Fire Safety Journal 46 (2011) 451–461

Contents lists available at ScienceDirect

Fire Safety Journal

journal homepage: www.elsevier.com/locate/firesaf

Characterization of thermal properties and analysis of combustion behavior of PMMA in a cone calorimeter

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ARTICLE INFO

Article history:
Received 10 January 2011
Received in revised form
14 July 2011
Accepted 18 July 2011
Available online 9 August 2011

Keywords:
PMMA
Cone calorimeter
FTIR
Heat release rate
Mass loss rate
Emission yields
Effective heat of combustion
Thermal properties
ISO 5660 standard

ABSTRACT

This paper deals with the thermal degradation of a black poly(methyl)methacrylate (PMMA) in a cone calorimeter (CC) in air with a piloted ignition. The influence of several heat fluxes (11 kW m^{-2} and 12 kW m^{-2}, and ten values from 15 to 60 kW m^{-2} in steps of 5 kW m^{-2}) on PMMA sample degradation and the decomposition chemistry has been studied. Thus, thermal properties have been deduced and calculated from ignition time and mass loss rate (MLR) curves. During our experiments, among compounds quantified simultaneously by a Fourier transformed infrared (FTIR) or gas analyzer, five main species (CO_2, CO, H_2O, NO and O_2) have been encountered, regardless of the external heat flux considered. The main product concentrations allow calculation of the corresponding emission yields. Thus, mass balances of C and H atoms contained in these exhaust gases were able to be compared with those included in the initial PMMA sample. Using the standard oxygen consumption method, heat release rate (HRR), total heat release (THR) and effective heat of combustion (EHC) have been calculated for each irradiance level. Therefore, these different results (thermal properties, emission yields, HRR, THR and EHC) are in quite good accordance (same order of magnitude) with those found in previous studies.

1. Introduction

Plastics and polymers, such as poly(methyl)methacrylate (PMMA), are used as replacements for conventional materials (e.g. wood, metals, glass, etc.) in numerous domains such as electrical appliances, light diffusers, optical fibers, furniture, transport, hygiene and health, etc. Indeed, these widespread kinds of synthetic compounds, with good technical, mechanical, chemical, optical performances, etc., are easily manufactured for a moderate cost and can be used in a wide range of applications. Thus, compounds made of PMMA can be used in numerous applications as signs and signboards (illuminated panels, 3D lettering, indicator panels, etc.), POS (point-of-sale) advertising (display stands, testers, notice-boards, etc.), interior design (shop-fitting, furniture, projection screens, glazing, etc.), transport (deflectors, sun visors, registration plates, ship portholes and windows, etc.) or industrial (machine guards, dials, precision parts, etc.) devices. In spite of these various uses linked to numerous advantages, plastics (highly combustible materials) constitute a grave danger (human injuries and deaths) in case of fire, as under the right conditions, they readily ignite and burn vigorously.

As a reference fuel material used in a cone calorimeter (CC), solid acrylic PMMA polymer has been widely used – with or without filler – during previous studies for assessing polymer flammability and characterizing the mass loss rate (MLR) during combustion processes [1–14]. Only some of these previous studies and other specific studies propose the chemical analysis and quantification of the effluents emitted during PMMA thermal degradation, and so include the calculation of the heat release rate (HRR), which is the most important parameter in fire characterization studies [1–5,15–22]. Finally, a few studies propose a chemical kinetic mechanism for predicting the PMMA degradation in a CC [23,24]. Generally, only the assumption of a single-step degradation corresponding to depolymerization and formation of MMA is carried out.

The present paper deals with a complete and detailed study of thermal degradation of a black non-charring PMMA in a CC, including the characterization of thermal properties and the quantification of exhaust gas concentrations of this typical polymer. Thus, the main purpose of this work is to characterize the influence of a widespread range of irradiance levels (external heat flux) on the MLR of a PMMA sample and on the product amounts released during this combustion process. Next, the HRR was determined based on the O_2-consumption principle in a CC.

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doi:10.1016/j.firesaf.2011.07.005

Nomenclature

Greek notations

ε	emissivity
ϕ	oxygen depletion factor
$k\rho c$	thermal effusivity, kJ^2 m^{-4} K^{-2} s^{-1}
ρ	density, kg m^{-3}
σ	Stefan–Boltzmann constant 5.6704×10^{-8} W m^{-2} K^{-4}

Notations

A	sample area exposed to cone calorimeter heat flux, cm^2
c	specific heat, kJ kg^{-1} K^{-1}
CC	cone calorimeter, –
CHF	critical heat flux, kW m^{-2}
ΔH_g	latent heat of gasification, kJ g^{-1}
E	net heat release per unit mass of oxygen consumed, MJ kg^{-1} of O_2
E_{CO}	net heat release per unit mass of oxygen for CO, MJ kg^{-1} of O_2
EHC	effective heat of combustion, kJ g^{-1}
$\overline{\text{EHC}}$	averaged effective heat of combustion, kJ g^{-1}
FHF	flame heat flux, kW m^{-2}
FHF_{net}	net flame heat flux, kW m^{-2}
FID	flame ionization detector, –
FTIR	Fourier transformed infrared, –
h_c	convective heat transfer coefficient, W m^{-2} K^{-1}
HRR	heat release rate, kW m^{-2}
$\overline{\text{HRR}}$	averaged heat release rate, kW m^{-2}
k	thermal conductivity, kW m^{-1} K^{-1}
m	mass, g
M_{Air}	molar mass of air, g mol^{-1}
$\dot{m}_{Air}$	mass flow rate of the incoming air, g s^{-1}
M_i	molar mass of species i, g mol^{-1}
$\dot{m}_i$	mass flow rate of species i in the exhaust duct of CC, g s^{-1}
$\dot{m}_e$	mass flow rate in the exhaust duct of CC, g s^{-1}
MLR	mass loss rate, g s^{-1}
NDIR	non-dispersive infrared, –
P	pressure, Pa
PMMA	poly(methyl)methacrylate, –
$\dot{q}''_{ext}$	external heat flux, kW m^{-2}
R	universal constant of perfect gas 8.314472 J mol^{-1} K^{-1}
SMLR	s mass loss rate, g m^{-2} s^{-1}
$\overline{\text{SMLR}}$	averaged specific mass loss rate, g m^{-2} s^{-1}
t	time, min or s
T	temperature, K
t_{ig}	ignition time, min or s
T_{ig}	ignition temperature, K
T_0	initial (ambient) temperature, K
THR	total heat release, MJ m^{-2}
$\dot{V}_e$	volumetric flow rate in the exhaust duct, L s^{-1}
V_m	molar volume, L mol^{-1}
X_i^0	mole fraction of species i in the incoming air, –
X_i	mole fraction of species i in the exhaust gas measured by analyzer, –
Y_i	emission yield of species i, g_i/g_{sample}

Finally, the MLR and HRR parameters have been correlated with main gaseous compound evolutions and their emission yields to propose a description of physical and chemical phenomena occurring during PMMA thermal degradation.

2. Experiments

2.1. Materials

The material used in this study is a black non-charring PMMA, commonly known as Altuglas, supplied by the company VACOUR and synthesized via radical polymerization. The PMMA elementary analysis was conducted by a combination of catharometry and non-dispersive infrared (NDIR) detection. Table 1 presents the averaged composition along with the analysis methods that were repeated three times and provided a dispersion of $\pm$0.3 wt%.

Table 1
Elemental analysis of black poly(methyl methacrylate).

Elements	Composition (wt%)
Carbon (C)	59.1
Hydrogen (H)	7.9
Oxygen (O)	31.9
Nitrogen (N)	<0.3
Sulfur (S)	<0.2
Chlorine (Cl)	0.1
Water (H2O)	0.6
Total	<100.1

Elementary analysis results show that no inert load, flame retardants or fillers were used during the manufacturing of the PMMA sample; neither chlorine- nor sulfur-based additives were found. Indeed, 100 wt% of the total sample mass was composed of C, H, O, N and S atoms. This result is in good accordance with various compositions of such PMMA reported in [25]. Based on this elementary analysis composition, the raw chemical formula of the virgin PMMA was determined to be $(C_{4.9}H_{7.8}O_{2.0})_n$ (with n=PMMA polymerization degree).

Its molecular weights and molecular weight distributions were obtained from an Agilent Technologies Size Exclusion Chromatography (SEC) calibrated with a polystyrene standard. Samples of 25 and 70 mg (1 and 2 in Table 2) were dissolved in chloroform and then injected into the SEC. Table 2 shows the molecular weights (Mn and Mw), molecular weight distributions (Ip) and polymerization degree (n) of each sample analyzed.

Molecular weight distribution (Ip), with a value around 3.7, shows that PMMA is a polymolecular compound obtained by radical polymerization ($\text{Ip}\geq2$) according to the definition given by some authors in the literature [26,27]. From these results, the polymerization degree (n) of the PMMA sample can be determined as equal to value ranging from 1500 to 1800.

Table 2
Characterization of black poly(methyl)methacrylate mass (SEC analysis).

Elements	Mn	Mw	Ip=Mw/Mn	*n*
1	178,670	639,340	3.6	1785
2	150,440	578,480	3.8	1503