

SYNERGISTIC EFFECTS OF ZINC BORATE AND ALUMINUM TRIHYDRATE ON FLAMMABILITY BEHAVIOUR OF AEROSPACE EPOXY SYSTEM

A. De Fenzo^{1,2}, Cristina Formicola^{1,2}, Mauro Zarrelli^{1,2*}, Alberto Frache³
Michele Giordano^{1,2} and Giovanni Camino³

¹ IMCB – Institute of Composite and Biomedical Materials, CNR – Research National Council,
P. E. Fermi 1, Portici 80055, ITALY

² IMAST – Technological District on Polymeric and Composite Materials Engineering,
P. E. Fermi 1, Portici 80055, ITALY

³ Material Science and Chemical Engineering Dept., Polytechnic of Turin in Alessandria,
Via Teresa Michel 5, 15100 Alessandria, ITALY

*mauro.zarrelli@imcb.cnr.it

SUMMARY

Flame retardancy of mono-component epoxy resin, used for aerospace composites, treated with zinc borate (ZB), aluminum trihydrate (ATH) and their mixtures at different percentages have been investigated by morphological and thermal characterization. Cone calorimeter data reveal that peak HRR decreases when synergistic effects between additives occur.

Keywords: Epoxy Resin; Fire retardancy; Zinc borate; Aluminum trihydrate; Cone calorimeter

INTRODUCTION

Zinc borate is an effective inorganic flame retardant and it possesses characteristic properties of flame retardancy (FR), smoke suppression, promoting charring, etc.[1-2] particularly important according to new fire standards. Zinc borate is commonly used as multifunctional flame retardant in combination with other halogenated or halogen-free flame retardant systems to boost FR properties [3-4]. Its efficacy depends upon the type of halogen source (aliphatic versus aromatic) and the used polymer root. The zinc borate can generally display synergistic effects with antimony oxide in fire retardancy. In the presence of aluminium trihydroxide (ATH) or magnesium hydroxide (Mg(OH)₂), this synergy can be augmented significantly [5]. Previous studies [6-8] have demonstrated that there are major advantages in using a combination of zinc borates with other flame retardants in several kinds of polymers (EVA, PVC, Polyamides, etc...). Furthermore, different authors [9-11] analyzed the fire and smoke behaviours of zinc borate and its synergist effect only in thermoplastic systems or in thermosetting bi-component matrices.

In this work, the synergistic effect of zinc borate and aluminium trihydroxide on the flame retardancy, smoke suppression, and thermal degradation behaviour of a

monocomponent epoxy resin (RTM6) is investigated. The considered epoxy system is widely used in primary and secondary composite structures within the aerospace sector (Ariane 5 and Airbus A380 [12]) for which fire behaviour represents an important feature upon the final application. The fire retardancy of different samples, characterized by various percentages of each additive and their combinations is exploited by cone calorimeter, TG-DTG and SEM analysis.

Materials and processing

The epoxy resin used is a commercially available pre-hardened epoxy-amine system labelled RTM6. The system was provided by Hexcel Composites (Duxford, UK). The ultra fine zinc borate ($2\text{ZnO} \cdot 3\text{B}_2\text{O}_3 \cdot 3.5\text{H}_2\text{O}$) and the aluminium trihydroxide ($\text{Al}(\text{OH})_3$) were supplied respectively by Joseph Storey & Co. (UK) and by Dadco (UK). The composite were prepared by mixing the epoxy resin with ZB and ATH both separately and in combination. For the separate mixtures 5 % w/w, 10 % w/w, 20 % w/w, 30 % w/w and 40 % w/w were used while for the combination they were mixed at 1:1 ratio in mass at 10 % w/w, 20 % w/w, 30 % w/w and 40 % w/w. The mixing was performed by using a Heidolph RZR mechanical stirring equipment. The samples were prepared by mixing RTM6 with ZB and ATH for 10 min at 1050 rpm and 10 min at 2000 rpm. Obtained mixture was then degassed for 30 min at 90°C under vacuum to eliminate entrapped air and absorbed humidity. The final liquid mixture was then poured in aluminium mould and cured by a two stage temperature profile (160°C and 180°C respectively for 90 min and 120 min) according to the curing schedule sheet of the neat epoxy resin. Preliminary TGA scans on neat additives were also performed to evaluate their maximum degradation temperatures. It was found that zinc borate and aluminium trihydroxide degrade respectively at 436°C and 299°C well below the set curing conditions.

Experimentals

Cone calorimeter tests were performed using a Fire Testing Technology Ltd. equipment according to the ASTM E1354-04 procedure. Samples, with nominal dimensions of $100 \times 100 \times 7 \text{ mm}^3$, were tested horizontally under an incident flux of 50 kW/m^2 . This level was chosen as it corresponds to the evolved heat during a fire. Thermogravimetric analysis was carried out using a TGA 2950 by TA Instruments. All measurements were conducted under nitrogen flow, with a sample weight of about $7 \pm 0.5 \text{ mg}$; for each test the heating rate was $10^\circ\text{C}/\text{min}$ from ambient to 800°C . The precision on the temperature measurements during each scan, according to the calibration procedure was $\pm 0.5^\circ\text{C}$ in the range $30\text{-}400^\circ\text{C}$ and $\pm 1^\circ\text{C}$ in the range $400\text{-}800^\circ\text{C}$. SEM and optical micrographs of additive powder, composites and residuals were taken respectively by 1450VP LEO SEM microscopy.

Results and discussion

Thermogravimetric analysis (TGA) of derivative signal (DTG) represents a quantitative methodology useful to analyze the stability of materials. TGA scans were performed on all composite samples for each concentration. In the table 1, onset and maximum

degradation temperatures for ZB and ATH filled samples at different percentages are reported. Analysis of the TGA curves and their DTG signals reveals that onset temperature, which corresponds to the value at 5% of weight loss, are significantly augmented in the case of 30 %w/w and 40 % w/w content for both mixtures, RTM6/ATH and RTM6/ZB

Table 1 TGA values of treated RTM6 with ATH and ZB at different concentrations

Sample	T onset	T max	Sample	T onset	T max
RTM6 neat	327±5	389±4			
ATH 5%	332±3	395±3	ZB 5%	342±3	380±2
ATH 10%	325±5	393±3	ZB 10%	348±4	382±4
ATH 20%	321±5	392±4	ZB 20%	352±5	388±3
ATH 30%	360±4	411±2	ZB 30%	368±3	418±5
ATH 40%	368±5	413±3	ZB 40%	379±3	426±4

The synergy between the ZB and ATH was investigated on four different percentages (10 % w/w, 20 % w/w, 30 % w/w and 40 % w/w with 1:1 ratio in mass) and the corresponding DTG curves are reported in Figure 1.

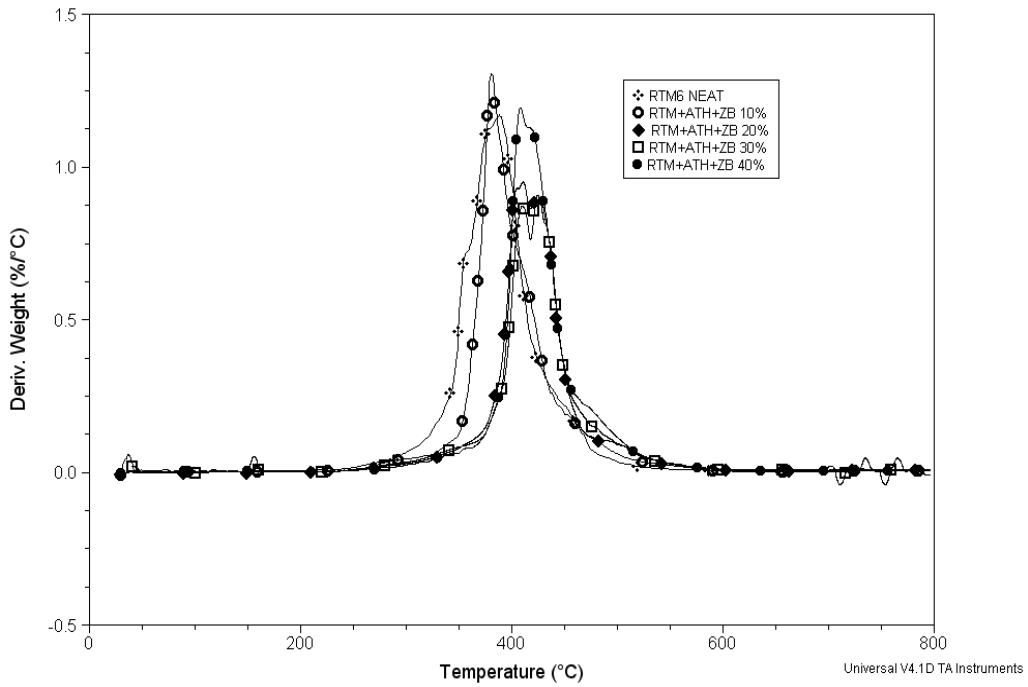


Figure 1 DTG curves of RTM6/ATH/ZB system at different concentrations

Table 2 reports the onset and maximum degradation temperatures for all concentrations considered of ATH/ZB loaded samples according to the thermogravimetry.

Table 2 TGA values of treated RTM6 with ZB+ATH at different concentrations

Sample	T onset (°C)	T max (°C)
RTM6 neat	327±5	389±4
RTM6+ZB+ATH (10%wt)	345±4	381±4
RTM6+ZB+ATH (20%wt)	352±4	417±4
RTM6+ZB+ATH (30%wt)	365±3	428±3
RTM6+ZB+ATH (40%wt)	375±5	434±5

It can be noticed that small variations are found for both parameters if the filler content is lower than 20% weight; whereas, for higher weight content (i.e. higher than 15 % w/w for each filler) appreciable increase of both temperature levels are found. The combination of these two types of flame retardant reduces the overall concentration level needed to achieve a higher flammability resistance, therefore minimising the risk of adverse effects, such as mechanical property degradation and density increasing of the hosting materials. It can be concluded that the addition of ZB and ATH synergistically retards the degradation behaviour of neat matrix system enhancing the flame retardancy of the overall hosting system at lower concentration respect to the stand alone filler loading.

Cone calorimeter test

Cone calorimeter represents a small-scale testing configuration which provides important correlating parameters with real fire scenario; data obtained from cone calorimeter can provide plentiful information on fire scenario behaviour of a specific material [13-15]. The values provided by cone calorimeter are mainly: Time To Ignition (TTI), which corresponds to the period that a combustible material can withstand when exposure to a constant radiant heat flux before igniting and undergoing sustained flaming combustion; Heat Release Rate peak (PHRR) and average (HRR average) are a quantitative measures of the amount of thermal energy released by a material per unit area when exposed to a fire radiating at constant heat flux (or temperature). The cone calorimeter data reported in Table 3 were averaged over three replicate experiments. The HRR value is considered the single most important fire reaction parameter as it represents the most valuable indicator of the fire hazard for a combustible material. Figure 2 reports the HRR curves for the neat epoxy and loaded systems with different ZB content. For the RTM6/ZB compound, the presence of the filler at 5 % w/w, 10 % w/w and 20 % w/w does change substantially neither TTI nor HRR peak parameters. The presence of zinc borate at higher concentrations (30 % w/w, 40 % w/w) improves flame retardant behaviour of the neat resin system enhancing time to extinction of flame and lowering PHRR and HRR average values. Reduced values for the PHRR and HRR average may be correlated with the decomposition of filler and formation of a protective glassy char layer over the sample surface, during the combustion process.

Table 3 Main cone calorimeter parameters evaluated for RTM6 epoxy with ZB and ATH at different concentrations

Sample	TTI [s]	Δ TTI [s]	PHRR [kW/m ²]	HRR Average [kW/m ²]	Δ PHRR [kW/m ²]
RTM6	43±2	-	702±3	382±4	-
RTM6+ZB 5%	44±5	5	682±2	354±3	20
RTM6+ZB 10%	48±4	1	523±3	265±2	179
RTM6+ZB 20%	49±3	6	428±2	251±4	274
RTM6+ZB 30%	58±2	14	396±3	193±3	306
RTM6+ZB 40%	63±2	20	315±2	148±2	387
RTM6+ATH 5%	33±6	-10	815±4	413±2	-113
RTM6+ATH 10%	41±3	8	728±4	383±2	-26
RTM6+ATH 20%	52±3	9	510±5	368±3	192
RTM6+ATH 30%	64±2	21	468±5	324±1	234
RTM6+ATH 40%	93±2	50	453±2	193±2	249
RTM6+ZB+ATH 10%	52±2	9	679±3	337±2	23
RTM6+ZB+ATH 20%	52±3	9	468±2	285±3	234
RTM6+ZB+ATH 30%	55±3	12	431±1	249±2	271
RTM6+ZB+ATH 40%	87±2	44	437±4	74±3	265

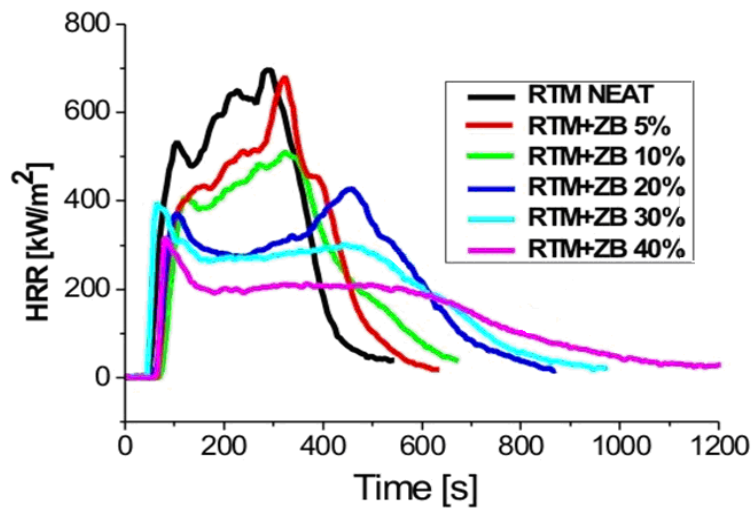


Figure 2 - HRR curves of RTM6/ZB at different concentrations

In the case of ATH filler, it was found that the presence of the micro-sized particles has a detrimental effect at lower concentrations compared with the neat epoxy system (Figure 3).

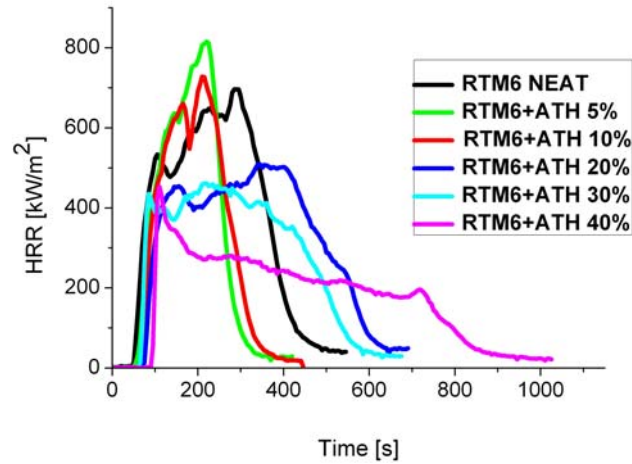
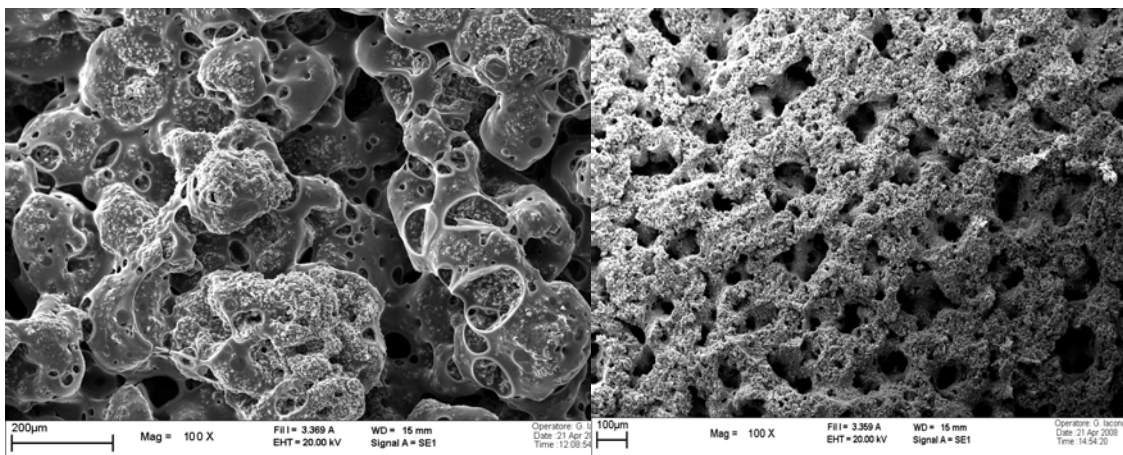


Figure 3 HRR curves of RTM6/ATH at different concentrations

Analysis of cone calorimetry results for RTM6/ATH compound indicates that the filler effect on HRR averaged values is also very noticeable for ATH content higher than 20 % w/w. The presence of the filler shows a flattening of the curve with a reduction of the HRR averaged value. Analysis of SEM micrographs on residual of system of epoxy resin, zinc borate and aluminium trihydroxide indicates that char topography varies from a compact like-amalgam structure for the RTM6/ZB (fig.4a) to a granular porous-like structure characterized by very small particles of additive along with some residual carbon from the resin for the ATH mixture (fig. 4b).



a)

b)

Figure 4 SEM micrographs of residual samples of RTM6/ZB (a) and of RTM6/ATH (b)

Different results can be drawn in the case of ATH and ZB mixture filler content. The synergistic effect of these two additives becomes effective with a weight content of each filler higher than 10% (Fig.5). In fact, the averaged HRR undergoes a slight drop from 382 kW/m² for the epoxy resin to 285 kW/m² for system RTM6/ZB/ATH 20 % w/w, with a further reduction to 249 kW/m² and 74 kW/m², respectively for the 30 % w/w and 40 % w/w of RTM6/ZB/ATH (see Table 3).

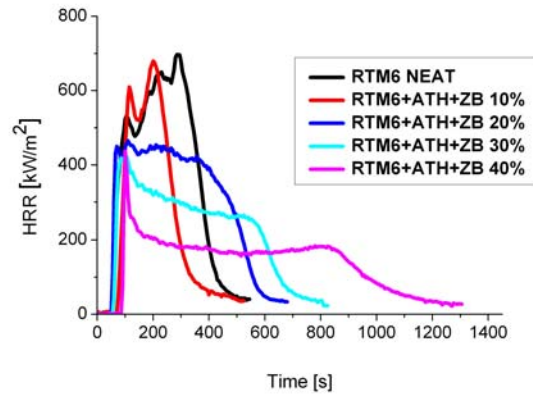


Figure 5 HRR curves of RTM6/ZB/ATH system at different concentrations

This indicates that the concentration of the each filler can be lowered in the case of ATH/ZB mixture loading if compared with the corresponding single-filler system due to the synergistic effect associated with the presence of both additives. Comparing the ΔTTI and the HRR average values for RTM6/ZB 20% w/w, RTM6/ATH 20% w/w and RTM6/ZB/ATH system at 40 % w/w, the filler synergy improves significantly the flame retardancy, respectively from 6 s to 9 s to 44 s; and from 251 kW/m² to 368 kW/m² to 74 kW/m². A SEM micrograph of residual sample of RTM6/ZB/ATH is reported in figure 6. The char is characterised by an amalgam structure due to ZB filler and a porous whitish morphology typical of the ATH residue.

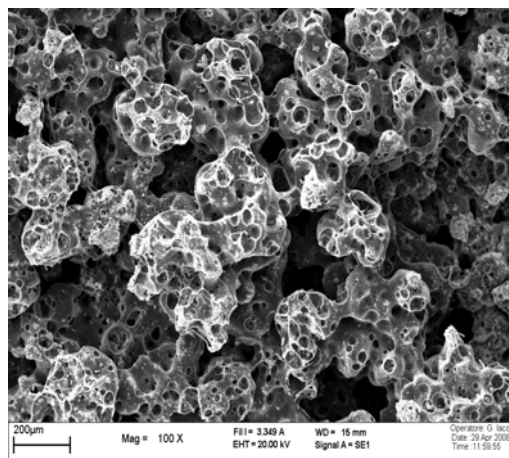


Figure 6 SEM of residual samples of RTM6/ZB/ATH system

Conclusion

The synergic effect of zinc borate and aluminium trihydroxide on flammability behaviour of mono-component epoxy resin has been studied in this work. Cone calorimeter experiments and results, obtained by thermogravimetric analysis, report clearer evidence that content of zinc borate and aluminium trihydroxide higher than 20 % w/w makes the neat resin system resistant to flame. Moreover a combination of the two fillers, at lower specific content, will affect synergistically the flammability behaviour of the neat system minimising the risk of adverse effects of original materials. Characteristic parameters, obtained by cone calorimeter tests, such as PHRR, HRR average and TTI reach higher values, indicating improved fire behaviour. The synergic effect of zinc borate with aluminium trihydroxide on the RTM6 epoxy resin can be reasonably proved not only comparing the TGA experimental curve with a mixture law based model but also analysing the cone results related with the 20 % w/w combined loads. Scanning electron micrographs indicate that the synergistic flame retardant effects of these additives results from the excellent quality of char which compromises the ZB and ATH char morphology enduring the oxidation at high temperatures slowing, at same time, the degradation of epoxy resin.

ACKNOWLEDGEMENTS

The activities were performed in the framework of project “Piros” granted to IMAST Scarl by Italian Ministry M.I.U.R.

References

1. Giüdice C.A., Benitez J.C: Zinc borates as flame-retardant pigments in chlorine-containing coatings. *Progress in organic coatings*, **42**, 82-88 (2001).
2. Schubert D.M.: Zinc borate. 5,472,644, United States (1995).
3. Fu H.Q., Huang H., Zhang X.Y., Chen F.Q.: Synergist flame retarding effect of ultrafine zinc borate on LDPE/IFR system. *Journal of Applied Polymer Science*, **103**, 3667-3674 (2007).
4. Maurer O.: New reactive, halogen-free flame retardant system for epoxy resins. *Polymer Degradation and Stability*, **88**, 70-73 (2005).
5. Shen K.K., Kochesfahani S., Jouffret F.: Zinc borates as multifunctional polymer additives. *Polymer Advanced Technology*, **19**, 469-474 (2008).
6. Bourbigot S., Le Bras M., Leeuwendal R., Shen K.K., Schubert D.: Recent advances in the use of zinc borates in flame retardancy of EVA. *Polymer Degradation and Stability*, **64**, 419-425 (1999).
7. Ning Y., Guo S.: Flame-Retardant and Smoke-Suppressant Properties of Zinc Borate and Aluminium Trihydrate-Filled Rigid PVC. *Journal of Applied Polymer Science*, **77**, 3119-3127 (2000).

8. Bourbigot S., Le Bras M., Duquesne S., Rochery M.: Recent Advances for Intumescent Polymers. *Macromolecular Materials and Engineering*, **289**, 499-511 (2004).
9. Bourbigot S., Duquesne S.: Fire retardant polymers: recent developments and opportunities. *Journal of materials chemistry*, **17**, 2283-2300 (2007).
10. Carpentier F., Bourbigot S., Le Bras M., Delobel R., Foulon M.: Charring of fire retarded ethylene vinyl acetate copolymer-magnesium hydroxide/zinc borate formulations. *Polymer Degradation and Stability*, **69**, 83-92 (2000).
11. Genovese A., Shanks R.A.: Structural and thermal interpretation of the synergy and interactions between the fire retardants magnesium hydroxide and zinc borate. *Polymer Degradation and Stability*, **92**, 2-13 (2007).
12. www.hexcel.com/...../HexFlowRTM6.pdf
13. Xie R.C., Qu B.J.: Expandable graphite systems for halogen-free flame-retarding of polyolefins. I. Flammability characterization and synergistic effect. *Journal of Applied Polymer Science*, **80**, 1181-1189 (2001).
14. Franchini M.C., Fabbri P., Frache A., Ori G., Messori M., Siligardi C., Ricci A.: Bentonite-based organoclays as innovative flame retardant agents for SBS copolymer. *Journal of nanoscience and nanotechnology*, **8**, 6316-6324 (2008).
15. Schartel B., Hull TR.: Development of fire-retarded materials-Interpretation of cone calorimeter data. *Fire and Materials*, **31**, 327-354 (2007).