

## FLAMMABILITY OF ORGANOCLAY/GFRP COMPOSITES

Q. T. Nguyen<sup>\*</sup>, T. Ngo, P. Mendis, P. Tran

University of Melbourne, Department of Infrastructure Engineering, Parkville, Australia 3010  
[\\*thuy.nguyen@unimelb.edu.au](mailto:*thuy.nguyen@unimelb.edu.au)

**Keywords:** Nanoclay, Flammability, Composites, Cone calorimetry.

### Abstract

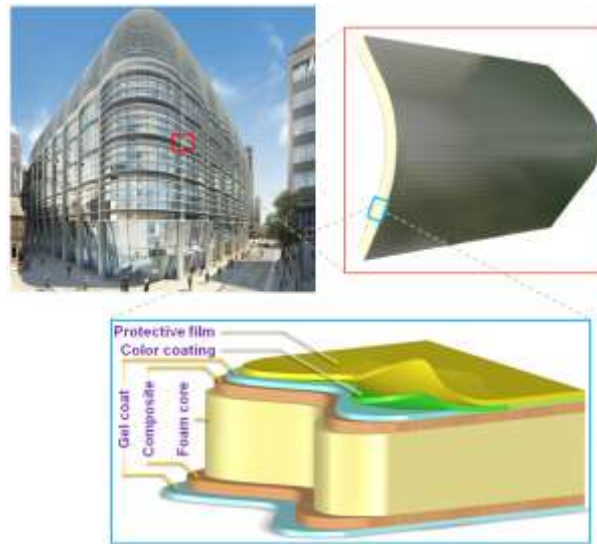
*One of the major issues that hinder the extensive use of composite structures in high-rise building is related to their fire resistance performance. Clay nanoparticles are well-known as potential precursors for nanocomposites. However, the effect of nanoclay on the fire performance of hybrid composites has not been studied comprehensively. This study investigates the effect of nanoclay on the fire performance of epoxy/glass fibre composites. Cone calorimetry with horizontal configuration is used as the bench-scale test to determine the heat production from samples with nanoclay contents ranging from 1% to 5%. The results show that a low percentage of less than 3% nanoclay results in scattered nanoparticle dispersion and, therefore, is insufficient for char formation. At 5% nanoclay replacement, a delay of 20 seconds in heat release rate, 22% lower total heat release, and 15% lower total smoke production are observed.*

### 1. Introduction

Composites made from glass fibre reinforcement and polymeric matrix offer excellent alternatives of strong, lightweight, flexible and cost-effective materials when compared with conventional materials used in building construction (such as aluminium and steel) (**Figure 1**). While glass fibre reinforced polymer (GFRP) composites possess the required strengths with low embodied energy, the main obstacle preventing application of GFRP in building construction is its poor performance when exposed to fire hazards. The highly flammable resin contributes mostly to this inferior fire performance, and the glass fibre reinforcement exacerbates the flammability of the composite due to the “candle-wick effect”[1]. Improving its flame retardancy is, therefore, the key to converting GFRP into a superior construction material. For sandwich structures used in façade systems, the foam core can be designed especially for high flame retardancy; however, the composite layers are still sensitive to fire, thus require critical improvement to pass fire performance requirements in the built environment.

Many researchers have investigated the influence of nanoclay on improving the properties of nanocomposites at low levels of replacement (3–5%). Most of them were interested in the mechanical, electrical and thermal properties [2-7]. The effect of nanoclay on the fire retardancy of thermosetting resin-based composites was also investigated. Liu et al. [8] dispersed organo-modified clay Nanocor I.30 into epoxy with different hardeners. The

composites have been tested using a cone calorimeter at a heat flux of 50 kW/m<sup>2</sup>. The sample of bisphenol A epoxy/diethyl toluene diamine (as the hardener) and 5% nanoclay gave a PHRR of 16.5% lower than the neat resin. However, the laminates with nanoclay showed more severe combustion properties. This could be attributed to the dispersing technique, as the nanoclay and the resin had been mixed mechanically for one hour. The performance of the nanocomposite has been known to depend greatly on the dispersion of the nanoparticles in the mixture. The properties of composites with poorly dispersed nanoclay have been observed to fall in the same range as traditional microcomposites.



**Figure 1.** An example of a building façade made from sandwich structures

In this study, the effect of organoclay on the fire performance of epoxy-based composites will be investigated. Apart from mechanical mixing, sonication energy is used to improve the dispersion of organoclay into the resin before fabrication. The composites are reinforced with E-glass fabrics, and the fire performance of the composites will be studied using the cone calorimeter method, which is one of the most effective bench-scale tests for heat release rate of polymer-based materials. Organoclay will be added to the resin at three different replacement levels and the corresponding samples will be fabricated by the vacuum-assisted infusion technique.

## 2. Experimental work

### 2.1 Materials

Epoxy (Kinetix) obtained from ATL Composites is used as the resin. Kinetix contains bisphenol A (more than 60% by weight) and bisphenol F. Kinetix is diluted by 1, 6-hexanediglycidyl ether and aliphatic glycidylether C12-C14 alcohols. The reinforcement composes of six layers of 410 *gsm* biaxial E-glass fabrics (0°/90°/0°/90°/0°/90°). The 0° fabric layer weighs 236 *gsm*, while the weight of the 90° layer is 174 *gsm*. Nanoclay from Sigma-Aldrich Australia, designed especially for flame retardant purposes, is used in this work. Nanoclay contains 35–40% wt. of the organic modified agent. The clay nanoplates are 200–

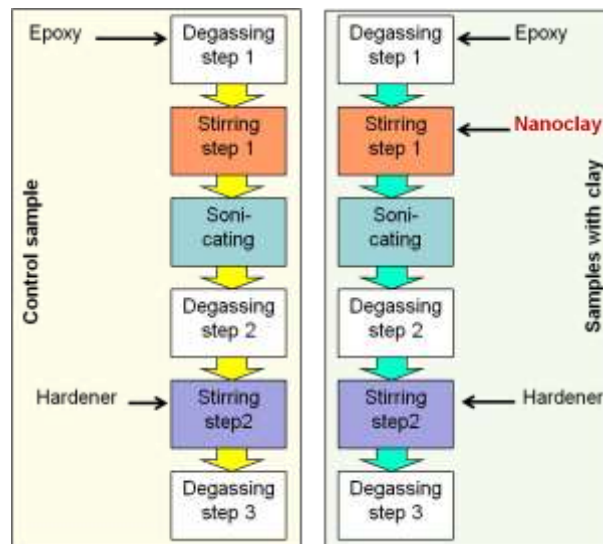
300 nm in lateral dimension and 1 nm in thickness. After surface treatment, the clay has an average particle size of 10–11  $\mu\text{m}$ .

## 2.2 Nanoclay dispersion

The dispersion of clay into epoxy is illustrated in Figure 2. The material compositions of four sets of samples with varying Nanoclay contents are presented in

**Table 1.** Material compositions with varying nanoclay fraction

. An overhead mechanical mixer with a speed of 500 rpm is used to mix the resin for 30 minutes. It is observed that the mixtures were in a slurry-like form. To ensure good dispersion of nanoclay into the resin, the slurry-like mixture is sonicated in the bath sonicator in two steps: degassing for 10 minutes, and then sonicating for 30 minutes. The control sample without nanoclay is treated using the same procedure to ensure consistency.



**Figure 2.** Schematic of the nanoclay dispersion process into the epoxy resin

**Table 1.** Material compositions with varying nanoclay fraction

Samples	Kinetix epoxy (grams)	Nanoclay (grams)	Hardener (grams)
E0	400	-	100
E1	395	5	100
E3	385	15	100
E5	375	25	100

## 2.3 Fabrication and characterization of composites

The composite laminates are fabricated using a vacuum-assisted infusion process, where six layers of glass fibre fabric are cut to a size of 380 mm x 540 mm and are stacked together.

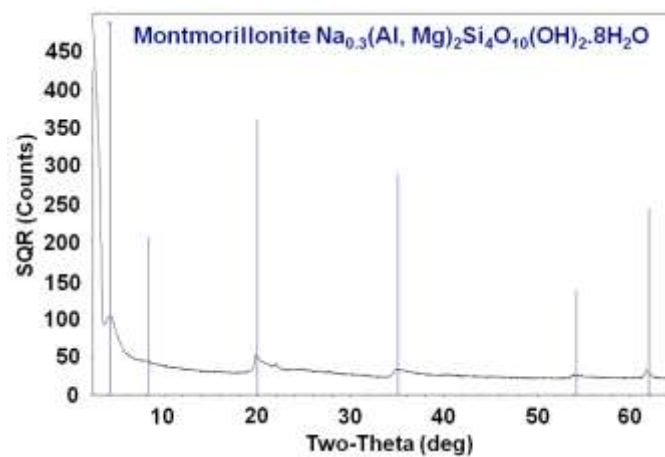
The hardener is added to the treated/control resin with a weight ratio of 1:4. Mixtures are then degassed for 30 minutes at 98% vacuum level in the resin trap.

The structure of the selected nanoclay was investigated by X-ray diffraction analysis with Cu K $\alpha$  radiation operating at 40 kV and 30 mA at room temperature. Diffraction patterns are collected at  $2\theta = 2^\circ$ – $65^\circ$  with a step size of  $0.008^\circ$  and four seconds per step. Elemental analysis of the samples is carried out using a Phillips XL30 EDS scanning electron microscope (SEM). This is a high vacuum SEM equipped with an Oxford instruments ISIS energy-dispersive X-ray spectrometer (EDS) X-ray microanalysis system. Fire retardancy of the composite is evaluated using cone calorimeter tests conducted at Victoria University's Centre for Environmental Safety and Risk Engineering (CESARE) laboratories, in accordance with ISO 5660-1. The samples are tested in a horizontal orientation. They are cut from post-cured panels to the size of 100 x 100 x 3 mm and are exposed to a 50 kW/m<sup>2</sup> radiant cone. The field emission SEM (Phillips XL30) is used to study the distribution of nanoclay particles over the surface of the infused panel. Samples are also coated with gold in the Dynavac SC100 magnetron sputter coater for 10 minutes, and scanned in the SEM at the an operating voltage of 10 kV.

### 3. Results and discussions

#### 3.1 Microanalysis of nanoclay and GFRP samples

X-ray diffraction patterns of the used organoclay are compared with the pristine montmorillonite (MMT), as can be seen in Figure 3. The organoclay XRD pattern shows an excellent match with the MMT  $\text{Na}_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ . The appearance and magnitude of the peaks at  $2\theta = 4.1, 19.9, 35.2, 54.2, 62.0$  in the organoclay and MMT XRD patterns prove the microstructure and chemical characteristics of the used organoclay.

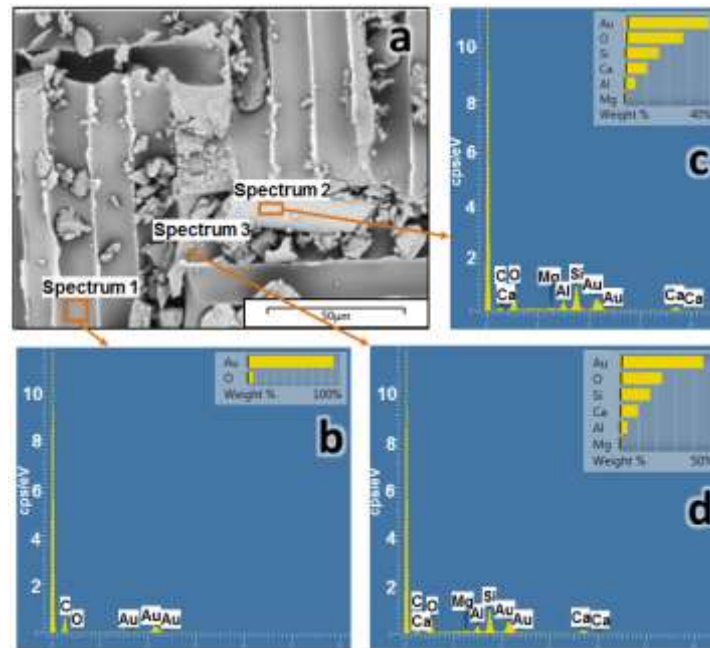


**Figure 3.** X-ray diffraction patterns of organoclay in comparison with pristine montmorillonite  $\text{Na}_{0.3}(\text{Al}, \text{Mg})_2\text{Si}_4\text{O}_{10}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$

Microanalysis conducted with the SEM-EDS analyser provides the elemental details of the phases in the samples. SEM-EDS together with the XRD results give a complete picture of the used organoclay and contribute to the analysis of nanoclay distribution in the samples, which will be discussed in Section 3.4.

Figure 4 **Error! Reference source not found.**a shows the image of sample E3 at 3000x magnification. Three spectrums are collected at different locations, which represent the epoxy

resin (spectrum 1, Figure 4b), large tactoids (spectrum 2, Figure 4c) and smaller particles (spectrum 3, Figure 4d). Element Au (gold) is shown in all the spectrums because the sample is coated in a gold layer in the sputter prior to the tests. The appearance of only element C, H and O (apart from element Au) in spectrum 1 shows a typical point of the resin with an organic composition. Spectrums 2 and 3 show similar elements present, such as Si, Ca, Al and Mg. These results further confirm the appearance of the MMT crystal in the composite structure.



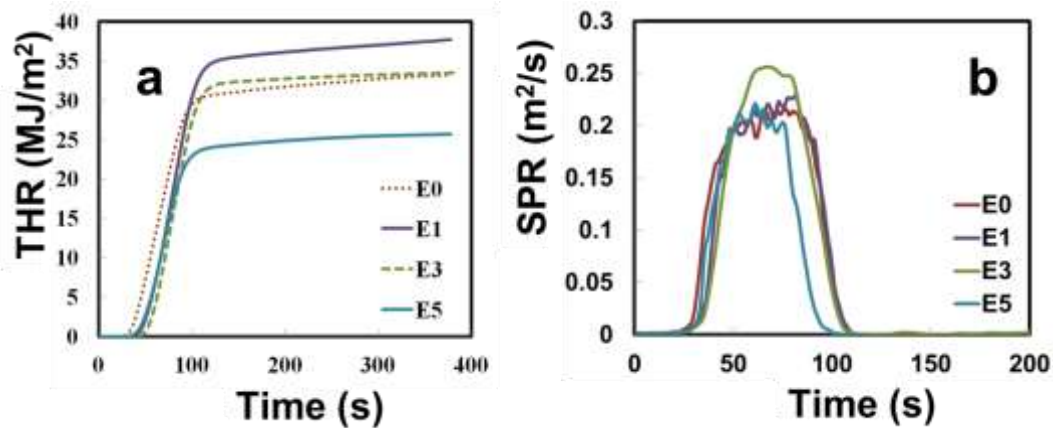
**Figure 4.** (a) SEM-EDS analysis of sample E3 with 3% organoclay. Spectrums at different locations, representing: (b) epoxy resin, (c) 54  $\mu\text{m}$  tactoids, and (d) 4  $\mu\text{m}$  particles

### 3.2 Heat release rate

Mass loss curves of all the samples are shown in Figure 5. The mass loss curves of the E0 and E1 samples are quite similar, while that of the E3 sample indicates the smallest residual mass fraction of 59.3%. This mass reduction level of sample E3 could be attributed to various factors, including an insufficient char layer induced by the combustion of nanoclay, clustering of clay nanoparticles on the surface, and combustion of the organic modified agent described in Section 3.3. The 3% nanoclay in sample E3 seems to have some flame retardant effects, but it is not clear due to dominance of other factors such as distribution of nanoclay and combustion of the organic surfactant. On the other hand, sample E5 has a final mass of 64%. The low PHRR, high final mass and low total heat release (THR) (Table 2) confirm the formation of a char layer during burning.

This low conductive char layer helps to isolate the heat from the flame and, therefore, reduces further combustion. Table 2 also shows that THR of both samples E0 and E3 are close to each other at the end of the cone tests. The same heat of combustion calculated for E0 and E3 suggests that the addition of 3% nanoclay in the composite's resin seems to balance the combustion of the organic agent and the nanoclay's flame retardant effect. The fire performance improvement using a 3% nanoclay replacement level is observed; nevertheless,

the network of newly formed char is still insufficient to compensate the combustion of the organic agent. In short, the experiment with sample E3 seems to indicate an “equilibrium” configuration with this level of 3% nanoclay inclusion.



**Figure 5.** Time evolutions of: (a) total heat release, and (b) smoke production rate (SPR) of samples with no nanoclay, 1%, 3%, and 5% nanoclay (E0, E1, E3, and E5, respectively) exposed to 50 kW/m<sup>2</sup> heat flux in the cone calorimeter test

**Table 2.** Comparisons of the total heat release (THR) and heat of combustion for four samples with varying nanoclay fraction

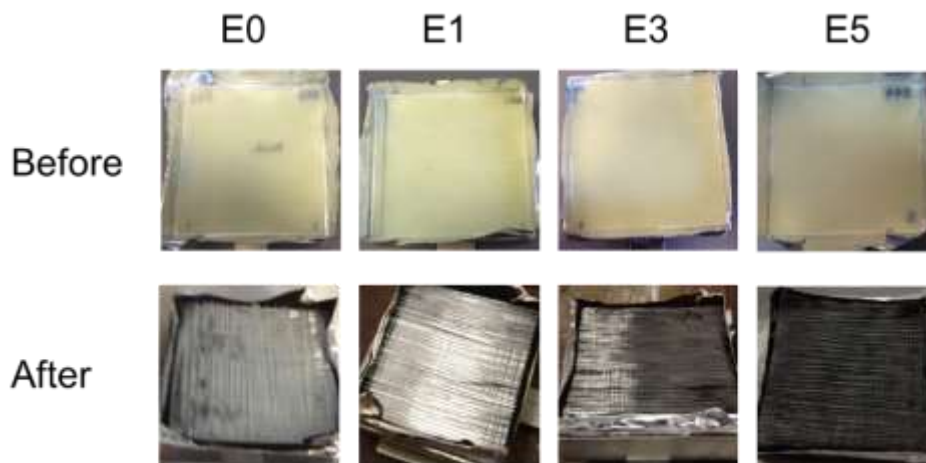
Sample	THR (MJ/m <sup>2</sup> )	Heat of combustion (MJ/kg)
E0	31.20	20.70
E1	35.53	25.12
E3	32.40	20.80
E5	24.33	18.98

### 3.3 Char formation and nanoclay distribution

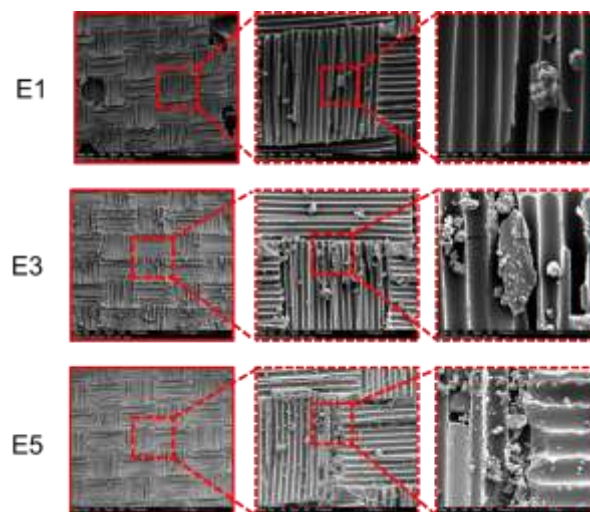
Figure 6 presents images of the control sample (E0) and other samples with nanoclay additives (E1, E3, E5) before and after the cone test at heat flux of 50 kW/m<sup>2</sup>. As clearly seen from this figure, the addition of clay nanoparticles up to 5% wt. does not affect the colour and translucence of the composite samples. Sample E0 and E1 are burnt and the glass fibres are exposed to the heat, with very little char formation observed after the tests. Sample E3 with 3% nanoclay is observed to have approximately half of its surface covered with a thin layer of char, while a thicker layer of char is found to cover the whole surface of sample E5.

This observation is elaborated by SEM images of the samples taken at different magnifications of 200x, 800x and 3000x, as shown in Figure 7. With low percentages of nanoclay (1%), images of sample E1 show a very scattered distribution of clay nanoparticles. Agglomeration also takes place with a diameter of nanoclay less than 25 μm. These two

factors, plus the presence of an organic surfactant, lead to the increase in combustion of the composite sample. As a result, both the heat and smoke released from sample E1 are higher than those obtained from the control sample E0. The higher amount of nanoclay in E3 clearly leads to more formation of char. However, the agglomeration of 3% nanoclay in E3, as visualised in the SEM results, is in considerably large clay aggregates with sizes of up to 50  $\mu\text{m}$ . This clay aggregation deters the effectiveness of nanoclay in improving the flame retardancy of the composite samples. On the other hand, sample E5 achieves good distribution of clay with small particles less than 10  $\mu\text{m}$ . This creates a network of clay nanoparticles on the surface and contributes to the formation of the thick char layer. This newly formed layer plays a key role in lowering the heat release as well smoke production from the laminate. It is important to note that not only increasing the amount of nanoclay but also minimising agglomeration and optimising the clay nanoparticles distribution, is equally important to improve the flame retardancy of epoxy composites.



**Figure 6.** Images of samples before and after the cone calorimeter tests



**Figure 7.** SEM images of E1, E3, and E5 samples at different magnifications: 200x, 800x and 3000x

#### 4. Conclusions

The effect of nanoclay in GFRP was investigated with different replacement levels of organoclay. The composites were fabricated by a vacuum-assisted infusion method. At low levels of nanoclay replacement, the combustion of the organic amine used as a surface modified agent was observed to dominate the effect of the nanoclay. This led to a rise in peak heat release rate (PHRR) at 1% (E1) and 3% (E3) levels. Mass loss curves, THR and heat of combustion of sample E3 pointed to some enhancements with nanoclay inclusion. However, the formed layer of char was not sufficient to overcome the effects of combustion associated with an organic surfactant. Sample E5 had the highest percentage of nanoclay (5%) and had a well distributed clay nanoparticle network, which evidently showed the best improvement in fire performance with the lowest THR, heat of combustion and total smoke production. This 5% level of nanoclay was also found to contribute to the delay of the PHRR compared to the control sample (E0). Further work on higher fractions of nanoclay, as well as a detailed study on char formation with nanoclay presence will be continued in order to understand the mechanisms of nanoclay in improving the flame retardancy of GFRPs.

## Acknowledgments

The authors would like to acknowledge Dr. Jinghan Lu for her assistance in fabricating the specimens; and Joe Abraham and Ariza Sharikin Abu Bakar for performing the cone calorimeter tests. The experimental work is conducted with financial support from ARC Linkage Grant LP110100429.

## References

- [1]Liu, Y., et al., *An efficiently halogen-free flame-retardant long-glass-fiber-reinforced polypropylene system*. Polymer Degradation and Stability, 2011. **96**(3): p. 363-370.
- [2]Poorabdollah, M., et al., *Cure kinetic study of organoclay-unsaturated polyester resin nanocomposites by using advanced isoconversional approach*. Polymer Composites, 2013. **34**(11): p. 1824-1831.
- [3]Ozkaraca, A.C. and C. Kaynak, *Contribution of nanoclays to the performance of traditional flame retardants in ABS*. Polymer Composites, 2012. **33**(3): p. 420-429.
- [4]Nevalainen, K., et al., *Characterization of melt-compounded and masterbatch-diluted polypropylene composites filled with several fillers*. Polymer Composites, 2013. **34**(4): p. 554-569.
- [5]Mohanty, S. and S.K. Nayak, *Effect of clay exfoliation and organic modification on morphological, dynamic mechanical, and thermal behavior of melt-compounded polyamide-6 nanocomposites*. Polymer Composites, 2007. **28**(2): p. 153-162.
- [6]Mohapatra, A.K., S. Mohanty, and S.K. Nayak, *Poly(lactic acid) and layered silicate nanocomposites prepared by melt mixing: Thermomechanical and morphological properties*. Polymer Composites, 2012. **33**(12): p. 2095-2104.
- [7]Pandey, P., et al., *Flammability and thermal characterization of PMMA/clay nanocomposites and thermal kinetics analysis*. Polymer Composites, 2012. **33**(11): p. 2058-2071.
- [8]Liu, W., R.J. Varley, and G.P. Simon, *Understanding the decomposition and fire performance processes in phosphorus and nanomodified high performance epoxy resins and composites*. Polymer, 2007. **48**(8): p. 2345-2354.