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Synergistic fire retardancy of colemanite, a natural hydrated calcium borate, in high-impact polystyrene containing brominated epoxy and antimony oxide

Cevdet Kaynak*, Nihat Ali Isitman

Department of Metallurgical and Materials Engineering, Middle East Technical University, Ankara TR-06531, Turkey

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ABSTRACT

This study explores for the first time the synergistic fire retardant action of natural hydrated calcium borate, namely the mineral colemanite, which partially replaces antimony oxide in brominated flame retardant high-impact polystyrene compounds. Various antimony oxide to hydrated calcium borate ratios were employed keeping the brominated flame retardant additive at a constant loading level. With partial colemanite substitution for antimony oxide, lower heat release rate, total heat evolved and fire growth index was obtained under forced flaming fire conditions. Synergism was also seen in limiting oxygen index along with maintained V-0 classification in UL-94 tests. Regarding fire behaviour and flammability ratings, a large antimony oxide to calcium borate ratio provided ultimate fire retardant performance whereas magnitudes of synergism in average heat release rate and total heat evolved tend to be higher towards a smaller ratio. Effective heats of combustion and structural/morphological characterization of fire residues ascribed the underlying mechanism demonstrated by hydrated calcium borate to the formation of a consolidated residue that co-operates with the dominant gas phase fire retardancy originating from bromine–antimony synergism. It is thus proposed that coupling is achieved between gas phase and condensed phase modes of action increasing the overall fire retardant effectiveness. Along with enhanced fire retardancy, thermal stability and mechanical properties were satisfactorily maintained with the use of hydrated calcium borate at a variety of loading levels in compounds.

1. Introduction

Due to their inherent flammability, polymeric materials, particularly those intended for use in electrical and electronics applications are compounded with flame retardant additives where products are required to fulfil fire resistance criteria forced by legal regulations. As a typical example, high-impact polystyrene (HIPS) representing a large fraction of plastic housings for electrical and electronics equipment is expected to meet these stringent criteria.

The mechanisms by which flame retardant additives operate are generally classified as condensed phase and gas phase operative mechanisms. Condensed phase activity encompasses several mechanisms including the most common modes of action, i.e. protective char formation and endothermic decomposition. Gas phase active flame retardants strongly interfere with the combustion process either by scavenging of hot radicals, what has been called flame poisoning, or by generating considerable amounts of less-combustible gases. The general mechanism of action for halogen–antimony flame retardant systems is the effective removal of H• and OH• radicals from the flame thereby suppressing exothermic combustion reactions.

Boron compounds have attracted considerable research interest for use as fire retardant additives in polymers, especially as synergists used in conjunction with halogenated, phosphorus- and mineral-type primary flame retardant additives. Zinc borates with a general formula $xZnO \cdot yB_2O_3 \cdot zH_2O$ were investigated in a number of studies seeking for synergistic interactions with aluminium and magnesium hydroxides [1–7], phosphorus-based intumescent systems [8–11] and organophosphorus compounds [12–14]. A recent review [15] summarizes the synergistic fire retardancy and smoke suppressant characteristics of zinc borates used in combination with antimony oxide (AO) in chlorine and bromine containing polymer compounds. It was shown that zinc borates can either partially or fully replace antimony oxide while maintaining satisfactory flammability ratings along with lower smoke production, higher comparative tracking index and strong afterglow suppression.

However, apart from zinc borates, boron containing substances such as boron-silicon containing preceramic oligomers, boron phosphate, ammonium pentaborate and calcium borates have only

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* Corresponding author. Tel.: +90 312 210 5920; fax: +90 312 210 2518.
E-mail address: ckaynak@metu.edu.tr (C. Kaynak).

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rarely been investigated so far [16–20]. In fact, results of these limited studies disclose strong indications for synergistic interactions between boron compounds, particularly calcium borate [18], and conventional flame retardants leading to reduced flammability of polymers. Among all known calcium borates, natural hydrated calcium borate (HCB) known as mineral colemanite with a formula $2CaO\cdot 3B_2O_3\cdot 5H_2O$, originating from major deposits in Turkey, is promising for use as a hydrated mineral type additive in polymers owing to its relatively high dehydration temperature above 300 °C.

It has also been an interesting task to find out whether specific combinations of gas and condensed phase active mechanisms act in a synergistic manner. In this respect, it was proposed in the literature that partial substitution of halogen–antimony fire retardants with hydrated natural fillers might compensate for the loss in gas phase fire retardancy by the endothermic dehydration reactions and fuel dilution or cooling by water vapour release. Such replacements are expected to provide a balance between mechanical and fire retardant properties and enable the reduction of fire toxicity and smoke production. In this respect, hydrated calcium borate [20], hydromagnesite/huntite [21], magnesium hydroxide [22], and talc [22,23] were considered.

The approach used in these studies [20–23] was that a great portion, e.g. 50%, of the halogen–antimony fire retardant system comprised of a brominated flame retardant (BFR) and antimony oxide were replaced by mineral fillers. This caused, in many cases, reductions in fire retardant performance, i.e., antagonism occurring in terms of limiting oxygen index (LOI) and classifications of UL-94 standards. Accordingly, in this study, it is attempted through a new approach to obtain substantial synergistic fire retardancy with the incorporation of natural hydrated calcium borate in expense of antimony oxide keeping the brominated flame retardant content at a constant level in high-impact polystyrene. By exploiting the potential synergistic interaction of hydrated calcium borate with the bromine–antimony system, it is aimed to improve the fire retardant performance of halogen containing flame-retardant high-impact polystyrene while maintaining thermal stability and mechanical properties at satisfactory levels.

2. Experimental

2.1. Materials, compounding and shaping

Extrusion grade high-impact polystyrene (Dow Styron A-Tech 1175) was used as the matrix material. Ground colemanite, a natural hydrated calcium borate (HCB), with formula $2CaO\cdot 3B_2O_3\cdot 5H_2O$ was kindly donated by ETI Mine Works (Bigadic region, Turkey). It contained 42.3% B_2O_3 and 27.9% CaO. Brominated flame retardant (BFR), a tribromophenol end-capped brominated epoxy oligomer (molecular weight 15,000 g/mol, ~53 wt% Br), and antimony oxide (AO) with formula Sb_2O_3 were industrial grade products obtained from commercial sources. Particle size analysis was performed using a laser diffraction particle size analyzer (Malvern Mastersizer S) which revealed similar mean particle sizes, $d(0.5)$, for HCB and AO as 9.3 μm and 8.1 μm, respectively.

Table 1 summarizes the compositions and designations of samples investigated in this study. Total additive content, BFR + synergist(s), was kept constant at 27 wt% in the compounds. Hydrated calcium borate and antimony oxide were used at 4 wt%, 5 wt% and 6 wt% in expense of BFR. At a synergist content of 4 wt% where BFR content is 23 wt%, various weight ratios of HCB to AO were employed as 1:3, 1:2, 1:1, 2:1 and 3:1 to gain a complete insight of potential synergistic interactions.

Materials were compounded using a lab-scale co-rotating twin-screw extruder (Rondol Microlab 10 mm, L/D:20) operated at 80 rpm screw speed within a temperature range of 145–215 °C controlled over five heating zones. Compression moulding (180 °C, 100 bar) was used to obtain $100 \times 100 \times 4$ mm^3 square samples for mass loss calorimeter fire testing. Samples for mechanical and flammability tests were shaped to final dimensions using a lab-scale injection moulding device (DSM Xplore 12 ml) operated at barrel and mould temperatures of 210 °C and 50 °C, respectively, with 10 bar injection pressure.

Table 1
Sample designations and compositions (wt%).

	Brominated flame retardant (BFR)	Antimony oxide (AO)	Hydrated calcium borate (HCB)	AO:HCB weight ratio
HIPS	–	–	–	–
HIPS/10%HCB	–	–	10	–
HIPS/27%BFR	27	–	–	–
21%BFR, 6%AO	21	6	–	–
22%BFR, 5%AO	22	5	–	–
23%BFR, 4%AO	23	4	–	–
21%BFR, 6%HCB	21	–	6	–
22%BFR, 5%HCB	22	–	5	–
23%BFR, 4%HCB	23	–	4	–
23%BFR, 3%AO–1%HCB	23	3	1	3:1
23%BFR, 2.7%AO–1.3%HCB	23	2.7	1.3	2:1
23%BFR, 2%AO–2%HCB	23	2	2	1:1
23%BFR, 1.3%AO–2.7%HCB	23	1.3	2.7	1:2
23%BFR, 1%AO–3%HCB	23	1	3	1:3

2.2. Characterization and testing

Heat release and mass loss rates during forced flaming combustion were determined following the procedure explained in ISO 13927 using a mass loss calorimeter with chimney and thermopile attachments (Fire Testing Technology, FTT) under a calibrated external heat flux of 35 kW/m^2. Reference measurements indicated that the obtained heat release rates were reproducible within ±10%. Flammability was assessed by limiting oxygen index measurements according to ISO 4589 on an FTT Oxygen index apparatus and classifications of the UL-94 standard at 3.2 mm thickness with vertical orientation on a custom flammability meter.

Tension tests were performed on ISO 527 Type 1BA samples by using a universal testing machine (Instron 5565A, 5 kN) at a cross-head speed of 1 mm/min. Young's Moduli were calculated as the slope of tensile stress - strain curves within a strain range of 0.0005–0.0025 mm/mm. Impact tests were performed using a pendulum-type impact testing machine (Ceast Resil Impactor, 4J) on bar samples (ISO 179-1, machined notch Type A).

X-ray diffraction (XRD) analysis of ground and homogenized mass loss calorimeter fire residues were done on an x-ray diffractometer (Rigaku D-Max 2200, CuK$_\alpha$) over $10° < 2\theta < 80°$ diffraction angle range. Residues from oxygen index tests were characterized for their morphology by a scanning electron microscope (SEM; JEOL JSM 6400, 20 kV). Thermal analysis was performed on simultaneous thermogravimetric/differential thermal analysis equipment (Netzsch Model STA 449 F3 Jupiter) at a heating rate of 10 °C/min under flowing nitrogen at 20 ml/min.

3. Results and discussion

3.1. Fire retardancy

Forced flaming combustion behaviour was evaluated by mass loss calorimeter tests under an external irradiation of 35 kW/m^2 representing a mild-to-intermediate fire scenario. Fig. 1 displays the rates of heat release and mass loss from samples elucidating the

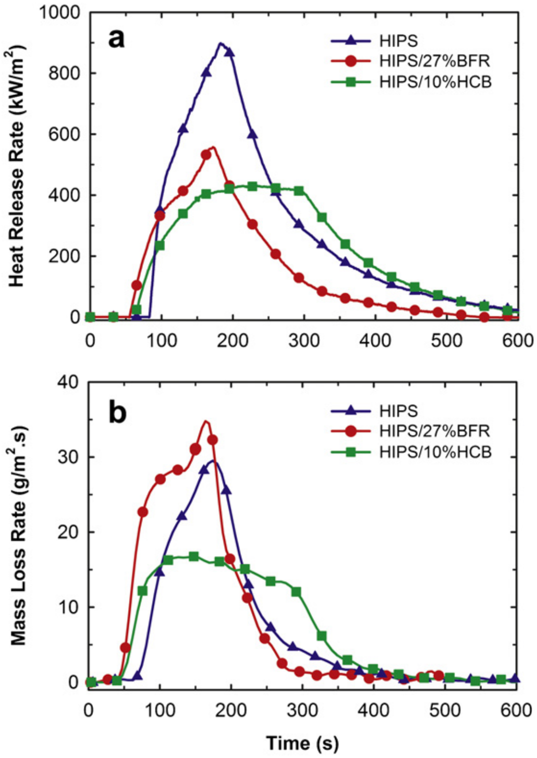

Fig. 1. Effects of brominated flame retardant and hydrated calcium borate on (a) heat release and (b) mass loss behaviour of high-impact polystyrene.

effects of brominated flame retardant (BFR) and natural hydrated calcium borate (HCB) on the combustion behaviour of high-impact polystyrene. It is interesting to note that although it was present at a lower weight fraction in the compound, HCB suppressed heat release in a more effective manner compared to BFR. Hydrated calcium borate influenced heat release and mass loss rates in a similar manner identifying its condensed phase action. Contrarily, when incorporated in HIPS, brominated flame retardant reduced the heat release rate while increasing mass loss rate throughout combustion. Although rate of fire degradation increases in the presence of BFR, the evolved gases during decomposition possess significantly lower heat of combustion and/or combustion efficiency leading to lower heat release rate. This could be attributed to the well-established gas phase flame inhibition mechanism of halogenated compounds through the evolution of hydrogen halides [24,25].

Fig. 2 shows the changes in heat release behaviour of brominated flame retardant HIPS with a replacement of certain BFR portion either with hydrated calcium borate or antimony oxide (AO) in an attempt to achieve synergistic fire retardancy. It is clear that both HCB and AO effectively reduced heat release rates during combustion. Almost the same trends were observed when various hydrated calcium borate (Fig. 2a) or antimony oxide (Fig. 2b) contents (4, 5, and 6 wt%) were utilized in expense of the brominated flame retardant. Therefore, the investigated relative amounts of HCB or AO with respect to BFR did not play an important role on the heat release behaviour.

It is depicted in Fig. 2(c) that AO had a slightly stronger synergistic interaction with BFR compared to that of HCB which led to lower heat release rates. This could well be attributed to the interactions of brominated additive and antimony oxide leading to the release of $SbBr_3$ working as an effective hot radical scavenger (flame poison) in the gas phase [25].

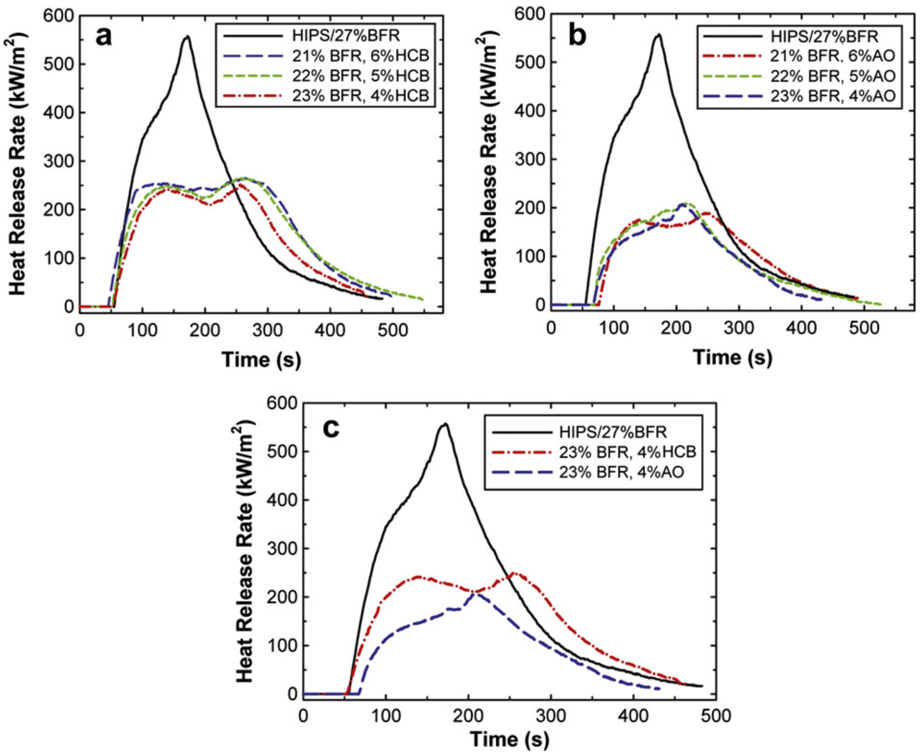

Fig. 2. Effects of (a) hydrated calcium borate and (b) antimony oxide as synergistic agents on the heat release behaviour when used separately in conjunction with brominated flame retardant, and (c) comparison of heat release rate curves corresponding to representative compounds containing hydrated calcium borate and antimony oxide.

In order to reveal the possible synergistic effect of HCB used in conjunction with AO at various ratios, fire properties interpreted from mass loss calorimeter data were plotted in Fig. 3. It is clear without exception that, at all levels of HCB used in expense of AO, mass loss calorimeter fire performance of compounds deviated remarkably in a synergistic manner from the linear “rule of mixtures” relationship. Negative interaction terms existing between HCB and AO provided deviations towards lower peak and average heat release rates, total heat evolved and fire growth index (defined as the ratio of peak heat release rate to time to ignition [26]).

The magnitudes of synergistic deviations (percent reductions) from linear relationships in Fig. 3 were generally larger towards the HCB rich part of the provided diagrams. In particular, this trend was predominant for average heat release rate and total heat evolved; for instance at a HCB:AO ratio of 2:1, attained reductions reached their maximum of 19% and 23%, respectively. At the same time, peak heat release rate and fire growth index were decreased by 27% and 30%. However, the global minima representing ultimate fire performance of compounds could be satisfied at the AO rich side, in particular, the lowest peak heat release rate and fire growth index were observed at a AO:HCB ratio of 3:1.

Among the interpreted parameters from mass loss calorimeter data, maximum attained heat release rate throughout combustion is considered as an important parameter determining the severity of flashover of a fire and the rate of flame spread [27]. In this respect, a significant feature of this paper is that it suggests reductions in peak heat release rate ranging from 22 to 27% with HCB substitution for AO keeping the total loading level of additives at a constant level.

In order to gain a more detailed insight of the combustion behaviour, heat release and mass loss rate curves of representative formulations are compared in Fig. 4. Incorporation of hydrated calcium borate at a HCB:AO ratio of 1:1 (23%BFR, 2%AO–2%HCB) altered the heat release behaviour such that a plateau-like behaviour of lower peak heat release rate was observed. It is also interesting to observe typically that reductions in rates of heat release in the presence of HCB were accompanied by strong reductions in mass loss rates indicative of condensed phase flame retardancy. It can then be concluded that with the incorporation of HCB, owing to the condensed phase action, the evolution of flame inhibiting volatiles formed by the interactions of BFR and AO was slowed down. In this manner, the effective gas phase action arising from bromine–antimony synergism was spread over a more extended period of time throughout combustion. Accordingly, flame retarding mechanism of HCB in the condensed phase was synergistically coupled with the gas phase mechanism of bromine–antimony system providing increased fire performance.

In order to evaluate the flammability properties of samples under non-forced flaming combustion conditions, limiting oxygen index and UL-94 tests were done. Neat HIPS supports flaming combustion at a significantly low oxygen concentration of 17.8% and apparently classified as non-rated (NR) according to UL-94V test. LOI was increased to 22.4% with the incorporation of BFR; however, the UL-94 rating remained as non-rated. No drips, either flaming or non-flaming, were observed for HIPS and brominated flame retardant HIPS during UL-94 tests.

Fig. 5 reveals the influence of HCB:AO ratio on the flammability ratings. Bromine–antimony synergism reached a relatively high LOI (24.7%) accompanied by a V-0 rating whereas the sample containing HCB in combination with BFR could only prove a LOI of 22.2% and classified as non-rated in the UL-94V test. It is clear that largest synergistic improvements (positive interaction term) in LOI were obtained towards the antimony oxide rich side, i.e., AO:HCB > 1, the optimum AO:HCB ratio being 3:1 which ascertained a LOI of 25.8%. With the incorporation of HCB in halogen–antimony system at various HCB:AO ratios, UL-94 ratings were maintained at the self-extinguishing level (V-0) with an exception of HCB:AO ratio of 3:1 where a V-1 rating was obtained.

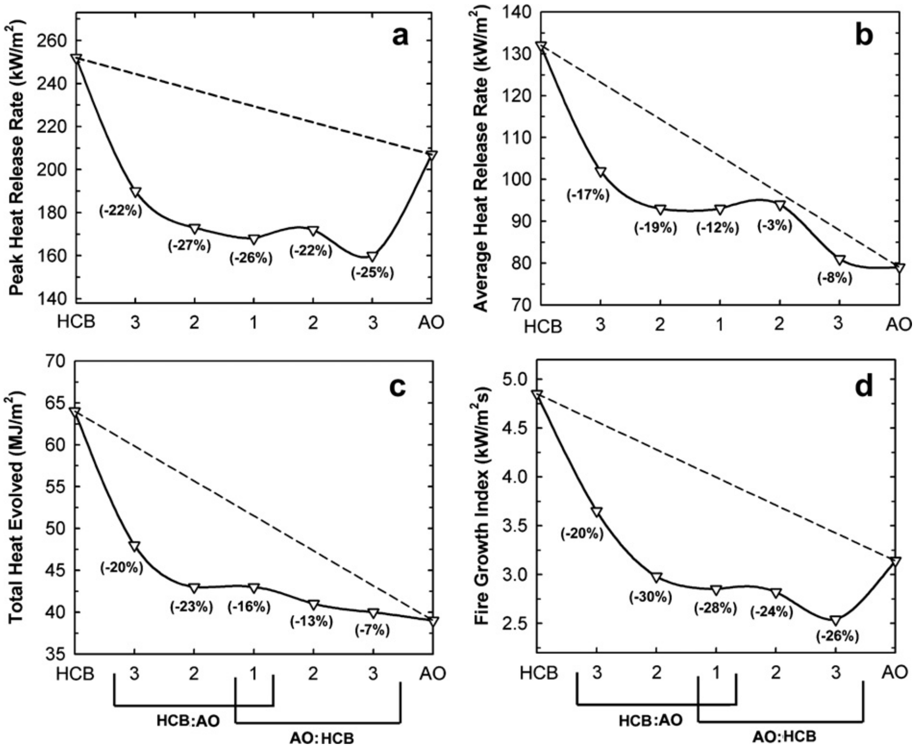

Fig. 3. Synergistic fire retardancy effect of hydrated calcium borate when used in conjunction with antimony oxide at various ratios (dashed lines stand for “rule of mixtures” while solid lines represent apparent fire performance of compounds). Loading level of AO + HCB = 4 wt%, loading level of BFR = 23 wt%.

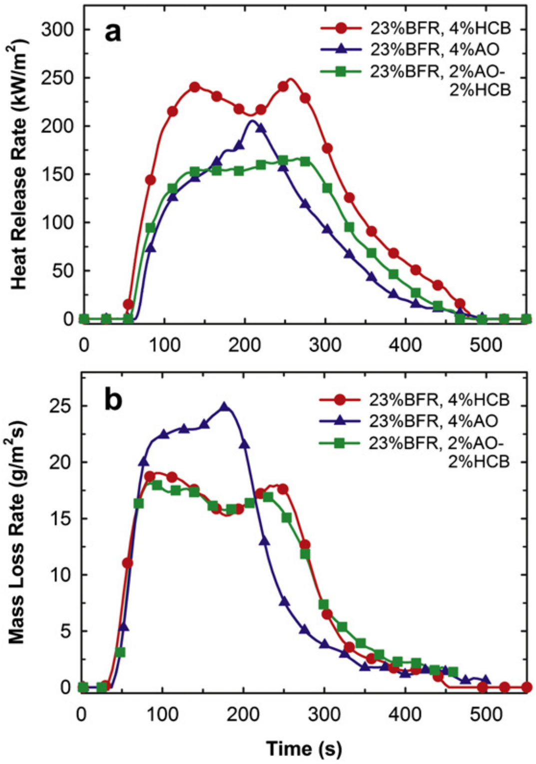

Fig. 4. (a) Heat release and (b) mass loss rates during combustion in the mass loss calorimeter. Synergistic action of hydrated calcium borate is seen when used in combination with antimony oxide at a AO:HCB ratio of 1.

3.2. Fire-retardant mechanism

3.2.1. Decomposition of colemanite

In order to reveal the fire-retardant mechanism, thermal decomposition of hydrated calcium borate was investigated in depth by thermal analysis. Thermogravimetric (TG) and differential thermal analysis (DTA) curves provided in Fig. 6 show that HCB undergoes a major endothermic mass loss attributed to fast dehydration which starts at around 370 °C and attains the maximum rate of mass loss at 401 °C. DTA heat flow signal displays closely overlapping sharp peaks at 387 °C and 403 °C (the whole process denoted as dehydration, T_d) showing that dehydration actually occurs in two steps within a narrow temperature range. These steps were attributed respectively to the formation of water molecules from structural hydroxyl groups, and, breaking of hydrogen bonds between water and borate chains [28]. The second step is accompanied by catastrophic release of water vapour properly termed as explosive dehydration which is typically observed during thermal decomposition of hydrated crystalline solids such as colemanite, dickite, ulexite and vermiculite [29–31]. The formed water molecules are entrapped within the coherent and strong retaining lattice as internal water which, upon further heating, blasts the crystal by the act of developing internal vapour pressure and results in the formation of a porous residue capable of heat insulation. The remaining water is gradually released at higher temperatures (above 700 °C), extending to above the glass transition temperature which conforms to an earlier mass spectrometer study [32].

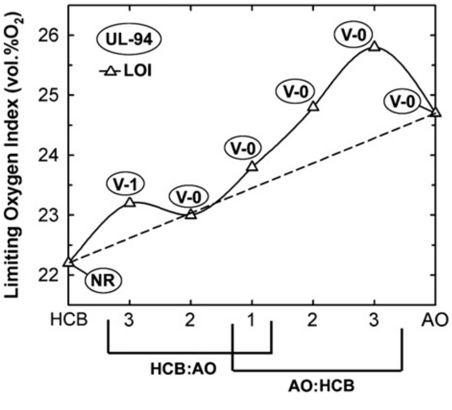

Fig. 5. LOI and UL-94 ratings of compounds showing the influence of hydrated calcium borate to antimony oxide ratio. Loading level of AO + HCB = 4 wt%, loading level of BFR = 23 wt%.

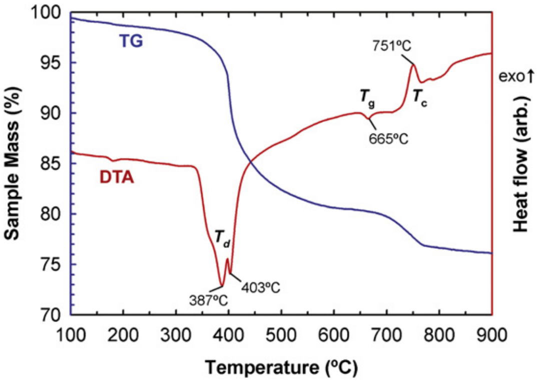

Fig. 6. Thermogravimetric sample mass and differential thermal analysis heat flow curves of hydrated calcium borate.

Upon dehydration that maximizes at around 400 °C, an amorphous residue is formed which undergoes glass transition and recrystallization processes at around 665 °C and 751 °C, respectively. The structural relaxation endotherm accompanying the glass transition, i.e., heat associated with glass transition, conforms to the study by Waclawska [33] stating that, unlike molten glasses, some elements of the primary crystal are preserved following dehydration in thermally amorphized borates. Interestingly, as explained in more detail in Section 3.2.4, this was evidenced in the present study as partially crystalline solid fire residues upon combustion in the mass loss calorimeter.

3.2.2. Thermal degradation of compounds

Fig. 7 contains the thermogravimetric and differential thermogravimetric (DTG) curves of investigated compounds. Temperatures corresponding to onset of degradation ($T_{10\%}$), half-way degradation ($T_{50\%}$), and maximum degradation rate (T_{max}) together with peak mass loss rates (DTG_{max}) and char yields at 600 °C are outlined in Table 2.

With the incorporation of BFR in HIPS, degradation temperatures were lowered around 47–58 °C accompanied by sharpening of the DTG curve and increased peak mass loss rate. Decreased thermal stability was related to macroradical formation due to hydrogen abstraction from the polymer during debromination of BFR in flame retardant HIPS compounds [25].

Considering formulations with AO, sharp peaks were observed in DTG curves at relatively lower temperatures around 358–361 °C besides main mass loss steps around 378–393 °C. This could be attributed to the decomposition of BFR facilitated by AO to form $SbBr_3$ that evolves into the gas phase acting as a hot radical scavenger [25]. Compared to HIPS/27%BFR, the lower char yield in the presence of AO indicates that the extent of debromination of BFR was increased through $SbBr_3$ formation as opposed to the case

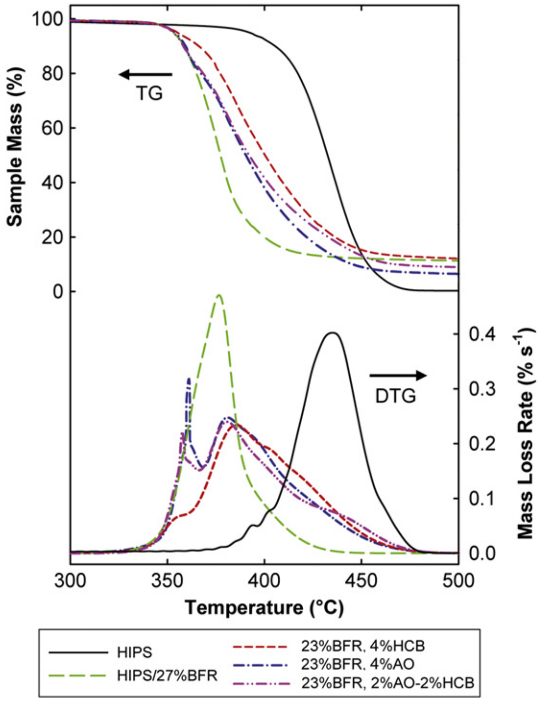

Fig. 7. Thermogravimetric and differential thermogravimetric curves of representative samples.

without AO where incomplete debromination and retained organic bromine compounds in the condensed phase are encountered.

Combination of BFR and HCB provides improved thermal stability and a markedly decreased peak mass loss rate during thermal degradation compared to HIPS/27%BFR. No early sharp peak was observed in DTG which suggests that debromination was not enhanced.

Samples with ternary BFR–AO–HCB formulations demonstrated degradation temperatures ($T_{10\%}$, $T_{50\%}$ and T_{max}) fairly similar to those with binary BFR–AO. However, peak mass loss rate corresponding mainly to $SbBr_3$ evolution (initial sharp peak in DTG) decreases with increasing HCB:AO ratio whereas an increasing trend was observed regarding char yields.

3.2.3. Effective heats of combustion

By considering the total heat evolved/total mass loss ratio as a measure of effective heat of combustion, a notion regarding the mechanism of flame retardancy could be gained [34–36]. As outlined in Table 3, the effective heat of combustion of volatiles was reduced to a great extent with the incorporation of BFR in HIPS. Therefore, it may be concluded that BFR is effective in the gas phase and that the gas phase action is amplified in the co-existence of BFR and AO leading to a significantly lower effective heat of combustion.

Table 2
Thermogravimetric data for compounds.

	$T_{10\%}$ (°C)[a]	$T_{50\%}$ (°C)[b]	T_{max} (°C)[c]	DTG_{max} (%/s)[d]	Char (%)[e]
HIPS	406	432	436	0.40	–
HIPS/27%BFR	359	377	378	0.47	9.9
23%BFR, 4%AO	359	390	361/382	0.31/0.24	5.5
23%BFR, 3%AO–1%HCB	361	406	360/392	0.29/0.22	5.7
23%BFR, 2.7%AO–1.3%HCB	360	393	362/385	0.27/0.21	6.4
23%BFR, 2%AO–2%HCB	358	392	358/382	0.22/0.24	7.7
23%BFR, 1.3%AO–2.7%HCB	361	397	356/384	0.15/0.23	9.5
23%BFR, 1%AO–3%HCB	360	404	359/393	0.12/0.22	10.2
23%BFR, 4%HCB	366	401	386	0.23	10.3

[a] Temperature at 10% mass loss.
[b] Temperature at 50% mass loss.
[c] Temperatures at maximum degradation rates.
[d] Peak mass loss rates.
[e] Non-volatile fraction at 600 °C.

The effective heat of combustion was lowered to some extent with the incorporation of HCB in brominated flame retardant HIPS which could arise from the largely endothermic dehydration reaction of HCB providing cooling and dilution of flame. Heat of combustion for the sample containing ternary BFR–AO–HCB formulation (23%BFR, 2%AO–2%HCB) assumed a value in between those for 4 wt% AO and 4 wt% HCB containing brominated flame retardant HIPS samples. Therefore, it could be considered that no apparent synergistic interactions persist between hydrated calcium borate and BFR/AO system regarding gas phase flame retardancy.

The condensed phase flame retarding action of HCB, proposed in the present study by carefully examining the combustion and thermal degradation behaviours, was supported by the amounts of solid fire residues listed in Table 3. While slight residues (<2 wt%) were obtained with bromine–antimony synergism, HCB containing samples yielded around 5–6 wt% fire residues.

3.2.4. Residue characterization

Phase identification of solid fire residues shown in Fig. 8 indicates that, either present in binary BFR–HCB or ternary BFR–AO–HCB combinations, hydrated calcium borate undergoes dehydration and demonstrates a partially crystalline structure. Unexpectedly, the corresponding dehydrated calcium borate ($2CaO \cdot 3B_2O_3$) did not form, instead, calcium borate of lower B_2O_3 content ($CaO \cdot B_2O_3$, orthorhombic) and boron oxide (B_2O_3, cubic) were observed as crystalline constituents of the fire residues. The results of phase identification of fire residues are in agreement with the above results regarding thermal decomposition of HCB that upon dehydration some elements of the primary crystal structure are preserved along with amorphization.

Fig. 9(a–c) displays the digital photographs of representative solid fire residues (whole 10 × 10 cm^2 sample surfaces). Due to the very low amounts of remaining char upon combustion of compounds with binary BFR–AO formulation (Table 3), fire residues were too thin and weak, and virtually had no structural integrity (Fig. 9c) to impart a remarkable condensed phase barrier action. Contrarily, residues from compounds that contain the hydrated calcium borate (Fig. 9a and b) demonstrated thicker and stronger characters with markedly increased capabilities of impeding heat and mass transfer during combustion. In particular, the formed barriers from compounds with ternary BFR–AO–HCB formulations appear to be free of macro-voids and cracks as opposed to those from compounds with binary BFR-HCB formulations.

Fig. 9 also shows the SEM images of residues upon combustion in oxygen index tests of compounds with binary BFR–AO and

Table 3
Heats of combustion and amounts of fire residue on combustion.

	Effective heat of combustion (kJ/g)[a]	Fire residue (wt%)[b]
HIPS	41.6	–
HIPS/27%BFR	18.8	<2
23%BFR, 4%AO	8.7	<2
23%BFR, 4%HCB	14.5	5.5
23%BFR, 2%AO–2%HCB	10.0	5.4

[a] Reported as the ratio of total heat evolved to total mass loss.
[b] Fire residue measured at flame-out in mass loss calorimeter.

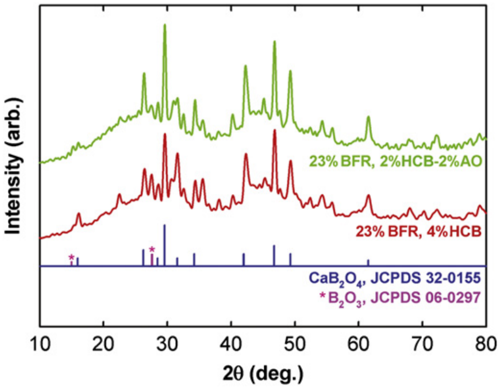

Fig. 8. Representative XRD patterns of solid fire residues from compounds with hydrated calcium borate. Partially crystalline calcium borate/boron oxide structures are demonstrated.

ternary BFR–AO–HCB formulations both exhibiting micro-porous structures (Fig. 9d and e). Although a lower porosity (denser) residue was observed for compounds with binary BFR–HCB formulation (Fig. 9d), corresponding solid fire residues suffered from major cracks (Fig. 9a) during combustion in the mass loss calorimeter. Not surprisingly, it appears in Fig. 4 that, compared to the compound with binary BFR–HCB, compound with ternary BFR–AO–HCB displayed slightly lower mass loss rates throughout combustion. This could be related with the formation of a macroscopically crack-free consolidated residue (Fig. 9b) that co-operates with the dominant gas phase action originating from bromine–antimony synergism.

Thus, we may conclude that coupling of gas phase flame retarding mechanism demonstrated by compounds with BFR–AO formulations and condensed phase mechanism by hydrated calcium borate was achieved for compounds with ternary BFR–AO–HCB formulations. A similar phenomenon was observed by Zanetti et al. [37] between condensed phase acting nanofillers and gas phase effective halogenated flame retardants.

3.3. *Mechanical properties*

Fig. 10 discloses the effects of BFR addition and replacement of certain BFR fraction with synergistic additives AO or HCB on the tensile and impact properties of HIPS compounds. It is seen that BFR imparts a clear improvement of Young's modulus while having no significant influence on ultimate tensile strength. However, ductility under tension loading and impact toughness were reduced. Decreased ductility and toughness and increased modulus, could be attributed to the presence of phase-separated, hard and brittle brominated epoxy phase. High melting aromatic compounds were previously shown to act as inert fillers that are immiscible in both polystyrene and rubber phases increasing modulus but at the same time decreasing impact toughness [38,39]. Those fillers possessing very low interaction with the polymer phases were previously stated [38] to have a deteriorative effect on ductility and impact properties via dilution of the rubber phase and de-bonding at polymer/filler interfaces upon loading.

With the incorporation of AO or HCB at various loading levels (4, 5, and 6 wt%) in expense of BFR, tensile strength, ductility and impact toughness were decreased to some extent. The presence of such rigid ceramic fillers had a dominating effect on reducing

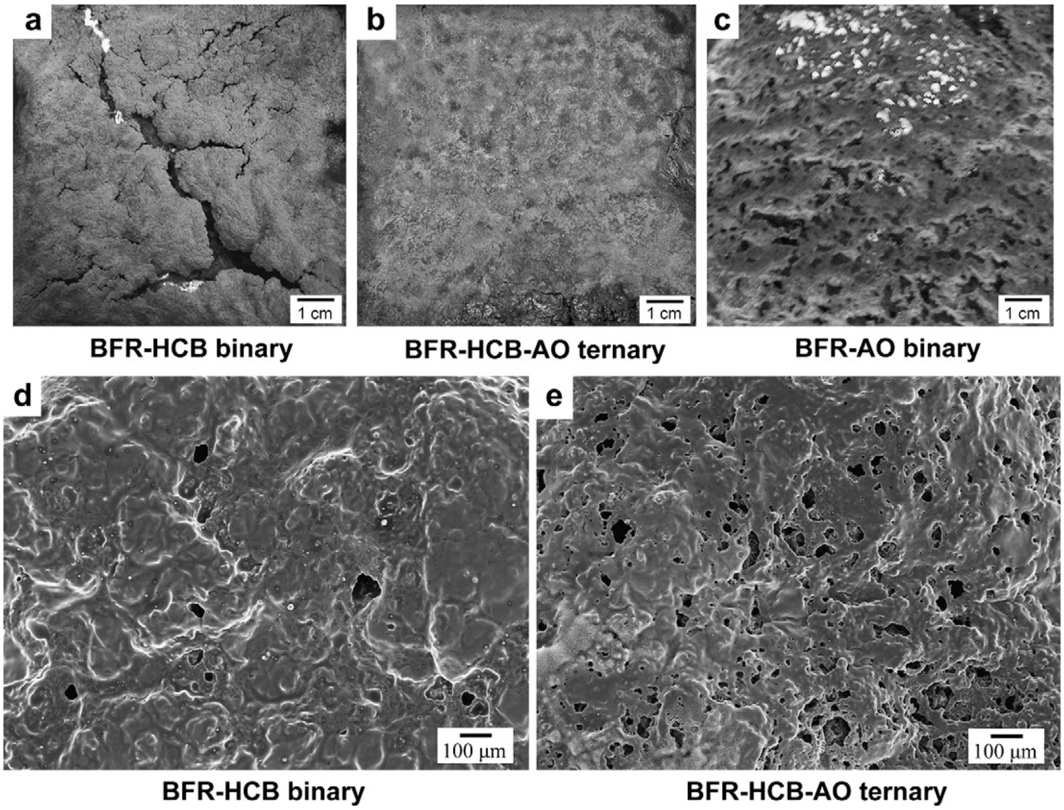

Fig. 9. Digital photographs of mass loss calorimeter fire residues upon flame-out; (a) 23%BFR + 4%HCB (around 5.5 wt% fire residue), (b) a representative compound with ternary BFR–AO–HCB formulation (around 5.4 wt% fire residue), (c) 23%BFR + 4%AO (negligible amount of residue), and, SEM images of residues from oxygen index tests of compounds with (d) BFR–HCB binary and (e) BFR–AO–HCB ternary formulations.

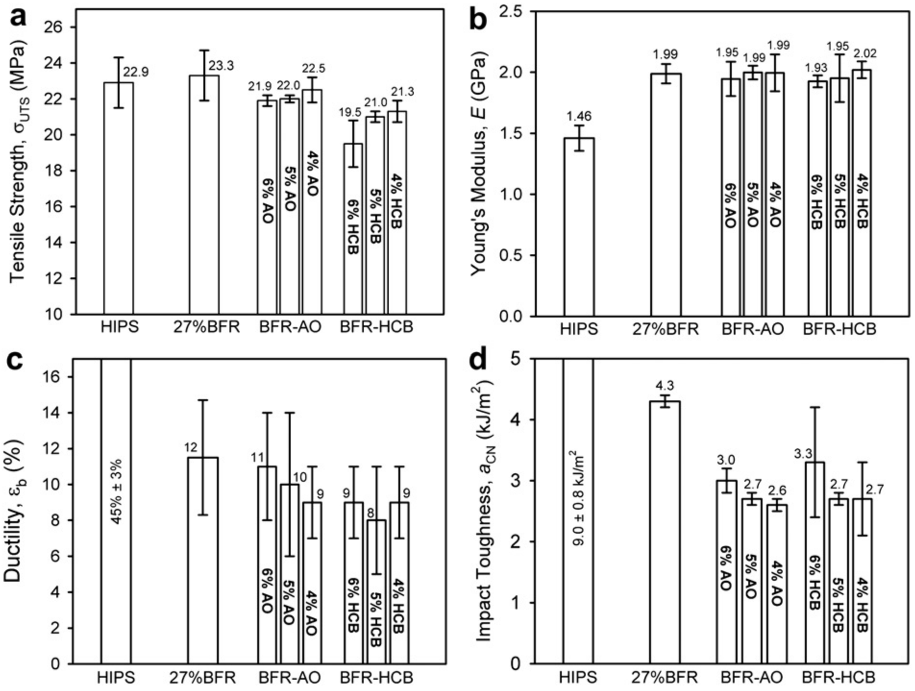

Fig. 10. Mechanical properties of samples; (a) tensile strength, (b) Young's modulus, (c) ductility, and, (d) Charpy impact toughness.

mechanical properties especially measured under very high strain rates (impact testing). Tensile strength and ductility were slightly lower with compounds containing BFR–HCB compared with those containing BFR–AO which might be related to greater stress concentration at HCB/polymer interfaces due to particle morphology, dispersion or compatibility issues.

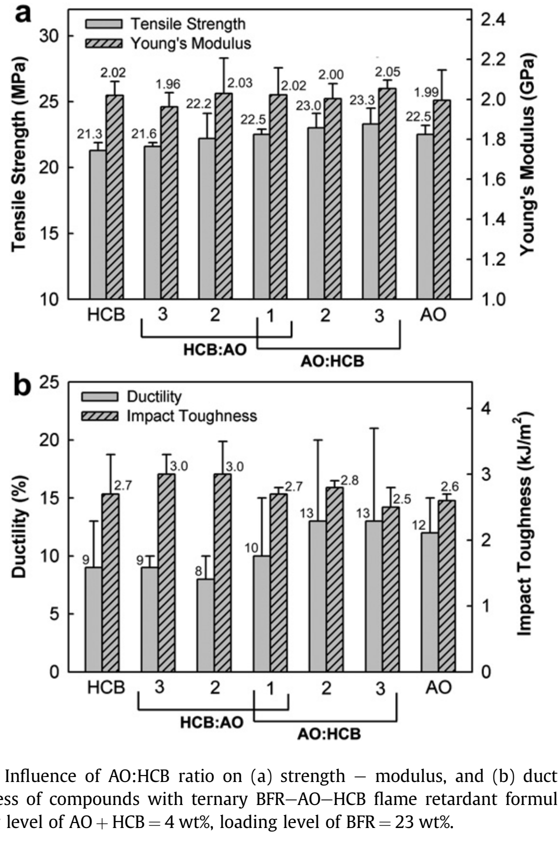

Fig. 11. Influence of AO:HCB ratio on (a) strength – modulus, and (b) ductility – toughness of compounds with ternary BFR–AO–HCB flame retardant formulations. Loading level of AO + HCB = 4 wt%, loading level of BFR = 23 wt%.

For compounds with ternary BFR–AO–HCB formulations that generally demonstrated superior fire retardant performance, there appears to be no remarkable influence of HCB:AO ratio on tensile and impact properties (Fig. 11). Nonetheless, although fairly marginal, tensile strength and ductility were higher close to the AO rich side whereas impact toughness was higher towards the HCB rich side.

To conclude, mechanical properties tested under tensile and impact loading conditions were similar for AO and HCB containing formulations meaning that HCB did not impart any remarkable deteriorating effect. Compounds with ternary BFR–AO–HCB flame retardant formulations benefiting from the strong synergistic fire retardant action of hydrated calcium borate displayed mechanical properties that are well-comparable to established compounds with binary BFR–AO formulations.

4. Conclusions

Compounds benefiting from strong bromine–antimony synergism showed significantly lower heat release rate and effective heat of combustion compared to brominated flame retardant HIPS, and high levels of flame retardancy were obtained as far as flammability ratings (LOI and UL-94) are concerned. Samples with binary combinations of brominated flame retardant and hydrated calcium borate demonstrated clear suppressions of heat release and mass loss under forced flaming combustion compared to brominated flame retardant HIPS while no synergism was seen in terms of limiting oxygen index and UL-94 classifications.

Most importantly, lower peak and average heat release rates, total heat evolved and fire growth index, as important mass loss calorimeter fire properties of samples, were obtained with compounds containing ternary BFR–AO–HCB formulations formed by the replacement of certain portion of antimony oxide with hydrated calcium borate at various AO:HCB ratios. The most significant result of this study is the reductions obtained in peak heat release rate ranging from 22 to 27% with the incorporation of hydrated calcium borate in expense of antimony oxide keeping the total loading level of additives constant.

Ultimate fire-retardant performance, i.e., lowest peak heat release rate and fire growth index, was obtained at a large AO:HCB ratio of 3:1. In addition to improvements attained under forced flaming conditions, synergistic improvements in limiting oxygen index were seen with compounds containing ternary BFR–AO–HCB formulations together with maintained UL-94 ratings (V-0), especially towards the AO rich formulations where AO:HCB > 1.

Regarding the mechanism behind synergistic improvements in flame retardancy with the use of hydrated calcium borate in halogen–antimony systems, it is proposed that coupling is achieved between gas phase action from bromine–antimony synergism and condensed phase action by hydrated calcium borate. By this means, gas phase flame inhibition arising from halogen–antimony synergism is spread over a more extended period of time throughout combustion increasing its effectiveness.

The presence of hydrated calcium borate significantly improved the thermal stability of brominated flame retardant HIPS whereas no remarkable effect was observed when used in conjunction with bromine–antimony synergism apart from lower peak mass loss rates and increased char yields.

Mechanical performance of compounds with ternary flame retardant formulations were well-comparable to those with binary BFR–AO in a sense that hydrated calcium borate did not impart a remarkable deteriorating effect.

This paper showed that colemanite, a natural hydrated calcium borate, might be a successful candidate as partial substitute for antimony oxide in halogen containing fire retardant polymers. Along with improved fire performance, colemanite offers significant cost benefits over antimony oxide. While antimony oxide continues price gains peaking at around USD 11,000 per tonne in the last quarter of 2010 due to shortage in supplies, ground colemanite costs USD 325 per tonne, and, since it is a readily available mineral in 2.3 billion tonne reserves, it is certainly sustainable in the long term. These unofficial figures might introduce colemanite as a commercially attractive alternative for the market.

Zinc borates were already proved as effective smoke and afterglow suppressants and anti-tracking agents when used in halogenated and halogen-free systems. The reader is referred to a comprehensive review article by Shen et al. [15]. Therefore, in addition to the cost effectiveness of colemanite, similar property improvements can also be attained with colemanite substitution for antimony in halogenated systems. However, further studies are required in respect of smoke/afterglow suppression and anti-tracking properties.

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