

Zinc-based compounds as smoke suppressant agents for an aerospace epoxy matrix

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Abstract

Smoke is considered to be the main hazard of fires involving epoxy resins but its production depends on many variables, principally the chemical character and the burning rate of the polymer plus the availability of oxygen. The work reported aimed to study the smoke suppressant effect and flammability performance of zinc-based compounds (FR system) in epoxy matrix composites used in the aerospace and aeronautical industry. The flammability performance of neat and FR-loaded systems was screened using microcombustion calorimetry, while smoke generation, in terms of carbon monoxide (CO) and carbon dioxide (CO₂) production, was analysed under dynamic conditions using cone calorimetry. Final results indicate that the dispersion of zinc borate and zinc hydroxystannate (ZHS) into epoxy matrices leads to a significant variation in flame retardant properties reducing both total heat release by about 25 and 30%, respectively, and heat release capacity by about 30 and 50%, respectively. The system containing ZHS shows an enhancement in all smoke suppressant properties; both tin compounds (zinc stannate (ZS) and ZHS) give a reduction of CO₂/CO ratio from 41 to 25 for ZS and from 41 to 36 for ZHS compared to neat matrix.

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Keywords: polymer flame retardancy; microcombustion calorimetry; epoxy; smoke suppressant; zinc compounds

INTRODUCTION

Epoxy resins are widely used in the manufacture of high-performance composites. These thermosetting systems are adopted when a higher level of functionality is needed hence when a greater number of crosslinking points per epoxy group is required, as for instance in some of the higher performance resins used in aerospace applications. Decomposition of most epoxies takes place with dehydration of secondary alcohol at a temperature of about 300 °C, which leads to the formation of weak allylic bonds. The scission reactions decompose 80–90% of the original polymer weight into almost 100 different volatile compounds, which are mainly various types of substituted alkylated phenols, aromatic ether derivatives and other flammable organic species. These compounds provide a fuel source for the decomposition reaction until the epoxy is completely degraded. Some 10–20% of the original polymer weight is transformed into a highly porous char, and, in the presence of air, this will start to oxidize above 550 °C.

The high yield of flammable volatiles produced in the decomposition reaction is the main reason for the relatively poor fire performance of epoxy matrix composites.¹ Recent studies^{2–4} to develop flame retardants have used inorganic tin compounds such as zinc hydroxystannate (ZHS) and zinc stannate (ZS) due to their low toxicity. Further investigations⁴ of inorganic tin compounds such as ZS and ZHS revealed that these compounds outperform tin oxides in terms of flame retardancy and smoke suppression via enhanced char formation. Cusack and co-workers^{3,5–8} indicated that ZHS and ZS could be used as highly effective flame retardants when compared to antimony compounds. Moreover toxic decomposition products (e.g. HCl) evolved during the combustion process of halogenated polymers

were observed when using antimony compounds as flame retardants with high specific optical density smoke production.¹ Xu *et al.*⁹ have investigated the flame retardant and smoke suppressant properties of inorganic tin compounds for poly(vinyl chloride) (PVC). It was demonstrated that ZS and ZHS reduced the initial decomposition temperature of PVC and their action as flame retardants of PVC led to rapid char formation. Several studies have been reported on the mechanism of action of tin compounds as flame retardants and smoke suppressants for halogenated polyester thermosets^{10,11} and Horrocks *et al.*¹² have reported the usage of ZS and ZHS as smoke suppressants in various polymers. However, few studies have been published on flame retardant and smoke suppression properties of inorganic tin compounds hosted in an epoxy system.

Polymer composites, generally, release dense smoke that limits visibility and can cause disorientation for people attempting to escape from a fire. The smoke generally consists of agglomerated fine soot particles originating in three distinct steps: nucleation, growth and agglomeration. In fact nucleated 'embryonic species' grow to spherical particles 10–50 nm in diameter following an agglomeration stage after thermal decomposition of the polymers.¹ In the case of composite materials, organic fibres

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can also be present in the smoke. Smoke can also contain microscopic fragments of non-combustible fibres, although these usually account for a small percentage of the total smoke content. The relevance of smoke in human survival in a fire has prompted the characterization of smoke properties for a wide variety of thermosetting and thermoplastic matrix composites.¹³

Microcombustion calorimetry (MCC) has been proposed and studied as valid tool for assessing the fire behaviour of milligram-sized samples.^{14–17} The MCC methodology combines the constant heating rate and flow characteristics of thermal analysis methods such as thermogravimetry with the capability to determine heat of combustion typical of oxygen bomb calorimetry. However, MCC determines the heat release and heat release rate using the oxygen consumption method, so that it corresponds to fire calorimetry rather than to thermal analysis. MCC was originally developed by the US Federal Aviation Administration (FAA) under the name of pyrolysis flow combustion calorimetry, and the technique has shown success in measuring the flammability of pure polymers, polymers with fire retardants and systems of fire-retarded polymers with additives.

Lyon and Walters¹⁵ measured the rate and total amount of heat released by the combustion of fuel gases generated during thermal decomposition using MCC. Scharrel *et al.*¹⁶ used MCC to determine the flammability of a polycarbonate blend containing various flame retardants and additives. Furthermore, Morgan and Galaska¹⁷ analysed the flammability performance of polymer nanocomposite, flame retardant, and polymer nanocomposite with flame retardant systems through the use of MCC.

Recently, Formicola *et al.*¹⁸ studied the synergistic effects of zinc borate (ZB) and aluminium trihydroxide on the flammability behaviour of the same aerospace epoxy system investigated in the present work. Analyses of flame retardancy, smoke suppression and thermal degradation behaviour were carried out on various samples, characterized by various concentrations of each additive, and also their combinations, using cone calorimetry, thermogravimetry/differential thermogravimetry and SEM analysis. They found that amounts of ZB and aluminium trihydroxide higher than 20 wt% enhanced the fire behaviour of the neat resin, preserving at the same time the processability feature of the system. Moreover, a combination of the two fillers, at lower specific content, can act synergistically on the flammability behaviour of the neat resin minimizing the risk of adverse effects of original materials.

Smoke behaviour is extremely important for the considered resin system (RTM6 epoxy matrix) in the light of the recent development of stringent aeronautic regulations by aviation authorities. The effect of zinc-based flame retardants on the degradation behaviour of RTM6 was reported by De Fenzo *et al.*¹⁹ Flammability behaviour of neat and loaded epoxy, considering various concentrations (5, 10, 20, 30 and 40 wt%), was investigated experimentally using cone calorimetry. Moreover, as the considered epoxy system is specifically designed for the manufacture of composite elements by liquid infusion processes, a preliminary chemo-rheological characterization was performed. An increase of viscosity, due to high filler contents, would lead to unacceptable levels of injection pressure and possibly to the complete non-processability of the system by liquid moulding. A concentration of 30 wt% was found as an optimal content to balance the fire performance and processability requirements as a result of the preliminary chemo-rheological analysis performed. Finally, degradation analysis of RTM6 using two models, the Kissinger and Flynn–Wall–Ozawa, has shown

that ZHS compounds, compared to neat epoxy, ZB and ZS, lead to two different decomposition steps instead of one.¹⁹

It has been found consistently that smoke, released by the materials discussed above, indeed represents a potential hazard to people's lives; in fact, not only for transportation applications but also for furniture and accessories, smoke-related parameters are considered critical features for developing safety procedures and evacuation plans. Within this scenario, the effects of various smoke suppressants on flammability and smoke suppression of a flame-retarded monocomponent epoxy have been studied using MCC and cone calorimetry. A filler content of 30 wt% was assumed as suitable, as this content gives better flame retardancy with appropriate resin specification according to the requirements of vacuum infusion processes employed to manufacture long-fibre composite elements.¹⁹

EXPERIMENTAL

Materials

The epoxy system (RTM6) considered in this paper is a monocomponent resin generally used in the aerospace/aeronautical sector. This system is commonly processed using the liquid infusion technique due to its suitable viscosity profile which can vary from a very high value (3000 Pa s) at 20 °C to a lowest level of 50 mPa s at 120 °C. RTM6 is a pre-catalysed resin and its polymerization reaction is achieved by temperature only. Three different smoke suppressant compounds supplied by Joseph Storey Company, namely ZB, ZS and ZHS, were used as flame retardants.

Sample preparation

Epoxy mixtures were prepared by mechanical stirring. Each zinc-based compound (ZB, ZS and ZHS) was gradually added at 30 wt%, while the epoxy resin was kept at an isothermal temperature of 90 °C. This temperature allowed better processability of the resin ensuring a suitable level of viscosity for the dispersion of the micro-sized filler and an uncured state of the resin during the whole mixing stage.

Mixing was performed for 10 min at 1050 rpm followed by 10 min at 2000 rpm. The system was then degassed for 30 min at 90 °C under vacuum to eliminate entrapped air, volatiles and humidity. Finally the liquid system was poured into an aluminium mould and cured at 160 and 180 °C for 90 and 120 min, respectively, according to the cure kinetics.

Microcombustion calorimetry

MCC measurements were carried out according to the ASTM D7309-07 standard¹⁴ using a FAA microcalorimeter instrument supplied by Fire Testing and Technology Ltd (UK). The heating rate was 1 °C s⁻¹ and the maximum pyrolysis temperature was 700 °C with a combustion temperature of 900 °C for the evolved gases. The flow was an O₂/N₂ mixture at a ratio of 20/80 cm³ min⁻¹ and the sample weight was 5 ± 0.5 mg. Each measurement was repeated on three different samples for repeatability purposes, so the values reported are averaged ones.

Cone calorimetry

Cone calorimetry measurements were carried out according to the ASTM E1354/ISO 5660 standard on samples with nominal dimensions of 100 × 100 × 7 mm³ using a Fire Testing Technology Ltd instrument. All measurements were repeated three times and the results averaged according to the standard

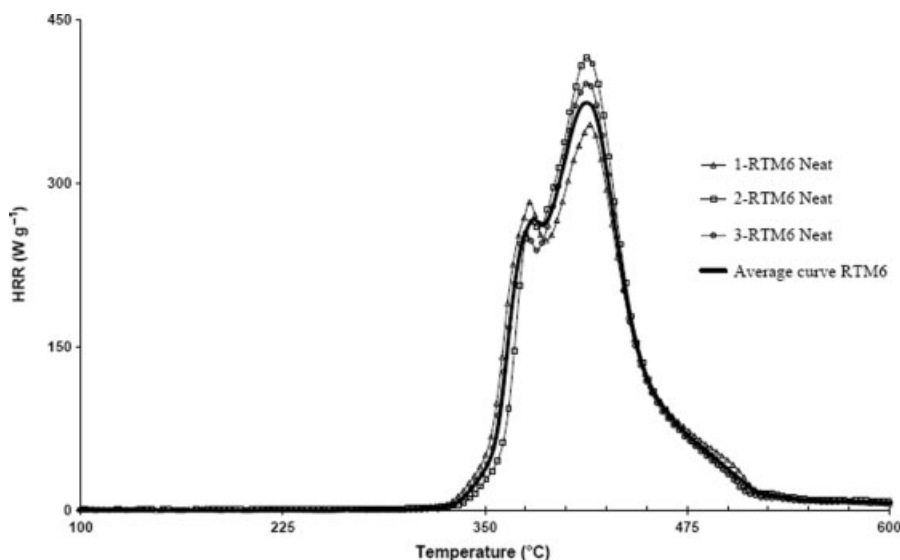


Figure 1. MMC tests for the neat RTM6 epoxy system. The bold curve represents the averaged curve.

specification. Due to irregularities of the wet-cutting process, a sample surface of 100 cm² was assumed for the purpose of heat release rate calculations. All cone calorimetry data were considered to have an error of ±5%.²⁰ An incident heat flux of 50 kW m⁻² was used to represent a well-ventilated developing fire condition. The cone calorimeter measured the optical density of the smoke by monitoring the intensity of light transmitted from a helium–neon laser beam located in the exhaust duct of the cone calorimeter. Yields of CO and CO₂ were measured using a CO–CO₂ gas analyser located in the exhaust duct.

RESULTS AND DISCUSSION

MCC results

MCC testing was carried out on neat and loaded epoxy systems to evaluate total heat release and heat release capacity. This technique allows the measurement and calculation of the following parameters.

- Heat release capacity (HRC; J g⁻¹ K⁻¹): described as the maximum specific heat release rate (HRR) during controlled thermal decomposition divided by the heating rate in the test, expressed as

$$\text{HRC} = \frac{q_{\max}}{\beta} = \frac{(1 - \mu)h_c^2}{eRT_{\max}^2/E_a} = \frac{\text{HR}}{\Delta T_p}$$

where β is the heating rate, μ the char yield, E_a the global activation energy for pyrolysis, T_{\max} the sample temperature at maximum HRR q_{\max} and ΔT_p the pyrolysis temperature interval.

- Total heat release per unit initial mass (total HR; kJ g⁻¹): defined as the maximum HRR divided by the constant heating rate.
- Heat release rate peak (pHRR; W g⁻¹): corresponds to the maximum amount of heat liberated by a material during the combustion process, and it often occurs over a very short period of time. The pHRR is considered a critical property controlling the maximum temperature and flame spread rate.

Sample	HRC (J g ⁻¹ K ⁻¹)	Total HR (kJ g ⁻¹)	pHRR (W g ⁻¹)	T_{peak} (°C)
RTM6 neat, sample 1	542.3	28.5	282.1	351.8
RTM6 neat, sample 2	465.8	28.3	264.2	411.0
RTM6 neat, sample 3	542.3	27.8	247.3	389.3
Averaged value	516.8	28.2	264.5	377.1
Standard deviation	44.2	0.4	17.4	29.9
Coefficient of variation (%)	8.5	1.4	6.6	7.8

- Temperature to peak (T_{peak} ; °C): represents the temperature at which the pHRR occurs.

Figure 1 shows three different microcombustion curves obtained from specimens of neat resin. The curves are repeatable, although a slight variation of the main peak height is recorded. Data show that the MCC tests are highly repeatable with a coefficient of variation below 10%. A comparison of the MCC HRR curves shows that the shapes of the curves are repeatable although a slight variation of the height of the two characteristic peaks is recorded. The flammability parameters for all three MCC curves of the neat epoxy system are reported in Table 1 along with averaged values and standard deviations. Two distinct values for pHRR and T_{peak} are identified, as a double peak is obtained for all replicate tests performed on various samples. Degradation analysis of epoxy resin performed using thermogravimetric measurements shows that, in air flow, two distinct decomposition steps occur at 370 and 570 °C while dehydration of secondary alcohol is generally observed at 250 °C as a pre-stage, corresponding to 1.1% mass lost, within the range 30–250 °C, as also reported by others.^{19,21,22} A similar behaviour is recorded during the burning process using MCC. The first peak of HRR occurs at 375 °C and the second is observed at 410 °C. The MCC curve shows also a slight shoulder,

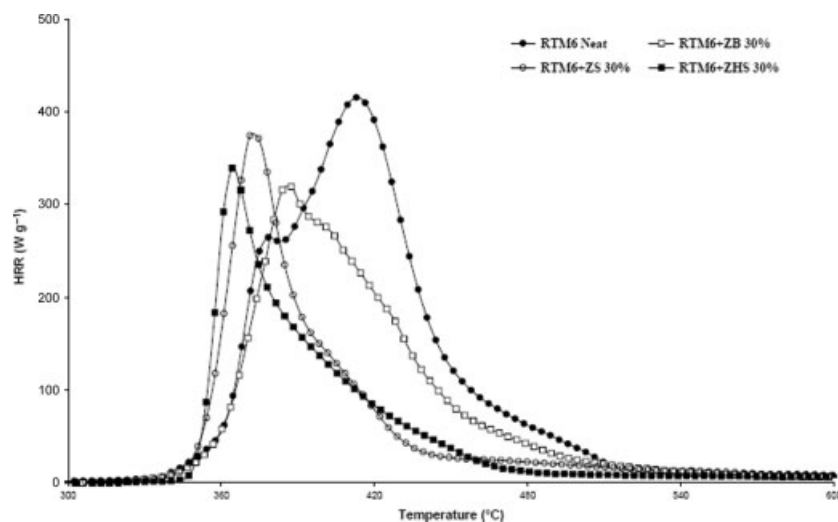


Figure 2. HRR curves as a function of temperature.

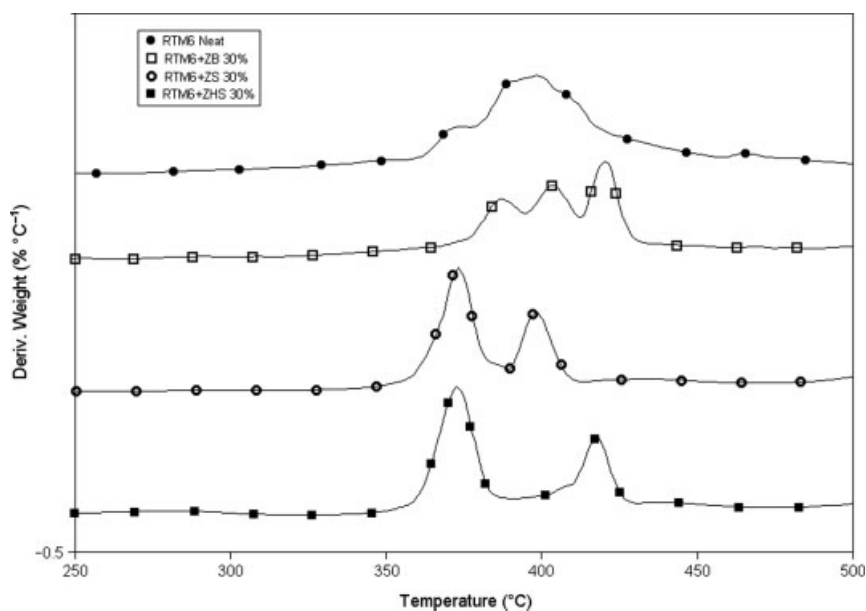


Figure 3. Differential thermogravimetry curves for RTM6 and RTM6 loaded with 30 wt% ZB, ZHS and ZS under air flow at a heating rate of $20\text{ }^{\circ}\text{C min}^{-1}$.

identified at a very high temperature scan using TGA, which can be associated with the equilibrium lag due to the temperature rate, more accentuated in the case of MCC for which the temperature rise during the pyrolysis of the sample is at a rate of $1\text{ }^{\circ}\text{C s}^{-1}$.

Figure 2 shows HRR *versus* temperature curves for the loaded epoxy system compared to the neat epoxy resin, Fig. 3 shows TGA curves for the same samples obtained in air at $20\text{ }^{\circ}\text{C min}^{-1}$ and displayed in the temperature range between 300 and $500\text{ }^{\circ}\text{C}$ and Table 2 gives the values obtained from tests carried out using MCC. It can be seen that the addition of zinc compounds is effective in lowering the heat release of the neat epoxy matrix as also reported previously using TGA.¹⁹ The peak for the mixture of resin and ZB at about $380\text{ }^{\circ}\text{C}$ (Figs 2 and 3) is due to the mechanism of action associated with ZB. ZB decomposes at elevated temperature and releases water which dilutes organic volatiles in the flame and thereby contributes to a reduction in the flame temperature.¹ The addition of ZB, as shown in Fig. 3, leads to the appearance of three

peaks. The first two peaks between 380 and $410\text{ }^{\circ}\text{C}$ are similar but delayed compared to those observed in the curve of pure resin which is due to dehydrogenation of the resin, resulting in breakage of the polymer chains. The third peak occurring around $430\text{ }^{\circ}\text{C}$ is due to oxidation of char, which creates a compact ceramic structure to protect the surface.¹⁹ The addition of ZB to the epoxy resin results in a reduction of about 22% in HRC, from 405 to $317\text{ J g}^{-1}\text{ K}^{-1}$ (Table 2), associated with the formation of a glass layer over the combusted surface of the sample which reduces volatile emission during the combustion stage. The total HR is reduced by 24% for the ZB-containing system while the pHRR value is reduced by 22% at a temperature of $385\text{ }^{\circ}\text{C}$. This is due to the structure of the compact ceramic char that is created on the surface.

Regarding the ZS- and ZHS-containing systems, a rough decomposition temperature region has been estimated at $350\text{--}380\text{ }^{\circ}\text{C}$ as reported in the literature.²³ In fact the two peaks

Table 2. MCC heat release parameters and char structure

Sample	HRC (J g ⁻¹ K ⁻¹)	Total HR (kJ g ⁻¹)	pHRR (W g ⁻¹)	T _{peak} (°C)
RTM6 neat	405 ± 2	28.1 ± 2.2	411 ± 10	412 ± 3
RTM6 + ZB 30 wt%	317 ± 2	21.4 ± 1	320 ± 12	385 ± 2
RTM6 + ZS 30 wt%	369 ± 5	15.5 ± 0.9	374 ± 9	372 ± 6
RTM6 + ZHS 30 wt%	332 ± 3	14.1 ± 1.1	337 ± 10	363 ± 2

of the TGA curves in Fig. 3 at a temperature of 360 °C are due to the initial decomposition of these additives. The first peak for both additives is due to dehydrogenation of the resin, resulting in splitting of the polymer chains, while the second peak is due to oxidation of char. The only difference between ZS and ZHS is due to release of water by ZHS involving a peak temperature of 360 °C instead of 380 °C for ZS and which is observed in Fig. 2. Instead, in Fig. 3, we see the so-called second peak at a temperature of ca 400 °C for ZS and 430 °C for ZHS. This difference is caused by the fact that ZHS losing water cools the surface of the material thus delaying the oxidation of char. Table 2 shows a reduction in HRC by about 10 and 20% for ZS- and ZHS-containing systems and a reduction in total HR by about 45 and 50% for ZS- and ZHS-filled epoxy systems.

Cone calorimetry results

Cone calorimetry data, such as total smoke released (TSR), specific extinction area (SEA) and CO and CO₂ production, were used to

evaluate the effect of the zinc compounds on smoke reduction compared with the neat thermoset system. As TSR represents the cumulative smoke yield over a 4 min time period, this parameter is generally assumed as an indicator of the amount of smoke generated in a full-scale fire. Moreover, the time derivative of the evolution curve may be considered a valid indication for the setting of evacuation times and general safety procedures.

Smoke release curves for the three loaded systems and the neat epoxy as a function of time are shown in Fig. 4, while smoke suppressant parameters are reported in Table 3. As can be seen, the tin compound noticeably lower the total amount of smoke released while ZB induces a appreciable variation in the smoke production per time unit (slope of the curve), being almost constant the final plateau value of smoke released. The neat RTM6 burns releasing a total of 9610 m² m⁻² very close to the recorded value of 9416 for RTM6/ZB; a reduction of around 30% is measured for ZS (6609 m² m⁻²) and ZHS (6561 m² m⁻²). SEA is defined as the total obscuration area per unit mass of sample consumed in a fire and this parameter is generally expressed as average SEA over a period of time. This parameter may be an indication of the smoke production but also of the density and the consistency of the released smoke. SEA values decrease from 1126 m² kg⁻¹ for the RTM6 epoxy resin to 916 m² kg⁻¹ for the RTM6/ZHS formulation. Smoke parameter (SP) and smoke factor (SF), reported in Table 3, are calculated using the corresponding pHRR values: SP is the product of pHRR and SEA, whereas SF is the product of pHRR and TSR.

The effect of smoke suppression is evident when comparing the neat RTM6 and samples containing ZS and in particular ZHS. In fact, especially for ZHS, a decrease of all smoke suppressant parameters (SEA, TSR, SP and SF) is observed. ZHS shows superior

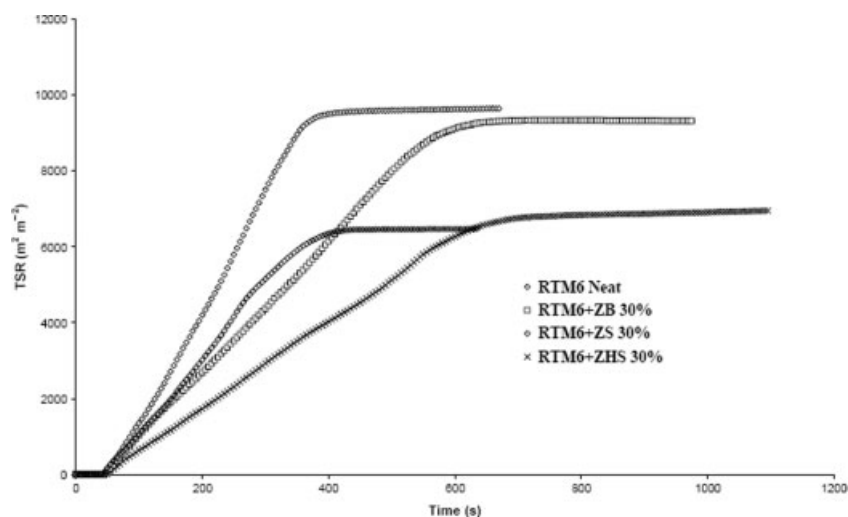


Figure 4. TSR measured using cone calorimetry.

Table 3. Smoke emission data from cone calorimetry measurements

Sample	Average SEA (m ² kg ⁻¹)	TSR (m ² m ⁻²)	TSR slope (m ² m ⁻² s ⁻¹)	SP (MW kg ⁻¹)	SF (MW m ⁻²)
RTM6 neat	1126 ± 56	9610 ± 475	30.5	790 ± 38	6500 ± 322
RTM6 + ZB 30 wt%	1238 ± 60	9416 ± 465	17.3	490 ± 20	4077 ± 205
RTM6 + ZS 30 wt%	981 ± 43	6609 ± 328	20.5	540 ± 26	3586 ± 178
RTM6 + ZHS 30 wt%	916 ± 47	6561 ± 318	11.7	347 ± 16	2549 ± 126

smoke suppressant and flame retardant properties as indicated by pHRR values. The gas products released during the combustion process for composite materials depend on the chemical nature of the organic constituents, oxygen availability and the temperature of the fire. Measurements of CO and CO₂ in conjunction with smoke become fundamental evidence from two perspectives. First, CO and CO₂ are major constituents of fire gases and higher concentrations of CO in a densely smoking fire can lead to carbon monoxide poisoning due to hindered escape. Second, the analysis of carbon oxides (CO and CO₂) generated during burning of a polymer can provide valuable information on the decomposition mechanism of the polymer. Lower values of the CO₂/CO ratio suggest inefficiency of combustion inhibiting the conversion of CO to CO₂. Furthermore, CO and CO₂ production is dependent on the availability of oxygen, chemical constituents of the polymer and the temperature of the fire.²⁴ The yields of CO and CO₂ are not significant in the early burning period because the mass loss rate is higher and gas production is lower compared to gas evolution after the complete combustion process of samples. Table 4 gives the total amounts of CO and CO₂ produced after complete combustion of filled epoxy systems along with the corresponding CO₂/CO ratio.

Table 4. CO₂ and CO data from cone calorimetry measurements

Sample	CO ₂ (kg kg ⁻¹)	CO (kg kg ⁻¹)	CO ₂ /CO
RTM6	33 ± 4	0.8 ± 0.01	41
RTM6 + ZB 30 wt%	40 ± 3	1.6 ± 0.03	25
RTM6 + ZS 30 wt%	22 ± 5	0.9 ± 0.02	24
RTM6 + ZHS 30 wt%	25 ± 6	0.7 ± 0.02	36

Figure 5 shows the curves of CO and CO₂ evolution as a function of time.

Figure 5 shows clearly that the addition of the zinc compounds, especially ZHS, in the RTM6 epoxy matrix reduces the emissions of CO and CO₂. Furthermore the ZHS-containing system shows a second peak towards the end of the burning period. This means that CO is a major reaction product of the incomplete combustion of volatiles to the end of the fire. Table 4 gives the CO and CO₂ data obtained using cone calorimetry. From the table it is evident that the addition of ZS and ZHS to the pure resin reduces CO and CO₂ formation. The CO₂/CO ratio is noticeably smaller than that of

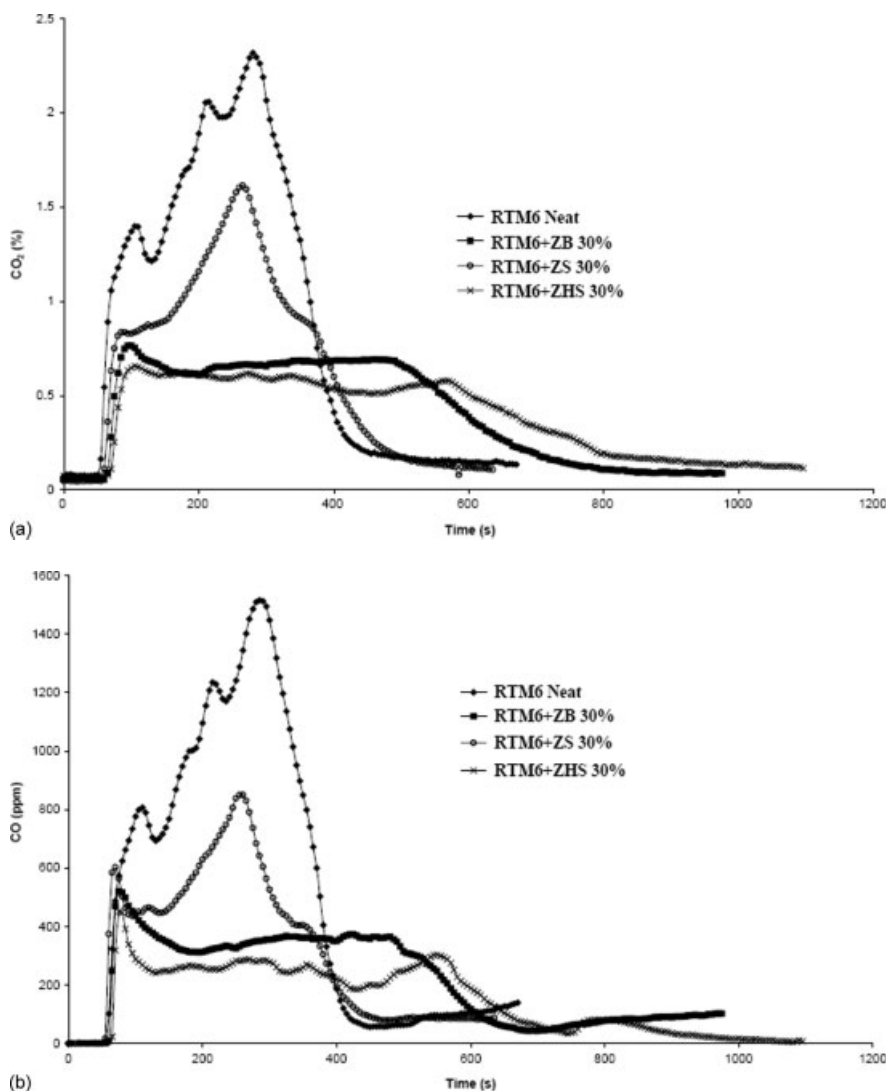


Figure 5. Curves for (a) CO₂ and (b) CO released as a function of time during cone calorimetry tests.

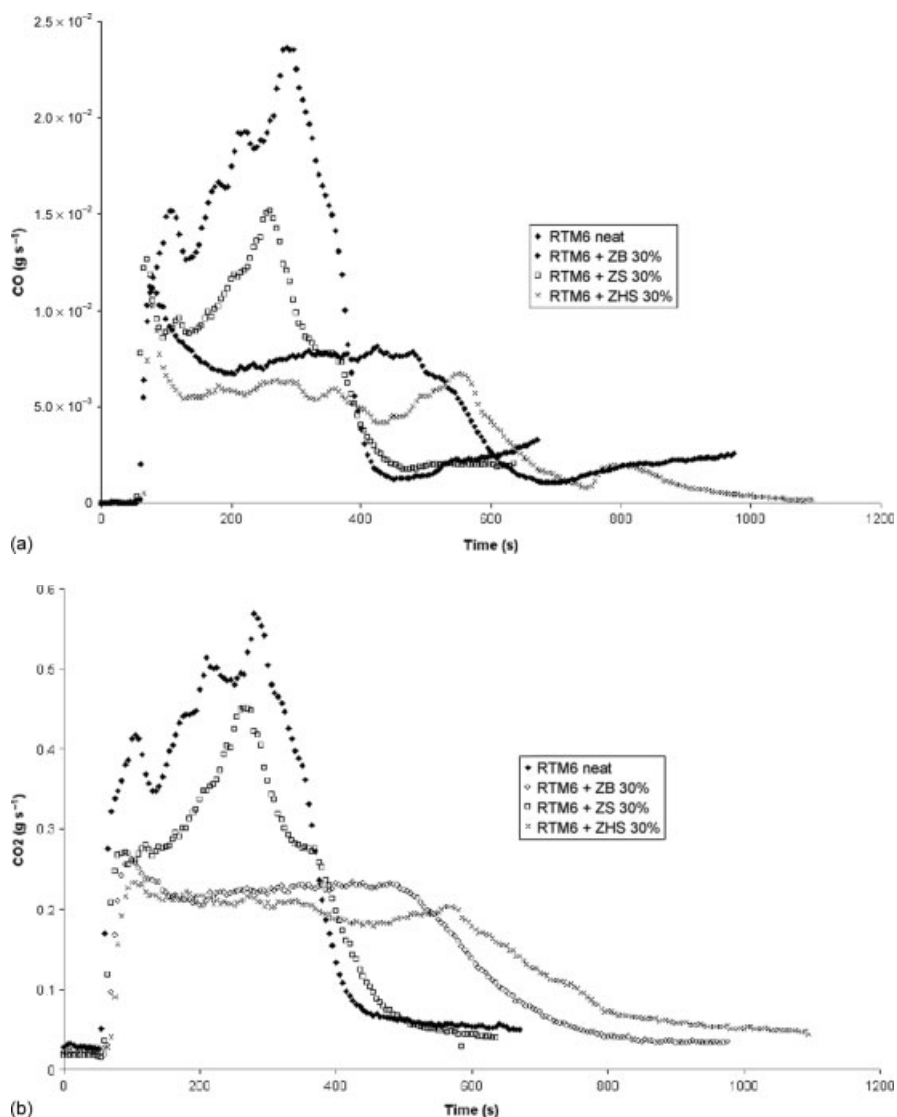


Figure 6. (a) CO and (b) CO₂ evolution rate as a function of time.

RTM6; in fact the CO₂/CO value for epoxy resin is 41 compared to that for epoxy resin with ZS of 24. The gas evolution rate for loaded and unloaded epoxy systems is shown in Fig. 6; a second peak at the end of the combustion process is observed for RTM6/ZHS.

CONCLUSIONS

The effects of various zinc compounds on flammability and smoke suppression of a flame-retarded monocomponent epoxy resin were investigated using MCC and cone calorimetry analysis. Based on previously published results, a fixed composition of 30 wt% for each zinc additive in the RTM6 epoxy system was assumed as a suitable compromise between processability requirements and flame retardant effects. The following important conclusions can be drawn from the experimental data presented.

- The addition of ZB decreases total HR and HRC by about 30% from 28.1 to 21.4 kJ g⁻¹ (total HR) and from 405 to 317 J g⁻¹ K⁻¹ (HRC).
- The addition of ZHS decreases total HR by about 50% from 28.1 to 14.1 kJ g⁻¹ and reduces HRC from 405 to 332 J g⁻¹ K⁻¹.
- In the case of smoke suppressant behaviour, the system containing ZHS shows a decrease in all smoke suppressant parameters: average SEA, TSR, SP and SF.
- The reduction of CO₂ production is evident with the addition of ZS and ZHS: from 33 to 22 kg kg⁻¹ for ZS and from 33 to 25 kg kg⁻¹ for ZHS.
- The presence of the zinc compounds strongly reduces the rate of smoke production. In fact, a different rate of production represented by the slope of the TSR curve is recorded for all three cases.
- Plateau level of the TSR curve is almost unchanged for ZB, but, in contrast, it is noticeably lowered by the presence of the tin compounds (ZS and ZHS), reducing the smoke production in terms of total amount of smoke released.

Future work will focus on the effects of these micro-sized fillers on the mechanical behaviour of the epoxy matrix. This will be in order to assess the potential application of these additives to reduce smoke evolution and flammability without any detrimental effects on the mechanical performances of the matrix and therefore matrix-dependent composite properties.

REFERENCES

- 1 Mouritz AP and Gibson AG, *Fire Properties of Polymer Composite Materials, Solid Mechanics and its Applications*, vol. 143. Springer, Dordrecht, pp. 19–98 (2006).
- 2 Cusack PA, Monk AW, Pearce JA and Reynolds SJ, *Fire Mater* **14**:23–29 (1989).
- 3 Andre F, Cusack PA, Monk AW and Seangprasertkij R, *Polym Degrad Stab* **40**:267–273 (1993).
- 4 Bains RS, Cusack PA and Monk AW, *Eur Polym J* **26**:1221–1227 (1990).
- 5 Cusack PA, Heer MS and Monk AW, *Polym Degrad Stab* **58**:229–237 (1997).
- 6 Cusack PA and Hornsby PR, *J Vinyl Additive Technol* **5**:21–30 (1999).
- 7 Cusack PA, *Fire Mater* **10**:41–46 (1986).
- 8 Cusack PA, Monk AW, Pearce JA and Reynolds SJ, *Fire Mater* **14**:23–29 (1989).
- 9 Xu J, Zhang C, Qu H and Tian C, *J Appl Polym Sci* **98**:1469–1475 (2005).
- 10 Atkinson PA, Haines PJ and Skinner GA, *Thermochim Acta* **360**:29–40 (2000).
- 11 Atkinson PA, Haines PJ and Skinner GA, *Polym Degrad Stab* **71**:351–360 (2001).
- 12 Horrocks AR, Smart G, Price D and Kandola B, *J Fire Sci* **27**:495–521 (2009).
- 13 Brown JR and Mathys Z, *Composites A* **28A**:675–681 (1997).
- 14 ASTM D7307-07, *Standard test method for determining flammability characteristics of plastics and other solid materials using microscale combustion calorimetry*. ASTM, West Conshohocken, PA (2007).
- 15 Lyon RE and Walters RN, *J Anal Appl Pyrol* **71**:27–46 (2004).
- 16 Schartel B, Pawlowski KH and Lyon RE, *Thermochim Acta* **462**:1–14 (2007).
- 17 Morgan AB and Galaska M, *Polym Adv Technol* **19**:530–546 (2008).
- 18 Formicola C, De Fenzo A, Zarrelli M, Frache A, Giordano M and Camino G, *Express Polym Lett* **3**:376–384 (2009).
- 19 De Fenzo A, Formicola C, Antonucci V, Zarrelli M and Giordano M, *Polym Degrad Stab* **94**:1354–1363 (2009).
- 20 Zhao L and Dembsey NA, *Fire Mater* **32**:1–26 (2008).
- 21 Rose N, Le Bras M, Delobel R, Costes B and Henry Y, *Polym Degrad Stab* **42**:307–316 (1993).
- 22 Rose N, Le Bras M, Bourbigot S and Delobel R, *Polym Degrad Stab* **45**:387–397 (1994).
- 23 Wrobel G, Piech M, Dardona S, Ding Y and Gao PX, *Cryst Growth Design* **9**:4456–4460 (2009).
- 24 Mouritz AP, Mathys Z and Gibson AG, *Composites A* **37**:1040–1054 (2006).