

# EXAMINING THE INFLUENCE OF GRAPHENE SPECIES ON TOUGHENING MECHANISMS IN INDUSTRIALLY RELEVANT EPOXY RESINS

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## ABSTRACT

In this study, a proprietary epoxy system from Solvay Advanced Materials UK (Cycom EPXX) is modified using graphene oxide (GO) in order to improve its mechanical properties. Thermal and spectral analyses are used to characterize the uncured resin blend, while blending conditions are optimized to achieve both dispersion and desirable morphology following cure. The analyses demonstrate that the incorporation of a modest quantity of GO may lead to enhancements of thermal and mechanical characteristics as evidenced by fracture toughness data.

## 1 INTRODUCTION

Epoxy resins are used widely in commercial engineering solutions as resins in composite materials due to their ease of manufacture and wide availability, but they are inherently brittle and require modification to enable their use in engineering applications. The toughening of brittle thermoset matrices for composite materials has traditionally utilized thermoplastic particles to effect increases in fracture toughness [1]. Whilst this approach does yield the desired increases in fracture toughness, the incorporation of thermoplastic particles also reduces the stiffness of the cured resin. Recently the use of nanomaterials, such as carbon nanotubes or graphene, has demonstrated increased fracture toughness with unaffected or increased stiffness of the resin matrix. However, to-date the literature on the toughening of thermosets with graphene particles has tended to focus on improving base resins that contain no other toughening agents, see for example [2-4]. These reports, whilst giving scientific understanding, lack direct relevance to technological application, for although undoubted increases in toughness are obtained, they do not significantly increase the toughness beyond existing proprietary systems. For instance, Park *et al.* [5] found that addition of 0.04 wt% graphene gave a 150% increase in the fracture toughness of a cured simple epoxy, when tested in compact tension. Bortz *et al.* [4] found similar improvements in fracture toughness (28 - 63% increases for  $K_{Ic}$  and 29 - 111% for  $G_{Ic}$ ) and glass transition temperature when incorporating 0.1 - 1 wt% graphene oxide (GO) in epoxies; with the greatest gains observed with lower loadings. Rafiee *et al.* [6] observed similar improvements with GO and found that an addition of 0.125 wt% of GO increased the fracture energy of the samples dramatically (115%), although beyond 0.15 wt% the value falls (and by 0.5 wt% there is no improvement over the original epoxy value). The improvement in fracture toughness have been attributed to the GO prohibiting crack propagation by generating a large amount of plastic deformation [7]. Crack deflection is also a large contributor as it generates an increase in the total fracture surface area, resulting in greater energy absorption [8]. When a crack is deflected, there becomes a height difference between the original crack front and the deflected crack front, which causes the cracks to pursue a more torturous path [9]. Conversely, the decrease in fracture toughness at higher graphene loadings has been attributed to the aggregation of graphene, thus the microcracks within and surrounding the graphene coalesce and allow cracks to propagate more easily [5]. In contrast with

other studies, the present study explores the feasibility of investigating the mechanism through which GO improves the fracture toughness in a complex, highly formulated toughened epoxy resin system (Cycom EPXX).

## 2 EXPERIMENTAL

### 2.1 Formulation

The graphene oxide used in this work was prepared at the University of Manchester using previously published methods [10]. Cycom EPXX is a Solvay proprietary toughened epoxy system. Its components were supplied individually and used without further purification. The formulation was manufactured in house (ACCIS, University of Bristol) using a Solvay procedure. This sample is hereinafter referred to as EPXX. A suspension of graphene oxide (GO, 0.5 wt%) in acetone (15 cm<sup>3</sup>) was prepared and sonicated in a water bath (*ca.* 25 °C, 2 hours). All the resin system components were then added to this solution. The complete blend (EPXX-GO) was then poured into a mould and degassed under vacuum for a maximum of 3 hours at 120°C until any bubbles had disappeared from the resin. The mould was then placed into a temperature controlled oven and cured at 180°C for 2 hours (2 K/min ramp rate from RT to 180°C).

### 2.2 Thermal analysis

Differential scanning calorimetry (DSC) was undertaken using a TA Instruments Q200 running TA Universal V4.7A software on samples (12.0 ± 0.005 mg) in hermetically sealed aluminium pans. Experiments were conducted on the blends at a heating rate of 5 K/min. from 25 °C to 300 °C (heat/cool/heat) under flowing nitrogen (50 cm<sup>3</sup>/min.). Dynamic mechanical thermal analysis (DMTA) (in single cantilever mode at a frequency of 1 Hz) was carried out on cured neat resin samples (*ca.* 15 x 55 x 2.5 mm<sup>3</sup>) using a TA Q800 in static air from 20 °C to 400 °C at 3 Kmin<sup>-1</sup> at 0.1 % strain.

### 2.3 Mechanical testing

To create the test samples, a steel mould was used that was composed of two parts held together by bolts and has the inner dimensions of 138 x 63 x 29.5 mm<sup>3</sup>. The density of the cured EPXX was determined by repeated measurement on multiple samples to be 1.3561 g cm<sup>-3</sup>. Using this value, the mass of resin required to fill the mould to the required thickness was calculated. The chosen test method followed the ASTM D4045 standard for a single edge notched beam (SENB) test [11]. Therefore, once cured, the resin blocks were cut into samples (63 – 68.5 mm long, 11-14.4 mm wide, *ca.* 5.5 – 7.3 mm thick), using a diamond-tipped saw and sanded to yield regular rectangular samples, which conformed to the ratio of dimensions required by the standard. The initial notch was cut using a diamond tipped saw and widened using a hacksaw. To initiate a crack in the SENB specimen, a new razor blade was tapped into the material with a small hammer. Each sample was loaded into the test machine (Figure 1). Mechanical testing was conducted using an Instron 3343 Universal testing machine with a 1 kN load cell and a displacement rate of 10 mm/min.

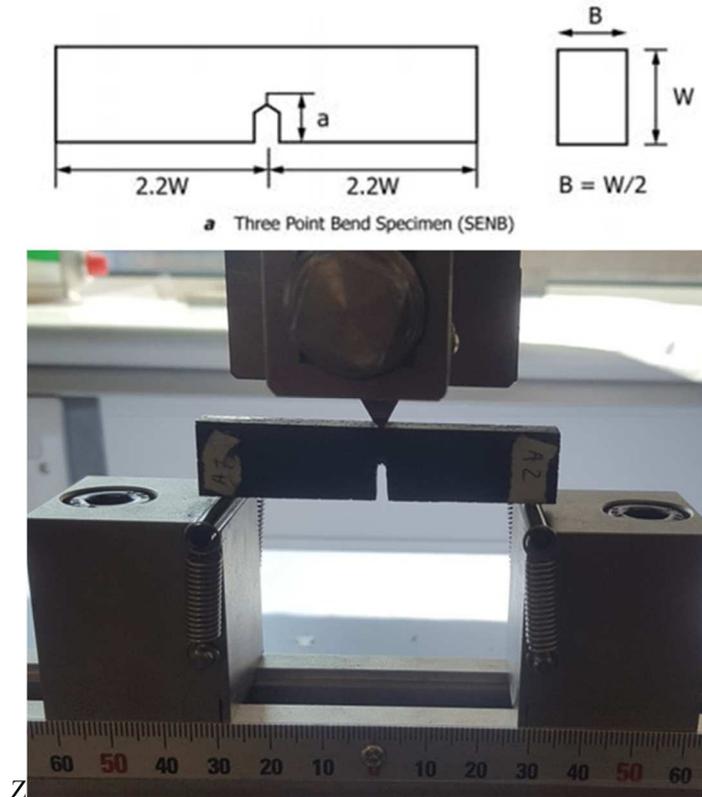


Figure 1: Test configuration of single etch notch beam (SENB) (top) and sample under test (bottom)

Once the testing was completed, the crack depth was measured on both parts of each failed specimen in 3 locations. This was in order to get an average value of the crack depth within each specimen for the fracture toughness calculation, the equation for which is shown below.

$$K_{Ic} = \frac{P_q}{BW^{0.5}} f(x) \quad (1)$$

where  $B$  is the thickness,  $W$  is the width,  $f(x)$  is a function of  $a/W$  and  $P_q$  is the load, details of how to find  $P_q$  are found in the D4045-14 standard [11]. When measuring the crack length and calculating  $a/W$  some of the specimens were outside the range of 0.45 to 0.55 and so these samples were discounted. It ruled out nine of the unmodified samples and two of the GO-modified samples, which left the final results being from seven unmodified samples and eleven GO samples.

#### 2.4 Scanning electron microscopy

To ascertain the effect on morphology of adding graphene oxide to the formulated epoxy resin the cured resin samples were analysed using SEM (Figure 2). This initially involved etching the samples using a superacid mixture that dissolved the thermoplastic component. Following this procedure, the samples were analysed using a Hitachi TM3030 SEM operating at an accelerating voltage of 15 kV. Fractured surfaces from the tested samples were also analysed using the same instrument.

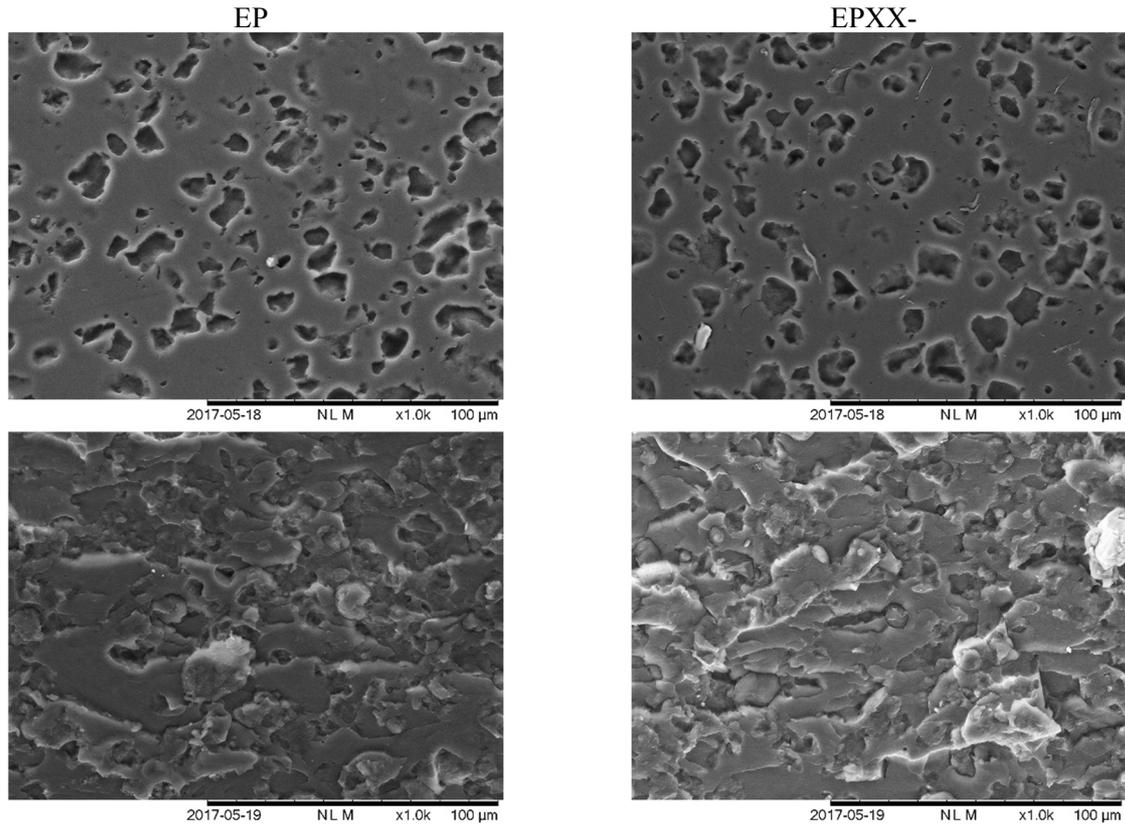


Figure 2: SEM analysis of the morphology (top) and fracture surfaces (bottom) of the formulated CYCOM EPXX epoxy resins.

The EPXX system already develops a secondary phase during cure (from the incorporation of the thermoplastic toughening agent), but although the loading of GO is modest (0.5 wt%), additional features are visible on the 977-GO images (Figure 2, bottom right) arising from the incorporation of the nanofiller.

### 3 RESULTS AND DISCUSSION

#### 3.1 Thermal analysis

Differential scanning calorimetry (DSC) was used to investigate the curing characteristics of the resin blends. Initial DSC analysis shown below in (Figure 3) indicate that the cure characteristics of both blends are very similar with polymerization occurring within a similar temperature regime, similar enthalpy yields and glass transition temperatures (Table 1).

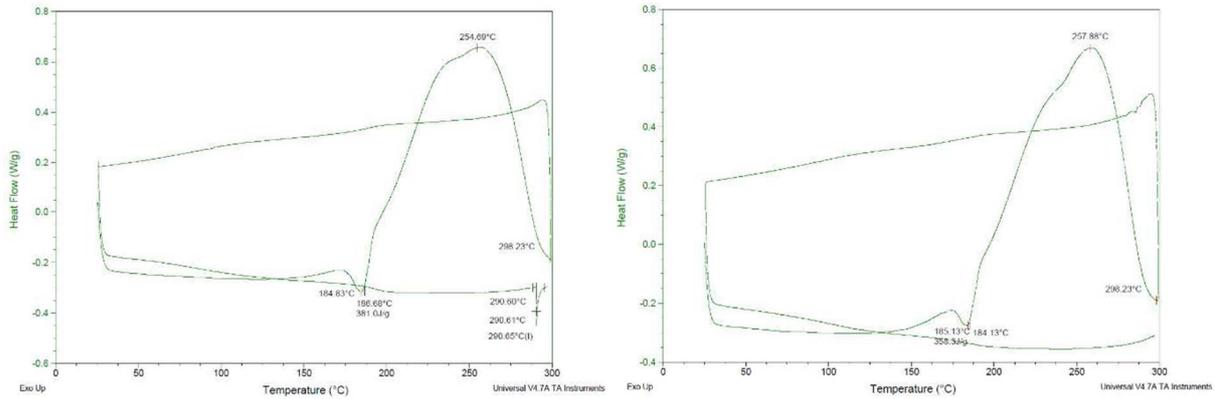


Figure 3: DSC results of Cycom EPXX (left) and Cycom EPXX with 0.5 wt% GO (right) for uncured resin samples

It is apparent that the presence of the GO leads to a change in the profile of the reaction exotherm, suggesting the acceleration of the epoxy ring opening reaction.

Table 1: DSC data for uncured 977 in the absence and presence of GO (nitrogen, 10 Kmin-1).

Material	$T_{g0}$ (°C)	$T_{max}$ (°C)	Polymerisation enthalpy ( $\Delta H_p$ , J/g)	Glass transition temperature ( $T_g$ )
EPXX	187	255	381	180-200
EPXX-GO	185	258	358	165-180

Key:  $T_o$  = onset of polymerization exotherm,  $T_{max}$  = peak maximum of polymerization enthalpy,  $\Delta H_p$  = Enthalpy of polymerization.

### 3.2 Blending for neat resin samples

After creating the first test sample (Figure 4, A), the blend was far from perfect: the upper surface of the sample, still contained bubbles which had not been removed during the degassing step. When the sample was sectioned, a range of differently sized air pockets were revealed within the bulk of the sample (Figure 4), along with very small particles which had not been mixed in properly during the blending. It was initially thought that the reason for the high porosity of the sample was due to rapid stirrer, trapping too much air within the mixture. The blend is very viscous even at high temperatures and so it is easy for small air bubbles to form within the sample when it is being blended at high speeds. To counter this, the next sample was mixed at a slightly slower speed (50-60 RPM), especially during the addition of powdered reagents. Additionally, the charge was reduced by half (two moulds of 10 g) to allow the resin more space to expand within the mould. The blending and degassing conditions were progressively changed with improvements observed in the quality of the sample; the best (Figure 4, E) reflects an increase the degassing time (180 minutes) and an increase in the mixing time of the thermoplastic toughening agent.



Figure 4: Cured Cycom EPXX blend showing the influence of degassing conditions on porosity: A = 90 mins @120°C, B = 120 mins @90°C, C = 150 mins @90°C, D = 150 mins @120°C, E = 180 mins@120°C.

### 3.3 Blending for neat resin nanocomposites samples

In a modified procedure, the GO was sonicated for up to 150 minutes in an ultrasound bath in order to maximise the dispersion in the resin. In common with the unmodified EPXX blend, the first sample was very porous and contained a particulate residue (Figure 5, A), which was again assumed to be the toughening agent.

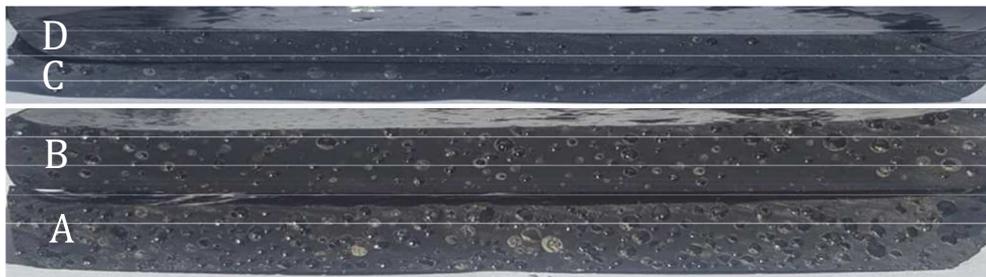


Figure 5: Cured Cycom EPXX/GO blend showing the influence of sample thickness on porosity (note samples A and B prepared using a 55 mm dia. mould; C and D prepared using a 70 mm dia. mould).

Fewer air pockets were observed on the top surface, but when sectioned there were still a considerable number of voids present within the sample. By changing the rate of application of vacuum and increasing the diameter and depth of the mould allowed the resin blend more space to expand during degassing. This process is still being optimised (and so these GO blends offer preliminary data), but nevertheless the upper samples (Figure 5, C and D) show considerable improvements over the initial samples (Figure 5, A and B).

### 3.1 Dynamic mechanical analysis

Dynamic mechanical thermal analysis (DMTA) was performed on cured neat resin samples (Figure 6) as rectangular plaques.



Figure 6: Cured samples of Cycom EPXX resin (top) and Cycom EPXX with GO (bottom)

Initial DMA results show a slightly high flexural modulus at lower temperatures (the storage moduli of both blends are very similar, with the loss modulus maximum increasing by 2 °C (Table 2), reflecting an increase in the  $T_g$ ) a broader tan delta response for the nanocomposite blend (Figure 7), suggesting a range of molecular structures and associated greater damping characteristics.

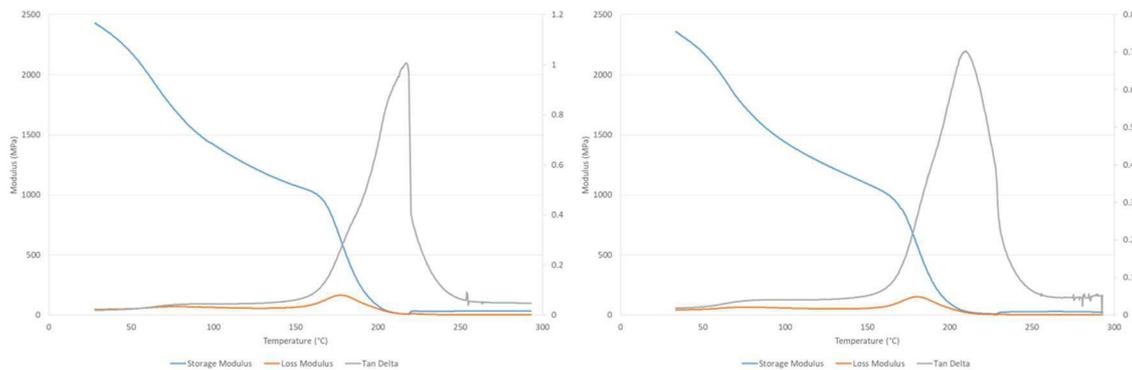


Figure 7: DMA results of Cycom EPXX (left) and Cycom EPXX with 0.5 wt% GO (right) for cured resin samples

Dynamic mechanical thermal analysis (DMTA) was used to investigate the thermomechanical properties of the cured blends.

Table 2: Storage moduli (DMTA) for cured samples of EPXX and EPXX-graphene oxide blend.

Sample	Storage modulus [°C]		Loss modulus, $T_{max}$ [°C]	Tan delta	
	2000 MPa	1000 MPa		maximum	$T_{max}$ [°C]
EPXX	65	170	178	1.00	217
EPXX-GO	65	174	181	0.72	210

### 3.1 Mechanical testing

The samples were both tested following the ASTM D4045 standard for a single edge notched beam (SENB) test and the force/displacement data are displayed for EPXX (Figure 8) and EPXX-GO (Figure 9) respectively. It is notable that the gradients are similar for each set of samples, but there is some scatter in the data. The fracture toughness of the two sets of samples was calculated from the force/displacement data (Table 3) with a modest increase in the mean KIC value

for the GO-modified blend. However, these are preliminary measurements made on a relatively small set of samples. Work is currently underway in the Bristol Composites Institute to increase the size of the dataset for mechanical tests.

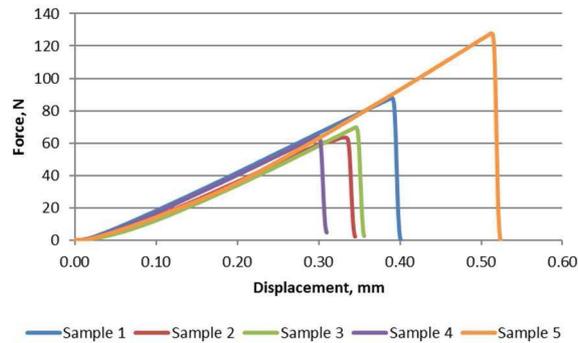


Figure 8: Force-Displacement Curves for the Unmodified Specimens

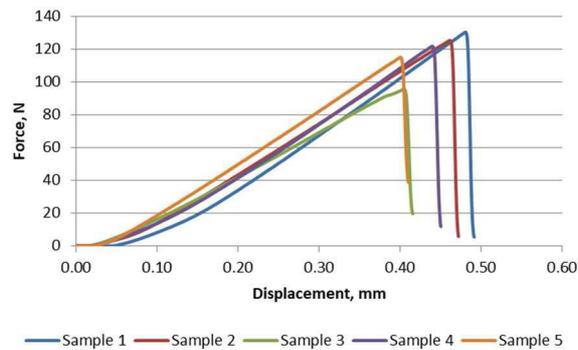


Figure 9: The Force-Displacement Curves for the separate GO blocks

Table 3: Fracture toughness data for cured samples of EPXX and EPXX-graphene oxide blend.

Sample	Mean $K_{IC}$	Standard deviation
EPXX	40.69	7.47
EPXX-GO	41.15	3.54

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## 9 CONCLUSIONS

This preliminary study has shown that the incorporation of GO has been possible within a very complex epoxy formulation and still show tangible benefits through improved physical and mechanical characteristics. Owing to the complexity of the blend and the formulation schedule, the method has not yet been fully optimised to accept GO and form a void free sample. However, work continues to improve the quality of the samples and to increase the number of samples tested for their mechanical properties. These data will be reported in a full paper in due course.