



# Quantifying effects of graphene nanoplatelets on slowing down combustion of epoxy composites

Qiangjun Zhang<sup>a</sup>, Yong C. Wang<sup>a,\*</sup>, Colin G. Bailey<sup>b</sup>, Richard K.K. Yuen<sup>c</sup>, Joshua Parkin<sup>a</sup>, Wei Yang<sup>c</sup>, Cristina Valles<sup>a</sup>

<sup>a</sup> University of Manchester, Oxford Rd, Manchester, M13 9PL, United Kingdom

<sup>b</sup> Queen Mary University of London, Mile End Rd, London, E1 4NS, United Kingdom

<sup>c</sup> City University of Hong Kong, 83 Tat Chee Ave, Kowloon Tong, Hong Kong

## ARTICLE INFO

### Keywords:

Graphene nanoplatelets  
Combustion behaviour  
Barrier effect  
Pyrolysis simulation  
Epoxy composites

## ABSTRACT

This paper investigates the effects of graphene nanoplatelets (GNP) on combustion behaviour of epoxy resin (ER). In particular it presents, for the first time, a numerical modelling methodology that quantifies the effects of GNP in reducing the peak rate of heat release of epoxy resin with different amounts and types of GNP.

Five different GNP/ER composites were prepared via the solution mixing method. Geometric characteristics and dispersion state of GNP in epoxy resin were characterized by three-dimensional (3D) X-ray CT scan. Thermogravimetric analysis (TGA) tests were carried out on pure epoxy and GNP/ER composites in N<sub>2</sub>. Bench-scale cone calorimeter tests were used to obtain combustion properties of the prepared nanocomposites. These test results provide input data for validating the modelling methodology.

The cone calorimeter tests found significantly lower peak heat release rate (PHRR) for GNP/ER composites than pure epoxy. For example, at 3 wt% GNP loading, the PHRR was reduced by 47%. This drastic reduction in PHRR due to GNP is attributed to two principal contributions of GNP: reduced permeability to slow down movement of volatiles to the surface to cause combustion, and reduced radiant conductivity of GNP/ER at high temperatures owing to GNP being able to promote the formation of a continuous and compact char layer, which decreases temperatures and hence slows down chemical reactions. This paper provides a new method, through numerical pyrolysis modelling, to quantify these two contributions and their effects in reducing PHRR of GNP/ER. A comparison between numerical simulation results and test results confirms assumptions of this quantitative method. This simulation model has the potential to improve material design process of graphene based composites and predict the fire behaviour of such composites in realistic fire conditions.

## 1. Introduction

With the growing demand for lighter, stronger and safer aircrafts, there has been considerable academic and industrial interest in graphene-based polymer composites. Since the discovery of graphene, a great number of researchers have been working on developing composite materials with graphene, hoping to transfer the superb properties of graphene from micro-scale nanosheets to macro-scale bulk composites. So far numerous studies have reported huge potential of graphene as reinforcement filler for polymers to achieve multiple performance improvements, including increased thermal and electrical conductivity and mechanical properties [1–4].

Fire hazard in aircrafts is a critical safety concern due to high flammability of polymer resins. An accidental electrical failure could start a fire, leading to potentially disastrous consequence for aircrafts.

This concern has led many researchers to investigate combustion behaviour of epoxy composites with graphene and its derivatives. For example, Liu et al. [5] reported a 56.9% reduction in the peak heat release rate (PHRR) of epoxy composites with a loading of 5% by weight (1 wt%) of graphene nanosheets (GNS) in cone calorimeter testing. Jiang et al. [6], Wang et al. [7] and Wang et al. [8] arrived at similar findings for GNS/ER composites. Graphene oxide and reduced graphene oxide has also been shown to reduce PHRR of epoxy with a low loading of 1 wt% [9,10].

This suppression effect on PHRR by graphene was qualitatively explained by the so-called barrier effect in literature. Some researchers speculate that graphene flakes act as blocking walls to hinder the escape of gas volatiles during pyrolysis thereby slowing down combustion and hence lowering PHRR [8]. This explanation is qualitatively justifiable as graphene is reported to be impermeable even to helium and has been

\* Corresponding author.

E-mail address: [yong.wang@manchester.ac.uk](mailto:yong.wang@manchester.ac.uk) (Y.C. Wang).

**Nomenclature**

E	Activate Energy (kJ/mol)
A	Pre-exponential factor ( $s^{-1}$ )
n	Reaction order
PHRR	Peak heat release rate ( $kW/m^2$ )
EHC	Effective heat of combustion (MJ/kg)
PMLR	Peak mass loss rate ( $g/m^2 s$ )
K	Thermal conductivity (W/m K)
C	Specific heat capacity (J/kg K)
D	Characteristic dimension of pores (m)
$\Delta H$	Heat of volatilization (J/kg)
$k_a$	Absorption Coefficient ( $m^{-1}$ )

$\varepsilon$	Emissivity
$\alpha$	Aspect ratio
$\phi$	Volume Fraction of GNP in epoxy resin
$\tau$	Tortuosity factor
$\sigma$	Reduced pore diameter factor
q	Mass flux per unit area (m/s)
$\Delta P$	Pressure gradient (Pa/m)
k	Intrinsic permeability of the medium ( $m^2$ )
$\mu$	Gas viscosity (Pa·s)
$\gamma$	Radiant conductivity
$\Psi$	Porosity
$\alpha_r$	Conversion rate of thermal decomposition

reported to possess efficient gas barrier properties in different polymers [11]. Other researchers claim that the improved char structure after adding GNP will also contribute to better combustion performance of composites, particularly a lower PHRR [12].

Whilst it is intuitively correct to attribute reduced PHRR to barrier effects and improved char structure due to GNP, there has been no research to quantitatively demonstrate and explain the observed results. Without a quantitative model it would not be possible to design graphene based composites, nor be able to predict the behaviour of such composites in fire conditions. Providing a quantitative model that is able to calculate the reduced PHRR of graphene based composites is the main focus of this research.

Because different researchers have used different materials, it is difficult to use their data in a quantitative way for development of a prediction model due to a lack of some details. Therefore, in this study, the authors have carried out independent, and additional, tests for epoxy composites filled with different loadings and types of GNP, including X-ray CT scan, TGA, cone calorimeter and SEM of char.

In conventional combustion modelling related to fire safety, the pyrolysis gases are assumed to move instantly to the surface from inside the solid in order to reduce computation time. This assumption is acceptable for materials with high permeability. However, if material permeability is low, the time it takes for gas volatiles to move to the surface will have an important effect on peak combustion and it is important that this effect is considered in combustion modelling, as it is in the present paper.

This paper uses Gpyro [13] to simulate cone calorimeter tests. Gas movement inside the solid phase is simulated by Darcy's law and is controlled by gas permeability of GNP/ER composite and its char after combustion. Therefore, such a quantitative model to predict combustion behaviour of graphene modified composites requires data on the internal structure of the composite, which provides input to calculating gas permeability of the composite. Different GNP types with different geometric information will be added into epoxy resin to make different GNP/ER composites for comparison. Furthermore, radiant conductivity of the char will need to be taken into consideration for different char structures of GNP/ER.

The results of numerical pyrolysis modelling presented in this paper demonstrate validity of this model in quantifying the effects of GNP in reducing PHRR of epoxy, due to reduced permeability (barrier effect) and lower radiant conductivity (improved char structure). The numerical modelling approach provides the foundation to developing a comprehensive understanding of the fire performance of graphene-based epoxy nanocomposites which will be a powerful tool for future design of graphene modified composites for fire safety.

**2. Experimental methods****2.1. GNP/ER composite samples**

Three types of GNP (M5, M15, M25) were provided by XG Sciences in the U.S.A. Table 1 lists the geometric information of GNP. The epoxy and hardener were Araldite LY5052 and Aradur 5052 respectively. GNP was first sonicated in acetone for 2.5 h at a ratio of 1 mg per 1 ml. Epoxy was then added and sonicated for a further 2.5 h. After removing acetone and leaving only epoxy and GNP mixture, hardener was added to the mixture at a ratio of 100:47 (epoxy: hardener in volume). The mixture was then cast in moulds with dimensions of 100 mm  $\times$  100 mm with a thickness of 4 mm. Samples were left to cure for 24 h at ambient temperature followed by a further heated curing at 100 °C for 4 h.

Five different composites were made, as listed in Table 2. Composites #1, #2 and #5 have the same GNP (M15) type and investigate the effects of different GNP loading by weight (0.1 wt%, 1 wt% and 3 wt%). Composites #2, #3 and #4 investigate the effects of using different types of GNP (M5, M15 and M25) while maintaining the same loading by weight (1 wt%). Three samples of each composite were tested. Sample #0 is the reference case with pure epoxy without any GNP.

**2.2. Tests**

In total, four different types of tests were carried out: 3D X-ray CT scan, Thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and cone calorimeter. 3D X-ray CT scans provide information of internal structures of the GNP/ER composites which can be used to assess the dispersion state of GNP/ER composites. The TGA results provide input data on mass loss rates and the cone calorimeter test results are used for validation of the pyrolysis modelling. The SEM test images provide qualitative information of char structures to aid assumptions of gas permeability and radiant conductivity of char.

**2.2.1. 3D X-ray CT scan test**

The ZEISS Xradia 810 Ultra XCT was used to observe the dispersion state and morphology of GNP inside epoxy resin. The field of view was 65 microns and the resolution was 50 nm.

**2.2.2. Thermogravimetric analysis (TGA) test**

Thermogravimetric analysis (TGA) was performed on a Netzsch TG

**Table 1**  
Geometrical Characteristics of selected GNP materials.

	Average Lateral Size ( $\mu m$ )	Average Thickness (nm)	Density ( $g/cm^3$ )	Bulk Density ( $g/cc$ )
M5	5	6–8	2.5	0.03–0.1
M15	15	6–8	2.5	0.03–0.1
M25	25	6–8	2.5	0.03–0.1

Download English Version:

<https://daneshyari.com/en/article/7211973>

Download Persian Version:

<https://daneshyari.com/article/7211973>

[Daneshyari.com](https://daneshyari.com)