



Experimental and modelling studies on the kinetics and mechanisms of thermal degradation of polymethyl methacrylate in nitrogen and air



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ARTICLE INFO

Article history:

Received 29 October 2015

Received in revised form 17 June 2016

Accepted 23 June 2016

Available online 25 June 2016

Keywords:

Polymethyl methacrylate

Thermogravimetric analysis

Fourier-transform infrared spectroscopy

Mechanism of degradation

Gaseous phase

Pyrolysis model

ABSTRACT

Modelling of spread of fires and their extinguishment in solid materials still present a significant challenge. In order to reliably predict the behaviour of a material in a fire scenario, an adequate description of the processes occurring at the gas/solid interface is highly crucial. In this context, those fire scenarios involving polymeric materials are of primary importance because of their increasing use as components in buildings and in transportation. The purpose of this study is to propose an accurate model for the thermal degradation of polymethyl methacrylate (PMMA) by primarily using thermogravimetric analysis (TGA). TGA in non-isothermal conditions, together with Fourier-transform infrared spectroscopy (FT-IR), was applied to investigate the thermal degradation of black PMMA in inert (nitrogen) and oxidizing (air) atmospheres, at different heating rates. The volatile degradation products as well as mass loss history provided sufficient information regarding the kinetics and possible degradation mechanisms of PMMA. A genetic algorithm (GA) was applied to estimate the kinetic parameters, which showed an excellent agreement with corresponding experimental observations for several heating rates and at different atmospheres (0, 10.5, 15 and 21 vol.% O₂).

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1. Introduction

Over the past several decades, polymeric materials are being increasingly used as building components, house-hold articles and in transportation. However, these materials can be highly combustible under degradative conditions and in oxidative atmospheres. Thus, it is important to understand how polymers behave in a fire scenario, and also to be able to explain the complex physio-chemical processes and associated coupling of the reactions between condensed and gas phases that lead to a sustainable flaming combustion.

Generally, fire safety investigations are commonly done using specific models of simulation. In these models, the thermal effect is investigated through a “model of pyrolysis”, where degradation of solid materials is treated classically. For instance, the calculations follow directly from heat release rates, where the effective heat of combustion is treated as a constant, or a kinetic model is assumed permitting calculation of the mass loss rate using a global

reaction (generally an Arrhenius-type reaction with one or two steps) [1–3]. The above assumptions could generate several errors, notably through a poor description of the rate process(s), and also owing to the fact that the thermal degradation of different fuels takes place in several steps (not necessarily by one or two steps).

The kinetics of degradation of solid fuels can be described by different models of different complexities. They can be also divided into two main categories: simple one-step global models and detailed degradation models (with multi-step reaction mechanisms and semi-global reaction mechanisms). However, the chemical processes underpinning these models are not generally well understood. In order that these models to be implemented, a set of apparent kinetic parameters are needed to be determined for each step of the degradation process. On the contrary, often degradation kinetic data are only empirical in nature, and are considered in most cases to be a first-order reaction, with little or no justification behind this choice [1–3]. In actual practice, an accurate determination of the kinetic parameters of material undergoing thermal degradation is crucial for predicting its behaviour in a fire.

The overall aim of the present study is to propose a new model of pyrolysis by employing a systematic and thorough analysis of various attributes of degradation of PMMA. The primary objective

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Nomenclature

Symbol	
m	Mass (mg)
Mn	Number average molecular weight (g/mol)
Mw	Weight average molecular weight (g/mol)
T	Temperature (°C)
TG	Thermogravimetric
w	Weight (wt.%)
C _p	Heat capacity (Jg ⁻¹ k ⁻¹)
TGA	Thermogravimetric analysis
PDI	Polydispersity index
MLR	Mass loss rate (ms ⁻¹)
MMA	Methyl methacrylate
SEC	Size exclusion chromatography
TDT	Thermal degradation temperature
FTIR	Fourier transform infrared spectroscopy
ρ	Density (kgm ⁻³)
n	Order of the reaction
A	Pre-exponential factor (s ⁻¹)
k	Reaction rate constant (s ⁻¹)
m _{sap}	Mass of sapphire (g)
y _{O2}	Mass fraction of oxygen
HF	Heat flow (mW)
GA	Genetic algorithm
φ	Fitness
ω _i	Reaction rate
α	α-PMMA
β	β-PMMA
γ	γ-PMMA
ε	ε-PMMA
α	Degree of conversion or degradation
g	Gas
p	Pyrolysis
r	Residue
Sap	Sapphire
0	Initial
t	Time (s)
ν	Reaction stoichiometry
E _a	Activation energy (J mol ⁻¹)
β	Heating rate (°C min ⁻¹)
C _{psap}	Heat capacity for the sapphire (Jg ⁻¹ k ⁻¹)
HF _{sap}	Heat flow for the sapphire (mW)

is to determine the various steps of the degradation and subsequently to describe the rate of each degradation reaction with a view to proposing the best realistic model possible. Over the past ten years, newer approaches to model the pyrolysis of different fuels have been proposed and developed, notably by Rein et al. [4,5], Lautenberger et al. [6], and Matala [7]. These studies used a similar methodology- i.e. from the evolution of the mass loss rates, obtained during TGA investigations, the authors proposed various mechanisms of degradation and then calculated the kinetic parameters for each of such reactions. However, the main drawback of such investigations was that none of them gave due consideration regarding the gaseous phase component(s). In fact, it is crucial to gauge the gaseous products of combustion, as this would enable one to formulate the degradative steps involved in the condensed phase that led to their production in the first place. Therefore, a close examination of both the solid and gaseous phases is pivotal in developing a scientifically robust and reliable thermal degradation model.

Thermogravimetric analysis (TGA) is the most conventional measurement technique to study the decomposition of materials

Table 1

Elemental composition of black PMMA.

Element	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 (H ₂ O)	0.6

[8]. This technique, generally, provides information that allows one to infer the probable decomposition mechanisms of solid materials in pre-set experimental conditions. In the present study, TGA technique was coupled with a Fourier-transform infrared spectroscopy (FTIR) in order to derive the rate parameters and to elucidate the kinetics of the mass loss rate of the solid. The technique also, in tandem, enabled us to identify the major gaseous species that emanated from the degrading solid substrate in real time. Thus by coupling data obtained from both phases allowed us to describe the decomposition mechanism(s) that are in agreement with the most probable physiochemical processes accompanying the degradation of PMMA. Credible and scientific analyses of the changes in solid phase, as well as the real time of analyses of gaseous components as a function of time (or temperature), are rarely reported in the literature.

In the present work, we focussed our efforts to clarify the thermal degradation and kinetic processes of non-charring thermoplastic polymers, such as PMMA, which has already been the subject of numerous publications [9–19]. The mechanisms and kinetics of the processes underlying the degradation of PMMA have been examined by employing various techniques, and also under several environments that included vacuum, nitrogen, oxygen, argon and helium. However, there are only fewer reports in the literature regarding its degradation studied under normal atmospheric conditions (i.e. air as the medium) [6,10,13,15,16]. It should be also noted that such reports also widely differ in the identification of the number and nature of various degradative steps. Generally, it is established for PMMA that the thermal degradation is initiated by the scission of weaker links (for example, at the end-groups) and random scissions, followed by a de-propagation step, and a first-order termination reaction. PMMA also undergoes almost complete degradation, leading to little or no char. However, a very nominal amount of char can be formed by the elimination of methoxycarbonyl side chains, under an oxidative atmosphere, between 370 and 420 °C. It is highly relevant to note here that the disagreement with regard to the degradation steps and/or associated products, among various reports, could primarily stem from the fact that solid substrates under consideration could widely vary in terms of their micro-structures and morphology. For instance, the molecular weights and its distribution, micro and nature and distribution of minor structures, weak linkages, nature of end groups, etc. could all vary amongst the substrates that were studied. However, by and large, PMMA is considered to yield almost quantitative yield of its monomer through a first order degradative pathway.

2. Materials and methods

Generally, unmodified PMMA is a colourless and transparent material, but for some applications where a colour is required, an appropriate additive (i.e. a colourant) is added. In the present work virgin polymer, mixed with a colourant (black), was used. This sample is often referred to as black PMMA, or Altuglas, and was supplied by Vacour company (see Table 1 for the elemental composition). The molecular weights and their distribution were obtained through size exclusion chromatography (SEC) using an

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