11] are provided for reference in Table 1:

Table 1 Typical composition of PMMA [11]

Elements	Composition (wt%)
Carbon	59.7
Oxygen	32.3
Hydrogen	8.0

Combustion tests were conducted on mass loss calorimeter (with chimney and thermopile) produced by Fire Testing Technology, UK. Experiments were performed according to ISO 13927 [10]. Mass loss calorimeter was placed in custom-made fume hood assembly, shown in Fig 1. The extraction system (pipes, fan, sampling probe) was constructed according to ISO 5660 [12]. Samples were exposed to four heat fluxes levels: 20, 30, 40, and 50 kW/m^2. Before the experiments, appropriate calibrations of the thermopile system with methane burner were

performed. Volumetric flow in the extraction system was set at 0.024 m^3/s, according to the recommendation from ISO 5660 [12].

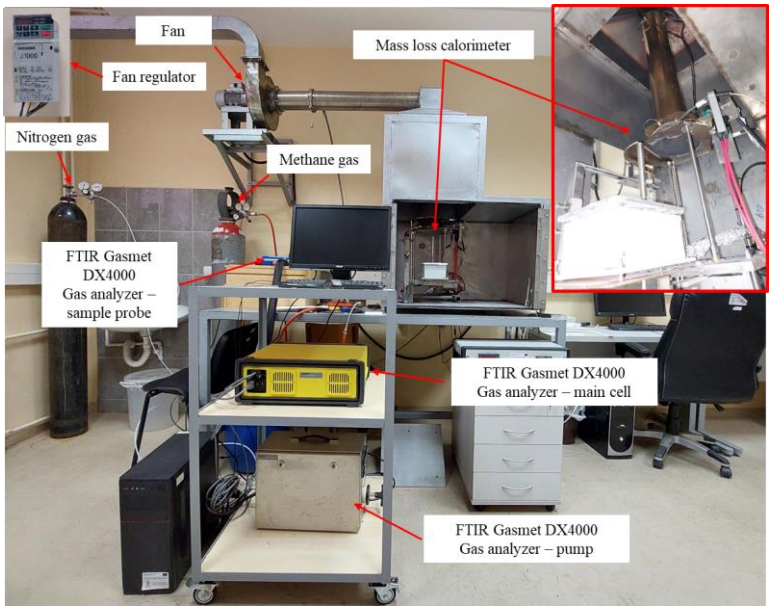

Fig. 1 Custom made assembly: mass loss calorimeter, extraction fume hood assembly, and FTIR gas analysis system

Experiments were performed with piloted ignition. Generally, critical heat fluxes with piloted ignition tend to be lower than fluxes with unpiloted ignition. Hence, for fire hazard assessment it is conservative to use the lower values. Each test was repeated three times and average values are reported.

Fire effluents emitted during the combustion experiments were cautiously and simultaneously measured with an FTIR spectrometer, Gasmet, Finland. A sampling probe, constructed according to ISO/TS 21397 was used for effluents sampling from the extraction system [13]. Sampled gases were transported to FTIR gas cell through a heated PTFE sampling line conditioned at 180^0 C. Spectrometer characteristics are provided in Table 2.

Table 2 Main characteristics of FTIR spectrometer

Spectrometer	Interferometer: Gasmet Technologies Oy's GICCOR interferometer Resolution: 8 cm^{-1} Scan frequency: 10 spectra/second Aperture: 1'' Detector: Thermo-electrically cooled mercury cadmium telluride (MCT) detector IR source: Ceramic (SiC), at 1550 K temperature Beam splitter: ZnSe Optical window material: ZnSe Wavenumber range: 900 – 4200 cm^{-1} with ZnSe/MCTP

Following 16 gases were continually measured: Water vapor (H_2O), Carbon dioxide (CO_2), Carbon monoxide (CO), Nitrous oxide (N_2O), Nitrogen monoxide (NO), Nitrogen dioxide (NO_2), Sulfur dioxide (SO_2), Ammonia (NH_3), Hydrogen chloride (HCl), Hydrogen fluoride (HF), Methane (CH_4), Ethane (C_2H_6), Ethylene (C_2H_4), Propane (C_3H_8), n-Hexane (C_6H_{14}) and Formaldehyde (CHOH). According to producer information, Gasmet's FTIR analyzers do not need any span or re-calibrations after the initial factory calibration. Gas sampling was performed on a 3 s interval which is theoretical minimum, regarding the technical limitations of the instrument. Gases evolved during the combustion flow through the extraction system and after that through the PTFE tube up to the spectrometer. Hence, there was a certain time delay between the moment when the gases evolve in the mass loss calorimeter until the moment when fluid stream screening was made. That time delay, the inertia of the hyphenated mass loss calorimeter - FTIR effluents measuring system, was determined before the experiments. Appropriate adjustments were made to temporarily align the data from the mass loss calorimeter and FTIR instrument.

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Results regarding the flammability characteristics

During polymer specimens exposure to external heat fluxes two distinctive phases can be delineated [14]:

- Pre-heating to ignition phase and
- Flaming burning phase.

3.1.1. Pre-heating to ignition phase

Rhodes and Quintiere [14] proposed an integral transient burning model for obtaining the approximate solution to the non-linear ignition. Detailed derivation procedure is omitted but two chief equations are presented below:

$$t_{ig} = \frac{2}{3}(k\rho c)\frac{(T_{ig} - T_o)^2}{(\dot{q}'')^2} \tag{1}$$

and

$$\dot{q}'' = \frac{1}{\varepsilon}[h_c(T_{ig} - T_o) + \varepsilon\sigma T_{ig}^4] \tag{2}$$

where: t_{ig} - is time to ignition; k - is material thermal conductivity; ρ - is material density; c - is material specific heat; h_c - is heat transfer coefficient; T_o - is ambient temperature; ε - is emissivity; σ - is Stefan Boltzmann constant and T_{ig} - is ignition temperature.

Combining these equations, an elegant form of ignition temperature t_{ig} formula evolves [4]:

$$\frac{1}{\sqrt{t_{ig}}} = \left[\frac{\varepsilon}{\sqrt{\left(\frac{2}{3}\right)k\rho c(T_{ig} - T_o)}}\right]\dot{q}'' - \left[\frac{h_c(T_{ig} - T_o) + \varepsilon\sigma T_{ig}^4}{\sqrt{\left(\frac{2}{3}\right)k\rho c(T_{ig} - T_o)}}\right] \tag{3}$$

The main advantage of this representation is that it enables straightforward estimation of important material flammability characteristics, directly from data. Experimentally obtained data are presented in Figure 2 in scatterplot form. Moreover, to test the validity of the proposed experimental installation, data from two similar studies [4], [14] were included. For comparative analysis, just the data up to external heat flux of 50 kW/m^2 from these two studies was used (20, 30, 40 and 50 kW/m^2). The lines were fit to experimental data. Results for best line fits (slope and intercept) are reported in Table 3. Regression lines were extrapolated up to the intersection with the x-axis. The x values of intersection points represent the theoretical critical heat flux [4].

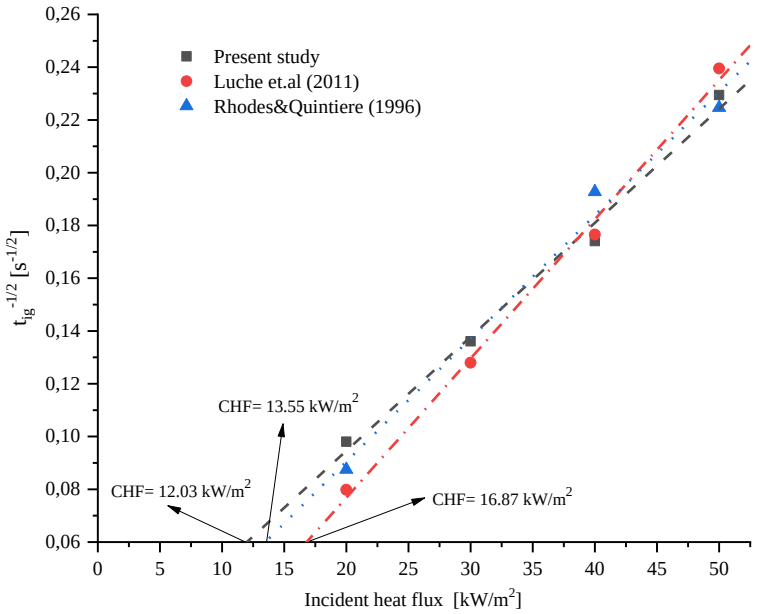

Fig. 2 Ignition data for PMMA: Present study, Luche et al. (2011) and Rhodes & Quintiere (1996)

It can be concluded from Figure 2 that results from the present study correspond well with results from the literature. Values of critical heat flux calculated this way, with reduced data set, for two studies [4] and [14] were considerably higher than the values reported in the original articles. Interestingly, the obtained values of theoretical heat flux with reduced data set correspond much better to real, experimentally determined critical heat flux for PMMA. The experimentally determined value of critical heat flux as reported by Luche et al. [4] was 11 kW/m^2. The number of external heat flux values selected in the experimental design phase directly affects the slope of the regression line and that consequently reflects on the values of critical heat flux. This effect should be further elaborated.

Table 3 Regression line parameters and theoretical critical heat flux for three studies

	Present study	Luche et al. (2011)	Rhodes et al. (1996)
Slope	0.00432	0.00528	0.00467
Intercept	0.00818	-0.02868	-0.00297
R square	0.98567	0.99306	0.97622
Theoretical critical heat flux (CHF), kW/m^2	12.03	16.87	13.55

Additionally, experimentally obtained data could be used for calculating ignition temperature. The slopes of regression curves from (3) are:

$$slope = \left[\frac{\varepsilon}{\sqrt{\left(\frac{2}{3}\right) k\rho c (T_{ig} - T_o)}} \right] \tag{4}$$

After elementary algebraic manipulations, ignition temperature yields:

$$T_{ig} = T_o + \frac{\varepsilon}{slope \sqrt{\left(\frac{2}{3}\right) k\rho c}} \tag{5}$$

The formula for ignition temperature (5) highly depends on the value of $k\rho c$. This effect is evident from the figures presented in Table 4.

Table 4 Ignition temperatures for three studies

	Present study	Luche et al. (2011)	Rhodes et al. (1996)
Ignition temperature, ^{0}C, $k\rho c$ = 0.352	497.85	410.97	462.00
Ignition temperature, ^{0}C, $k\rho c$ = 2.1	215.64	180.07	200.98

Calculated ignition temperature values in the first row correspond to $k\rho c$ = 0.352 and in second-row $k\rho c$ was set to 2.1. The first value was adapted from [15], while the second corresponds to the value reported by Rhodes [14], and was calculated from the experimental data. In both cases, ε was set to 1, and T_o was equal to 20 ^{0}C. Discrepancies are enormous. Calculated values in the second row closely correspond to measured ignition temperatures during the experiments [15].

3.1.2. Flaming burning phase

After the ignition, the flame-burning phase commences. In Fig. 3 graphical representation of external heat flux vs. average specific mass loss rate (SMLR) is shown for data from this study and data from studies [4] and [14]. The specific mass loss rate was calculated by dividing the mass-loss rate data with the surface exposed to the radiation heater (A=88.4 cm^2 as defined by ISO 13927 [10]). This data was averaged to yield the average specific mass loss rate.

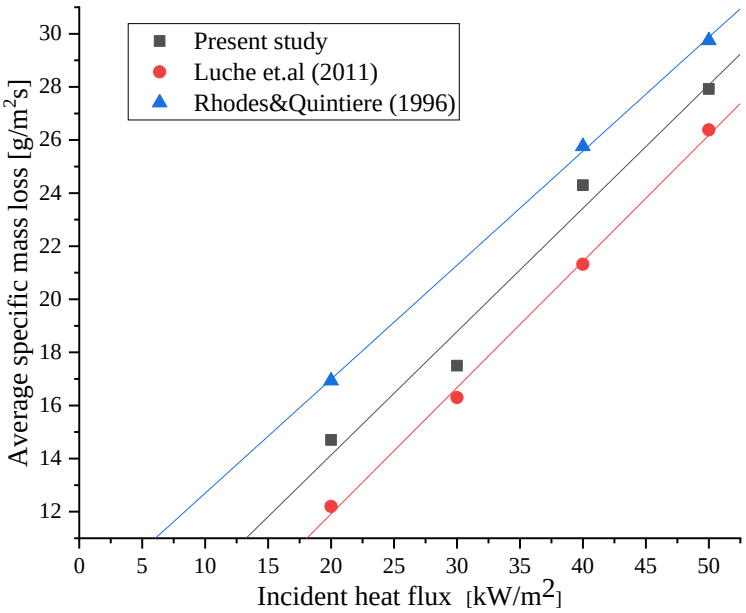

Fig. 3 Steady mass loss rate vs. external heat flux for PMMA: Present study, Luche et al. (2011) and Rhodes & Quintiere (1996)

The lines were fit to experimental data. Regression results for best line fits (slope and intercept) are reported in Table 5. Regression lines were extrapolated up to the intersection with the x-axis.

Table 5 Regression line parameters for three studies

	Present study	Luche et al. (2011)	Rhodes et al. (1996)
Intercept	4.844	2.404	8.40357
Slope	0.4646	0.4756	0.42936
R square	0.96279	0.99644	0.9988

This graphical representation is very useful as it enables direct calculation of heat of gasification using [16]:

$$slope = \frac{1}{\Delta H_g} \tag{6}$$

Substituting the value of line slope from Table 4, the heat of gasification yields the value of 2.15 kJ/g. This value corresponds well with the values from literature which are in the span from 1.34 – 2.77 kJ/g [4].

3.2. Results regarding the gas concentrations

While 16 gases were continuously monitored with FTIR just four gases had emission levels higher than 10 ppm, the value which was set as the threshold limit. Results regarding the evolution of fire effluents during the combustion phase of PMMA samples, for different heat fluxes, are shown in Fig. 4.

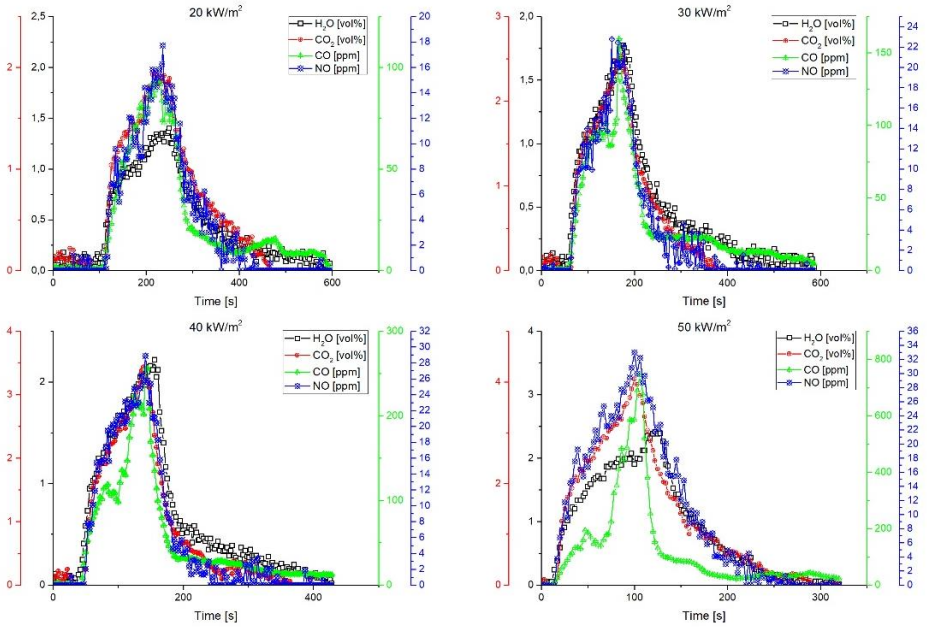

Fig. 4 Fire effluents emission as function in time for different heat fluxes for PMMA samples

For constructing water vapor profiles values corresponding to the humidity of ambient air were substracted from measured FTIR values. For this reason, water vapor concentration before the intensive gasification was zero. All combustion gases evolution curves had similar profiles following effluent curves from the literature [4]. A single, distinct peak on the curve was a common hallmark for all profiles. Curves' evolution closely followed mass loss rate. The time interval before the intensive gasification of fuel was, as expected, reduced with increased exposed heat flux. Interestingly, intensive evolution of gases happened almost simultaneously for all measured species. Moreover, all species had peak values corresponding to the same time moment. Measured maximal emission values for all detected species were in good agreement with findings from other studies [4].

4. CONCLUSIONS

In this work, thermal degradation of PMMA samples for different external heat flux values was studied. Experiments were performed in custom-made installation based on mass loss calorimeter and FTIR gas analysis system. The number of fire properties of

PMMA such as critical heat flux, ignition temperature, the heat of gasification as well as effluent emissions during the combustion phase were determined. Obtained results for critical heat flux were somewhat lower (12.03 kW/m^2) as opposed to other studies (13.55 kW/m^2 in [14] and 16.87 kW/m^2 in [4] – regression results for a reduced number of external heat flux values). Calculated ignition temperature in this study, for deducted values of the thermal inertia of PMMA according to [14], was 215 ^{o}C which is in agreement with [15]. The result for the heat of gasification (2.15 kJ/g) was in agreement with the values reported in the literature [4]. Moreover, emission levels during the combustion phase were in line with the values from [4].

Obtained results suggest that the proposed installation can be used with confidence in testing PMMA samples. However, further work is needed to test the experimental assembly of other plastic materials and compare results with literature findings.

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ISPITIVANJE POŽARNIH KARAKTERISTIKA PMMA U KALORIMETRU ZA MERENJE TOPLOTNE SNAGE UPARENIM SA FTIR GASNIM ANALIZATOROM

U ovoj studiji, PMMA uzorci su bili izloženi toplotnom zračenju intenziteta: 20, 30, 40 i 50 kW/m^2. Eksperimenti su izvedeni u namenski izrađenoj instalaciji koja se sastoji od kalorimetra za merenje toplotne snage, sistema za ekstrakciju i sistema za analizu efluenata sa FTIR spektrometrom. Cilj istraživanja je bio dvostruk: provera podobnosti namenski izrađene instalacije za ispitivanje upaljivosti i požarnih karakteristika polimera, i drugi, da se dobijeni rezultati uporede sa nalazima iz literature. Izmerene i izvedene požarne karakteristike PMMA (kritični toplotni fluks, temperatura paljenja i toplota gasifikacije), kao i emisije efluenata u toku faze sagorevanja, se u velikoj meri poklapaju sa rezultatima iz literature.

Ključne reči: *PMMA, kalorimetar za merenje toplotne snage, ISO 13927, FTIR, parametri upaljivosti, efluenti*