# Phase morphology of nanofibre interlayers: Critical factor for toughening carbon/epoxy composites

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## ARTICLE INFO

## ABSTRACT

Electrospun thermoplastic nanofibres were employed to toughen carbon/epoxy composites by direct deposition on carbon fibre fabrics, prior to resin impregnation and curing. The toughening mechanism was investigated with respect to the critical role of phase morphology on the toughening effect in carbon/epoxy composites. The influences of solubility in epoxy and melting characteristics of thermoplastics were studied towards their effects on phase structure and delamination resistance. For the three different thermoplastic nanofibre interlayers used in this work, i.e. poly(ε-caprolactone) (PCL), poly(vinylidene fluoride) (PVDF) and polyacrylonitrile (PAN) nanofibre interlayers, only PCL nanofibres produced toughening. Although cylinder-shaped fibrous macrophases existed in all three interlayer regions, only PCL nanofibres had polymerisation-induced phase separation with epoxy, forming ductile thermoplastic-rich particulate microphases on the delamination plane. These findings clearly show that the polymerisation-induced phase separation is critical to the interlayer toughening by thermoplastic nanofibres. An optimal concentration (15 wt.%) of PCL solution for electrospinning was found to produce composites with enhanced mode I interlaminar fracture toughness ($G_{IC}$), stable crack growth and maintained flexural strength and modulus.

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## 1. Introduction

Nanofibres exist in nature as basic building blocks in both animals and plants. For example, collagen nanofibres are abundant structures in animal bodies such as tendons and ligaments [1,2] and cellulose nanofibres are commonly found in green plants [3]. Polymeric fibres with diameters ranging from submicrons to nanometres (e.g. $10 \times 10^{-3}$–$100 \times 10^{-3}$ μm) exhibit amazing characteristics such as very high surface area to volume ratio, flexibility in surface functionalities and superior mechanical performance (e.g. stiffness and tensile strength). These unique properties made polymer nanofibres optimal candidates for many important applications such as filtration [4,5], tissue engineering scaffold [6,7], drug delivery carrier [8,9], protective clothing [10], electronic and semiconductive materials [11], and reinforced nanocomposites [12,13]. In particular, nanofibres have recently emerged as important fibrous materials for reinforcing and modifying polymer matrices [14,15].

For structural fibre reinforced composites, the lack of plastic deformation of the matrix and the low transverse and interlaminar shear strength of laminates are the main reasons for their strong vulnerability to impact [16]. Once a certain stress level is exceeded, irreversible damage by fracture will occur, resulting in local and structural degradation and failure. Polymer nanofibres have been shown to remedy this issue when they are inserted as interlayers in composite laminates. Although polymer nanofibres can be fabricated by a number of processing techniques such as electrospinning, drawing, template synthesis, phase separation, self-assembly, electrospinning is the most effective method to produce continuous nanofibres [17]. The basic electrospinning system consists of a hollow needle spinneret, a high voltage power supply and an electrode collector. During electrospinning, the polymer solution charged with high voltage is drawn into a Taylor cone, which becomes a jet when the solution at the apex can overcome the surface tension. Once the jet ejects into the electric field, it undergoes a whipping movement to stretch itself thinner. Solvent evaporation from the filament leads to solidification of the filament into nanofibres that form randomly orientated nanofibre mat in most cases [18,19]. More than 100 polymers and many inorganic materials have been electrospun into nanofibres with different morphologies such as core-sheath, side-by-side structure and porous-surface, for various applications in filtration, tissue engineering scaffold, energy storage and conversion [17,20], etc. Recently, new needleless electrospinning technique has been reported to produce nanofibres on significantly large scale for wide usage in practice [21].

Dzenis et al. [22,23] firstly reported the use of nanofibres to reinforce carbon fibre composite laminate, and they found that entangled nanofibres showed improvement in the interlaminar fracture resistance. Li et al. [24] compared the toughening effect of

polysulfone (PSF) film and PSF electrospun nanofibres as interlayers in carbon/epoxy laminates. They claimed that the inhomogeneous phase separation of PSF nanofibres along nanofibre directions led to better mechanical properties of composites compared to those with PSF film interlayers. However, the mechanism of multiple phase changes observed in the nanofibre interlayer region was not clear. Magniez et al. [25] also used electrospun poly(vinylidene fluoride) (PVDF) nanofibres to toughen an epoxy matrix composite. However, 20% reduction in the mode I interlaminar fracture toughness was reported. In our previous work [14], we have investigated electrospun polyetherketone cardo (PEK-C) nanofibres for toughening structural carbon/epoxy laminates. The composites exhibited considerably enhanced mode I interlaminar fracture toughness, with ductile PEK-C-rich particulate phases found on the delamination plane. However, how the phases transform in the interlayer region was still not clear. Phase separation may play an important role for nanofibre interlayer to toughen structural composites, which has not been elucidated to date. In this work, the phase behaviour of different nanofibres in carbon/epoxy composites was examined to clarify the toughening mechanism. The focus of this investigation is on the important factors such as the melting characteristics and the solubility of thermoplastic polymers in epoxy that may greatly affect the phase behaviour of nanofibres with epoxy, which are not understood previously.

In this work, nanofibres electrospun from three different polymers, poly(ε-caprolactone) (PCL), poly(vinylidene fluoride) (PVDF) and polyacrylonitrile (PAN), were used as modifiers. The selection of polymer materials in this study was based on the easy clarification of the toughening mechanism. PCL, PVDF and PAN were selected because of the noticeable difference in melting point. PCL has a melt point at 60 °C, and the melting point of PVDF is 165 °C, however PAN does not melt. PCL has been widely used as a thermoplastic modifier for toughening of epoxies [26–29], although PCL nanofibres have not been used for toughening carbon fibre/epoxy composites. PVDF is an engineering thermoplastic possessing excellent mechanical strength and toughness, high heat and chemical resistance, and low moisture absorption. PVDF nanofibres have recently been studied to toughen a carbon/epoxy composite, however, decrease in the mode I fracture toughness was obtained [25]. PAN was also used to study the existence form of its nanofibres in cured composites and the relationship between the nanofibre morphology and toughening effect on epoxies. The phase structure was investigated by both optical and electron microscopic techniques, combing with mechanical characterisations using double cantilever beam test and flexural tests.

## 2. Experimental

### 2.1. Materials

PCL ($M_n \sim$ 80,000), PVDF ($M_w \sim$ 534,000) and PAN ($M_w \sim$ 86,200) were obtained from Sigma–Aldrich. PEK-C was obtained from Xuzhou Engineering Plastics Co. The epoxy resin was composed of triglycidyl amino phenol (TGAP, Araldite MY0510, Hunstman, Australia) with epoxy equivalent 95–106 and a 4,4′-diamino diphenyl sulfone (DDS, Aldrich, purity > 97%) cure agent. Solvents N,N-dimethylformamide (DMF), chloroform and acetone from Aldrich were used as received. Formax multiaxial carbon fibre reinforcements [C12 K, 450, −45/+45] were used for preparing carbon/epoxy composite laminates. The stitching thread is polyester and the stitch weight is 7 g/m² (GSM).

### 2.2. Sample preparation

PCL pellets were dissolved in a solvent mixture of DMF and chloroform (50:50, vol:vol) to form 12 wt.% (12 g PCL in 100 ml solvent), 15 wt.% and 20 wt.% solutions. PVDF powder was dissolved in a solvent mixture of DMF and acetone (50:50, vol:vol) to form a 16 wt.% solution. PAN powder was dissolved in DMF to a 13 wt.% solution. The polymer solution was placed into a 5 ml syringe with a metal syringe needle (21 Gauge) which was connected to a syringe pump (KD scientific). Single layer carbon fibre fabric mounted on a metal roller at a distance of 12–15 cm from the needle tip was used as a substrate to collect nanofibres. The electrospinning was performed under an applied voltage of 15 kV with a solution flow rate of 1 ml/h. During electrospinning, the nanofibres were collected onto the carbon fabric mounted on a drum collector rotating at a constant speed of 100 rpm.

The carbon fabrics with one side deposited with nanofibres were laid up with epoxy resin (epoxy/carbon 1:1, wt/wt) applied on the other side. Only one layer of nanofibre mat was placed in the mid-plane of the prepared composite laminates. To maintain the same nanofibre weight fraction in the composite laminates, approximately 0.2% in the present investigation, the electrospinning time was adjusted for different solution concentrations. The electrospinning time was 101 min for the 12 wt.% PCL solution, 81 min for the 15 wt.% PCL solution, 61 min for the 20 wt.% PCL solution, 76 min for the PVDF solution and 93 min for the PAN solution. The composite laminates [0/90]₄ were finally cured in an oven with a low positive pressure of 3.5 kPa, following a cure schedule of 125 °C for 1.5 h and 175 °C for 2 h. As a control, a composite laminate without nanofibre interlayer was prepared using the same process. Thermoplastic/epoxy blends for phase behaviour observation were prepared by solvent casting on glass slides with further cure in a convection oven.

### 2.3. Characterisations

Mode I interlaminar fracture toughness was measured by double cantilever beam (DCB) tests on an Instron 5569 universal tester according to the protocol of the European Structural Integrity Society [30]. A 15 μm thick aluminium foil was treated with release agent and then inserted between the mid-layers prior to processing. A crosshead speed of 2 mm/min was used for DCB tests. The cured thickness of composite laminates was about 1.95 mm. Correction factors for large displacements and stiffening by the end blocks were applied for calculating the mode I critical strain energy release rate, $G_{IC}$. Three-point-bending flexure tests were conducted according to ASTM D790. Five specimens were tested for each type of composite laminates, when the DCB and flexure tests were performed.

Dynamic mechanical thermal analysis was performed using a TA Q800 analyzer at a fixed frequency of 1 Hz with a heating rate of 3 °C/min. A single cantilever mode was adopted. The microstructure analysis was conducted by using both optical microscopes (Leica DMLM and Nikon Eclipse 80i) and scanning electron microscope (SEM) (Zeiss Supra 55VP). The average diameters of the electrospun fibres were calculated based on the SEM micrographs using an image analysis software (Image J). For each polymer type, 100 fibres were counted and the average diameters were determined from the histogram graphs of size distribution. The weight fractions of thermoplastic nanofibres in composites were calculated based on the flow rate of the polymer solution being electrospun, the electrospinning time, polymer concentration and the weight of carbon fabrics and epoxy resin.

## 3. Results and discussion

### 3.1. Nanofibre morphology

Fig. 1 shows the morphologies of electrospun nanofibres. PCL nanofibres showed bead-on-string morphologies, whereas PVDF