Effect of Boric Acid on Volatile Products of Thermooxidative Degradation of Epoxy Polymers

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Abstract. The polymeric materials are characterized by high flammability. The use of flame retardants in order to reduce the flammability of polymers can lead to the formation of toxic gaseous products under fire conditions. In this work we studied the effect of boric acid on the volatile products of thermooxidative degradation of epoxy polymers. The comparative investigations were carried out on the samples of the unfilled epoxy resin and epoxy resin filled with a boric acid at percentage 10 wt. %. The analysis of the volatile decomposition products and thermal stability of the samples under heating in an oxidizing medium was performed using a thermal mass-spectrometric analysis. It is found that the incorporation of boric acid into the polymer matrix increases the thermal stability of epoxy composites and leads to a reduction in the 2–2.7 times of toxic gaseous products.

1. Introduction

Polymeric materials are widely used in industry and everyday life due to such properties as low density, high strength, chemical stability, ease of processing etc. A significant disadvantage of polymeric materials and products made of them is high flammability. Burning of polymeric materials in fire leads to environmental pollution by combustion products; it causes human injury and deaths as well as entails huge economic losses [1–4]. Thermal decomposition and combustion of polymers is accompanied by the release of heat, smoke and toxic gases such as carbon monoxide, carbon dioxide, formaldehyde, water, methane, ethylene, propylene, and others [5, 6]. Among the toxic gases carbon monoxide is considered the major cause of fire deaths.

Decrease in flammability and combustibility of polymers is an urgent problem. One of the methods of this problem decision is the incorporation of flame retardants into the polymers. The use of conventional halogenated flame retardants (bromine and chlorine) can lead to highly dangerous and persistent toxicants, having also carcinogenic action, such as phosgene, cyanogen compounds, dioxins. Therefore, current studies aimed at finding and developing environmentally friendly flame retardants [7–10].

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Epoxy resins are thermosetting polymers which dominate in composite industry. They are widely used in electronic, aerospace, automotive industries and other structural applications. Epoxy resins possess good mechanical and electrical insulating properties, excellent adhesion, high chemical and corrosion resistance. They are applied as paint, coating, adhesive, matrices for composites. With the increasing epoxy resin market, it is of great importance to develop epoxy systems based on environmentally friendly flame retardants and study their thermal characteristics and volatile products under fire conditions. The evolved gases analysis by means of thermogravimetry, FTIR and mass spectrometry during thermal degradation of epoxy resin revealed that the main volatile product are carbon monoxide CO, carbon dioxide CO_2, water H_2O, formaldehyde CH_2O, a number of hydrocarbons [11–13].

The aim of this study was to investigate the influence of boric acid used as filler for reducing flammability, on gaseous products of thermal oxidative degradation of epoxy composites by means of a thermal analyzer coupled with a mass spectrometer. The dominant volatile products such as CO, CO_2, CH_2O were selected for the analysis and their evolution is discussed in this study.

2. Experimental

The samples of epoxy polymers were prepared from an epoxy resin ED-20. The curing of the epoxy resin was carried out using polyethylene polyamine (PEPA). The fine powder of boric acid was used as filler. In this study we investigated the thermal characteristics and the volatile products of two samples: 1) the sample E0 was the unfilled cured epoxy resin; 2) the sample EB10 was the epoxy resin filled with boric acid of concentration 10 wt. %. The studied samples were grinded to powder in mortar for all the experiments.

Analysis of gaseous products released during heating of the samples, was performed using a quadrupole mass spectrometer QMS 403 Aëolos coupled with a simultaneous thermal analyzer STA 449C Jupiter (Netzsch, Germany). Approximately 5 mg of the samples were placed in an Al_2O_3 crucible. The samples were heated from room temperature up to 800 °C at a heating rate of 10 °C/min in air with a gas flow rate of 50 mL/min. For mass spectrometry analysis, mass-to-charge ratio (m/z) values from 10 to 100 were collected and m/z intensities of interest (28, 30 and 44) were monitored with time.

3. Results and discussion

Figure 1 shows the evolution of the volatile products with mass-to-charge ratio $m/z = 28$; 30 and as a function of temperature. The ions with $m/z = 28$ and 44 correspond to carbon monoxide $[CO]^+$ and carbon dioxide $[CO_2]^+$, respectively. The value $m/z = 30$ indicates the release of ions of formaldehyde $[CH_2O]^+$. The main volatile gas released during thermooxidative process is carbon monoxide.

a)   b)
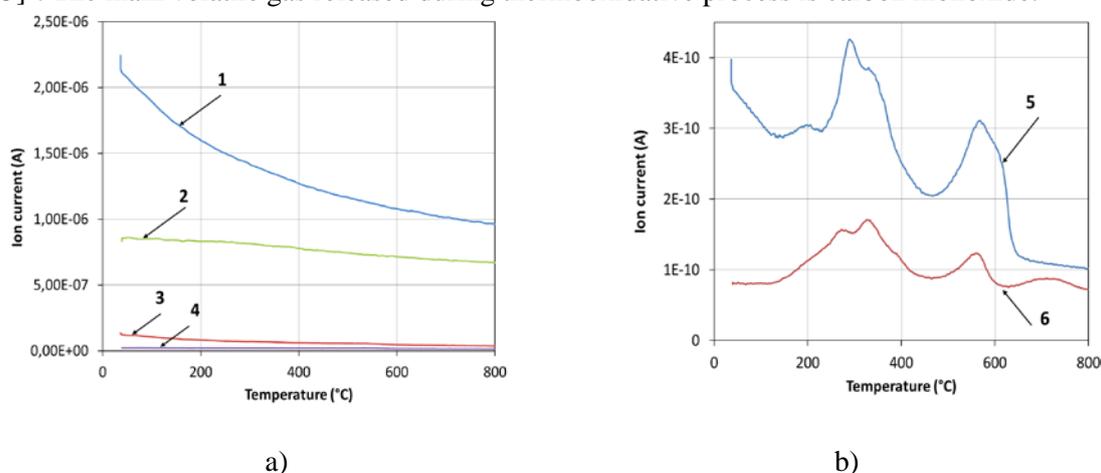
Figure 1. Dependence of ions current on temperature a) $m/z = 28$ (1 and 2) and 44 (3 and 4); b) $m/z = 30$ (5 and 6): 1, 3, 5 – unfilled epoxy polymer; 2, 4, 6 – epoxy polymer filled with 10 wt. % boric acid.

The analysis of experimental data indicates that the incorporation of boric acid in the epoxy matrix as a filler decreases the intensity of the emission of volatile decomposition products of the epoxy samples at the heating. For the molecular ions $[CO]^+$ and $[CO_2]^+$ intense background signals are observed at mass thermograms. Nevertheless, the intensity of signals for the filled sample EB10 is less in 2–2.5 times than for the unfilled sample.

The analysis of the intensity of the ion current for the molecular ion of formaldehyde $[CH_2O]^+$ revealed that its emission during thermooxidative destruction of the samples occurs in three stages. Table 1 shows the results of analysis.

According to the data of table 1 the incorporation of boric acid in the epoxy matrix resulted in a decrease of the maximum temperature of the first peak of the ion current curve by 16 °C and the third peak by 8 °C. A decrease of the ion current over the entire temperature in 2.3–2.7 times is observed.

Table 1. The intensity of the ion current for the gaseous decomposition product with the mass number $m/z = 30$

Sample	Stage 1		Stage 2		Stage 3	
	T_{max} (°C)	I (A)	T_{max} (°C)	I (A)	T_{max} (°C)	I (A)
E0	288	$4.26 \cdot 10^{-10}$	330	$3.86 \cdot 10^{-10}$	568	$3.11 \cdot 10^{-10}$
EB10	272	$1.57 \cdot 10^{-10}$	330	$1.7 \cdot 10^{-10}$	560	$1.23 \cdot 10^{-10}$

Figure 2 shows the dependence of mass changes (TG) and heat release (DSC) during heating of the samples on the temperature. The results of thermal analysis of the studied samples are shown in table 2.

a)   b)
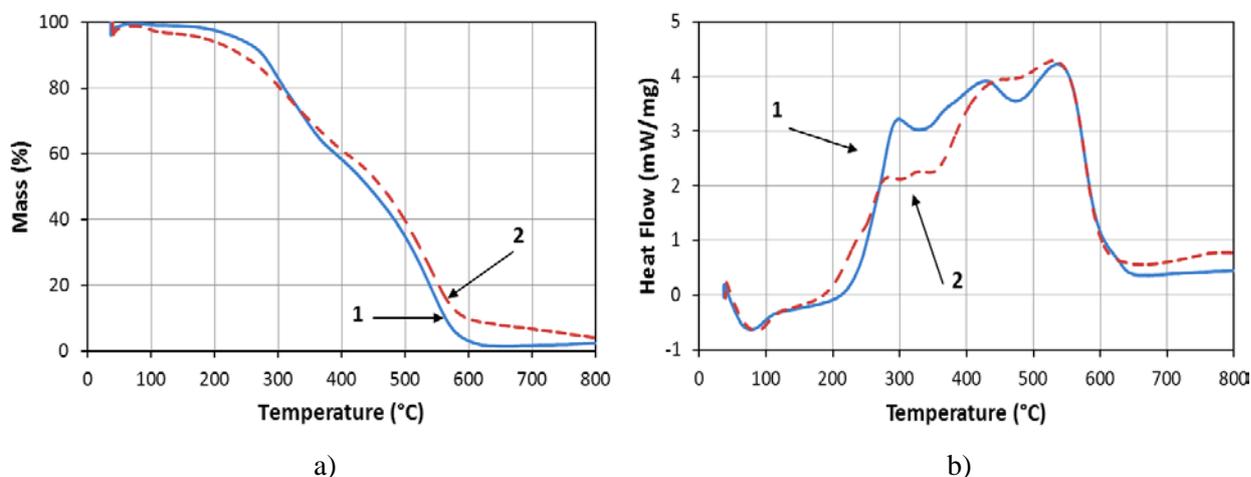
Figure 2. TG (a) and DSC (b) curves of the epoxy composites: 1 – unfilled epoxy polymer; 2 – epoxy polymer filled with 10 wt. % boric acid.

Table 2. The results of thermal analysis

Sample	Stage 1		Stage 2		Stage 3		Residue at 600 °C (%)
	Temperature range (°C)	T_{max} (°C)	Temperature range (°C)	T_{max} (°C)	Temperature range (°C)	T_{max} (°C)	
E0	236–328	298	328–473	429	473–603	535	3.0
EB10	196–345	284	345–467	430	467–600	530	9.8

The process of thermooxidative degradation occurs in three stages with heat release in each of them. The greatest amount of heat is released upon heating the samples on the second and third stages, which correspond to the oxidation of carbon residue. According to the thermal analysis data, the onset temperature of degradation (corresponding to the 5 % of mass loss) for the filled sample EB10 is lower by 40 °C than that for the unfilled epoxy sample. The residual mass of the filled sample EB10 at 600 °C is 9.8%, which is higher by 6.8% than for the unfilled sample E0. The increased residue yield of the sample EB10 compared with the unfilled sample E0 also indicates the reducing amount of the gaseous products. The total specific heat effect for the sample E0 is 15112 J/g, and for the sample EB10 is 13086 J/g. The thermal effect of the first stage for the filled sample is less in 1.5 times than for the unfilled epoxy resin.

These results are explained by the fact that at the heating of the filled sample endothermic decomposition of boric acid occurs with release and evaporation of water and the consequent formation metaboric acid HBO_3 and boron oxide B_2O_3 [14]. This contributes to cooling of the polymer surface and dilution of volatile products of the polymer degradation. The formation of non-flammable boron oxide layer reduces the flame spread of polymer surface.

4. Conclusion

We have investigated the effect of fine powder of boric acid used as filler in the epoxy resin, on gaseous products formed upon heating of the epoxy polymers in air up to 800 °C. The thermooxidative degradation characteristics and the volatile products were studied by means of thermogravimetry and differential scanning calorimetry coupled with mass spectrometer. The incorporation of boric acid into epoxy resin resulted in increased yield of the residue after thermooxidative degradation and reducing the amount of volatile products. The analysis of the gaseous products of thermal oxidative degradation indicates a decrease in 2–2.4 times of toxic gaseous products such as carbon monoxide CO, carbon dioxide CO_2, formaldehyde CH_2O.

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