1 General Introduction

Carbon nanotubes have been explored in composite materials to increase the electrical conductivity [1-3], the glass transition temperature and modulus. Continuous fiber-polymer composites fail in different damage modes under impact: intraply cracks, delamination and fiber fracture. Hence, any methods to improve matrix properties and delamination are under consideration for increasing the required penetration energy under impact, including matrix toughening by adding nanoparticles. Carbon nanotubes are of interest as reinforcement against impact, as they have a large aspect ratio and can form a network. Although the concept of multiscale reinforcement in composite materials has been thought advantageous, it is very difficult to fully infiltrate multiwall carbon nanotubes (MWNTs) through a continuous fiber reinforcement. In this study, the fabrication of interlayers of MWNTs within the laminate has been considered and electrospinning has been used to fabricate these MWNT interlayers.

Grujicic et al [4] carried out computational modeling of the impact process of hybrid glass fiber fabrics-MWNT interlayers-polyester composites and concluded that the optimum configuration for a MWNT-loaded continuous glass fiber laminate requires a 100 μm layer of MWNTs near the front face of a laminated structure.

In this study, electrospun MWNT-epoxy fibers have been explored, due to the fact that MWNT orientation in MWNT interlayers can also be exploited. The electrospinning process was fine tuned to achieve high voltage deposition of a mixture of oriented MWNT/epoxy nanofibers and MWNT/epoxy spray on a plain woven glass fiber fabric. Four MWNT coated fabric layers were laid in pairs within an 11 ply assembly near the face of intended impact (as optimized theoretically by Grujicic et al [4]), so that the MWNT coatings in each pair were face-to-face at a 0/90 configuration. Laminates were fabricated by resin transfer molding (RTM) and were tested in single low-speed impact tests.

2 Experimental

2.1 Materials

| Table 1. Properties of the glass fibre woven fabric |
|-----------------|-------------|
| Fabric type     | Y0212       |
| Fabric thickness| 0.48 mm     |
| Weave           | Plain       |
| Warp yarns      | 136x3 EC9 tex – 670 ends/m |
| Weft yarns      | 136x3 EC9 tex – 630 pics/m |
| Areal density (ρ_a) | 0.546 kg/m² |
| Filament diameter (D_f) | 10.5 10⁻⁶ m |
| Number of filaments in a yarn | 2090 |

An E-glass fiber plain woven fabric Y0212 from Fothergill Engineered Fabrics has been used in this study of areal density 0.546 kg/m², nominal thickness 0.5 mm, 670 ends/m in the warp direction and 630 pics/m in the weft direction. The resin system used was Araldite® LY 564 epoxy resin and hardener HY 2954 at a weight ratio of 100:35 Araldite®/ hardener. Elicarb® multiwall carbon

1 Defined as the weight in kilogram of a 1 square metre of fabric
nanotubes (MWNTs) from Thomas Swan were used in this study, of 10-30 nm average diameter and microns length.

A mixture of butanone with 1-methoxy 2-propanol in 3:1 weight ratio, respectively, was used as a solvent for the electrospinning of MWNT-epoxy fibers (solvents from Sigma Aldrich). After the stirring process, the MWNT solution was combined with the epoxy solution part to form the suspension to be used in the electrospinning process.

2.2 Electrospinning of MWNT-epoxy nanocomposite fiber mats

Electrospinning was carried out at 30 kV to deposit MWNT-epoxy nanocomposite fiber mats on glass-fiber fabrics, which were secured on a rotating drum. The MWNT-epoxy fibers were deposited in parallel fiber orientation. The most successful electrospinning runs involved an MWNT solution-epoxy (without hardener) mixture at a volume ratio of 1:1; this process resulted in a mixture of electrospun MWNT/epoxy fibers and MWNT/epoxy spray, where the epoxy was just uncured Araldite resin. A similar product but with fewer fibers and more spray was fabricated by using MWNT solution-epoxy and hardener mixture.

2.3 Manufacture of hybrid composite laminates

11 Layer plain weave glass fiber fabric-epoxy laminates were fabricated by RTM (Fig.1) and tested as a reference in the same way as the hybrid MWNT-plain weave glass fiber fabric-epoxy laminates. All laminates were of a fiber volume fraction in the range of 44-49%. The hybrid glass fiber fabric-MWNT-epoxy laminates were fabricated by assembling 11 plain weave glass fiber fabrics with four glass fiber fabrics having deposited electrospun MWNT-epoxy fibers/spray on one side of each of these four fabrics. Then these fabrics were laid on the RTM mould, so that the adjacent MWNT-glass fiber fabrics were laid with the MWNT sides face-to-face at 0/90, as presented in Fig.2. The RTM mold was then closed and the curing epoxy resin mixture was injected and let to cure and post-cure. The MWNT coated fabrics were placed near the face of the impact. Overall, the hybrid laminates contained MWNTs at 0.15 wt%.

3 Experimental results

The fabricated laminates were cut into discs of 140 mm diameter for impact testing in a CRAG test rig on an Instron mechanical testing machine (Fig.3). The impactor used in the impact experiments was a marble ball of 15.89 mm diameter. Single impact tests were performed at a speed of 2 mm/s.

The results demonstrated that the four interlayers of the electrospun MWNT/Araldite system, in two pairs of 0/90 face-to-face interlayers, strengthened the laminate by increasing its peak load by 4.5%, compared with the original 11 ply fabric-epoxy laminate. The four interlayers of the electrospun
MWNT/Araldite system also increased the total penetration energy by 22% and the damage area by 145%.

On the other hand, the MWNT/Araldite/hardener electrospun coatings, which were expected to have cured after electrospinning, were not so efficient under single impact: they actually resulted in a 6% decrease of the peak load, 5% larger total penetration energy and 87% larger total damage area than the standard plain woven glass fiber-epoxy laminate.

The process started first with the glass fibre fabric-epoxy laminate for which the experimental results of a multiple impact test are presented in Fig.4, including the photos of the impacted laminate and its damage area at selected peak loads. Loading and unloading at low strains, well below the appearance of initial matrix cracking provides the case study for the numerical fitting of the stiffness coefficients of the elastic deformation of the composite laminate, where initial values of the coefficients in the computer simulations were provided from data of tensile tests (Young’s moduli) and dynamic mechanical testing torsion tests (shear modulus) of the laminates.

Matrix cracking is seen at 0.2 mm for the glass fibre fabric-epoxy laminates, with some variability between specimens. The first delamination seems to occur at loads of 5-5.8 kN. The load displacement curve in Fig.4 seems to have a wide plateau of relatively high load, which can be attributed to the large number of well bonded layers in the thick laminate.

Given that it is not easy to fabricate laminates with exactly the same thickness (to ±0.1 mm), the effect of the laminate thickness on the absorbed energy under impact is of concern. Manufacturing glass fibre fabric-epoxy laminates of different thickness in the range of 4.7-5.4 mm, it was found that an increase of the laminate thickness by 8% (and subsequent decrease of the fibre volume fraction, Vf) produced an almost proportional increase in the penetration energy by 7.7%. This is an interesting finding for these laminates, as this effect of thickness is known but it is also known that a

4 Theoretical analysis

The problem is solved using ABAQUS Explicit in an explicit dynamic finite element analysis. The panels are modelled on a ply by ply basis (using solid elements). Two alternative modelling strategies are considered for the MWNT interlayer: (a) modelling it as a different type of ply or (b) incorporating the MWNT interlayer in the form of interface elements. Based on anticipated (reported) failure modes the constitutive model incorporates (i) fibre damage models, (ii) matrix damage models and (ii) a constrained crushing model. Computer simulations of multiple impact tests and progressive impact tests following a trial-and-error process of different values for the parameters and properties of the constitutive model and comparison of the predictions with the load displacement curves of the experimental part provide a means of fitting these properties and parameters to the experimental results.
decrease in $V_f$ leads to decreased impact performance.

Fig. 4. Load/displacement curve and pictures of impact damage of multiple impact test performed on a plain woven glass fibre fabric-epoxy laminate
5 Conclusions
The reinforcing effect of MWNTs on glass fibre woven fabric-epoxy laminates was investigated under impact. The MWNTs were introduced as two pairs of 0/90 face-to-face interlayers, deposited by electrospinning of MWNT-epoxy solutions with or without hardener. It has been concluded that the electrospun MWNT/Araldite fibre interlayers strengthened the laminate by increasing its peak load by 4.5%, compared with the original 11 ply fabric-epoxy laminate. The four interlayers of the electrospun MWNT/Araldite system also increased the total penetration energy by 22% and the damage area by 145%.

On the other hand, including hardener in the electrospinning solution, which was expected to have cured after electrospinning, deteriorated the performance of the laminate under impact.

References
