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Original

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Synergistic effects of zinc borate and aluminium trihydroxide on flammability behaviour of aerospace epoxy system

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Abstract. The flame retardancy of mono-component epoxy resin (RTM6), widely used for aerospace composites, treated with zinc borate (ZB), aluminium trihydroxide (ATH) and their mixtures at different concentrations have been investigated by morphological and thermal characterization. Cone calorimeter data reveal that combustion behaviour, heat release rate peak (PHRR) and heat release rate average (HRR Average) of RTM6 resin decrease substantially when synergistic effects of zinc borate and aluminium trihydroxide intervene. Thermogravimetric (TGA) results and analysis of the residue show that addition higher than 20% w/w of ZB, ATH, and their mixture greatly promotes RTM6 char formation acting as a barrier layer for the fire development. Depending upon the different used flame additives, SEM micrographs indicate that the morphology of residual char could vary from a compact amalgam-like structure, for the RTM6+ZB system, to a granular structure, characterized by very small particles of degraded resin and additive for the ATH.

Keywords: thermosetting resins, fire retardancy, zinc borate, aluminium trihydroxide, cone calorimeter

1. 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. The zinc borate can generally display synergistic effects with antimony oxide in fire retardancy. In the presence of aluminium trihydroxide

(ATH) or magnesium hydroxide ($\text{Mg}(\text{OH})_2$), this synergy can be augmented significantly [5]. Previous studies [6–11] 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, various authors [13–20] 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

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(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 concentrations of each additive and their combinations is exploited by cone calorimeter, TG-DTG and SEM analysis.

2. Experimental section

2.1. 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 composites were prepared by mixing the epoxy resin with ZB and ATH both separately and in combination. For the separate mixtures 5, 10, 20, 30 and 40% w/w were used while for the combination they were mixed at 1:1 ratio in mass at 10, 20, 30 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 and 180°C respectively for 90 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 degraded respectively at 436 and 299°C well below the set curing conditions.

2.2. Methods

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/m². 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°C/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 30–400°C and $\pm 1^\circ\text{C}$ in the range 400–800°C. SEM and optical micrographs of additive powder, composites and residuals were taken respectively by an 1450VP LEO SEM microscopy and an optical Olympus BX51 Instruments.

3. Results and discussion

3.1. SEM and optical microscopy

Multiple locations on different samples were observing by optical and SEM microscopy to verify the level of dispersion. Figure 1 reports a 10X optical micrograph of 20% w/w zinc borate and epoxy system, showing a uniform distribution through the matrix. At all considered concentrations either for ZB and ATH, the powder is well dispersed into the epoxy matrix maintaining also its original grain size as also confirmed by Figures 2a and 2b, where SEM micrographs, respectively of ZB as-received and RTM6/ZB mixing at 20% w/w are reported. An appreciable uniformity of filler within the hosting matrix where observed on all loaded samples for both ZB and ATH filler.

In order to study the synergistic effects of zinc borate with aluminium trihydroxide, samples of composite of RTM6 and ZB/ATH, dispersed at

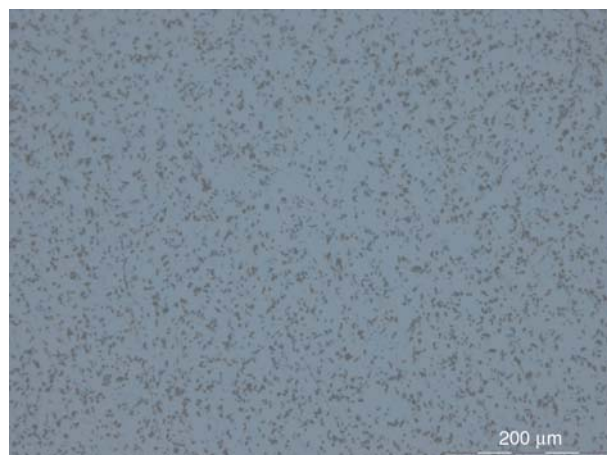


Figure 1. Optical microscopy of zinc borate dispersed into the epoxy resin (200 μm)

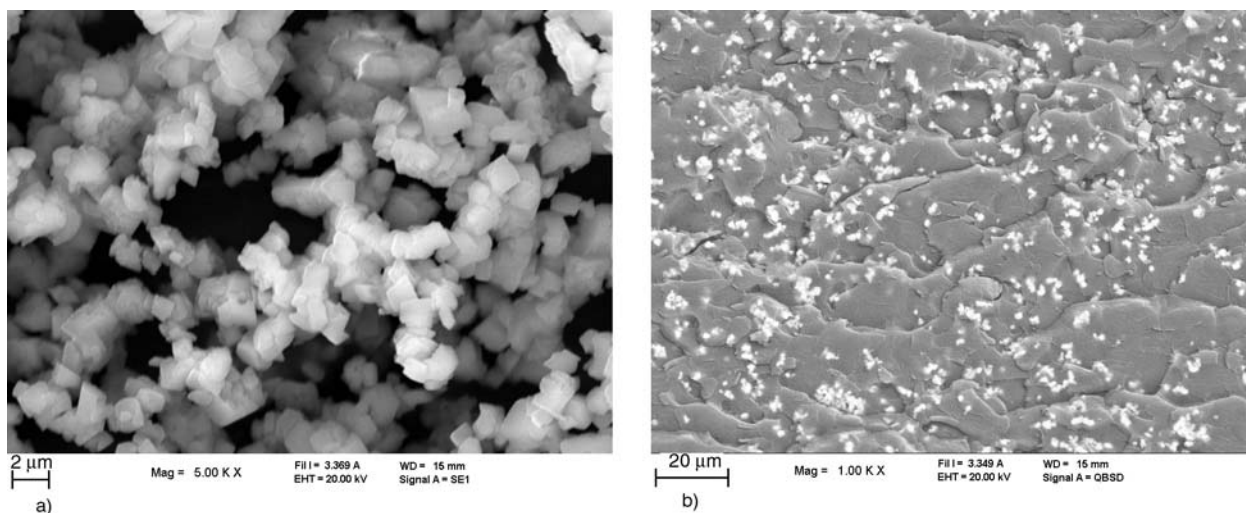


Figure 2. Scanning electron micrograph of zinc borate powder (a) and scanning electron micrograph of composites of RTM6 and ZB 20% w/w (b)

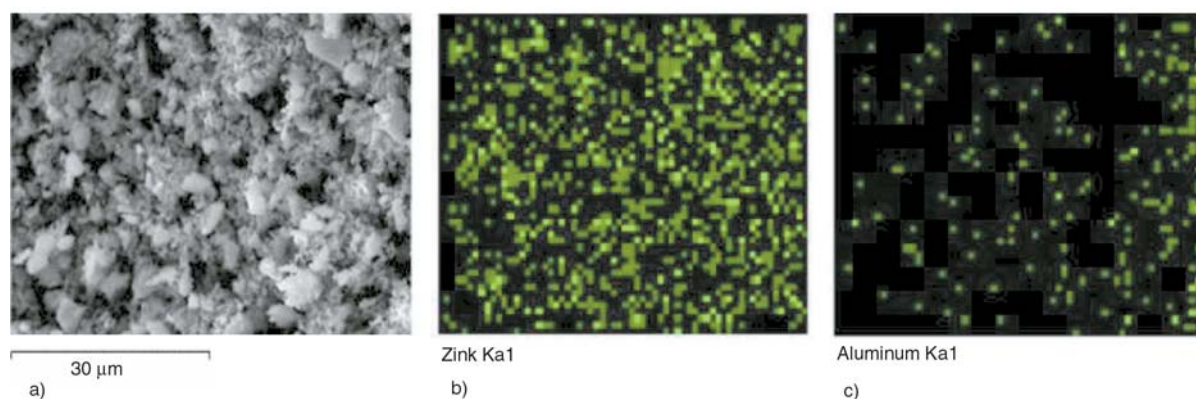


Figure 3. Mapping of ZB/ATH sample dispersed into the epoxy resin

total concentration of 20% w/w, were mapped by SEM. The presence of ZB and ATH, consistently found together within the same area of the sample, lead to the reasonable conclusion that an interaction between the two additives could be assumed (Figure 3). This conclusion is also confirmed by experimental TGA data compared with the corresponding calculated curves as reported in following paragraph.

3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) and derivative signal (DTG) represent a quantitative methodology useful to analyze the stability of materials. TGA scans were performed on all composite samples for each concentration. TGA theoretical curves (calculated curves) were then computed and compared to experimentally obtained thermographs to further understand the synergist effect of

ZB and ATH on the degradation behaviour of the RTM6 epoxy system.

Analysis of the TGA curves and their DTG signals reveals that onset temperature, which corresponds to the value at 5% of weight loss, are augmented significantly in the case of 30 and 40% w/w content for both mixtures, RTM6/ATH and RTM6/ZB. According to Table 1, in fact, measured values for onset and maximum temperatures fall within the same range, if the error bar is considered; thus highlighting the substantial inefficiency of the filler to act as flame retardant. As expected, it is neces-

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

sary to add a high weight content of filler to induce an active retardant effect to the degradation process of the hosting material.

In the case of ATH, the presence of the additives increases the onset temperature due to the decomposition reaction $[2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}]$ which takes place between 220 and 400°C. ATH decomposition is an endothermic reaction, which, ATH absorbs about 1 kJ/g of heat. The main endothermic peak of the reaction occurs at about 300°C, which means that the reaction is absorbing the most heat at a temperature below the service degradation temperature level of most polymers. Another important aspect of the reaction is the release of water vapour formed from the hydroxyl group bonded with aluminium. This water is released into the flame hindering the combustion process by diluting the concentration of flammable evolving gases and restricting the access of oxygen through the composite surface. An added benefit of the decomposition reaction is that no toxic or corrosive gases are produced unlike some other flame retardant compounds are present. ATH also operates as a heat sink extending the time to reach the polymer decomposition temperature. ATH has a higher heat capacity than most organic resins, enabling it to absorb heat and promoting a ‘cooling’ effect of the host polymer. It is believed that another mechanism of ATH is the formation of a refractory layer of Al_2O_3 following the decomposition of the ATH. The efficiency of the aluminium oxide layer with the consistency and thickness needed to be an effective thermal barrier is strictly depended upon the ATH content [21]. ZB acts as flame retardant in both condensed and gas phases of the combustion process. At elevated temperatures, this compounds decomposes, releasing crystallization water molecules (about 15% by weight of water in the temperature range of 290–450°C) which dilutes the concentration of H radicals and organic volatiles in the flame, reducing its temperature. After decomposition, the residual borate retained in the decomposed polymer will form a vitreous-like layer that slows the permeation of volatile compounds through the surface and restricts them from entering the gas phase [21]. Analysis of onset temperatures evaluated by TGA scans, lead to the main conclusion that both types of fillers do not enhance significantly the start of degradation process below a specific concentration,

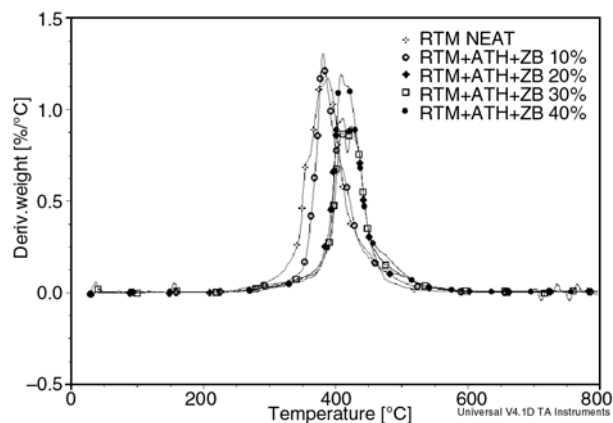


Figure 4. DTG curves of RTM6/ATH/ZB system at different percentage

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

as expected. Different observations can be made by analysing the TGA results of RTM6 and a combination amount of ZB and ATH. The synergy between the ZB and ATH was investigated on four different percentages (10, 20, 30 and 40% w/w with 1:1 ratio in mass) and the corresponding DTG curves are reported in Figure 4. Table 2 reports the onset and maximum degradation temperatures for all concentrations considered of ATH/ZB loaded samples according to the thermogravimetry. It can be noticed that small variations are found for both parameters if the filler content is lower than 20% w/w (i.e. 10% w/w of ATH and 10% w/w of ZB); 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; thus, minimising the risk of adverse effects, such as mechanical property degradation and density increase of the hosting materials. The analysis of experimental TGA and DTG curves with a law of mixture based model, hereby referred as calculated curves, could be very useful to proof the synergistic effect of flame retardancy associated with a combined amount respect to the percentage used of stand-

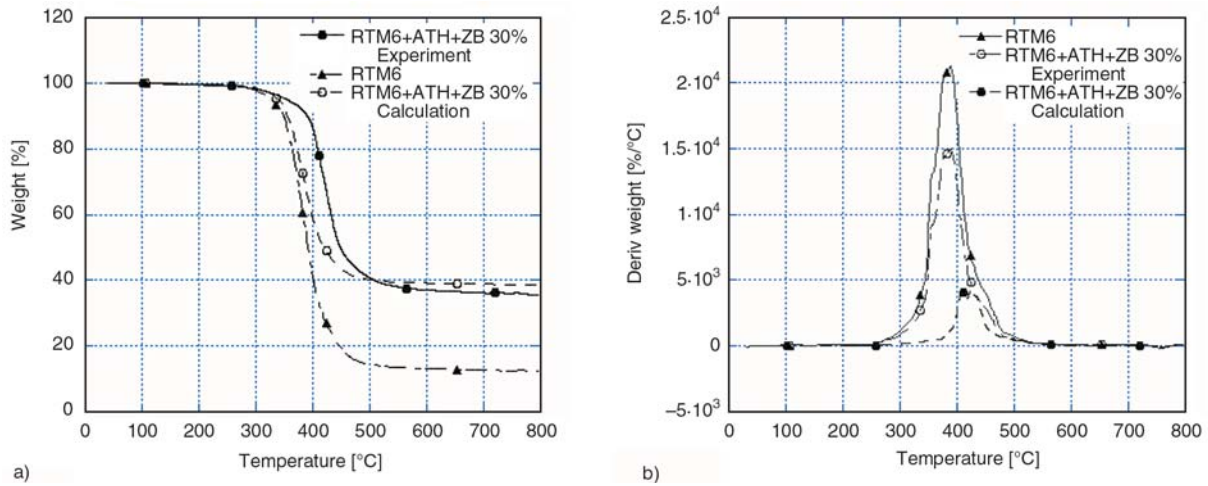


Figure 5. Experimental and calculated TGA (a) and DTG (b) curves for 30 wt%RTM6/ATH/ZB

alone filler. Calculated and experimental TG-DTG curves have been superimposed in Figure 5 for the 30% w/w ZB/ATH amount. Experimental curves are shifted to higher temperatures if compared with their corresponding calculated curves; therefore a superposition effect of flame retardancy due to the presence of each filler is not able to model accurately the experimental results. A synergic mechanism due to the combined amount of fillers can be assumed to occur on the degradation behaviour of the overall loaded system. Similar results were also obtained for all other considered total concentrations, leading to analogous results. The synergistic effect due to the presence of both, ZB and ATH, is quantified by substantial the increase of the onset and maximum degradation temperatures, respectively of 50 and 40°C for the highest total percentage compared with the neat epoxy system.

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.

3.3. 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 [22, 23]. Figures 6a and 6b report the HRR curves over three different tests, respectively for the neat epoxy and loaded systems along with their average. 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

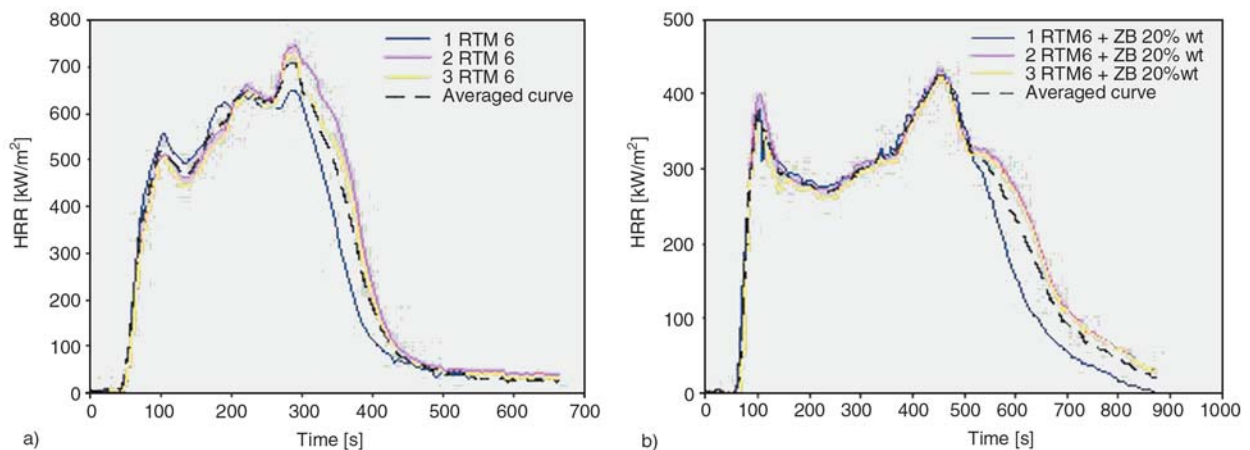


Figure 6. HRR curves for neat epoxy (a) and RTM6 loaded with 20% w/w of zinc borate (b)

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

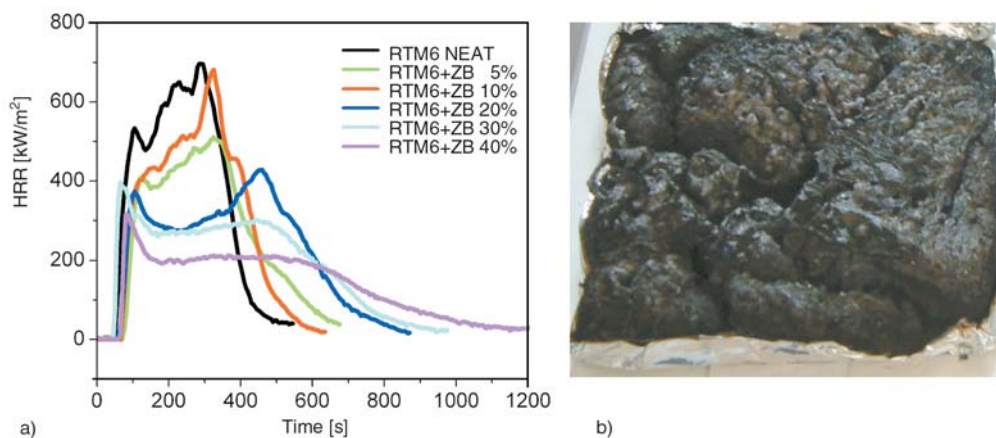
Sample	TTI [s]	Δ TTI [s]	PHRR [kW/m ²]	HRR Average [kW/m ²]	Δ PHRR [kW/m ²]
RTM6	43±2	–	702±3	382±4	–
RTM6+ZB 5%	44±5	5	682±2	354±3	20
RTM6+ZB 10%	48±4	1	523±3	265±2	179
RTM6+ZB 20%	49±3	6	428±2	251±4	274
RTM6+ZB 30%	58±2	14	396±3	193±3	306
RTM6+ZB 40%	63±2	20	315±2	148±2	387
RTM6+ATH 5%	33±6	–10	815±4	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

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 are averaged over three replicate experiments. The HRR value is considered the single most important fire reaction property as it represents the most valuable indicator of the fire hazard for a combustible material.

For the RTM6/ZB compound, data show that the presence of the filler at 5, 10 and 20% w/w does not change substantially neither the time to ignition or the heat release rate peak values. Instead, the presence of zinc borate at higher concentrations (30, 40% w/w) improves flame retardant behaviour of the neat resin system as supported by the recorded values of PHRR and HRR average which increase respectively by 15 and 20 kW/m².

The accentuate peak for the ZB 5% w/w curve, around 300 s, could be attribute to a local instability of the heat flux during the test which lead to a wider cracked area and therefore, a localised combustion growth. In Figure 7a the HRR curves of RTM6/ZB are characterised by an increased time period up to 1200 s in the case of 40% w/w content, with a progressive flatness of the curve height at highest content. Decreasing values for the PHRR and HRR average may be correlated with the decomposition of the filler and the formation of a protective glassy char layer over the surface of sample, during the combustion process (Figure 7b). The consistency of this formed layer, inevitably, reduces oxygen absorption and limits the permeation of volatile compounds through the surface of the fired system.

**Figure 7.** HRR curves of RTM6/ZB at different concentrations (a) and RTM6/ZB at 40% w/w residue (b)

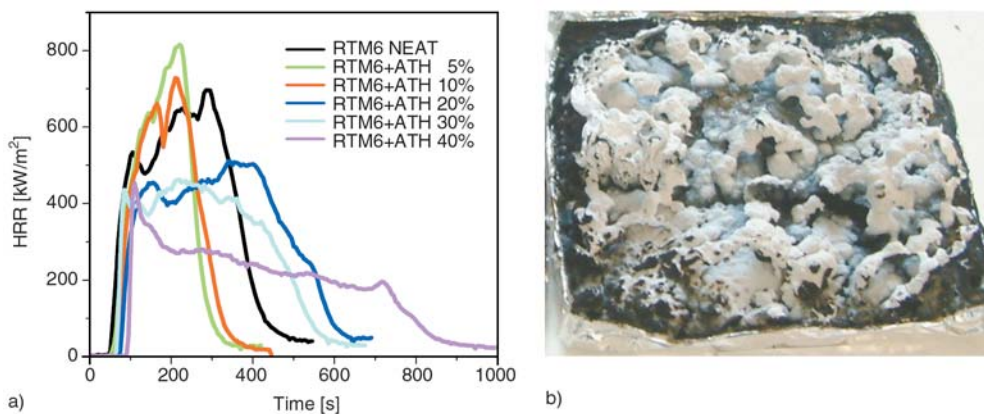


Figure 8. HRR curves of RTM6/ATH at different concentrations (a) and RTM6/ATH at 40% w/w residue (b)

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 8a). The two curves, in fact, are characterised by a higher peak value and a slight left shifting, probably due to the presence of filler which breaks the continuity of the hosting system providing a more opened morphology of the char for the propagation of the flame. Analysis of cone calorimetry results indicates that the HRR peak of the RTM6/ATH system is reduced from 815 to 510 kW/m², respectively for the 5 and 20% w/w and this value is further reduced with rising of filler concentration to 453 kW/m² for the maximum content of 40% w/w. The filler effect on HRR averaged values is also very noticeable varying of about 50% for the highest filler content (193 kW/m²) compared with the unloaded epoxy (382 kW/m²). For ATH content higher than 20% w/w the material behaviour is affected by the presence of the filler with more evidence: flattening

the curve and reducing the averaged HRR. In Figure 8b the image of the residue 40% w/w RTM6/ATH system with the whitish surface characteristic of the aluminium trihydroxide is reported. A visual inspection of the final residual sample reports the presence of the char layer (Figures 7b and 8b) characterised by a different morphology. 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 (Figure 9a) 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 (Figure 9b).

Different conclusions 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 both fillers higher than 10%. In fact, the averaged HRR undergoes a slight drop from 382 kW/m² for the epoxy resin to

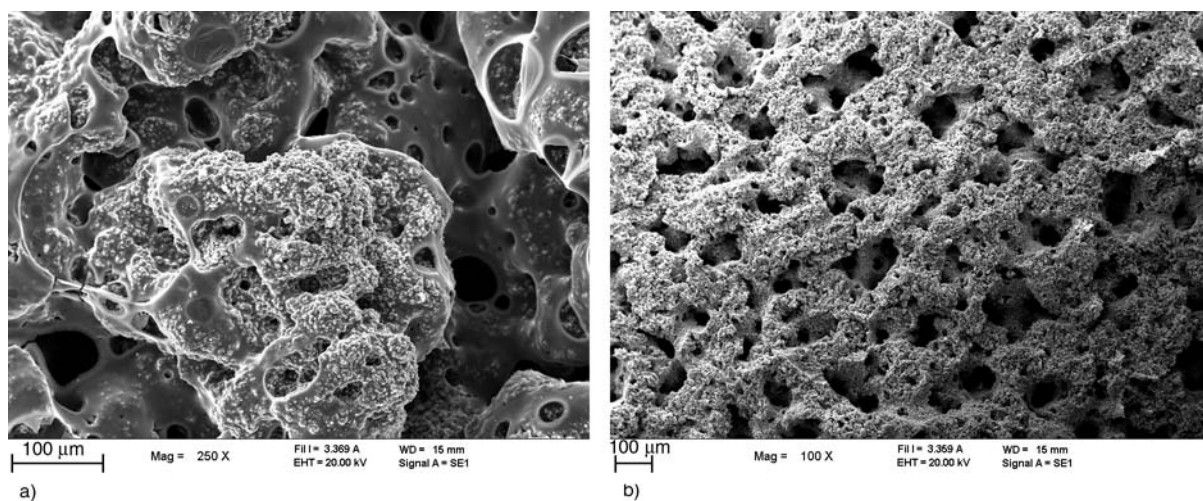
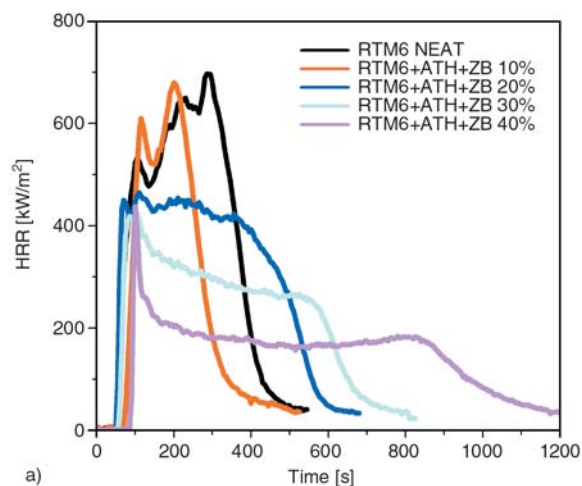


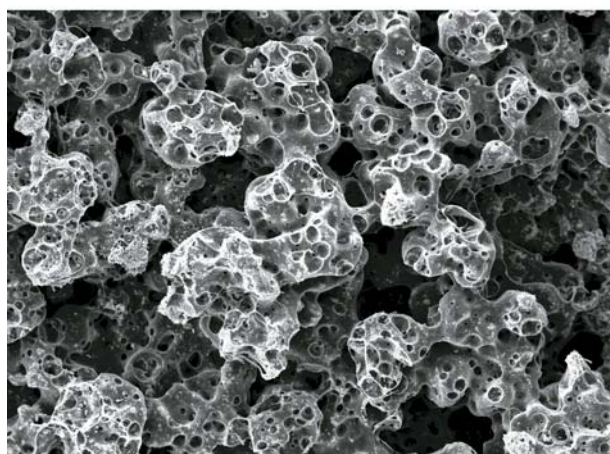
Figure 9. SEM micrographs of residual samples of RTM6/ZB 20 wt% (a) and of RTM6/ATH 20 wt% (b)



a)



b)



c)

Figure 10. HRR curves of RTM6/ZB/ATH system at different concentrations (a), RTM6/ZB/ATH system residue (b) and SEM of residual samples of RTM6/ZB/ATH system (c)

285 kW/m² for system RTM6/ZB/ATH 20% w/w, with a further reduction to 249 and 74 kW/m², respectively for the 30 and 40% w/w of RTM6/ZB/

ATH (Figure 10a). 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 Δ TTI 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 to 9 to 44 s; and from 251 to 368 to 74 kW/m². An optical image and an SEM micrograph of residual samples of RTM6/ZB/ATH are reported respectively in Figures 10b and 10c. The char is characterised by an amalgam structure due to ZB filler and a porous whitish morphology typical of the ATH residue is clearly showed by the SEM photo.

4. Conclusions

The synergistic 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 synergistic effect of zinc borate with aluminium trihydroxide on the RTM6 epoxy resin can be reasonably proved not only comparing the TGA experiential 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 synergist 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.

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