# The Low Velocity Impact Response of Nano Modified Composites Manufactured Using Automated Dry Fibre Placement

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## SUMMARY

The low velocity impact response of composite materials manufactured from dry fibre tows using the automated fibre placement technique has been investigated. Following fibre placement, the dry preforms were infused with an epoxy resin. The influence of incorporating graphene oxide (GO) nanoparticles into the matrix was investigated, and the impact response of these samples was compared to that of its plain resin counterpart. Flexural and low velocity impact tests were undertaken in this study to understand the influence of GO nano-filler loading on mechanical behaviour of the unreinforced epoxy resin. The introduction of GO into the resin showed nearly 50% increase in ductility compared with that of the neat polymer at a mere 0.1 wt% filler loading. However, GO had a negligible effect on the impact response of these novel composites. There was no observable difference between the load-displacement traces or the resulting damage in the plain and unmodified composites. It is possible that the polymer's ability to undergo larger non-linear deformation at lower rates of strain is suppressed when it is subjected to impact rates of loading.

**Keywords:** AFP, LCM, Impact, Graphene oxide

## 1. INTRODUCTION

Producing large complex composite parts for use in the marine and aerospace industries has been a challenge for many years. Liquid composite moulding (LCM) includes a number of manufacturing techniques, all of which require a vital, yet time-consuming, preforming step. Traditionally preforming was achieved by fabric draping, fabric stitching or weaving 3D profiles. These procedures are labour-intensive, expensive and rely heavily on textile processing capabilities. The automated fibre placement (AFP) technique, using dry fibres, offers potential for overcoming many preforming problems. The technique involves depositing fibres onto a complex mould at a high rate, overcoming any fabric structure variability and variations in local fibre volume fractions, while draping in tight corners. The dry fibre AFP process offers cost advantages over other preforming methods, while maintaining the advantage of keeping the finished preform at room temperature with unlimited shelf life. The lay-up operation in the dry fibre AFP approach is similar to that of the automated tape laying (ATL) approach, where the tows are either delivered to the head from a creel cabinet, or stored directly on the head[1,2]. Recently, a range of dry fibre tows, based on either a thermosetting or thermoplastic binding material, has been developed, examples being the dry unidirectional carbon fibre tapes from Hexcel, HiTape® and Cytec's UD-dry tape (TX1100™), both having a width of 6.35 mm.

The dry fibre placement process requires the use of a thermoplastic binding agent and a permeable veil between the fibres; the quantity used should be enough to tack to the mould and subsequent layers when heated, whilst retaining the preform shape prior to resin injection. However, the binder in the dry tows may obstruct the in-plane and through-thickness flow of liquid resin.

Preform permeability is an important parameter, since it determines the processability of the preform during the injection process. Rudd *et al.*[4] developed models to predict the permeability and elastic modulus of laminates produced by dry tow placement using a tackifier. The permeability models were also developed to consider fibre waviness and were validated experimentally for sinusoidal fibre paths. Through-thickness compression also plays an important role, given that the

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first ply will be compressed several times, while the last ply will be compressed only once. The resulting preform may be non-homogeneous in the through-thickness direction, given that fibrous preforms exhibit viscoelastic behaviour[5,6]. Preform compaction data are vital, since they should inform the placement software in order to achieve improved tow adjustment and compaction pressures, conditions that are required to achieve an optimum fibre volume fraction and part thickness. In order to allow high-speed production at high temperatures, a powerful heating source, such as a laser, has to be incorporated to activate the thermoplastic binder. Furthermore, the response time of the heating device needs to be as rapid as possible, to avoid any ply spring back[7]. Clearly, a detailed study is required to adjust the tow gap to achieve a superior flow behaviour and mechanical properties[8]. Belhaj *et al.*[9] studied three different preform configurations, by adjusting the tow gap, to study the permeability and compaction behaviour of preforms. They concluded that different configurations affected the resulting mechanical properties and that the creation of open channels to enhance the flow propagation during manufacture, did not increase the preform permeability to any significant degree.

To date, it is unknown to the authors whether research has been conducted to understand the processability of graphene in advanced composite manufacturing processes, such as the AFP technique. However, some literature is available on the application of carbon nanofibres (CNFs) and CNTs as fillers in polymer matrices using resin infusion processes[10-12]. There are several methods available to introduce nanoparticles into composite materials, but a relatively easy method is dispersing nanoparticles in the resin[13,14]. Though the process of particle dispersion is relatively simple, the loading of high surface area and aspect ratio nanoparticles causes an increase in the viscosity of the resin which makes it difficult to process further. Moreover, the increase in viscosity will affect the overall properties of the resulting composite laminates due to different fibre wetting mechanisms, and the first obvious manifestations are changes in some important mechanical properties. The following study investigates the low velocity impact response of carbon fibre laminates based on dry fibre preforms, manufactured using the AFP process. Attention, in particular, concentrates on the effect of introducing nanoparticles into the matrix material on the resulting impact resistance of the composite part.

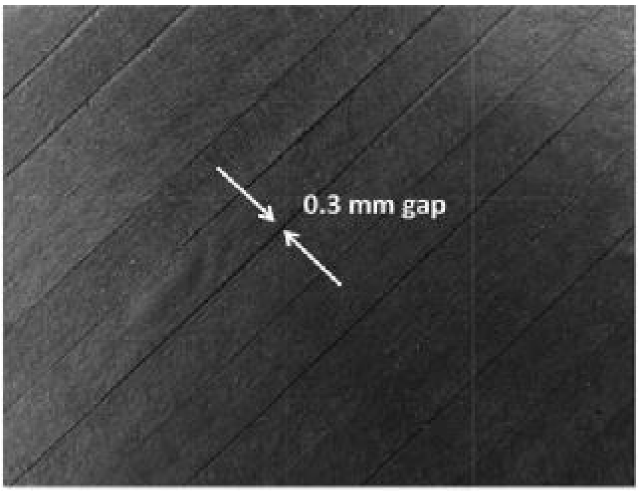
## 2. EXPERIMENTAL PROCEDURE

The dry fibre tows used in this study were supplied by Cytec Ltd. (Wrexham). Preforms, based on the dry fibre tows, were manufactured using the automated fibre placement (AFP) manufacturing technique. Here, a Coriolis AFP machine with KUKA robot and a 6 kW laser mounted on the end-effector, was used to place the fibres on a flat mould. The heat generated by the laser was sufficient to activate a thermoplastic binder that ensured bonding of adjacent tows. The panels were manufactured after adjusting optimum tow gap to facilitate resin flow. **Figure 1** shows a close-up of the manufactured preform with selected optimum tow gap of 0.3 mm.

Following the preforming step, the dry fibre preforms were infused with an epoxy resin, using the resin infusion manufacturing technique. A highly permeable flow medium, Gurit Knitflow40®, was used to facilitate the flow of resin through the thickness of the fibre bed, Prime™ 20LV two-part toughened epoxy was used with a fast hardener to infuse the fibre preform. One panel was infused using plain epoxy resin (henceforth referred to as plain samples) and a second was infused using a graphene oxide (GO) modified epoxy which had 0.1% by weight of GO nanoparticles mixed with epoxy using ultrasonication and mechanical stirring (henceforth referred to as modified samples).

Rheological tests of epoxy resin were performed using a TA Instruments Discovery Hybrid Rheometer with a Peltier plate fixture that used 25 mm disposable parallel plates. Batches of about 50 g epoxy resin, with GO contents of 0 and 0.1 wt.% and the appropriate amount of hardener were

**Figure 1. Close-up of the dry fibre preform after adjustment of optimum tow gap for resin flow**



mixed. Samples of approximately 2 ml mixed resin samples were pipetted onto the rheometer bottom plate. Rheological tests were performed with 0.5 mm plate gap at a constant shear rate 2.5 $s^{-1}$. Temperature sweep tests were completed for the prediction of temperature-dependent viscosity evolution, which were performed on both samples from 23 to 95 °C.

A glass mould, with line injection and a line vent, was used to manufacture both the panels. The mechanical properties of the plain resin and the modified resin were investigated under three point bending scheme. Specimens of 4 mm thickness were cast in a steel mould as per manufacturer's recommendations. Two weight fractions, 0.1 and 0.2 of graphene oxide were investigated. Samples with length and width dimensions of 80 mm and 13 mm, respectively were then removed from the plates and tested in three-point bending as per standard ASTM 7264. The support span of 64 mm was chosen and loaded centrally at a crosshead displacement rate of 1 mm/minute.

An initial series of perforation tests were undertaken at quasi-static rates of strain (crosshead displacement rate = 1 mm/minute) on an Instron 1484 universal test machine. Here, samples were supported on a steel ring with a 50 mm diameter internal opening. The tests were continued until the 10 mm diameter hemispherical steel indenter had fully perforated the test sample. Low velocity impact tests were undertaken using a falling-weight impact tower. Here, test samples were supported on the steel ring with a 50 mm diameter internal opening and impacted by a falling carriage with a 10 mm steel hemispherical head. The mass of the impactor was 1.38 kg and the impact energy was varied between 1.36 and 10.9 Joules by increasing the release height from 0.1 to 0.8 metres. After impact, the carriage was caught manually in order to avoid unwanted secondary impacts. The impact load was recorded using a piezoelectric load-cell located immediately above the hemispherical indenter and the associated displacement of the target was monitored using a high speed video camera positioned close to the impact rig. After testing, the front and rear surfaces of the samples were photographed and a number of samples were sectioned in order to elucidate the failure mechanisms occurring during impact loading.

## 3. RESULTS AND DISCUSSION

### 3.1 Mechanical Properties of the Matrix Material

The influence of adding graphene oxide particles to the epoxy resin was investigated through a series of flexural tests on unreinforced polymer samples. **Figure 2** shows typical stress-strain traces following the quasi-static flexural tests. An examination of the figure indicates that the incorporation of nanoparticles serves to increase the ductility of the polymer, with the strain to failure increasing by approximately 50% as the concentration of nanoparticles increased to 0.1%wt. Further increases in the weight fraction of nanoparticles does not result in a significant increase in failure strain. Similar increases in the properties of epoxy resins were observed elsewhere following the incorporation of 0.1%wt GO nanoparticles[15-17]. This evidence suggests that the nanoparticles trigger local plasticity, reducing the effect of stress concentrations, such as surface flaws or scratches. From **Figure 2**, it is also evident that the incorporation of nanoparticles results in a reduction in the flexural modulus of the polymer. Given the fact that the viscosity of the resin increased dramatically in passing from 0.1% to 0.2% by weight of modifier, all subsequent testing focused on laminates containing 0.1%wt. of graphene oxide.

Following the tests on the unreinforced resins, laminates were manufactured by infusing the dry fibre preforms with either the plain resin or the modified resin. The resin infusion was carried out using the SCRIMP (Seemann Composites Resin Infusion Moulding Process) variant where a highly permeable distribution medium was placed over the preform. This was done in order to overcome the very low in-plane permeability of the preform. From **Figure 3**, the modified resin is more viscous at room (processing) temperature than the unmodified resin; hence the mould filling time for the modified resin system was longer.

**Figure 2. Typical stress-strain curves following flexural tests on the plain resin and the graphene oxide-modified resin**

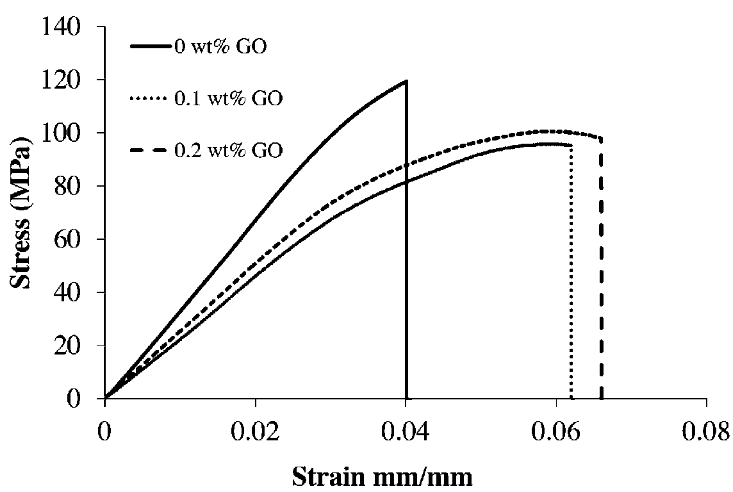


**Figure 3. Viscosity vs. temperature sweep for the modified and unmodified epoxy resins**

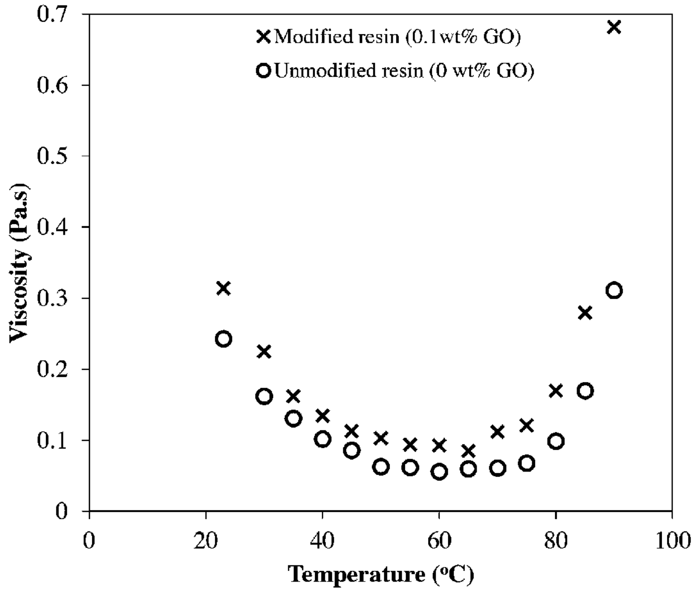



**Figure 4. Cross-sections of the plain composite following resin infusion**

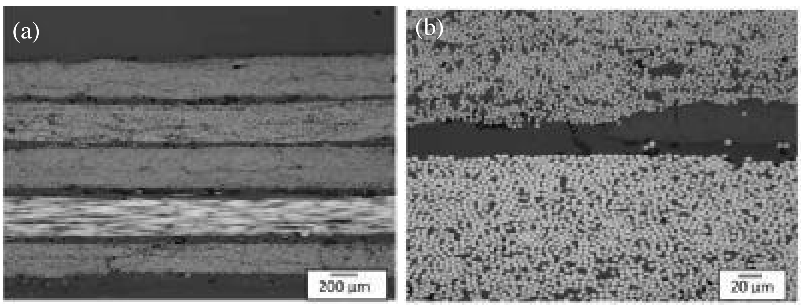
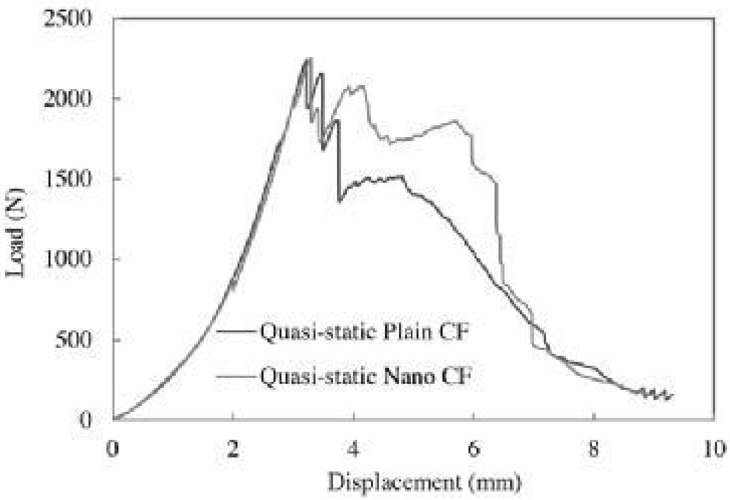



**Figure 5. Load-displacement traces following quasi-static perforation tests on the modified and plain CFRP samples**




Following manufacture, the panels were sectioned and polished prior to subsequent testing. **Figure 4** shows the cross-section of a plain panel. An examination of the micrographs highlights the presence of distinct resin-rich zones between the individual plies. These regions are associated with the presence of the thermoplastic binder and veil in the dry preform, the latter being introduced to tack fibre tows during automated layup. An inspection of **Figure 4a** suggests the presence of a number of voids between individual plies, defects that can be eliminated following further optimization of the manufacturing cycle. Closer examination of the laminate, **Figure 4b**, suggests that the resin had fully impregnated the individual plies. Similar trends were noted for the modified panel.

## 3.2 Quasi-static Perforation Tests

Initial tests were undertaken in order to both characterize the quasi-static perforation resistance of the laminates and to establish the range of incident energies required for impact testing. **Figure 5** shows typical load-displacement traces following quasi-static perforation tests on the plain and modified CFRP panels. An examination of the figure indicates that both traces exhibit similar trends with the force increasing to a maximum value before dropping in a series of short steps. It is interesting to note that the maximum force is similar for both the plain and modified laminates, in spite of the fact that the latter is based on a modified resin system. The measured force during the perforation phase of the impact event is slightly higher in the case of the modified resin, resulting in a slightly higher perforation energy (9.2 Joules for the modified system compared to 8.3 Joules for the plain laminate). Given that the differences between the two types of laminate occurs during the damage propagation phase, it is likely that the increased ductility associated with the modified resin has resulted in a higher delamination resistance and greater energy absorption in these quasi-static interlaminar fracture modes.

### 3.3 The Impact Properties of the Composite Materials

In **Figure 6**, the load-displacement traces following low velocity impact tests on the plain and modified laminates is shown. On examination, the response of the plain laminates in **Figure 6a** indicate the response at energies up to 2.7 Joules to be largely elastic, with the force rising to a maximum before unloading along a slightly lower load-displacement curve. Increasing the impact energy to 5.2 Joules and above results in the propagation of damage after the peak load, with the region over which damage propagation occurs increasing with impact energy. It is encouraging to note that the initial loading traces collapse onto one curve, and that the maximum force values associated with the onset of damage, are very similar, highlighting the reproducibility of the laminates. Similar trends to those observed in the plain composites are apparent in the traces for the graphene-modified composites, **Figure 6b**. Once again, the maximum force values (associated with the onset of fibre fracture) are similar for all energies greater than that required to initiate this form of damage. It is also evident that the maximum force values for the modified system are similar to those of the plain composite, suggesting that resin-modification has little effect on this failure threshold. A comparison of **Figures 6a** and **6b** also suggests that the damage propagation phases are similar in both systems. Finally, target perforation of the GO-modified system occurred following an impact of 10.4 Joules, a value that is slightly higher than the value required to perforate the plain resin system. **Figure 7** shows the variation of the maximum impact force with impact energy for both types of composite. Clearly, at low energies, increasing the impact energy results in

**Figure 6. Load-displacement traces following low velocity impact tests on (a) the plain CFRP samples and (b) the GO-modified composites. The incident impact energies are marked on the appropriate traces**

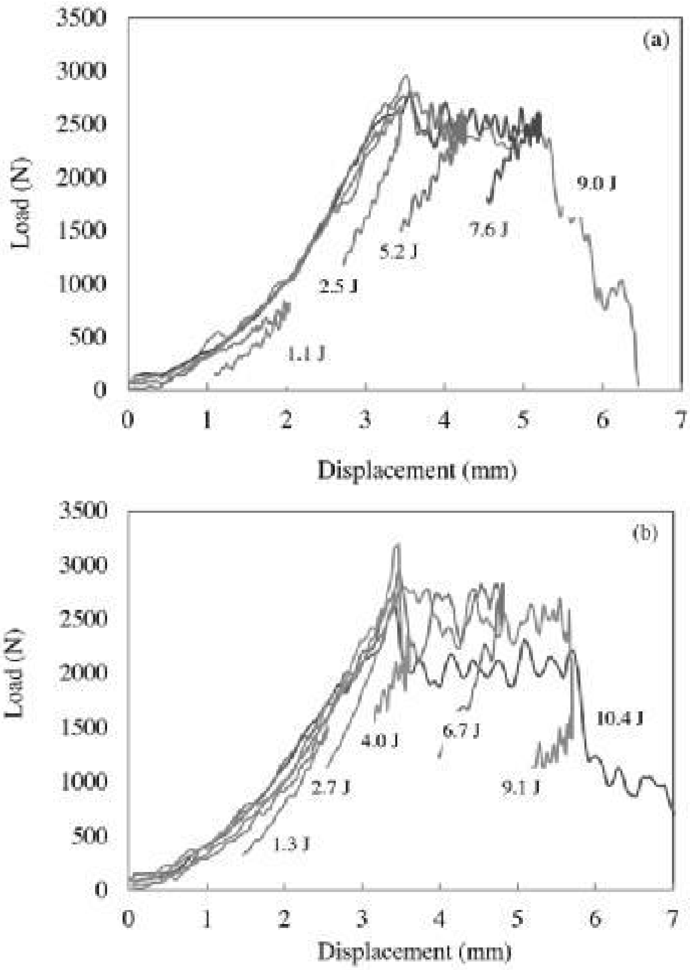



**Figure 7. The variation of the maximum impact force with impact energy for the plain and GO-modified composites**

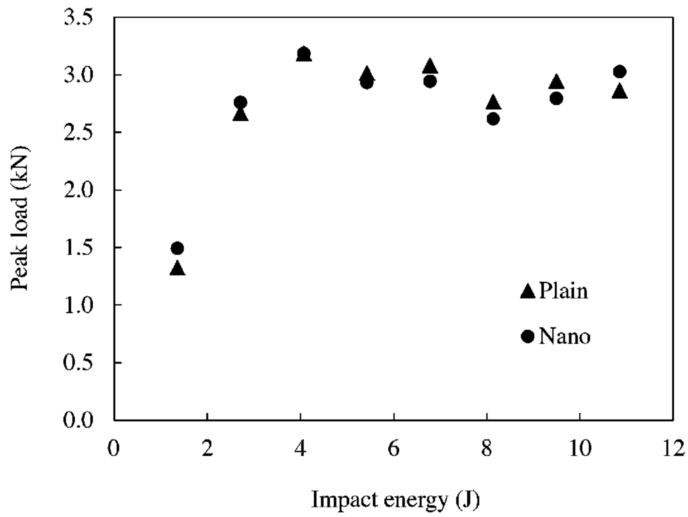


**Figure 8. The variation of absorbed energy with impact energy for the plain and GO-modified composites**

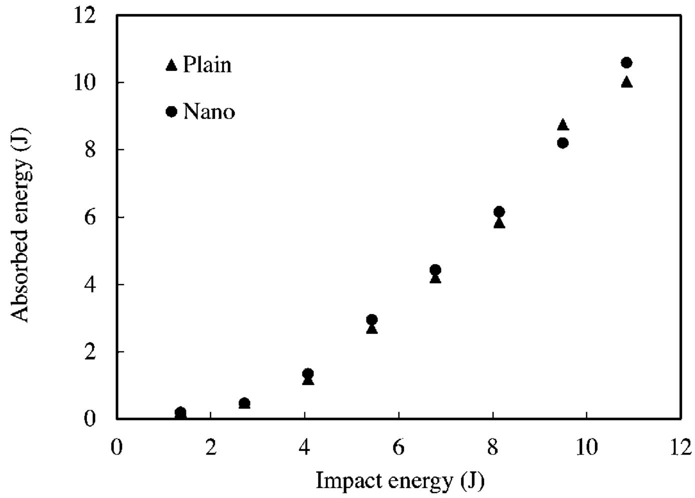



**Figure 9. Comparison of the rear surfaces of the plain and graphene-modified CFRP samples following impacts at increasing energy**

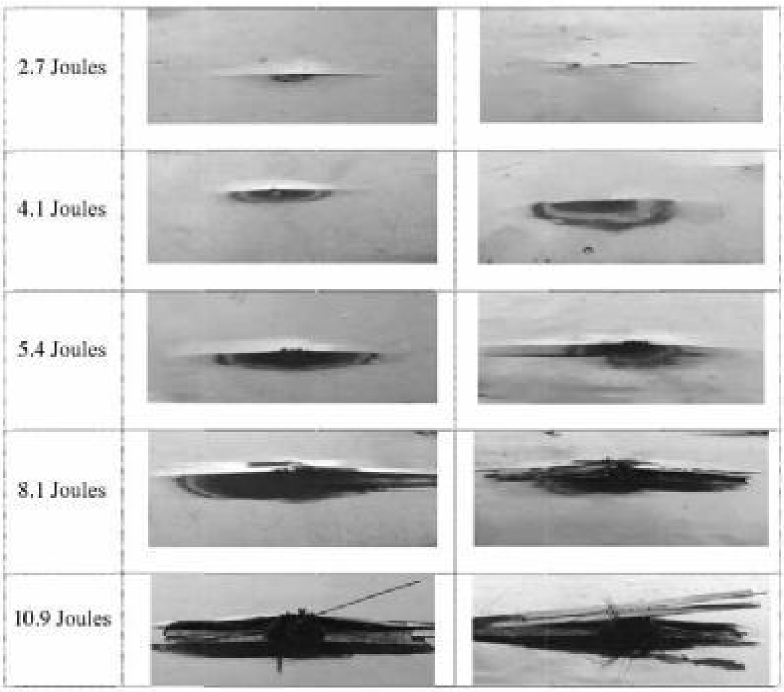
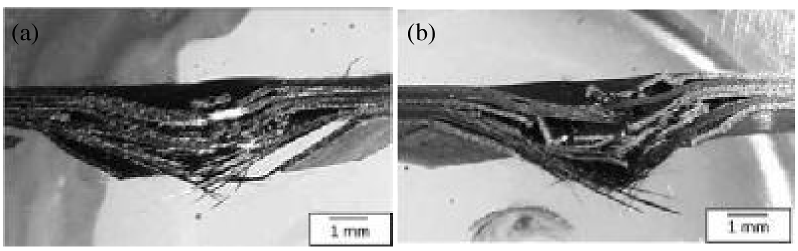



**Figure 10. Cross-sections of samples following impact perforation. (a) Plain sample and (b) GO modified sample**




a higher impact force. Once the energy is greater than approximately 4 Joules, the force tends to plateau at a value that is associated with the ultimate strength of the laminate. From the figure, it is clear that there is little difference between the two types of laminate with the modified system exhibiting similar values of maximum impact force to its unmodified counterpart. Given that the maximum impact force is associated with fibre fracture, it could be argued that modifications to the matrix material would have little effect on the magnitude of this critical threshold. The energy absorbed by the composites during the impact event was determined by calculating the energy within the load-displacement traces and the resulting values are presented in **Figure 8**. At the lowest energy, the impact event in largely elastic, with little energy being absorbed in fracture within the laminate. As the impact energy is increased the level of energy absorbed in inelastic processes increases, with virtually all of the energy being absorbed at the perforation threshold. Once again, there little difference between the responses of the plain and modified composites, suggesting that the incorporation of graphene particles has very little effect on the overall impact response. **Figure 9** shows the rear surfaces of samples impacted over a range of energies. At low energies, failure took the form of rear surface splitting parallel to the direction of the lowest surface ply. At higher energies, the fibres in the lowermost layer fail, leading to significant splitting along the fibre direction. An examination of the rear surfaces of the plain and modified samples highlights little difference in the failure modes, with both types of material exhibiting similar levels of damage for a given energy. **Figure 10** shows cross-sections of the perforation zones in the two types of laminate. From the figure, there is little difference between the two damage zones, with failure taking the form of extensive fibre fracture and localized delamination. Once again, there is no distinct benefit associated with the incorporation of the nanoparticles. Similar conclusions can be drawn following examination of the cross-sections of perforated samples in **Figure 10b**. Here, significant fibre fracture has occurred over a zone immediate to the point of impact.

The evidence presented in this study has suggested that whereas GO modification enhances the quasi-static response of the resin and possibly the composite, it appears to have little effect on the dynamic properties of the composite. Interestingly, Norhakim *et al.*[18] evaluated the mechanical properties of a GO-modified epoxy resin and noted that whereas the flexural properties were significantly enhanced by adding between 0.1%wt. nanoparticles, the impact strength remained unchanged. Indeed, adding greater quantities of GO resulted in a significant reduction in impact resistance.

## 5. CONCLUSIONS

The effect of graphene oxide modification on the low velocity impact response of composite laminates based on dry fibre preforms, manufactured using the automated fibre placement technique, has been investigated. Initial tests on the unreinforced resin showed that the incorporation of 0.1%wt. graphene oxide resulted in a fifty percent increase in the flexural strain to failure. Modifying the matrix in this way resulted in a modest increase in the quasi-static perforation resistance of the composites, probably due to greater energy absorption in resin-dominated failure mechanisms. These improvements were not reproduced under dynamic loading conditions, where there was little difference in the energy absorption characteristics or the levels of damage for a given impact energy. It is likely that the toughening mechanisms associated with the presence of the nanoparticles are not triggered under dynamic loading conditions. More specifically, it is probable that localized energy-absorbing mechanisms that occur quasi-statically do not occur to any significant degree under impact loading, thereby imparting little benefit to the overall impact toughness of the composite laminates.

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