Effect of bath concentration during electrophoretic deposition on the interfacial behaviour of hybrid CFRP composites

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Abstract:
Carbon fibre reinforced polymer (CFRP) composites a perfect structural material due to their outstanding malleable strength, great rigidity, light mass and pronounced thermal resistance. But their inferior out-of-plane properties which are controlled by the matrix–fibre interface restrict the use of CFRP composites in critical applications. Amalgamation of nano-filler in the CFRP composites has found to improve the matrix-fibre interface and there by out-of-plane response. Though matrix modification has contributed to the improvement of interface, fibre modification has a scope for higher levels of nano-filler incorporation and proper fibre nano-filler adhesion. Out of several methods available for fibre modification electrophoretic deposition (EPD) is an eye-catching method for monitoring as well for nanofiller deposition. In recent ages, Graphene has grabbed wonderful consideration Among the graphene based functionalised nano fillers Carboxyl functionalized Graphene (G-COOH) modified CFRP composites have shown better ILSS properties. This research primarily aims to fabricate a CFRP composite using G-COOH modified carbon fibres with varying nano-filler concentrations of 0.5g/ltr, 1g/ltr and 1.5g/ltr in the EPD bath and its impact on the mechanical properties of the FRP composites. The laminates thus obtained were subjected to short beam shear test for the determination of inter laminar shear strength (ILSS). Fractography of the tested samples to observe various failure modes has been carried out by using scanning electron microscope (SEM).

Keywords: Electrophoretic deposition, CFRP composite, G-COOH, ILSS.

1 Introduction
Carbon fibre (CF) is one of the significant reinforcing materials utilised for the processing of the well-developed composites for structural applications [1]. The properties of carbon fibre reinforced polymer (CFRP) composite are mainly dependent on the interfacial bond strength between the matrix and reinforcement [2]. Carbon fibres have superior in-plane properties, however the out-of-plane properties limit their capability to replace conventional materials in critical structural applications [3,4]. Few studies have suggested that the modification of the fibre by incorporating the nano-filler on to the fibre surface resulted in the improved interlaminar performance [5]. However untreated carbon fibres are prone to have low enactment due to bulky surface inertia and weak interface [6]. Extensive research has been devoted for surface modification to enhance the interfacial performance of CFs. In the recent times wide research has been dedicated to the modify the surface of CF to improve the interfacial properties of CFRP composites, a few prominent modification techniques are sizing route, electro-chemical technique, plasma based modification and nano filler hybrid fibre synthesis are a few modification procedures [6,7]. Among these methods, introducing graphene based nano-fillers on to the CF surface can increase the interfacial bonding considerably, especially ones with oxygen based functional group can very well adhere with the epoxy due to the presence of epoxide groups, can institute the hydrogen bonding with epoxy resin. Deposition of nano-fillers on CF surfaces affects the

surface morphologies of carbon fibres, and enhances the surface wettability of carbon fibres by increasing the surface free energy of the fibres [8]. This decoration of carbon fibre can be attained by the Electrophoretic deposition (EPD) which has been a successful technique for the incorporation of the nano-filler [9]. A colloidal process in which the suspended particles are deposited on the substrate by means of an electric field is called electrophoretic deposition (EPD). EPD, a favourable deposition procedure to create extensive nanoparticles strengthening for composite uses, that provides some benefits over other surface coating approaches, such as process ease, homogeneity of the deposited layers and better monitoring over the deposited dimensions [10] .

After the deposition of nano-fillers, the modified CF is subjected to thermal annealing to improve mechanical bonding at the interface[11]. Sheng-Yun Huang et al reported that mechanical properties of CFRP have improved due to increased surface wettability and the interfacial bonding between the nano-fillers and the CFs. Graphene based nano fillers when dispersed in water have very high tendency for sedimentation making it impossible to carry out efficient deposition at lower voltages [12]. In general, suspensions for EPD have to remain steady during the complete deposition process even in the presence of an electric field. During entire EPD process, in the existence of electric field steady suspensions are to be maintained. However simple approach that is available to make a stable suspension is addition of methyl violet (MV), which adsorbs on to the surface of the nano-filler and thereby improving the electrostatic stability of the suspension and apart from that it also helps graphene based nano-fillers attain a positive charge and thereby leading to a cathodic EPD which is desirable. Concentration of the nano-filler in the suspension affects the rate of deposition thereby the mechanical properties of the CFRP composite [13]. Here in this work GCOOH is chosen as the nano-filler to be deposited because of its high polarity and presence of oxide functional groups which help in proper bonding. Cathodic EPD is used to deposit various concentrations of GCOOH nano-fillers i.e. 0.5g/ltr,1g/ltr and 1.5g/ltr on the carbon fibres and the best concentration was chosen based on the mechanical properties of the CFRP composites fabricated with these modified carbon fibres.

Table.1. Nomenclature used for various laminates and fibres.

Nano-filler concentration (g/ltr)	Fibre nomenclature	Laminate nomenclature
0.5	**A**	**a**
1.0	**B**	**b**
1.5	**C**	**c**

2 Materials required

The following materials were used in this work.

- 216 Stainless Steel Sheets of 3mm thickness are used as anode (counter electrode) in EPD
- Carbon fabric from TORAY (25cmX25cm). 3K plain woven fabric is used as cathode (working electrode) in EPD.
- Graphene carboxyl (GCOOH) nano-filler (supplied by Platonic nanotech Pvt. Ltd)
- Methyl violet (as a stabilizer manufactured by Sigma Aldrich) is used as suspending agent.
- Diglycidyl ether of Bisphenol A (DGEBA) type epoxy and Triethylene tetra amine (TETA) was used as the hardener. Both these are manufactured by Atul Industries, India under the trade name Lapox L12 and K6 respectively as the matrix material.

3 Experimental setup for deposition and characterization

3.1 EPD technique

This investigation used Cathodic EPD for modifying the CFs where nano-filler deposits on the negative electrode. Prior to deposition desizing (removal of epoxide coating) of carbon fibres was carried out in a furnace maintained at 120°C for 2 hours. Carbon fibre which is fixed to the frame acts as cathode, and 216 Stainless steel plates having thickness of 3mm and dimensions 25mm×25mm fixed to the frame acts as counter electrode. To make a suspension of desired concentration the selected nano-filler was added to distilled water and subjected to a sonication at 100 KHz frequency for one hour followed by addition of MV and further mixture was sonicated for a period of one hour. The nano-fillers concentration was varied in the solution accordingly. The methyl violet concentration was fixed at 0.5g/ltr. After sonication, the solution was transferred into the cell for deposition. The electrodes were fixed in the frame and put into the solution to start with the deposition. With lapse of time, graphene based materials inherently get negatively charged when exposed to water and methyl violet interacts with graphene based materials which imparts positive charge to nano-fillers and finally gets deposited on cathode. Deposition was carried out by varying the voltage to maintain a constant current of 5A and the duration of deposition is 30 min, the voltage applied was varied according to the nano-filler used in the range of 6V-35V. After the deposition of GCOOH on the carbon fibres, it was dried for 24 hours at room temperature followed by exposing to acetone for two hour to remove MV and finally subjected to thermal annealing at 140°C for two hours in a furnace. These deposited fibres were then used in making laminates with epoxy as matrix. The investigations here used 12 layer laminates of thickness 3.85mm prepared by hand lay-up method. Then the obtained laminates were compressed in a hot press machine for 20 min at 60°C temperature and under an applied pressure of 10 kg/cm^2. The laminate after hot compression was cut to required size and polished to accurate dimensions followed by post curing for 6 hrs at 140°C in an oven. Fig.1. shows the schematic of EPD cell used in this work. Fig.2. shows a detailed flow chart of the processing and testing carried out in this work.

3.2 Short beam shear (SBS) Test

The ILSS of the CFRP composites were evaluated by SBS test standard (ASTM D 2344). The tests were performed on the same universal testing machine (Instron 5967) with a constant loading rate of 1 mm/min at room temperature conditions.

3.3 Surface topography and fractography

Surface topologies of the modified fibres (neat and hybrid) were characterized using a scanning electron microscope at 10 kV. Fibre was cut with scissors after deposition to observe the surface under an SEM. Investigation of the fracture mechanisms of tested CFRP composite was carried out by the fractography of the tested samples.

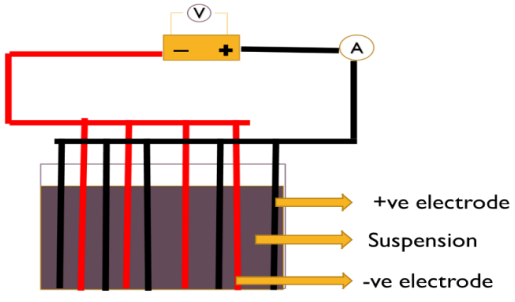

Fig.1. Schematic of the EPD cell

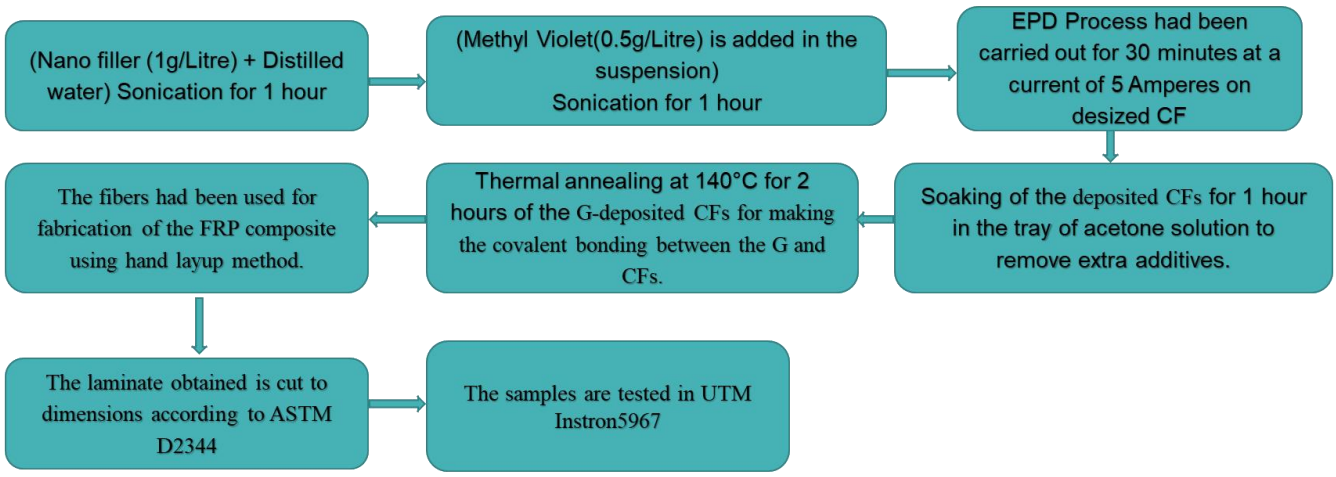

Fig.2. Flow chart of deposition and testing

4 Results and discussion

Fig.3 shows the SEM micrographs of neat and modified carbon fibres. The surface of neat carbon fibre is smooth as can be seen from Fig.3a and after the deposition of the nano-filler, the surface of carbon fibre has become relatively rough confirming the deposition of nano-filler. Fibre B has shown a good deposition in terms of uniformity (Fig.3c) when compared to fibre A and fibre C, the reason behind degradation in the quality of deposition from B to C might be the excessive concentration of nano-filler in the suspension that might have led to agglomeration. The reason behind fibre A showing non uniform deposition might be unavailability of required concentration of nano-filler for chosen deposition parameters. So it can be proposed that for a deposition time of 30 min and deposition current of 5 Amp optimum concentration of nano-filler to get a uniform deposition is 1g/ltr.

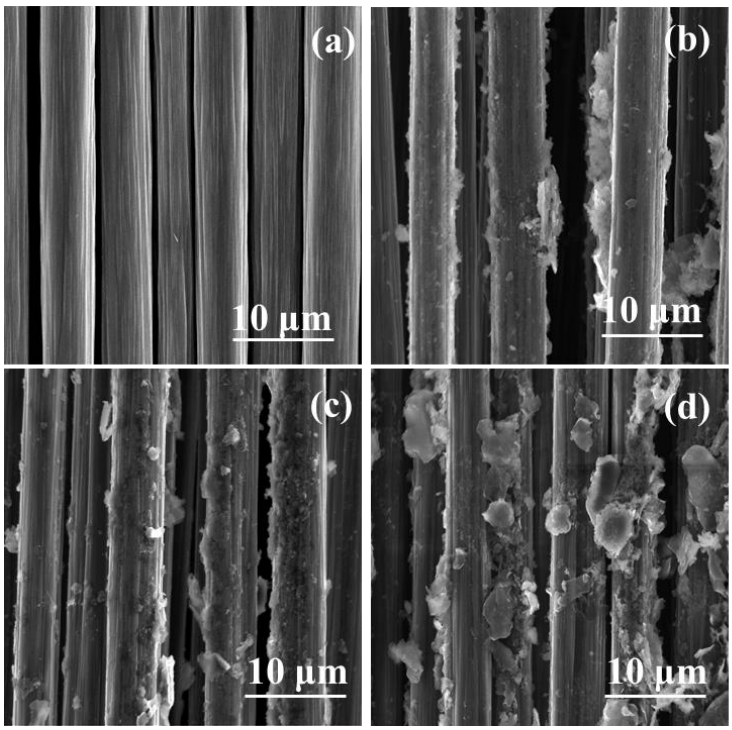

Fig.3. SEM images showing fibre morphology (a) Neat (b) 0.5 g/ltr (c) 1 g/ltr (d) 1.5 g/ltr

Fig.4a. shows the stress-strain curves of neat and modified composites by varying GCOOH nano-filler concentration. Neat sample exhibit catastrophic failure and samples a, b and c has shown some signs of pseudo-ductility. Laminate c tends to shows more pseudo-ductility in comparison to a, this

may be due to the increased nano-filler concentration on the CF. Pseudo-ductility is a peculiar behavior observed mainly in hybrid composites [14]. It can also be observed from the Fig.4a that with increasing concentration of nano-filler there was a consistent increase in ILSS and the strain to failure was also increasing. The improvement in ILSS with addition of nano-fillers might be because of the improved interface quality and larger interface available between the matrix and fibre facilitating proper stress transfer. The improvement in strain to failure may be correlated to the induced stiffening by addition of nano-fillers [15]. Fig.4b. gives the ILSS of various laminates. It was very clear from the Fig.4b that ILSS increases with increase in the concentration of the nano-filler in the suspension. All the modified CFRP composites have shown better ILSS than control sample, which makes it clear that modification of carbon fibre is improving ILSS. Laminate a has shown an improvement of 15.7%, b has shown an improvement of 22.8% and laminate c has shown an improvement of 25.4% in ILSS with respect to control sample. The improvement of ILSS from laminate 'a' to laminate 'b' was higher than that of laminate b to laminate 'c' which may be due to scattered deposition of GCOOH on CF as shown in Fig.3d.

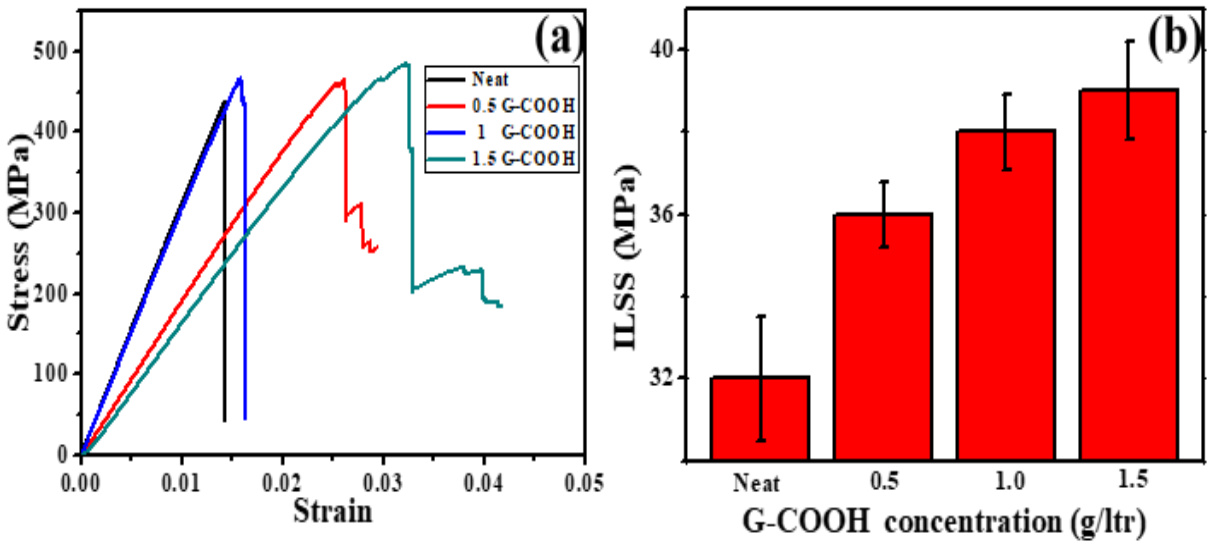

Fig.4. Short beam shear test of the Composite (a) Stress-Strain Curve (b) ILSS of Composite

Fractography of the tested samples revealed various modes of failure as seen in Fig.5. Fig.5a. shows the fibre pull-out and Fig.5d shows deformed matrix in sample b. Delamination in sample a was clearly shown in Fig.5b which is indicating a weak interface. In control sample matrix fracture was the primary mode of failure that can be observed in Fig.5c which indicates that load is not transferred from matrix to fibre because of absence of proper interface between matrix and fibre.

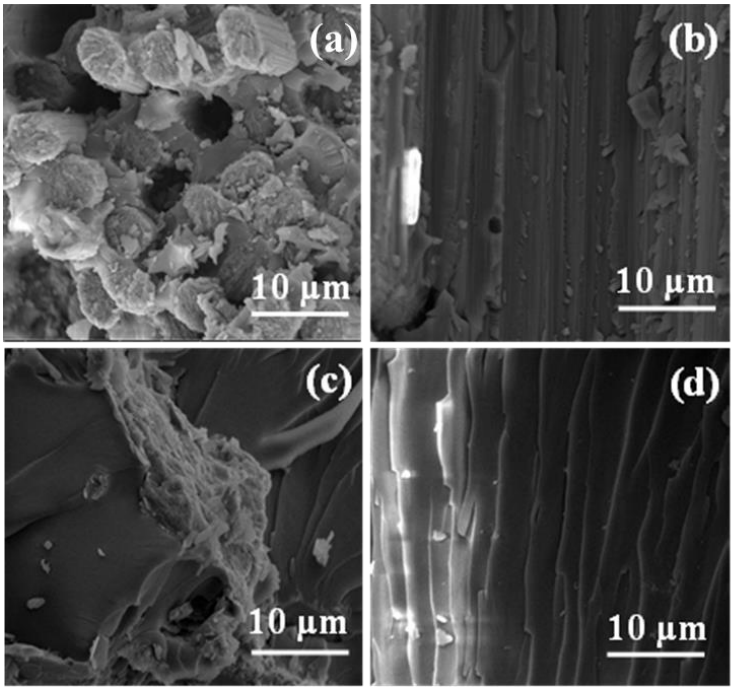

Fig.5. Modes of failure (a) fibre pull-out in 1 g/ltr (b) delamination in 0.5 g/itr (c) matrix fracture in neat (d) deformed matrix in 1 g/ltr

5 Conclusions

Present work proposes EPD as an effective technique for enhancing the interlaminar performance of CFRPs. The following conclusions can be drawn from this investigation.

1. ILSS increases with increase in the nano-filler concentration in the suspension i.e. 0.5 g/ltr has shown an improvement of 15.7 % compared to neat, 1 g/ltr has shown an improvement of 22.8 % compared to neat and 1.5 g/ltr has shown 25.4 % improvement compared to control sample.
2. The strain to failure increases with increasing nano-filler concentration because of the induced stiffening at the interface.
3. SEM analysis confirmed the deposition of the nanofiller and uniform deposition was observed in 1 g/ltr.
4. Fractography revealed various modes of failure i.e. matrix cracking, fibre pull out, delamination and deformed matrix in the modified CFRP composites.

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