

Thermal behavior and flammability of epoxy/glass fiber composites containing clay and decabromodiphenyl oxide

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Abstract Epoxy/glass fiber hybrid composites with organo-montmorillonite (OMMT) and decabromodiphenyl oxide (DBDPO) flame retardants were prepared by vacuum-assisted resin infusion technique. The effects of OMMT and DBDPO on the flammability properties of epoxy/glass fiber hybrid composites were evaluated through UL-94 vertical flammability test and limiting oxygen index (LOI). Thermal decomposition was studied by means of thermogravimetric analyzer (TG). Field emission scanning electron microscopy (FESEM) was used to study the char morphology of the epoxy hybrid composites after being subjected to UL-94 vertical flammability test. Epoxy/glass fiber/OMMT hybrid composites with DBDPO loading of 40 wt% showed V-1 rating, whereas an increase to 50 wt% loading showed V-0 rating. The LOI values increased from 22.7 to 39.9 % as the loading of DBDPO increased. The obtained TG results showed that the thermal stability of epoxy hybrid composites decreased as the DBDPO loading increased. DBDPO decomposed at a lower temperature to form bromine radicals, which reacted with the combustible gases to form hydrogen bromide to inhibit the flame spread in the gas phase. The condensed phase activity was shown in FESEM, in which a layer of compact and continuous char was formed in epoxy/glass fiber/OMMT/DBDPO hybrid composites.

Keywords Epoxy · Glass fiber · Organo-montmorillonite · Decabromodiphenyl oxide · Thermal properties

Introduction

Fiber-reinforced epoxy composites have become to be more commonly used in automobile, construction, and aerospace industries [1]. The inherently low flame resistance of epoxy resins has limited their development and application because of the greater potential of fire risk [2, 3]. Epoxy resins are susceptible to combustion because of its nature as an organic substance, the major concern being the structural integrity of the epoxy composite laminates during and after fire exposure [4]. To alleviate these concerns, the flame-resistant properties can be enhanced by incorporating flame-retardant additives or copolymerization with reactive compounds [5]. The existing flame-retardant additives and reactive compounds can be classified as halogenated and non-halogenated.

The most commonly used brominated flame retardants in polymeric materials include tetrabromobisphenol-A-bis(2,3-dibromopropyl ether), decabromodiphenyl oxide (DBDPO), ethylenebis(tetrabromophthalimide), hexabromocyclododecane (HBCD), bis(2-ethylhexyl)tetrabromophthalate, and tris(tribromoneopentyl) phosphate (TTBNP) [6–8]. DBDPO is used primarily in electrical and electronic as well as textile applications [9, 10]. Effects of DBDPO have been studied extensively in several polymer systems, e.g., polystyrene, ethylene-propylene copolymer, polypropylene, and high impact polystyrene [11–14].

Research on polymer/clay nanocomposites gave new insights on the potential of clay as flame-retardant agents. The main proposed mechanism of flame retardancy of nanocomposites involved the formation of an insulating char, which reduced the available amount of combustible volatile products for burning in the gas phase [15]. Over the last decade, an assortment of studies has revealed that the effectiveness of layered silicate clay in reducing flammability depended on several factors, which include clay loading,

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level of dispersion, and type of surface modifier [16–23]. Regardless of the effectiveness of layered silicate in reducing peak of heat release rate (PHRR), some research results pointed out that layered silicate clay was insufficient to act as stand-alone flame retardant in important regulatory flammability tests such as limiting oxygen index (LOI) and UL-94 [24]. Thus, an alternate strategy involving the combination of layered silicates and conventional flame retardants has been suggested to achieve self-extinguishing behavior [25, 26].

To the best of our knowledge, no studies on the combination of organoclay and DBDPO flame retardant have been reported for epoxy/glass fiber systems. The aim of this study is to improve the flame retardancy of epoxy/glass fiber using the combination of organo-montmorillonite (OMMT) and DBDPO flame retardants. In this research, epoxy/glass fiber/organoclay hybrid composites with flame retardants were prepared by vacuum-assisted resin infusion technique. The effects of OMMT and DBDPO on epoxy hybrid composites were evaluated through thermal analysis, flammability test, and char morphology.

Experimental

Materials

A bifunctional epoxy resin, diglycidyl ether of bisphenol A (DGEBA; DER331, Dow Chemical, Midland, USA), was selected for this study. The characteristics of the DGEBA are epoxide equivalent weight of 182–192 g eq⁻¹; viscosity of 11,000–14,000 cps at 25 °C; and density of 1.16 g cm⁻³ at 25 °C. The curing agent used was an isophorone diamine (IPD; clear epoxy hardener 8161, ZARM Scientific and Supply, Malaysia). The characteristics of the curing agent are amine hydrogen equivalent weight of 95 g eq⁻¹; viscosity of 300–600 cps at 25 °C; and specific gravity of 1.03. OMMT consisting of octadecyltrimethylamine intercalant (OMMT; Nanomer 1.28E) was supplied by Nanocor (USA). The mean particle size of Nanomer 1.28E is 8–10 μm, while the *d*-spacing is approximately 2.98 nm. Glass fiber fabric (HexForce 7544) was provided by Hexcel Corporation (USA). A single layer of glass fiber fabric has a thickness of approximately 0.49 mm with filament diameter of 9 μm. The brominated flame retardant that was used in this study was decabromodiphenyl oxide (DBDPO; grade DE-83R, Chemtura Corporation USA).

Sample preparation

Predetermined quantities of OMMT and DBDPO were added to the IPD curing agent and mixed at 1,000 rpm (revolutions per minute) for 60 min at room temperature.

Table 1 Material designations and compositions of epoxy hybrid composites

Material designation	Composition	
	OMMT/wt%	DBDPO/wt%
E/GF	–	–
E/GF/OMMT	2	–
E/GF/OMMT/DBDPO-10	2	10
E/GF/OMMT/DBDPO-20	2	20
E/GF/OMMT/DBDPO-30	2	30
E/GF/OMMT/DBDPO-40	2	40
E/GF/OMMT/DBDPO-50	2	50

Furthermore, ultrasonification was performed on the mixture for 60 min, followed by degasification. Finally, DGEBA was added to the IPD/OMMT/DBDPO mixture and mixed mechanically. Vacuum-assisted resin infusion process was performed at room temperature. The laminates containing six layers of glass fiber fabric were cured at room temperature for 24 h. Cured specimens with dimensions of 350 × 250 × 3.2 mm (length × width × thickness) were obtained. Test specimens for various tests were cut into specific dimensions according to ASTM standard. Table 1 shows the formulation of epoxy hybrid composites with various loadings of DBDPO flame retardants.

Measurements

Flammability tests

UL-94 vertical flammability test was performed according to ASTM 3801 with the following specimen dimensions: 127 × 12.7 × 3.2 mm (length × width × thickness) using Plastic HVUL Horizontal Vertical Flame Chamber (ATLAS Fire Science Product, Chicago, USA). LOI test was performed in a FTT oxygen index apparatus (Fire Testing Technology, UK) according to ASTM D 2863, with specimen dimensions of specimens of: 127 × 6.5 × 3.2 mm (length × width × thickness).

Thermal analysis

Thermal decomposition of epoxy hybrid composites was investigated using thermogravimetric analyzer (TGA, Pyris 6, Perkin Elmer, USA). TG tests were performed at a heating rate of 10 °C min⁻¹ in the temperature range of 30–600 °C under nitrogen gas. The sample mass was ~ 10 mg.

Morphological characterization

The char morphology of epoxy/glass fiber and hybrid composites after being subjected to UL-94 vertical flammability

Table 2 Effect of DBDPO on UL-94V ratings and LOI values for epoxy/glass fiber/OMMT hybrid composites

Sample	UL-94 vertical		LOI/%
	Mean total after-flame time/s	Rating	
E/GF	184 ± 13	NR	22.5 ± 0.2
E/GF/OMMT	170 ± 23	NR	22.7 ± 0.2
E/GF/OMMT/DBDPO-10	106 ± 19	NR	23.9 ± 0.2
E/GF/OMMT/DBDPO-20	80 ± 18	NR	27.4 ± 0.3
E/GF/OMMT/DBDPO-30	64 ± 14	NR	32.0 ± 0.2
E/GF/OMMT/DBDPO-40	20 ± 8	V-1	38.0 ± 0.2
E/GF/OMMT/DBDPO-50	5 ± 1	V-0	39.9 ± 0.2

NR no rating

test were examined using field emission scanning electron microscope (FESEM, Supra 35 VP, Carl Zeiss, Germany). Samples were sputtered with gold before FESEM examination. The elements present in char layer were analyzed by Energy Dispersive X-ray microanalysis (EDX 32, Genesis, Germany).

Results and discussion

Flammability of epoxy hybrid composites

Table 2 summarizes the results of flammability test on epoxy hybrid composites with OMMT and DBDPO. It was observed that the UL-94V rating and LOI of the epoxy composites improved as the DBDPO loading increased. The role of OMMT was found to be indistinctive in improving the flame retardancy of epoxy through the UL-94V flammability test as it failed to satisfy the minimum requirements for V-2 rating. This phenomenon was due to the lack of self-extinguishing ability of OMMT [27–30]. The UL-94V flammability test results showed that the DBDPO was ineffective in extinguishing the flame propagation with up to 30 wt% DBDPO loading. All composites with or lower than 30 wt% DBDPO loading burnt vigorously. A slight change in flame resistance was observed at 40 wt% DBDPO loading, in which the effect of DBDPO in inhibiting and extinguishing the flame propagation was observed. The mean total after-flame time upon two cycles of flame exposure was ~20.1 s, achieving V-1 rating for UL-94V flammability test. At 50 wt% DBDPO loading, excellent self-extinguishing behavior was achieved, with a mean total after-flame time of 5.4 s, which led to V-0 rating.

The LOI test measures the minimum volume percentage of oxygen in the test atmosphere needed to support ignition and flame combustion, which serves as a measure of ease of flame extinguishment of the materials [31]. The higher the LOI values, the harder it is for the materials to be

ignited and hence resulted in lower flammability. It has been documented that cross-linked epoxy resins were combustible, and their burning was self-supporting with LOI values in the range of 22–23 % [32]. In this study, the LOI value for the control sample of E/GF composites was found to be 22.5 %. The addition of 2 wt% OMMT loading has no significant effect on the LOI value. This result was in agreement with the observation reported by Schartel et al. [33]. However, some researchers found that the addition of 2–5 wt% modified MMT enhanced the LOI value [34–36].

The incorporation of DBDPO into epoxy/glass fiber/OMMT hybrid composites showed more drastic improvement in LOI values from the initial value of 22.7 % to 39.9 % as the flame-retardant loading increased. A 10 wt% DBDPO loading has marginal effects on the LOI value, while a 20 wt% DBDPO loading improved the LOI value by approximately four times compared with E/GF/OMMT/DBDPO-10. The further addition of DBDPO led to 9.3, 15.3, and 17.2 % increments in LOI values for 30, 40, and 50 wt% DBDPO loadings, respectively. In this study, the addition of 40 wt% DBDPO loading improved the UL-94V rating from “no rating” to V-1 rating, while a LOI value of 38 % was achieved. These results suggested the existence of a threshold of DBDPO loading to act in flame extinguishing mechanisms effectively.

Thermal properties

Figures 1 and 2 present the TG and DTG curves for epoxy/glass fiber/OMMT hybrid composites with and without DBDPO, respectively. Table 3 summarizes some data extracted from the TG curves, e.g., the decomposition temperature recorded at 5 % mass loss (T_5), the onset decomposition temperature at stages 1 and 2 (T_{O1} and T_{O2}), and char yield. From Fig. 1, it is seen that the epoxy hybrid composites (with various DBDPO loading) experienced two stages of decomposition. All composite samples showed similar decomposition curves: a slow degradation

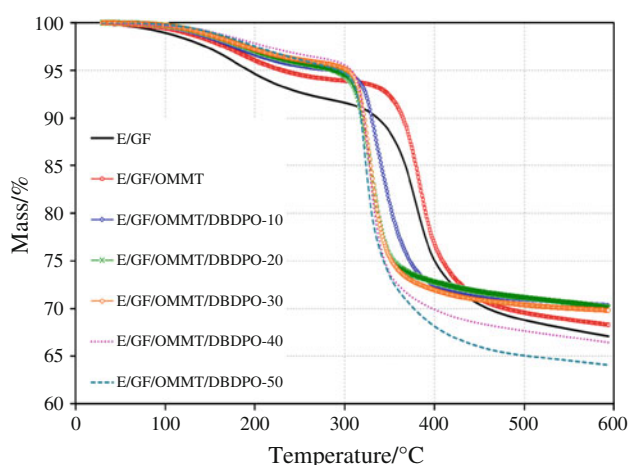


Fig. 1 TG curves of epoxy hybrid composites at various DBDPO loadings

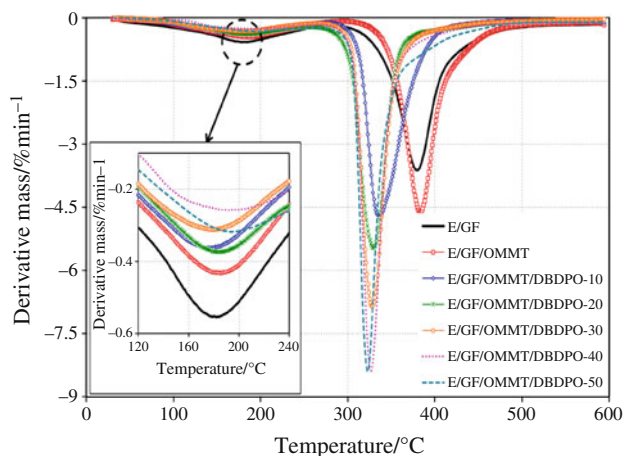


Fig. 2 DTG curves of epoxy hybrid composites at various DBDPO loadings

at lower temperature range of up to 280 °C, followed by a rapid decomposition, and left char residue ranging from 64.1 to 70.3 % at 600 °C. The first-stage decomposition was mainly caused by the pendant chain of the epoxy, while the second-stage decomposition resulted from the decomposition of the main chain in epoxy resin [37].

The addition of OMMT has enhanced the thermal stability of E/GF composites (c.f. Fig. 1). The onset decomposition temperatures for the first-stage and second-stage thermal degradations of E/GF/OMMT hybrid composites were slightly higher than E/GF composites. The improved thermal stability was related to the formation of carbonaceous silicate char which protected the bulk of sample from heat and hindered the volatilization, and the presence of inorganic phases with high thermal stability (e.g., SiO₂, Al₂O₃, and MgO) in the clay [38–40].

An interesting trend was observed when epoxy hybrid composites with DBDPO were subjected to thermal

decomposition. At the lower temperature decomposition stage, the addition of DBDPO enhanced the thermal stabilities of E/GF composites; while at the higher temperature decomposition stage, DBDPO destabilized the E/GF composites. The first-stage decomposition was predominantly due to dehydration and elimination of low molecular mass molecules. Referring to Fig. 1 and Table 3, it is noted that as DBDPO loading increased, the first onset decomposition temperature (T_{O1}) shifted to higher values. This occurrence suggested that DBDPO possessed higher thermal stability. Thus, when decomposition took place, DBDPO delayed the first-stage decomposition, which led to a higher first onset decomposition temperature.

The second stage of decomposition represents the thermal stability of the epoxy/glass fiber/OMMT/DBDPO hybrid composites. It was clear that as the loading of DBDPO increased, the second onset decomposition temperature (T_{O2}) decreased. A higher DBDPO loading into the epoxy hybrid composites caused the hybrid composites to decompose more readily. Thermal decomposition of polymers was often initiated by dissociation of covalent bonds to form radicals. Bond dissociation energies were particularly important as it can be used to explain the preferred decomposition path that was more likely to take place. The bond dissociation energies for C–Br, C–C, and C–O bonds were 280, 607, and 1,076 kJ mol⁻¹, respectively [41, 42]. It was noted that the bond dissociation energy for C–Br was much lower compared with C–C and C–O bonds. The presence of these weaker C–Br bonds explained the higher tendency of decomposition in E/GF/OMMT/DBDPO hybrid composites.

Similar observations were reported by Grause et al. [14], Lu and Wilkie [43], and Peng et al. [44] where the initial decomposition temperature decreased up to 68 °C at DBDPO loadings ranging from 13 to 20 wt%. The decreased thermal stability was mainly associated with the flame retardancy mechanism of DBDPO. The flame retardancy mechanism of DBDPO operated through the gas-phase mechanism. Under the application of heat, DBDPO decomposed before the epoxy matrix to form bromine free radicals and prevent the formation of combustible gases. Epoxy resin produced hydrogen radicals upon pyrolysis. Bromine free radicals functioned primarily by interfering chemically with the combustible gases in the gas-phase to form hydrogen bromide, HBr. The hydrogen bromide was believed to be a flame inhibitor by interrupting the vigorous chain branching caused by hydrogen free radicals [45]. It has been documented that a good flame retardant should decompose at ~50 °C below the host polymer [46]. The early decomposition produced bromine radicals to act effectively in the gas phase to inhibit the flame spread before the host polymer decomposes. In addition, the flame retardant was ineffective if it decomposed or volatilized after the polymers decompose.

Table 3 Thermal properties of epoxy hybrid composites recorded from TG

Sample	$T_{O1}/^{\circ}\text{C}$	$T_{O2}/^{\circ}\text{C}$	$T_5/^{\circ}\text{C}$	$*T_{\text{max}}/^{\circ}\text{C}$	Char yield/%
E/GF	118.4	352.8	192.7	380.0	67.1
E/GF/OMMT	124.0	363.2	230.2	383.3	68.3
E/GF/OMMT/DBDPO-10	119.1	320.1	287.7	337.8	70.3
E/GF/OMMT/DBDPO-20	123.3	312.6	287.9	328.8	70.1
E/GF/OMMT/DBDPO-30	116.1	313.7	303.1	328.0	69.8
E/GF/OMMT/DBDPO-40	127.5	314.7	307.6	327.4	66.4
E/GF/OMMT/DBDPO-50	129.1	313.2	293.0	323.5	64.1

T_{max} were obtained from DTG curves, T_{O1} = first onset decomposition temperature recorded from first-stage decomposition from TG curves, T_{O2} = second onset decomposition temperature recorded from second-stage decomposition from TG curves

Enhanced flame-retardant activity can be achieved by compounds which displayed more than a single mode of action that were capable of synergistic flame suppressant properties [47]. It was mentioned that DBDPO interfered with the combustion process by radical trap activity in the gas-phase. On the other hand, the decomposition of E/GF/OMMT at higher temperatures was attributed to the chemical and physical actions of the layered structure of OMMT, which formed stable carbonaceous char in the condensed-phase. The rate of radical generation by epoxy decomposition during flame propagation was sufficiently low to allow the HBr generated by DBDPO to interfere with the combustion process. The combination of both gas-phase and condensed-phase mechanisms were believed to be the effective mode of action in the flame retardancy mechanism for the epoxy hybrid composites in this study.

Char formation was an important condensed-phase mechanism for modifying the combustion process. It served as a barrier to heat and prevented the underlying material from converting to combustible gases. Table 3 showed the char yield for neat E/GF composites and E/GF/OMMT hybrid composites with various DBDPO loading. The char yield displayed a decreasing trend as the DBDPO loading increased. It was noted that the epoxy hybrid composites with up to 30 wt% of DBDPO gave higher char yield than neat E/GF and E/GF/OMMT hybrid composites. On the other hand, 40 wt% DBDPO loading onwards gave lower char yield than neat E/GF and E/GF/OMMT hybrid composites. This behavior suggested that the amount of char yield was not the exclusive factor in the flame retardancy of E/GF/OMMT/DBDPO hybrid composites. It has been reported combining DBDPO with different types of polymer matrix and synergist resulted in different amounts of char yield [48, 49].

The derivative thermogravimetry (DTG) curve gave the rate of change of mass as a function of temperature. The peaks shown in the DTG curve corresponded to various stages of decomposition. The area under the DTG curve was directly proportional to the mass change and the height

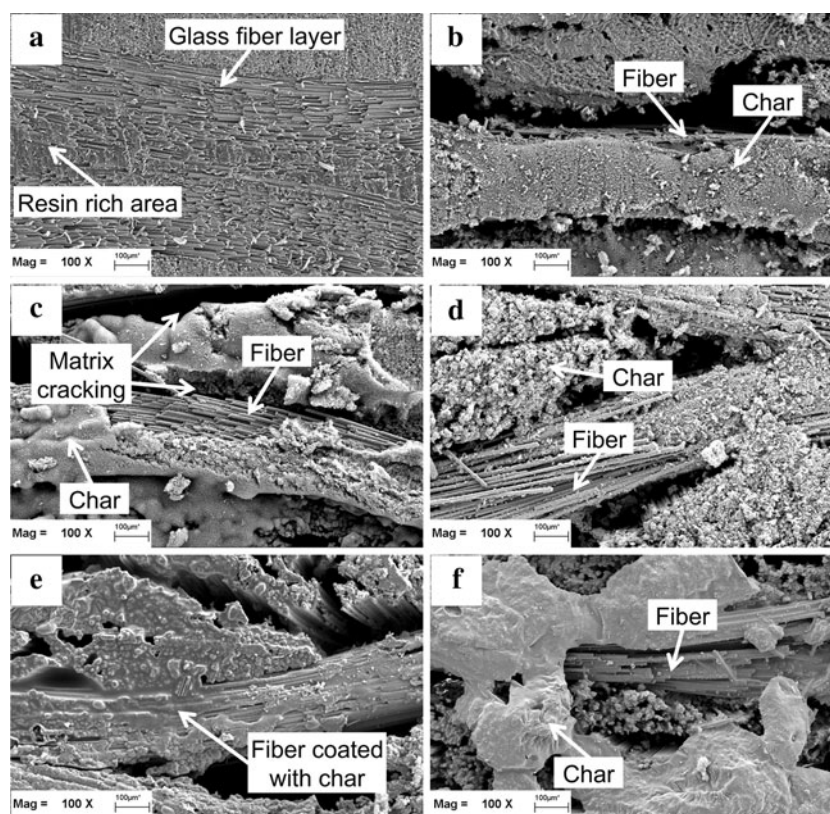
of the DTG peak gave the rate of mass change [50]. The two peaks that appeared in the DTG curves corresponded with two separate decomposition events of epoxy hybrid composites with DBDPO flame retardants. It was noted that there were two different trends in the peak shift pattern in Fig. 2. The peaks shifted to the right at the lower temperature range while the peaks at the higher temperature range shifted to the left as DBDPO loading increased. This trend suggested that the thermal stabilities of E/GF composites and E/GF/OMMT hybrid composites were improved with the addition of DBDPO at lower temperature range. At higher temperature range, DBDPO destabilized the E/GF composites and E/GF/OMMT hybrid composites, which led to lower T_{max} values.

Another trend that was observed from the DTG curve was that as DBDPO loading increased the peak height increased. This trend revealed that the rate of mass change increased as more DBDPO was added into the hybrid composite systems. As more DBDPO was added into the epoxy hybrid composites, the DBDPO constituent dominated the thermal properties of epoxy hybrid composites. As DBDPO loading increased, there were more C–Br bonds present in the hybrid composite systems, which readily decomposed into bromine radicals in the initial step of the flame retardancy mechanism.

Char morphology

The char morphologies of neat E/GF composites and epoxy hybrid composites with DBDPO after being subjected to UL 94V flammability test were examined using FESEM. Figure 3a showed the FESEM micrograph of E/GF composites before being subjected to UL-94V as a comparison. A few important characteristics of char were density, continuity, coherence, adherence, oxidation-resistance, thermal insulation properties and permeability [51]. It was noted that there was a thin layer of carbonaceous char on the glass fiber surface in E/GF composites even without the addition of OMMT or flame retardant (c.f. Fig. 3b).

Fig. 3 FESEM micrographs showing the char morphology of epoxy hybrid composites after subjected to UL-94V flammability tests. *Notes:* **a** E/GF (before UL-94), **b** E/GF, **c** E/GF/OMMT, **d** E/GF/OMMT/DBDPO-10, **e** E/GF/OMMT/DBDPO-30, and **f** E/GF/OMMT/DBDPO-50



The incorporation of OMMT into the epoxy composites has thickened the char residue in comparison to E/GF composites. However, it was observed that the E/GF/OMMT composites possessed loose structures that exhibited major cracks. In addition, Fig. 3c revealed that the glass fibers in E/GF/OMMT hybrid composites were highly exposed regardless of the char formation, which was the reason behind the low LOI value and “no rating” in UL-94V flammability test. The addition of 10 wt% DBDPO into E/GF/OMMT hybrid composites changed the char morphology by forming more homogeneous char that adhered on the glass fiber surface (c.f Fig. 3d). Figure 3e showed a more compact and uniform char morphology in E/GF/OMMT/DBDPO-30 hybrid composites. However, such char morphology was insufficient to pass the minimum requirements of the UL-94V flammability test. Drastic changes in char morphologies of E/GF/OMMT/DBDPO-50 hybrid composites were observed (c.f Fig. 3f). The formed char was thick, compact and continuous around the glass fibers, which was in agreement with the results obtained in the LOI and UL-94V flammability tests.

Figure 4a, b showed the EDX taken from the E/GF/OMMT/DBDPO-50 sample (at 100 \times and 1,500 \times magnification). The EDX results showed that the components of

char consisted of bromine, carbon, silicon and oxygen elements. It was observed that there was more Si element near the fiber surface than in the char-rich area, while the amount of bromine element in both the char-rich area and near the fiber surface was almost the same. This result suggested that only a portion of bromine in DBDPO formed bromine free radicals to inhibit the flame spread in the gas phase, while some remained in the condensed phase. It was proposed that once the OMMT decomposed, a Si-rich barrier was formed that helped shield the glass fibers and the remaining resin from heat and prevented the escape of volatiles, while DBDPO enhanced the char formation by forming swollen and compact char layer on top of the Si-rich barrier. According to Lu and Wilkie [43], the presence of bromine free radicals terminated the active radicals in the pyrolysis gas phase, resulting in incomplete combustion of the pyrolysis products. These incomplete combustion products enhanced the formation of soot and char that was observed in Fig. 3f. On the other hand, the DBDPO decomposed and converted to lower brominated derivatives such as nonabromodiphenyl oxide and octabromodiphenyl oxide [41]. These lower brominated derivatives remained in the condensed phase and contributed to char formation.

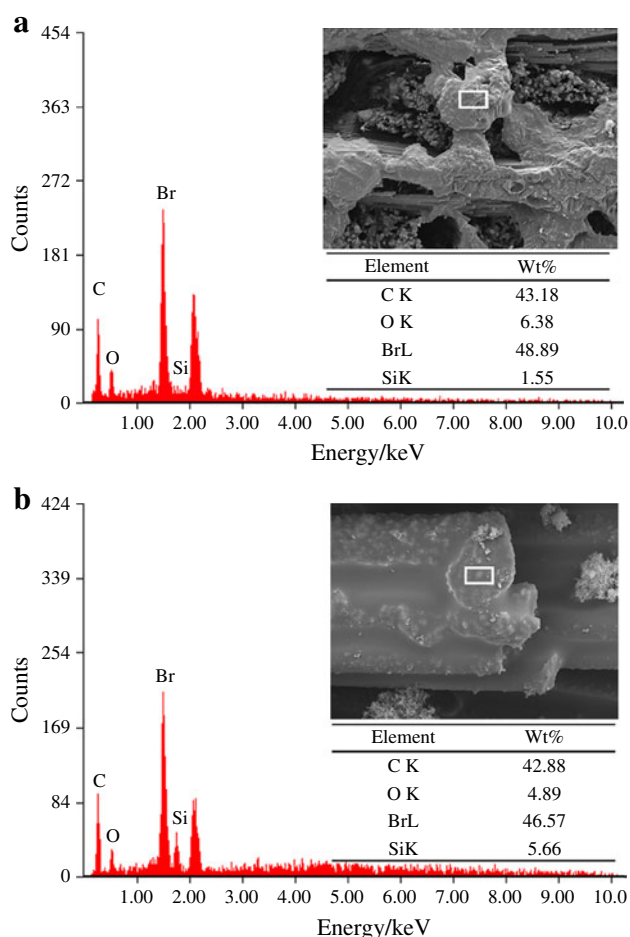


Fig. 4 EDX taken from the E/GF/OMMT/DBDPO-50 sample at **a** 100 \times , **b** 1,500 \times magnification

Conclusions

Epoxy/glass fiber/OMMT hybrid composites with various loadings of DBDPO flame retardant were successfully prepared by vacuum-assisted resin infusion technique. Based on the UL-94V, LOI, TG and microstructure analysis, the following conclusions were drawn.

A loading of 40 wt% DBDPO in E/GF/OMMT/DBDPO hybrid composites achieved V-1 rating in UL-94V flammability test, while increasing the DBDPO loading to 50 wt% achieved V-0 rating for the hybrid composites. The LOI of E/GF/OMMT hybrid composites (22.7 %) increased to 39.9 % with 50 wt% loading of DBDPO. The decreased thermal stability of the E/GF/OMMT/DPDPO composites was attributed to the decomposition of DBDPO to form bromine free radicals at a lower temperature than the decomposition temperature of the E/GF composites and E/GF/OMMT hybrid composites. These bromine free radicals reacted with the combustible gases from the epoxy pyrolysis to form hydrogen bromide, which improved the flame retardancy of the epoxy composites. This result was

supported by FESEM, which showed that increased DBDPO loading resulted in more compact and continuous char morphologies, indicating higher flame retardancy in the hybrid composites.

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