

A quantitative study of carbon monoxide and carbon dioxide evolution during thermal degradation of flame retarded epoxy resins

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Abstract

Thermogravimetric analysis (TGA) combined with infrared analysis of the evolved gases analysis (EGA) has been used to study the thermal degradation behaviour of epoxy resin both in air and nitrogen. The mass loss as a function of temperature has been correlated with the evolution of carbon monoxide (CO) and carbon dioxide (CO₂), and oxygen consumption as measured using an oxygen analyser. An analytical technique has been developed to quantitatively measure the carbon monoxide and dioxide gases evolved. The effect of a range of flame retardants containing phosphorus, nitrogen and halogen elements on CO and CO₂ evolution during thermal degradation of flame retarded epoxy resins has also been observed.

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1. Introduction

Organic polymers when exposed to heat, decompose and their decomposition products burn generating various fire gases and smoke. Invariably the products of combustion are highly toxic and the cause of most fire fatalities [1]. The prime toxic product is carbon monoxide (CO) accompanied with asphyxiant and carbon dioxide (CO₂). Fire gas toxicity is dependent upon material composition and the fire conditions [2]. The formation of CO in fires occurs at low temperatures in the early stages of fire development mainly due to incomplete combustion of the pyrolysed polymer volatile fuels. As the fire develops, the higher temperature favours the formation of CO₂, which is particularly dependent on oxygen availability to the fire [3]. The evaluation of the polymer flammability is carried out using a variety of techniques, most of which do not correlate well with each other. They tend to fall into two classes, namely those which are product based (e.g. the UL 94 (ISO 1210) [4] for assessing bulk polymer behaviour)

and science based (e.g. the Limiting Oxygen Index (ISO 4589) [5] and Cone Calorimeter tests (ISO 5660) [6]). Such test methods usually measure parameters such as ease-of-ignition, ease-of-extinction, rate of burning, the effect of oxygen concentration and heat release rate. All these techniques involve different sample sizes and need a few replicate tests for reliable results and none yield fundamental information regarding the mechanism of thermal degradation that underpins the burning process. Thermal analytical techniques, which involve only few milligrams of sample, are quite often used during new polymer developmental stages, because they give information about physical and chemical changes occurring on heating the polymer in a controlled atmosphere. Although thermal analytical results do not correlate with actual fire conditions, they give insight into mechanisms of thermal degradation, in particular when evolved gases are characterised analytically [7–14]. In this work a thermogravimetric analyser coupled with infrared analysers has been used to quantitatively measure the CO and CO₂ produced during thermal degradation of a typical epoxy resin of aerospace grade.

Thermoset epoxy resins are widely used in a variety of areas like aerospace, marine, automobile, adhesive and coating

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industries [15,16]. Chemically, epoxy resins may have variety of structures [15–17] but all contain epoxide groups ($-\overset{\text{O}}{\text{C}}-\text{C}-$) in their polymeric backbone. Like other organic polymers, epoxy resins can be flame retarded either by incorporating flame retardant additives or by copolymerization with reactive flame retardants [18]. In this work selected flame retardants (e.g. phosphorous–nitrogen, organophosphorous and halogen based) have been added to the resin prior to polymerization. The TGA–EGA technique has been used to give a chemical insight into the thermal decomposition of the different flame retardant resins.

2. Experimental

2.1. Materials

Chemicals used for calibration of EGA instrumentation:

- (i) Sodium bicarbonate, NaHCO_3 (Supercook, UK);
- (ii) calcium carbonate, CaCO_3 (Sigma Chemical Co., USA).

Resin:

Epoxy resin: triglycidyl-*p*-aminophenol (Vantico Ltd., UK); curing agent: 4,4-diamino diphenyl sulphone, DDS (Acros Organics BVBA, Belgium); thermoplastic toughener: Polyether sulphone, PES (Cytec, Netherlands).

Flame retardants:

These were selected based on the criteria that they should contain phosphorous and/or nitrogen; if bromine is present, P or N should be also present and they should be compatible with the resin. The following were selected as a consequence:

Phosphorous and nitrogen based:

- (i) Ammonium polyphosphate, APP (Antiblaze MC, Rhodia Specialities Ltd., UK),
- (ii) melamine phosphate, MP (Antiblaze NH, Rhodia Specialities Ltd., UK),
- (iii) melamine pyrophosphate, MPP (Antiblaze NJ, Rhodia Specialities Ltd., UK).

Organophosphorous based:

- (iv) Resorcinol bis-(diphenyl phosphate), RDP (Chemtura, UK),
- (v) bisphenol A bis-(diphenyl phosphate), BAPP (Chemtura, UK).

Halogen based:

- (vi) Tris(tribromoneopentyl)phosphate, FR372 (DSBG, Israel),
- (vii) tris(tribromophenyl)cyanurate, FR245 (DSBG, Israel).

2.2. Sample preparation

Epoxy resin samples with and without flame retardants have been formulated by a hot-melt method. The epoxy resin was heated to 120 °C to melt it and toughened and required amounts of flame retardants were added slowly while stirring with a mechanical stirrer. The mixture was further stirred for 30 min. The temperature was lowered to 100 °C, the curing agent DDS was added and the mixture was stirred at 100 °C for 30 min in order to yield a homogeneous mixture. The mixture was then degassed at 85 °C for 2 h. Small quantities (~200 mg) of uncured samples were stored for thermal analytical tests and the rest poured in aluminium moulds to cure for further flammability testing (results to be published in a forthcoming publication) [19]. The sample compositions are given in Table 1 and different samples prepared are listed in Table 2.

2.3. Equipment

The TGA experiments were carried out using a Polymer Laboratories TG 1000 instrument under flowing air or nitrogen atmosphere at 20 ml/min gas flow rate and at a heating rate of 10 °C/min from room temperature to 900 °C. About 2–3 mg sample was used. The TGA instrument was connected in series to gas analysers (O_2 , CO and CO_2) manufactured by Irriidium, City technology, UK, via an unheated gas line. CO and CO_2 were monitored using a nondispersive infrared analyser operating at 2000–2300 cm^{-1} wavelength and oxygen with an electrochemical sensor.

3. Results and discussion

3.1. Calibration of the TGA–EGA equipment

The combined TGA–EGA experiment has been calibrated using gases quantitatively derived from chemicals with known thermal degradation mechanisms, namely sodium bicarbonate (NaHCO_3) and calcium carbonate (CaCO_3).

During TGA–EGA experiments, the TGA records the changing mass of a sample with respect to time or temperature, while the gas analyser records evolved gas concentrations as percentage volume concentrations (e.g. CO, CO_2 , and O_2) in the purge gas with respect to time. The relationship between time and temperature can be drawn from the heating rate in TGA. In this work, the heating rate has been kept at 10 °C/min and so

10 °C increment in TGA = 1 min or 60 s

period in the gas analyser.

Table 1
Mass percentage of various components in the formulations

Samples	Epoxy resin	DDS	PES	FR
Epoxy resin	57.8	22.2	20	–
96% Epoxy + 4% FR	57.8	22.2	16	4
92% Epoxy + 8% FR	57.8	22.2	12	8

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