This is the published version:


Available from Deakin Research Online:

http://hdl.handle.net/10536/DRO/DU:30033583

Reproduced with the kind permissions of the copyright owner.

Copyright: 2010, American Institute of Physics
Properties of a Carbon-Fibre Composite Modified by Electrospun Poly (Vinylidene Fluoride).

K. Magniez a, C. De Lavigne ab and B.L. Fox a

a Institute of Technology Research and Innovation, Deakin University, Victoria, Warrn Ponds, 3217, Australia
b École nationale supérieure des arts et industries textiles (ENSAIT), Roubaix, 59056, France.

Abstract. The interlaminar toughening of a carbon-fibre reinforced composite by incorporation of electrospun polyvinylidene fluoride (PVDF) nanofibrous membranes was explored in this work. The nanofibres were electrospun directly onto commercial pre-impregnated carbon fibre materials under optimised conditions and PVDF was found to primarily crystallise in its β phase polymorphic form. There is strong evidence from DMA analysis to suggest that a partial miscibility between the amorphous phases of the PVDF nanofibres and the epoxy exists. The improved plastic deformation at the crack tip after inclusion of the nanofibres was directly translated to a 57% increase in the mode II interlaminar fracture toughness (in-plane shear failure). Conversely, the fracture toughness in mode I (opening failure) was slightly lower than the reference by approximately 20%, and the results were interpreted from the complex micromechanisms of failure arising from the changes in polymorphism of the PVDF.

Keywords: polyvinylidene fluoride; electrospinning; composites.

PACS: N/A

INTRODUCTION

For the past decade, the improvement in the fracture toughness of composite has been realised through the development of novel resin systems involving the use of rubbers and thermoplastics as toughening agents. Interlayer toughening described as the inclusion of discrete layers of a secondary material, in film, fibrous or particulate form, in the inter-plies has also been successfully applied [1]. Very recently, the interlayer toughening of carbon fibre reinforced composites using a nanofibrous substrate produced by electrospinning has been reported [2,3] but thus far this approach remains novel as very limited literature has been published. Polyvinylidene fluoride (PVDF) is a well-known thermoplastic that has shown excellent compatibility with epoxy resin [4]. For this reason, the interlaminar toughening of a carbon-fibre reinforced composite by incorporation of electrospun PVDF nanofibrous membranes was explored in this paper. The work aimed to determine the complex interfacial interactions between the nanofibres and the epoxy matrix, and understand how a secondary interlayer phase influences on the resistance to crack propagation in the resulting composites. The mode I and mode II fracture toughness results were correlated to the micromechanisms of failure and changes in polymorphic crystal forms in order to establish the structure-property relationships.

RESULTS

The electrospinning process a high molecular weight PVDF was found to be optimum at (20kV, 25wt%) where nanofibres free of defects with average diameter of 340nm ± 150nm and orientation in random directions could be observed (Fig. 1). PVDF nanofibrous membranes were electrospun directly onto pre-impregnated woven material (Toray G83C).

Double Cantilever Beam (DCB) (mode I) and End Notch Flexure (ENF) (mode II) fracture toughness tests were performed on the resulting composites. The mode I and mode II fracture toughness represent the resistance of a material to delamination in an opening and in-plane shear modes of failure, respectively upon crack propagation. It can be noted that the unmodified reference sample out-performed the other modified samples and displayed the best resistance to crack propagation with an average value $G_{IC}$ of 1.02 kJ/m². The resistance to crack propagation for the samples containing the PVDF films was found to be very poor with average $G_{IC}$ values as low as 0.2 kJ/m², and poor interfacial strength between the film and the epoxy was accounted for this result. The resistance to crack propagation for the samples containing the PVDF nanofibrous membranes was found to be slightly lower than the one of the
reference sample with an average value $G_{\text{IC}}$ of 0.8 kJ/m$^2$. This trend is somehow consistent with the recently reported literature showing no significant effects on the mode I results after incorporation of electrospun membranes in composite [2]. A cross section analysis of the DCB samples (not shown here for brevity) showed that the crack path transited from the mid-section of the nanofibrous interlayer region to the interfacial interlayer/resin region.

**FIGURE 1.** Morphology and statistical distribution of the high molecular weight (HMW) PVDF nanofibres (polymer flow rate 1.5 ml/min, tip to collector distance of 15 cm, DMF/acetone).

Displayed in Fig. 2 are the the plots of the mode I fracture toughness (referred to as $G_{\text{IC}}$) as a function of the crack growth and the mode II results.

**FIGURE 2.** Mode I and mode II fracture toughness results (left and right images, respectively) for the reference composite and composite modified with high molecular weight (HMW) PVDF film and nanofibres.

This type of behaviour has previously been described in interlayer toughened systems and it was attributed to complex changes in micromechanisms of failure during the loading [5]. SEM surface fracography analysis showed a combination of brittle and ductile regions which evidenced the complexity of the micromechanisms of failure. Plastic deformation of the matrix and the nanofibres was visible in the semi-ductile regions and typical brittle interlaminar fracture surfaces accompanied with the presence of nanofibres embedded within the epoxy matrix were also visible (Fig. 3).

**FIGURE 3.** Surface topography in the ductile (left) and brittle (right) region of the composite modified with PVDF nanofibres.
The polymorphic behaviour exhibited by the PVDF was detected by FT-IR spectra where the predominance of the less ductile β crystal phase was visible (not shown here for brevity). In light of these results, it is speculated that the polymorphic behaviour displayed by PVDF in the nanofibrous membranes strongly influenced the fracture toughness of the resulting composites.

Mode II results (Fig. 2) showed that the insertion of a PVDF film into the composite underperformed which highlights the inability for the epoxy matrix to plastically deform ahead of the crack tip. On the other hand, the introduction of electrospun PVDF membranes improved the $G_{IIc}$ by approximately 57%. The complex surface morphology after fracture with the presence of mixed brittle and ductile regions was also visible from the SEM images. It was found that the ductility of the epoxy matrix in the presence of the nanofibres was enhanced at the crack tip. The complexity in the crack path and micromechanisms of failure which have been aforementioned might have been in themselves contributing to the observed improvements.

DMTA analysis also showed no improvement in the dynamic response of the composite after inclusion of PVDF film or nanofibres. On the other hand, and despite the occurrence of interfacial phase separation, there is strong evidence to suggest that a partial miscibility between the amorphous phases of the epoxy and PVDF exists. Annealing at 185°C for 45 minutes resulted in a shift in glass transition temperature ($T_g$) which implicates partial miscibility between the amorphous phases and high compatibility (Fig. 4).

**FIGURE 4.** Tan ($\delta$) of the reference composite and composites modified with high molecular weight (HMW) PVDF film and nanofibres as such (left) and annealed (right).

**ACKNOWLEDGMENTS**

The authors thank Alfred Deakin Prof. Xugai Wang from the textile group at Deakin University for financial support of this research project. The authors gratefully acknowledge the helpful assistance of Associate Prof. Tong Lin and Dr. Jian Fang during this work and Glenn Bridgford from Arkema providing the Kynar® films.

**REFERENCES**