Investigation of thermal and fire performance of novel hybrid geopolymer composites

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Many advanced polymer composites consist of an organic phase of a highly cross-linked epoxy resin, thus the flammability of the virgin polymer matrix limits the use of these materials in many applications, such as marine platforms, automotive, and aerospace [1–3]. Various methods have been proposed for forming inorganic protective layers on the surface of burning polymers, but their positive effect is generally accompanied by certain disadvantages. Inorganic filler particles improve fire performance through a dilution effect and reduced heat feedback. Silica additives of high surface area are most efficient, as these particles accumulate on the surface instead of sinking into the polymer [4]. A current area of great interest involves polymer-clay (layered silica) nanocomposites, when introduced in intercalated or exfoliated form, which may accumulate on the surface of a polymer during burning to form a barrier layer to either outgoing degradation products or incoming gases [5, 6]. Their effect is clearly indicated by the reduced rate of heat release of horizontal samples in the cone calorimeter. Recent work also suggests that even very low levels (1–4%) of nano-clay lower the peak heat release rate in a cone-calorimeter by some 30% [7]. In particular, a family of new materials called geopolymers (poly-silates) has emerged during the last decade as one of the most promising replacement candidates, for plastics and even ceramics, in certain applications since they have certain advantageous physical properties of ceramics. The term "geopolymer" was first used by Davidovits [8, 9] to describe a family of mineral binders closely related to artificial zeolites.

The most attractive geopolymers (polysialates) are inorganic polymers made from alumino-silicates since they can be synthesized at low temperatures and have useful properties such as high compressive strength and are stable at temperatures up to 1300–1400 °C. By changing the Si/Al ratio, it is possible to produce composites with very high fire resistant properties. Polysialates are readily synthesized from natural aluminosilicates such as kaolinite, a very abundant source of alumina and silica. The formation of geopolymeric materials follows the same routes as that of most zeolites. Geopolymers are formed by the co-polymerization of alumino and silicate species, which originate from the dissolution of silicon and aluminium-containing source of materials at a high pH, in the presence of soluble alkali metal silicates. The current commercial use of geopolymers alone, compared to plastics, is limited because of the complexity of large scale processing, high density and problems with machining and molding, and most importantly, their brittleness. Generally geopolymers are linear poly(metasilicate), with tetra-coordinate aluminate crosslinks. The geopolymerization involves the chemical reaction of alumino-silicate oxides (Al^{3+} in IV-fold coordination) with alkali polysilicates yielding polymeric Si—O—Al bonds, the amorphous to semi-crystalline three dimensional silico-aluminate structures are of the poly(silate) type (—Si—O—Al—O), the poly(silate-siloxo) type (—Si—O—Al—O—Si—O—), the poly(silate-disiloxo) type (—Si—O—Al—O—Si—O—Si—O—).

In this paper synthesized geopolymer is incorporated into the cross-linked polymeric structure systems by manipulating the chemical composition of the geopolymer and hence compatibility, rather than physical blending. In so doing, we will make use of the processability and properties of the cross-linked epoxy resin, in combination with the geopolymers to produce inorganic organic hybrid materials, which have excellent mechanical properties such as stiffness and strength, and in particular are more fire resistant. Thus the first system reported involves the choice of a standard, bi-functional epoxy resin, diglycidyl ether of bisphenol A (DEGEBA) to be incorporated with the geopolymers. The results are also compared with a physically blended epoxy–kaolin blend to investigate any synergistic effect of producing a more homogeneously dispersed network on the fire performance. This paper presents, to our knowledge, the first investigation of the successful incorporation of a geopolymer system into an organic polymer system, such as an epoxy, and is advantageous to improving properties of the matrix.

Kaolin (HR1-F grade) with an average particle size of 38.20 μm was procured from Commercial Minerals, Sydney, Australia. The potassium silicate solution was obtained from PQ Australia Pty Ltd. Potassium silicate composition was $SiO_2/K_2O = 2.00$,

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SiO_2 = 29.3 (wt%) and K_2O = 14.5 (wt%) with density 1420 kg/m^3. 5M KOH solution was prepared in the laboratory from KOH pellets from Bdh, Merck Pty. Ltd. The epoxy resin used in the study was diglycidyl ether of bisphenol-A (DGEBA), commercially known as DER-331 from Dow Chemical Company, Australia. The curing agent used in this experiment was a mixture of 3,5-diethyltoluene-2,4-diamine and 3,5-diethyltoluene-2,6-diamine (Ethacure-100) obtained from Albemarle Corporation, USA.

Inorganic geopolymer was synthesized by the reaction of kaolin, potassium silicate and potassium hydroxide solution at room temperature. Initially, the desired amount of potassium silicate was mixed with 5 M potassium hydroxide solution and then 20 g kaolin was added and mixed for 5–30 min. The viscous mix was then added to a mixture of DGEBA epoxy resin and the curing agent with constant stirring for 15 min. The mixture was then placed in the Teflon coated mold and was cured at 60 °C for 6 h followed by post curing at 180 °C for 2 h.

To fabricate filler dispersed composites, 20 g of pure kaolin was mixed with the mixture of DGEBA epoxy resin and the curing agent for 1 h. The mix was then placed in a Teflon coated mold and was then cured at 80 °C for 6 h followed by post curing at 180 °C for 2 h. The sample was then cut, ground and polished for thermal, cone calorimetry and microstructure analysis.

The formation of geopolymers was characterized by X-ray diffraction analysis by Rigaku wide-angle goniometer. An acceleration voltage of 40 kV and current of 22.5 mA were applied using Ni filtered Cu K_α adiation. FT-IR spectra were recorded on a Perkin-Elmer FT-IR spectrometer. Wave numbers were recorded from 400–4000 cm^{-1}. The loss tangent, tan δ of cured samples was determined on a rheometric scientific dynamic mechanical thermal analyzer, DMTA IV. The cured samples were clamped in a medium frame using a small center clamp in the dual cantilever mode. Frequency sweep scans were performed from 80 to 260 °C at 2 °C/min. Thermo gravimetric analysis was performed on the cured samples using a TG-92 Setaram thermal analyzer. The thermographs were obtained at a heating rate of 10 °C/min using 10–15 g of the powdered sample. The experiments were made in a static air atmosphere. Fire performance tests including time to ignition (TTI), rate of heat release (RHR), time to reach maximum RHR, smoke density, carbon monoxide and carbon dioxide evolution and the sample mass loss were determined by cone. The heat flux produced was 50 kW/m^2 on the specimen, which had an exposed surface of 100 × 100 mm.

The glass transition temperature and dynamic-mechanical properties of DGEBA, 20% Kaolin-DGEBA and 20% Geopolymer-DGEBA has been determined. Fig. 1 shows the tan δ spectra from dynamic mechanical analyses of the cured of DGEBA and its composites respectively. Cured DGEBA showed a T_g around 201.0 °C. However, on addition of kaolin the T_g of the composites decreased to 195 °C. The effect on the T_g of clay addition has been widely studied by many researchers reporting an increase in T_g, [10, 11], whilst others found a slight decrease or no change [12, 13]. Becker [14] reported a decrease in T_g for higher functionality epoxy resins and suggested that the decrease in T_g of clay-modified composites was due to interference of the clay with crosslink density, epoxy homopolymerization and plasticization. Subsequently, addition of geopolymer into the DGEBA epoxy produced a lower T_g. The lower crosslink density of Kaolin modified DGEBA was confirmed by the greater height of the delta relaxation observed in Fig. 1. The lower relaxation strength and T_g of geopolymer-modified composites are believed to be due to structural inhomogenety which were observed by SEM images.

Thermo-gravimetric analysis was performed to examine the effect of geopolymer and Kaolin addition on

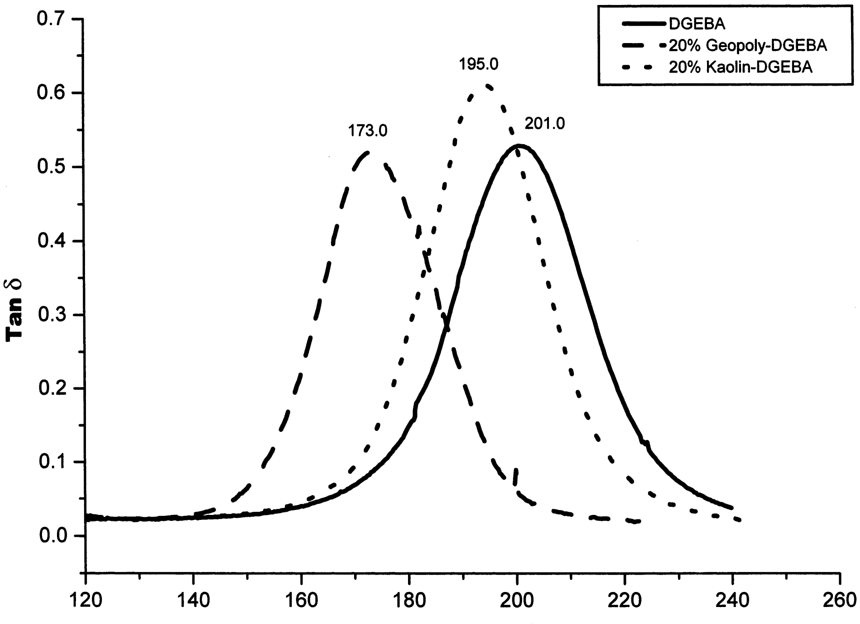


Figure 1 DMTA spectra of (a) cured DGEBA (b) cured 20% Geopolymer-DGEBA and (c) cured 20% kaolin-DGEBA.

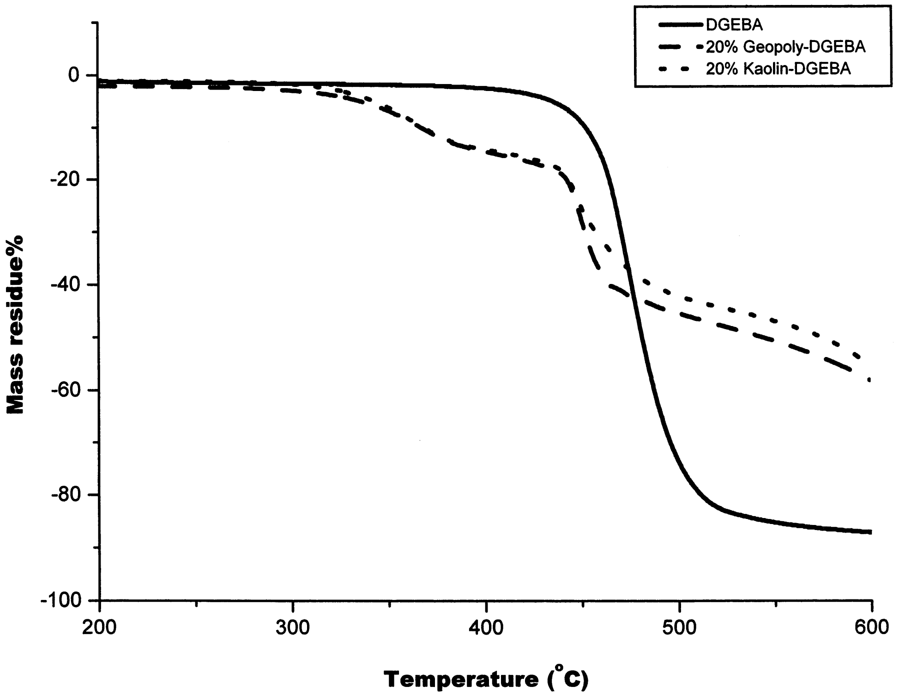


Figure 2 TGA spectra of (a) cured DGEBA (b) cured 20% Geopolymer-DGEBA and (c) cured 20% kaolin-DGEBA variation with temperature.

the thermal stability of cured DGEBA. Fig. 2 shows the weight loss for the unmodified DGEBA epoxy, kaolin modified DGEBA and geopolymer-DGEBA composites. Pure DGEBA epoxy resin showed a one-step degradation mechanism. However, kaolin or geopolymer modified DGEBA showed a three-step degradation mechanism. Table I reflects the thermal properties of pure DGEBA epoxy resin and modified-DEGBA epoxy resin. In the unmodified cured DGEBA system, initial degradation commenced at around 430 °C, however, the rate of degradation significantly increased above 450 °C and a char yield of 16% remained at 600 °C. The degradation temperatures at 10% weight loss were found 463 °C for DGEBA and around 380–384 °C for modified DGEBA composites. These results indicate that the thermal stability of modified epoxy resin at lower temperatures (<400 °C) is not superior to that of pure DGEBA epoxy resin. However, the char yield of modified epoxy resin at 600 °C is much higher than unmodified DGEBA epoxy resin. Only 20% addition of kaolin or geopolymer increased the char yield. High char yield formation prevents the production of combustible gas materials and thus decreases the thermal conductivity of the surface of the burning materials [13].

The cone calorimeter provides important information on the combustion behavior of a material under ventilated conditions. The peak rate of heat release of a material is one of the important factors to determine the potential behavior during fire. Fig. 3 shows the rate of heat release (RHR) of unmodified DGEBA and modified DGEBA variation with time at a heat flux of 50 kWm^{-2}. The peak rate of heat release for DGEBA is high at around 1400 kWm^{-2} after 150 s. However, 20% Kaolin modified DGEBA has a lower peak rate of release at 1100 kWm^{-2}, which is significantly reduced to 21.5% compared to unmodified DGEBA. In contrast, DGEBA modified with 20% geopolymer showed a peak release rate at 702 kWm^{-2}, which is 47% lower than that of unmodified DGEBA. The significant rate of heat release reduction is attributed to incorporation of geopolymer. An increase in flame retardancy in modified DGEBA was observed from the residual masses, or char, obtained during firing. A higher percentage of mass residue or char indicates a condensed-phase flame retardance mechanism [16]. Other important parameters obtained from the epoxy and modified epoxies by cone calorimetry are given in Table II.

Evaluation of fire performance of epoxy resins involves quantifying smoke generation at specific extinction area (SEA) and quantifies production of CO and CO_2. SEA measures the total obscuration area of smoke produced, divided by the total mass loss during burning, thus measuring efficiency of a given mass of flammable volatiles converted when it burns. Fig. 4 shows the SEA of DGEBA and kaolin/geopolymer modified DGEBA

TABLE I Thermal properties of DGEBA epoxy and modified DGEBA-epoxy composites

	Temperature (°C) at 10% wt loss	Char yield 400 °C (%)	Char yield 400 °C (%)	Char yield 400 °C (%)
Pure DGEBA epoxy	463	100.0	90.0	16.0
20% Kaolin modified-DGEBA	384	90.0	82.0	46.5
20% Geo-poly modified-DGEBA (30 min mix)	380	88.0	82.0	39.0

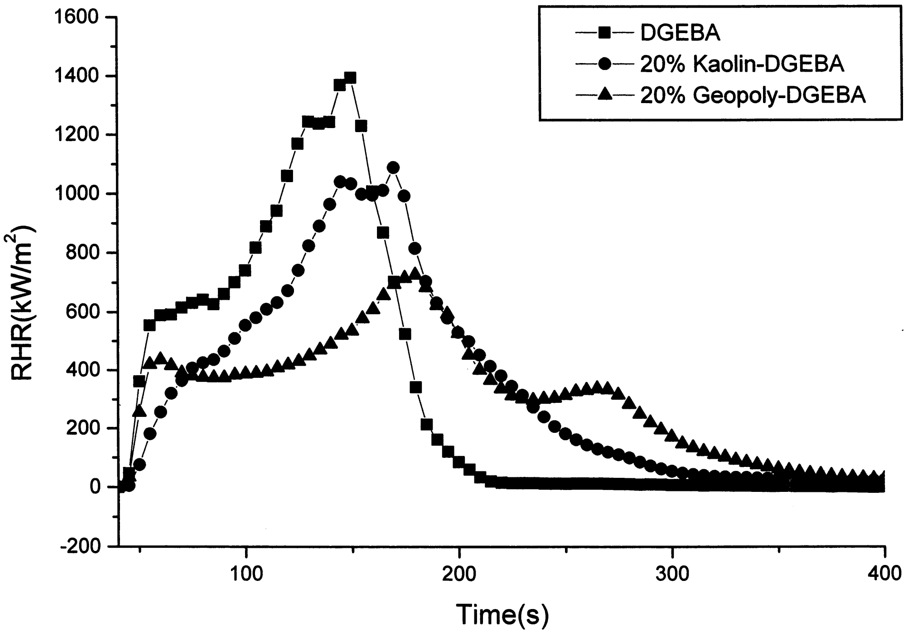


Figure 3 RHR spectra of (a) DGEBA (b) 20% Geopolymer-DGEBA and (c) 20% kaolin-DGEBA variation with time.

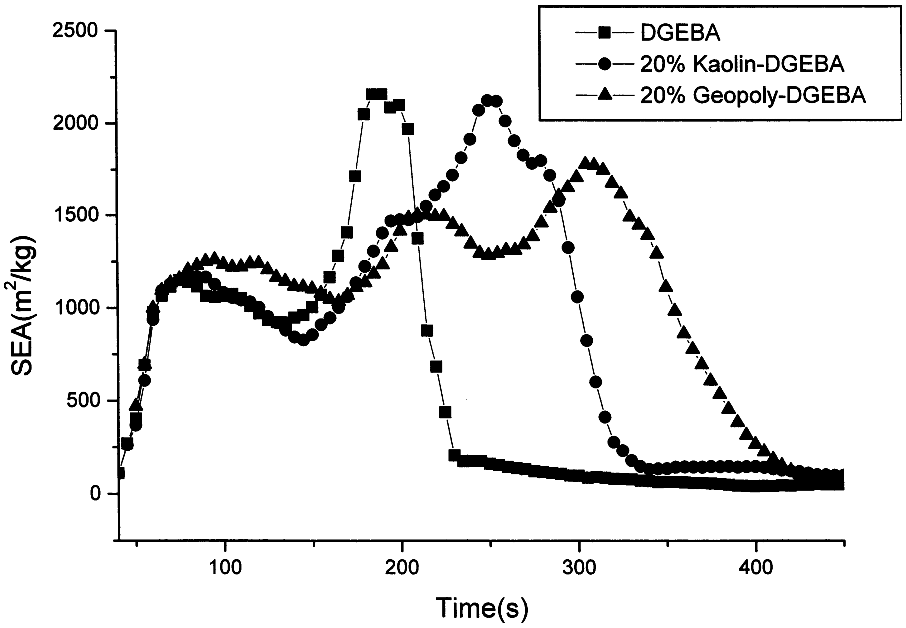


Figure 4 SEA spectra of (a) DGEBA (b) 20% Geopolymer-DGEBA and (c) 20% kaolin-DGEBA variation with time.

as a function of time. The SEA value of DGEBA was found to be maximum around 200 s and decreased rapidly. However, modified DGEBA showed relatively lower value at 200 s and maximum value observed at 250 and 325 s for kaolin and geopolymer modified DGEBA respectively. This can be explained by the fact that unmodified DGEBA is converted into smoke more easily when it burns, and does so over a longer period of time. CO emission for the modified DGEBA system remained constant for a longer period as found in Fig. 5. The higher CO production of unmodified DGEBA indicates incomplete combustion. The generation of a low volume of CO during a fire is desirable.

The fire performance of a material can also be calculated from the fire performance index, (FPI), which is the ratio between the time of ignition (time) and the peak rate heat release (RHR). Table III shows the fire performance index of unmodified DGEBA and modified DGEBA system. DGEBA without any modification showed the lowest fire performance at 0.046 sm^2/kW. However, when DGEBA was modified with kaolin the FPI increased to 0.062, an increase of 35%. In comparism, the geopolymer modified DGEBA FPI increased to 0.081 sm^2/kW and improved by 76%.

Fig. 6 shows the SEM micrographs of 20% kaolin modified DGEBA and 20% geopolymer-DGEBA mixed for 5 and 30 min respectively. It is clear from Fig. 6a that kaolin particles were homogeneously dispersed into the DGEBA matrix. No agglomeration was observed. However, in the geopolymer-DGEBA system a different microstructure was observed. The co-continuous structure of geopolymer composites was as observed in Fig. 6b. It is evident from the micrographs that incorporation of geopolymer into the organic polymeric system is possible with good microstructure. These types of microstructure, however, showed lower

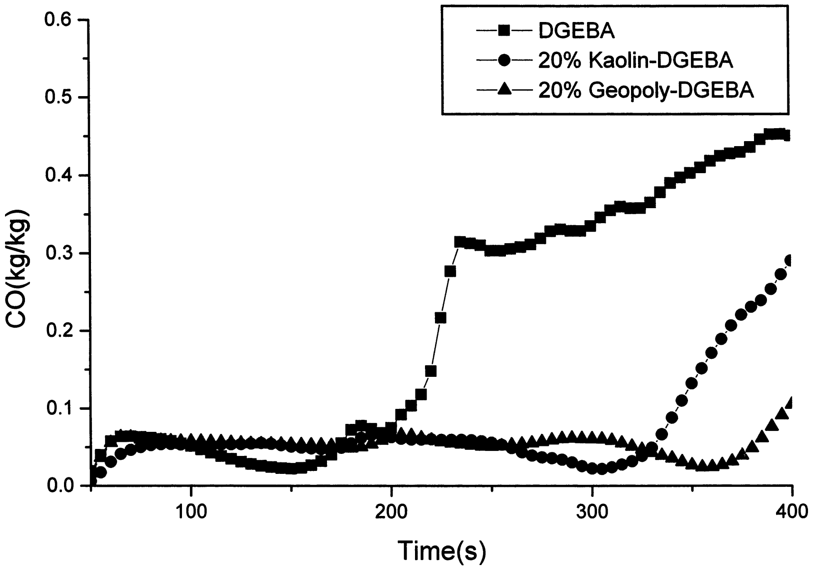
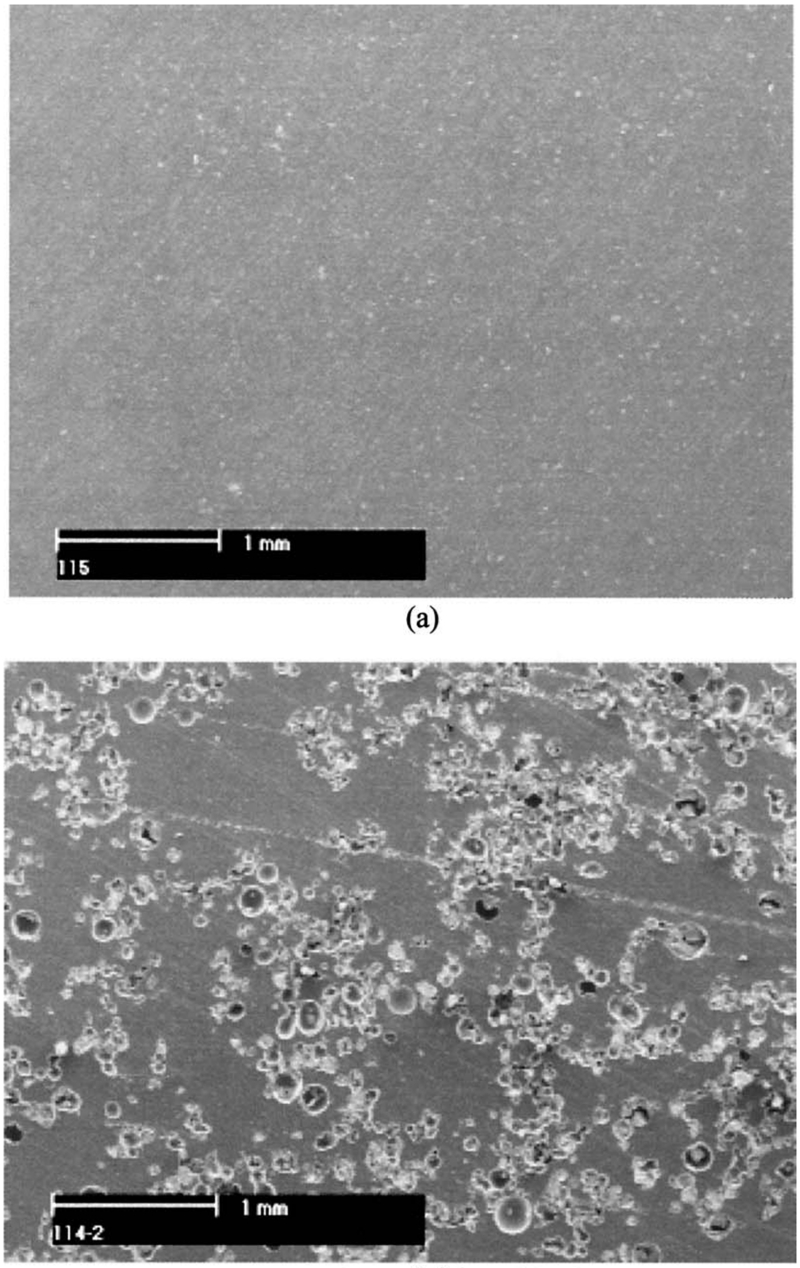


Figure 5 CO emission of (a) DGEBA (b) 20% Geopolymer-DGEBA and (c) 20% kaolin-DGEBA variation with time.



(a)

(b)

Figure 6 SEM images of (a) 20% kaolin-DGEBA and (b) 20% Geopolymer-DGEBA.

TABLE II Cone calorimetric data measured with an irradiance of 50 kWm^{-2}

Fire properties	DGEBA	20% Kaolin-DGEBA	20% Geo-poly-DGEBA
Time to ignition (s)	65	69	60
Peak RHR (kW/m^2)	1396	1100	735
Av. HRR (kW/m^2)	399.8	426	364.1
Av. HRR at 180 s	501	562.5	471
Time to max HRR(s)	155	170	185
Av. effective heat of combustion (MJ/kg)	21.2	25.3	24.7
Av. CO yield (kg/kg)	0.0454	0.06	0.059
Av. CO_2 yield (kg/kg)	1.48	1.99	1.955
Total heat evolved (MJ/kg)	89.65	115.24	95.68
Mass loss (%)	82.8	73.9	74.7

TABLE III Fire performance index of unmodified DGEBA and modified DGEBA system

DGEBA system	RHR (kW/m^2)	Time to ignition	FPI (sm^2/kW)
DGEBA only	1396	65	0.046
20% kaolin-DGEBA	1100	69	0.062
20% geopolymer-DGEBA	735	60	0.081

relaxation behavior and T_g but exhibited higher thermal stability and higher fire performance capability. Other properties of materials, mainly the mechanical properties before and after firing tests of the composites, should be investigated further.

References

1. R. A. DEMARCO, "Composites Applications at Sea, Fire Related Issues," in Proc. 36th Int. SAMPE Symposium, 15–18 April 1991, p. 1928.
2. W. T. HATHAWAY, "Fire Safety in Mass Transit Vehicle Materials," in Proc. 36th Int. SAMPE symposium, 15–18 April 1991, p. 1900.
3. R. G. HILL, T. I. EKLUND and C. P. SARKOS, "Aircraft Interior Panel Test Criteria Derived from Full-Scale Fire Tests," Reported DOT/FAA/CT 85/23(1985), USA.
4. T. KASHIWAGI, J. GILMAN, K. BUTLER, R. HARRIS, J. SHIELDS, A. ASANO and M. LEWIN (eds.), in "Recent Advances in Flame Retardancy of Polymeric Materials" (Stamford, 2000) Vol. 9.
5. WEI XIE, ZONGMING GAO, KUNLEI LIU, WEI-PING PAN, RICHARD VAIA, DOUG HUNTER and ANANT SING, *Thermochim. Acta* **367** (2001) 339.
6. JUN-CHAO HUANG, ZI-KANG ZHU, JIE YIN, XUE-FENG QIAN and YANG-YANG SUN, *Polymer* **42** (2001) 873.
7. J. GILMAN, T. KASHIWAGI, S. LOMAKIN, E. GIANNELIS, E. MANIAS, J. LICHTENHAN and P. JONES (eds.), in "Fire Retardancy of Polymers: The Use of Intumescence" (The Royel Chemical Society, Cambridge, 1998) p. 203.
8. J. DAVIDOVITS, Geopolymer 88, 1st Eur. Conf. Soft Mineralogy (1988) Vol. 1, p. 25.
9. *Idem.*, *Concrete Int.* **16** (1994) 53.
10. J. M. BROWN, D. CURLISS and R. A. VAIA, *Chem. Mater.* **12** (2000) 3376.
11. P. MUSTO, G. RAGOSTA, P. RUSSO and L. MASCIA, *Macromol. Chem. Phys.* **202** (2001) 3445.
12. J. MASSAM and T. J. PINNAVAIA, "Clay Nanolayer Reinforcement of a Glassy Epoxy polymer," Mater. Res. Soc. Symp. Proceeding 1998, p. 36.
13. A. LEE and J. D. LICHTENHAN, *J. Appl. Polym. Sci.* **73**(10) (1999) 1993.
14. O. BECKER, R. J. VARLEY and G. P. SIMON, *Polymer* **43** (2001) 4365.
15. E. M. PEARCE and R. LIEPINES, *Environmental Health Perspect* **11** (1975) 69.
16. J. R. EBDON, B. J. HUNT, P. JOSEPH, C. S. KONKEL, D. PRICE and K. PYRAH, *Poly Degrad Stab* **70** (2000) 425.

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