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Study of the thermal decomposition of flame-retarded unsaturated polyester resins by thermogravimetric analysis and Py-GC/MS

Everson Kandare*, Baljinder K. Kandola, Dennis Price, Shonali Nazaré, Richard A. Horrocks

Centre for Materials Research and Innovation, University of Bolton, Bolton BL3 5AB, UK

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ABSTRACT

The thermal degradation behaviours of flame-retarded unsaturated polyester resin formulations containing ammonium polyphosphate (APP), Cloisite 25A nanoclay and zinc based smoke suppressants have been studied using thermogravimetric analysis (TGA) combined with infrared analysis of the evolved gases (EGA) and pyrolysis/gas chromatography–mass spectrometry (GC/MS). In TGA–EGA experiments, the mass loss as a function of temperature has been correlated with the evolution of carbon monoxide (CO) and carbon dioxide (CO_2) and oxygen (O_2) consumption as measured by an oxygen analyser. The effect of APP, Cloisite 25A and the smoke suppressants on the evolution of CO and CO_2 has been examined. The decomposition behaviour of flame-retarded polyester resins under isothermal pyrolytic conditions was investigated and the evolved gaseous products were collected and qualitatively and semi-quantitatively analysed via GC/MS. The addition of APP does not yield many new gaseous products relative to the unmodified polyester resin neither does the presence of zinc borate (ZB) and zinc stannate (ZS) together with APP. Possible chemical interactions are discussed in an attempt to explain the observed results.

1. Introduction

Polyester resins are pre-polymer mixtures of unsaturated polyester chains and styrene with the latter serving as both a diluent and cross-linking agent during the subsequent radical polymerisation process [1]. Polyester resins constitute the binding matrix in fibre reinforced composites which are increasingly becoming common for industrial applications including aerospace, automotive, marine and load bearing infrastructure. This is because of their excellent ease of processibility, outstanding chemical resistance, high flexural moduli and low cost [2,3]. However, despite the above-mentioned advantages, polyester resins are prone to fire damage. Incomplete combustion of the volatiles evolved from the pyrolysed polymer during the initial stages of a developing fire may lead to the formation of carbon monoxide (CO), a highly lethal colourless and odourless gas. Depending on the availability of oxygen (O_2) at elevated temperatures, carbon dioxide (CO_2) is also produced.

There is need to improve the flame resistance of polymeric materials for which a wide range of flame retardants are available and under development for use with polystyrene and unsaturated polyester resins [4–8]. Phosphorus containing flame-retardant additives such as ammonium polyphosphate (APP) are becoming increasingly popular because they give rise to environmentally friendly products when incinerated. These additives achieve their purpose in the condensed phase and their effectiveness is highly dependent on the chemical structure of the polymer; they particularly are effective with high oxygen content polymers [9]. During thermal decomposition, phosphorus is converted to phosphoric and polyphosphoric acids, which consequently promote charring through esterification (cross-linking) of reactive polymer fragments [10]. Formation of carbonised char networks prevents or slows down the transfer of heat and combustible volatiles into the remaining virgin polymer and pyrolysis zone, respectively, thus retarding the flaming/combustion process [9]. Detailed mechanistic schemes describing the charring behaviour of polyester resin formulations containing the intumescent additive, APP have been discussed elsewhere [11].

When used alone flame-retardant additives have little or no effect on the amount of smoke hazard produced, hence the need to search for possible smoke suppressant additives with which they may be used in conjunction [12]. Zinc and tin containing compounds such as zinc stannate (ZS), zinc borate (ZB) and zinc hydroxystannate (ZHS) have been shown to exhibit very low toxicity, are compatible with a variety of flame-retardants while acting as smoke suppressants for various polymer systems [13–19].

* Corresponding author. Tel.: +44(0)1204 903512; fax: +44(0)1204399074.
E-mail address: ek1@bolton.ac.uk (E. Kandare).

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Synergistic effects are envisaged when these smoke suppressants are combined with conventional flame retardants and/or nanoclays.

The aim of this work is to investigate the combined effect of organically modified nanoclay, Cloisite 25A; flame retardant, APP; and smoke suppressants, ZS, ZB and ZHS on the quantity and composition of volatile products from decomposition and pyrolysis of unsaturated polyester resin formulations. The burning behaviours of the resin formulations are dependent on both condensed and gas phase chemical reactions in which the selected additives are expected to participate and the conditions under which the materials degrade. Thermal degradation under a slow heating rate using thermogravimetric analysis (TGA) combined with infrared analysis of the evolved gases (EGA) is used to gain an insight into the thermal decomposition of the different flame-retardant resins. In addition GC/MS has also been used to separate and identify pyrolytic gaseous products generated via fast pyrolysis in air. The information thus obtained is used to interpret possible decomposition mechanisms for flame-retardant, nanoclay and/or smoke suppressant containing resin formulations.

2. Experimental

2.1. Materials

The resin, unsaturated polyester, (orthophthalic, Crystic 471 PALV) was supplied by Scott Bader. Flame retardant (FR), ammonium polyphosphate (APP), (Antiblaze MCM) was supplied by Rhodia Specialities Ltd. Smoke suppressants; zinc stannate, $ZnSnO_3$, (ZS) (Flamtard S) and zinc hydroxystannate, $ZnSn(OH)_6$, (ZHS) (Flamtard H) were supplied by William Blythe Ltd., whilst zinc borate, $2ZnO \cdot 3B_2O_3 \cdot 3H_2O$, (ZB) (Firebrake ZB) was supplied by Borax UK. The nanoclay, Cloisite 25A (C), which is an alkyl ammonium cation modified montimorillonite clay was supplied by Southern Nanoclay Products, USA.

2.2. Preparation of unsaturated polyester resin formulations

Unsaturated polyester composites incorporating APP, zinc and tin containing smoke suppressants and Cloisite 25A nanoclays were prepared via *in situ* interactive polymerisation; predetermined weight fractions of respective additives were slowly added to the resin with vigorous mechanical stirring (900 rpm) for 1 h at room temperature to afford homogeneity. All samples were cast and cured at room temperature followed by post-curing after adding 1% catalyst w.r.t. resin at 80 °C for 8 h. Details of constitutional percent concentrations of respective additives are presented in Table 1.

2.3. Thermogravimetric analysis

TG curves were obtained by using a Polymer Laboratory TG1000 instrument for sample sizes of 5 ± 0.5 mg heated at a rate of 10 °C/min with air as the purge gas (flow rate, 40 ± 2 ml/min). The concentrations of carbon monoxide and carbon dioxide evolved from the TG furnace were monitored by using a non-dispersive infrared gas analyser and the concentration of oxygen was monitored by using an electrochemical cell oxygen sensor. The TG furnace and the gas analyser cell were connected by an unheated transfer line. The gas analyser records evolved gas concentrations as percentage volume concentrations in the purge gas with respect to time, whereas mass loss in TGA is recorded as a function of temperature. The time delay in detection of gases by the gas analysers has been accounted for while establishing the relationship between time and temperature [20]. The analytical technique for quantitative measurements of gases evolved during thermal decomposition has been calibrated using compounds of known thermal history and is described in detail elsewhere [21].

Table 1
Mass percentages of various components in the formulations

Sample	Mass (%)			
	Resin	Cloisite 25A	APP	Smoke suppressant
R	100	–	–	–
RA	83	–	17	–
RAZS	83	–	8.5	8.5
RAZB	83	–	8.5	8.5
RAZHS	83	–	8.5	8.5
RAZBC	79	4	8.5	8.5

2.4. Pyrolysis procedure

A Wilks Pyro-Chem filament type pyrolyser (Foxboro Analytical, USA) was used to flash pyrolyse unsaturated polyester resin formulations at a desired temperature in static air at atmospheric pressure. The pyrolysis chamber is composed of a stainless steel cell with an enclosed volume of *ca.* 60 cm^3 and an electrically heated Ni/Cr/Fe sample holder/filament. The sample holder/filament was cleaned by heating at 800 °C to burn off residual material from previous experiments. Pre-weighed sample amounts of 14.0 ± 0.5 mg were placed in the boat shaped filament and the cell was tightly sealed to retain all gaseous products. The pyrolysis temperature was set to a desired value of 700 °C and held for 40 s. Pyrolysis gases were slowly drawn up into a pre-heated gas tight syringe beginning 5 s after initiation of the reaction and continuing for the rest of the reaction time, 35 s [22]. Pyrolytic char was measured as the amount of residue remaining at the completion of the experiment. Experiments were performed in triplicate to assess experimental reproducibility.

2.5. GC/MS analysis

Separation of the collected products was accomplished by an HP 5890 gas chromatograph using a BPX 5 capillary column (25 m × 0.25 mm i.d., 0.25 μm film thickness), supplied by SGE with the following temperature program; initial oven temperature of 40 °C, held for 5 min; then raised to 220 °C at 20 °C/min and held for 10 min. The GC effluents were fed directly into the ion source of a Scientific Instruments Specialties TRIO-1000 mass spectrometer. Helium, (gas pressure of 5 psi) was used as the carrier gas. The mass range from $m/z = 40$ to 540 was scanned. Identification of the pyrolysis gaseous products was achieved by comparing the observed mass spectra to those in the NIST mass spectral library. Due to the lack of an appropriate standard mixture for calibration, percent fractional yields of gaseous pyrolysis products were calculated from the total integrated area of all products and expressed relative to the total mass lost during pyrolysis.

3. Results and discussion

3.1. Oxygen consumption and CO and CO_2 measurements

Solid-state chemical reactions (thermal degradation) lead to the evolution of gaseous products, which add to the purge gas hence diluting the oxygen concentration. In order to measure the actual oxygen concentration at any given time the following parameters need to be established;

Volume of total purge gas flow per second = f,
Volume of oxygen in purge gas per second = $f\mathrm{O}_2 = 20.94\%$ for air.
Volume of CO_2 evolved per second = $f\mathrm{CO}_2$,
Volume of CO evolved per second = fCO and
Calculated volume of gas flow per second, $F_{\mathrm{cal}} = f + f\mathrm{CO}_2 + f\mathrm{CO}$.