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## Accepted Manuscript

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Hybrid enhancements by polydopamine and nanosilica on carbon  
fibre reinforced polymer laminates under marine environment

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**Abstract:**

In this study, two enhancement methods, i.e., toughen the epoxy matrix by commercially available nanosilica and enhance the interfaces of fibres and matrix by autoxidation of dopamine were applied together in carbon fibre reinforced polymer laminates with potential large-scale applicability. Significant enhancements were found for Mode I interlaminar fracture toughness and interlaminar shear strength with the combined addition of nanosilica and polydopamine in the laminates. The enhancement mechanism is proposed as well. Salt spray tests were applied in this study to simulate a marine environment for the laminates. Model I interlaminar fracture toughness and interlaminar shear strength both decreased under the simulated marine environment with an increase in immersion time, but the deterioration was significantly mitigated when nanosilica and polydopamine were added together with still much higher mechanical properties measured after 3 weeks of salt spray immersion than in neat laminate without salt spray immersion, providing promising evidence for maritime engineering applications of such laminates.

**Keywords:**

A. Laminates; B. Fracture toughness; B. Environmental degradation; B.

Interface/interphase

## 1. Introduction

Growing demand exists for carbon fibre reinforced polymer (CFRP) composite materials with enhanced properties, which are essential for applications in engineering fields, especially in harsh environments. As CFRP is a combination of fibre and matrix, its properties are dominated by high strength and stiffness in fibres as well as low strength in the ductile polymer matrix and the interfaces between fibres and matrix. These poor polymer properties and weak interfaces between fibres and polymer significantly limit the applications of CFRP. Consequently, it is of interest to enhance the polymer resin as well as the interfaces between the resin and fibre of the CFRP composites to extend laminate applications in various fields.

Significant work has been done to enhance polymer matrix as well as interfaces in recently years, with some studies focusing on large-scale production and commercialization. The use of nanoparticles to toughen polymer matrix is one promising method, employing such particles as nanosilica, halloysite nanotubes, and carbonaceous nanoparticles such as graphene nanoplatelets and graphene oxide. Improvements in Young's modulus, fracture toughness and tensile strength have been reported [1-6]. However, one of the challenges in using nanoparticles is the achievement of homogeneous dispersion of high weight/volume ratio nanoparticles in matrix while maintaining comparatively low viscosity. The difficulty is that viscous resin systems cannot easily impregnate continuous fibres or fibre fabric during CFRP production. Meanwhile, based on a resin infusion process, the filtering of dense fibre bundles against agglomerated nanofillers can lead to severe segregation and depletion of nanofillers in matrices [7-8], also significantly offsetting the enhancement effects of nanoparticles in laminates. One of the solutions is the use of *in situ* synthesized

methods such as the sol-gel manufacturing process, whereby particle size and excellent distribution are unaffected during any further processes. Several commercially produced nanosilica-modified epoxies are available, such as Nanopox F400, a concentration of 40 wt% nanosilica in diglycidyl ether of bisphenol A (DGEBA) epoxy resin [9], with an average particle size of 20 nm and a narrow range of particle size distribution. In our previous research, only 2 wt% nanosilica added in the epoxy improved the fracture toughness and corrosion rate under a marine environment [9]. Meanwhile Sprenger reported using nanoparticles no longer further improvement the delamination fracture value when the value reached to 500 J/m<sup>2</sup>. Above that value, the dominated delamination fracture of laminate often changes from matrix failure to interfacial failure [10]. Therefore, the addition of a single type of nanoparticle did not further mitigate the occurrence of delamination fracture.

Sizing is a method of wetting out fibre surfaces to improve the poor interfacial adhesion of CFRP. Polydopamine (PDA) is a bionic material which has excellent adhesion to a range of solid surfaces, such as metals, oxides, polymers and ceramics by autoxidation of dopamine in basic aqueous solutions [11]. Recently, it has also been applied to modify nanoparticles such as carbon nanotubes [12], graphene [13] and clay [14], revealing excellent ability to improve the mechanical, thermal and electromagnetic interference shielding performance of polymer matrices. In addition, PDA has been used to modify short carbon fibres, revealing significant improvement in tensile strength and Young's modulus [12]. Furthermore, Yang et al. reported that the catechol groups in PDA were forming hydrogen bonds with polar groups in epoxy [15]. In addition, the interfacial covalent bonding was forming between PDA and epoxy because of the primary and

secondary amine groups in PDA may react with epoxy groups and the amine hardener may react with PDA [16, 17]. We reported using a simple method for surface modification to improve the load transfer between carbon fibre and epoxy matrix, increase the fractured interface friction and reduce unstable crack growth in CFRP composites [18].

The application of CFRP composites in maritime engineering was initially the demand of building lightweight, strong, corrosion-resistant durable naval vessels. CFRP can overcome corrosion problems experienced with steel or aluminium alloys and environmental degradation suffered by wood. As well, CFRP can significantly reduce the weight of a structure but still maintain the desired performance and structural integrity. However, under the marine environment, the mechanical properties of laminates degrade due to UV, moisture, temperature and ageing – creating the potential of accidentally creating fracture. Bastioli et al. reported water aging may strongly affect the matrix behaviour, by producing changes in its chemical and physical nature by itself or in conjunction with other chemical or physical agents such as heat and ultraviolet light [19, 20]. Moreover, the fibre/matrix interface can be degraded by a hydrolysis reaction of unsaturated groups within the resin under marine conditions [21-23]. A concern is the incomplete understanding and shortage database of using fibre reinforced composites as marine structures with long-term durability. Consequently, to efficiently enhance the properties of CFRP and extend its applications in the harsh marine environment, there is interest in improving the mechanical performance at least to offset the deterioration generated by that environment.

Current enhancements to interfacial adhesion rely on sizing wet-out fibre surfaces. However, the inherent poor properties of polymer matrix render these solutions inefficient. Furthermore, polymer matrix enhancement can only toughen the matrix itself, with less

enhancement of the interfaces. In this work, we demonstrate a feasible hybrid method to enhance the laminate, with potential large-scale application under marine environments. Commercially available nanosilica can provide the necessary polymer matrix toughness, while polydopamine on carbon fibre surfaces can provide significant interfacial adhesion among fibres and matrix. With those hybrid enhancements, laminates can offset deterioration under a simulated marine environment and still achieve superior mechanical performance to that displayed by neat laminate without salt water immersion.

## **2. Experiments**

### **2.1. Polydopamine for CFRP interfacial enhancement**

The as-received carbon fabric was submerged in acetone for 48 h to wash off the commercial sizing and impurity. For fabrication of the PDA sizing fibres, 4 g dopamine hydrochloride (Sigma, Australia) was dissolved in a mixed solution of deionized water (4000 mL) and aqueous solution of TRIS (3.6 g tris(hydroxymethyl)aminomethane, 1000 mL deionized water), with magnetic stirring for 30 min. 200 gm unidirectional carbon fibre fabrics (Hexcel, USA) were prepared into 8 layers with the size of 30 cm \*30 cm then placed in a container and the mixed solution was transferred to the container. The container was shaken by a benchtop orbital shaker (Labec, Australia) at 100 rpm for 24 hrs at ambient temperature. Then, the modified carbon fibre fabrics were collected, washed with deionized water several times to remove the residual dopamine, and dried in a vacuum oven at 40 °C for 24 hrs. Finally, the thickness of PDA layer on the carbon fabric was 50-100 nm. From our previous report, approximately 3.2 wt% of polydopamine was coated on the carbon fabric [20].



## 2.2. PDA-SiO<sub>2</sub>-CFRP composites preparation

A vacuum-assisted resin transfer moulding (VARTM) process was used to fabricate the CFRP composites, as shown in the schematic drawing in Fig. 1. In this procedure, a flat metal plate was first treated with a releasing agent. For the PDA-SiO<sub>2</sub>-CFRP, the raw resin was prepared by using a diglycidyl ether of bisphenol A (DGEBA) epoxy resin, Araldite-F (Ciba-Geigy, Australia) to dilute the commercialized Nanopox F400 resin (40 wt% nanosilica) to 2 wt% nanosilica epoxy resin. A piperidine (Sigma-Aldrich, Australia) hardener was added at the ratio of 100:5 by weight while being stirred slowly. A PDA-modified carbon fibre ply stack was next placed on the metal plate between two PTFE films, one above and one below the stack. A 10-um thick non-stick film was inserted in the middle layer of the stack to create the initial delamination. The peel films were placed between two infusion meshes (above and below the peel films). Then the mixture resin was placed in a vacuum oven to preheat to 80 °C and degassed as well. After that, the resin was pumped into the vacuum bag and placed in a hot press machine (Carver Inc. USA) with a pressure at 10 KN/m<sup>2</sup> and curing temperature at 120 °C for 24 hrs. Finally, the cured panel thickness was measured to be approximately 3 mm for all plates and the fibre volume was measured at nearly 32 vol.%. Test specimens were cut from the cured panels by means of bandsaw cutting and polisher polished. As controls for evaluation, pure CFRP and 2% SiO<sub>2</sub>-CFRP were prepared separately. Figure 1 illustrates the hybrid enhancement strategy used in this study.

## 2.3. Characterizations

The Mode I interlaminar fracture toughness was measured using double cantilever beam tests carried out on a universal testing machine (Instron, US) fitted with a 500 N load cell in

accordance with the ASTM D 5528 standard. The dimensions of the test specimen were 125 mm×25 mm×3 mm. Test specimens were clamped in the jaws of the machine via the block hinges with a load rate of 1 mm/min while the load–displacement data was recorded. The fracture surfaces of test specimens were examined using a scanning electron microscope (SEM; Inspect F50, FEI, US). The SEM samples were selected around the pre-crack tip area and coated with gold to form a thin 1 nm conductive layer. The interlaminar shear strength (ILSS) was measured using a 3-point short beam strength test following the ASTM D-2344 standard. The specimens were cut to the dimensions of 50 mm×12 mm×3 mm. A minimum of 8 specimens per batch were tested.

Specimens were placed in a salt spray test machine for periods of 1 and 3 weeks following the ASTM b117 standard. 5 wt% NaCl solvent was used to simulate marine water and the test temperature was 42 °C. Specimens were then washed in running water and oven dried at 60 °C for 48 hrs. Model I interlaminar fracture toughness and interlaminar shear strength were characterized after the immersion.

### **3. Results and discussion**

#### **3. 1. Hybrid enhancement on CRPF laminates**

Figure 2(a) shows load-crack opening displacement (COD) curves obtained from Mode I interlaminar fracture toughness tests for different laminates. The neat CFRP shows a saw-tooth shaped curve which forms as the load increases and decreases alternately, demonstrating unstable energy release during crack propagation. In comparison, for the SiO<sub>2</sub>-CFRP sample, the COD curve shows a saw-tooth shaped curve similar to that of the neat CFRP but with higher load capacity than that of the neat CFRP. For the PDA-SiO<sub>2</sub>-

CFRP specimen, however, the force regularly increases to the peak point and then drops in a relatively smooth movement, while the load capacity increases further, as shown in Figure 2(a). These COD curves indicate that the addition of nanosilica alone can increase the load capacity but may not improve the interface adhesion. With PDA added in the SiO<sub>2</sub>-CFRP specimen, however, the interfacial adhesion also improves [24]. Figure 2(b) shows typical Mode I delamination crack growth resistance curves (R-curves) calculated from the COD curves. Generally, the R-curves grow to a plateau with crack propagation.

The gradual formation of a fibre-bridging zone behind the crack front is the main toughening process in these CFRP composites [25]. The average value of  $G_{IC}$  during propagation is 540 J/m<sup>2</sup> for CFRP and 630 J/m<sup>2</sup> for SiO<sub>2</sub>-CFRP, with about 17% improvement which is attributed to the deflection of the cracking paths because of the presence of the rigid nanosilica particles consuming more energy [9]. The average propagation  $G_{IC}$  value for PDA-SiO<sub>2</sub>-CFRP is 750 J/m<sup>2</sup>, which is a 39% increment compared to that of CFRP, as the PDA can further provide strong adhesions between carbon fibre and epoxy resin [11]. Table 1 shows a summary of the  $G_{IC}$  values for the nanosilica enhanced CFRP and its improvement ratios. As shown in the Table, Tsai et al. reported that compared with neat laminate,  $G_{IC}$  values increased by 8.4% and 14.5% when 10 wt% and 20 wt% silica nanoparticles respectively were added in the laminate [26]. Obviously, the 2 wt% sol-gel form of nanosilica provided a greater increment of the  $G_{IC}$  than the 20 wt% unmodified nanosilica. Similarly, Zeng et al. reported that in laminates modified with 4 wt% and 6 wt% silica nanoparticles, the  $G_{IC}$  values increased by 15% and 19%, respectively [27]. However, further increases in the concentration of nanosilica did not further increased the  $G_{IC}$  value. Meanwhile, Carolan et al. reported the use of a hybrid

of nanosilica and polysiloxane core-shell rubber (CSR) to toughen the  $G_{IC}$ . They found that the use of 8 wt%  $SiO_2$  with 8 wt% CSR significantly improved the  $G_{IC}$  value by 41% compared to that of neat CFRP [28]. In comparison, the hybrid enhancement in the PDA- $SiO_2$ -CFRP of the current study used only 3 wt% PDA and 2 wt% nanosilica to achieve a 39% increment in the  $G_{IC}$  value. This result demonstrates a marked advantage over the use of enhancement of simple matrices by nanoparticles.

Table 1 also shows that the average ILSS value of the neat CFRP laminate is 55.7 MPa; this value increases to 59.9 MPa for  $SiO_2$ -CFRP and 67.8 MPa for PDA- $SiO_2$ -CFRP with increments of 8% and 22%, respectively. In the report of Zhang et al. [29], the ILSS values were 46 MPa and 50.7 MPa for laminates with 2.5 wt% and 10 wt% GO nanoparticles, the values increasing by 1% and 12% respectively compared with those of the neat laminate. Srivastava et al. found that, with 3% carbon blacks (CBs), 3% multi-walled carbon nanotubes (MWCNTs) and 3% graphene nanoplatelets (GnPs) added in the laminate, the ILSS values increased by -29%, 5% and 7%, respectively [30]. Thus a significant advantage has been demonstrated of hybrid enhancement as a feasible way to enhance the interlaminar properties of laminates, compared with single nanoparticle enhancement.

Figure 3 shows a schematic drawing of the proposed toughening mechanisms for different laminates, with SEM images of fracture surfaces. Figure 3(a) shows a clean and smooth surface of the fibres in a CFRP fracture surface, indicating that the fracture mechanism is primarily interfacial debonding. The epoxy resin detaches completely from the carbon fibre surfaces because of weak bonding in the interfaces. This finding indicates that fibre/epoxy debonding is the dominant failure mechanism, and the most likely failure site in the laminates is still the interface. Although the  $SiO_2$ -CFRP fracture toughness

surface is also clean and smooth, as observed in Figure 3(b), the fractured resin surface is rougher than that of the neat epoxy Figure 3(a), because the rigid nanosilica particles can deflect cracking paths, resulting in a higher  $G_{IC}$  and a rougher fracture surface, as shown in Figure 3(b). From our previous publication [18] regarding the PDA-CFRP laminate, with the enhancement on the interfaces, a higher  $G_{IC}$  value has been reported with rough fracture surfaces been observed, as shown in Figure 3(c). In contrast, in the PDA-SiO<sub>2</sub>-CFRP fractured surface, a significantly different interface microstructure is shown in Figure 3(d). A large amount of epoxy adhering to the PDA treated carbon fibre surfaces and the rough fractured epoxy surface indicate that the failure mechanism is a combination of epoxy resin fracture and interface debonding. The development of these microstructures is related to both PDA-enhanced interactions between carbon fibre and epoxy and nanosilica toughened epoxy matrix. Therefore, the overall  $G_{IC}$  value is significantly increased.

### 3.2 Marine environment effects on the hybrid enhancement of laminates

Figure 4(a) shows the Mode I interlaminar fracture toughness  $G_{IC}$  values after 0, 1 and 3 weeks' salt spray testing to simulate marine environment effects on laminate mechanical properties. Generally speaking, the marine environment will deteriorate Mode I interlaminar fracture toughness. As shown in the figure, after a week's salt spray test, the  $G_{IC}$  values decrease to 0.61 KJ/m<sup>2</sup> for SiO<sub>2</sub>-CFRP and 0.72 KJ/m<sup>2</sup> for PDA-SiO<sub>2</sub>-CFRP, respectively. Moreover, the  $G_{IC}$  values continue to decrease, reaching 0.58 KJ/m<sup>2</sup> for SiO<sub>2</sub>-CFRP and 0.68 KJ/m<sup>2</sup> for PDA-SiO<sub>2</sub>-CFRP after 3 weeks' salt spray testing. Such trends of deterioration effects have also been reported previously [9, 31]. After a period of salt water permeation, it is found that laminates began to swell, and the moisture sorption caused by the volume swelling gradually increased. Meanwhile, physical or chemical degradation,

such as hydrolysis of the polymer, chain breakage, creation of small molecules and extraction of these molecules from the composite began, and mass loss of composite occurred [32]. However, the deterioration of the laminate  $G_{Ic}$  values was diminished by the addition of nanosilica, as reported by us previously [9], with further mitigation when PDA and nanosilica were added together. As a result, the  $G_{Ic}$  values of SiO<sub>2</sub>-CFRP and PDA-SiO<sub>2</sub>-CFRP after 3 weeks' salt spray testing were still 7% and 26% higher respectively than those of the neat CFRP (0.54 KJ/m<sup>2</sup>) without any salt spray test. This finding shows that the hybrid enhancement significantly improved the Mode I interlaminar fracture toughness under the marine environment.

Figure 4(b) shows that the ILSS values of all laminates decreases after the salt spray test. The highest ILSS result after the salt spray test still comes from the PDA-SiO<sub>2</sub>-CFRP laminate, with reduction rates of 5% in 7 days and 9% in 21 days compared with that in 0 day as shown in Table 2. For the SiO<sub>2</sub>-CFRP laminate, it has the similar reduction rates of 5% in 7 days and 9% in 21 days, respectively. However, CFRP has a reduction rate of 9% in 7 days observed indicates that SiO<sub>2</sub> or PDA-SiO<sub>2</sub> are applied in CFRP can efficiently reduce the degradation of mechanical properties under marine environment. Interestingly, the ILSS value of the SiO<sub>2</sub>-CFRP laminate after the 3-week salt spray test decreases to a value which is even 2.3% lower than that of the neat CFRP without the salt spray test. However, the ILSS value of the PDA-SiO<sub>2</sub>-CFRP laminate is still 11% higher than that of the unmodified CFRP. Hence, it can be concluded that in terms of mechanical properties, PDA-SiO<sub>2</sub>-CFRP laminate is superior to SiO<sub>2</sub>-CFRP laminate under marine environment.

Figure 5 shows SEM images of interlaminar fracture toughness surfaces after different salt spray periods. The morphologies of the fracture surfaces changed significantly with the

salt spray duration. Figures 5(a)-(c) shows SEM images of the fracture surfaces of SiO<sub>2</sub>-CFRP without and after 1 and 3 weeks of salt spray tests. The fracture surfaces become smoother as the salt spray duration increases. Especially in Figure 5(c), the fracture surfaces of SiO<sub>2</sub>-CFRP after 3 weeks' salt spray were very similar to that of the neat CFRP fracture surface shown in the SEM image of Figure 3(a). This result indicates that, due to salt water permeation, the nanosilica/resin interfaces have been attacked by salt water, weakening the ability of rigid silica particles to deflect cracking paths. Therefore, the fracture surface of SiO<sub>2</sub>-CFRP becomes smoother. For PDA-SiO<sub>2</sub>-CFRP, as shown in Figure 5(d)-(f), significant amount of resin still adheres to the PDA treated carbon fibre surfaces. Although the resin surfaces are less rough, the PDA layers do not show significant damage. Therefore, most of debonding comes from the epoxy resin fracture, indicating that the salt water on the PDA layer may serve as an effective layer to slow the deterioration effects of swelling on the interfaces.

#### 4. Conclusion

In this study, with the use of hybrid enhancements of CFRP laminates by nanosilica and polydopamine, CFRP shows significant improvement of mechanical properties. Increments of 39% in Mode I interlaminar fracture toughness and 26% in interlaminar shear strength were obtained for the PDA-SiO<sub>2</sub>-CFRP compared with those of the neat CFRP. The enhanced mechanism was mainly the result of the enhancement of interfacial bonding among epoxy and carbon fibres by the PDA and the toughening of rigid nanosilica particles by the epoxy matrix. In the marine environment, the mechanical properties deteriorated with an increase in time. However, that deterioration could be effectively offset by the

combined enhancements from nanosilica and PDA, an outcome that successfully demonstrates a promising use of CFRP laminates under marine environments.

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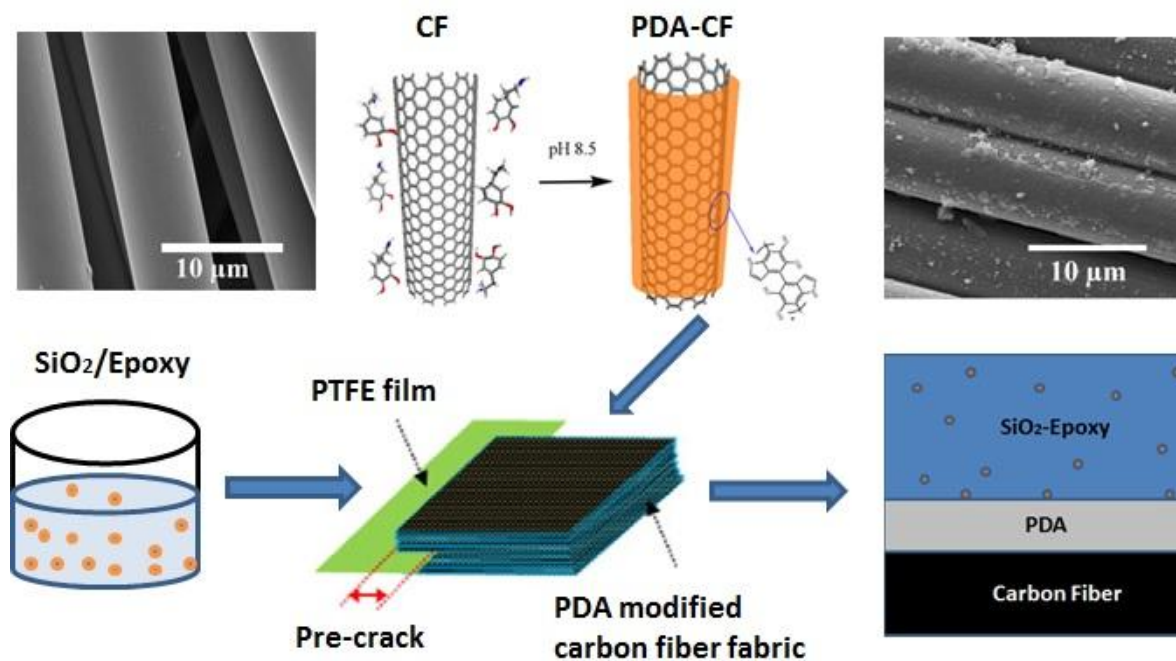


Figure 1. Schematic drawing demonstrating the hybrid enhancement strategy by toughening epoxy matrix with nanosilica and enhancing the interface by applying polydopamine on carbon fibre surfaces.

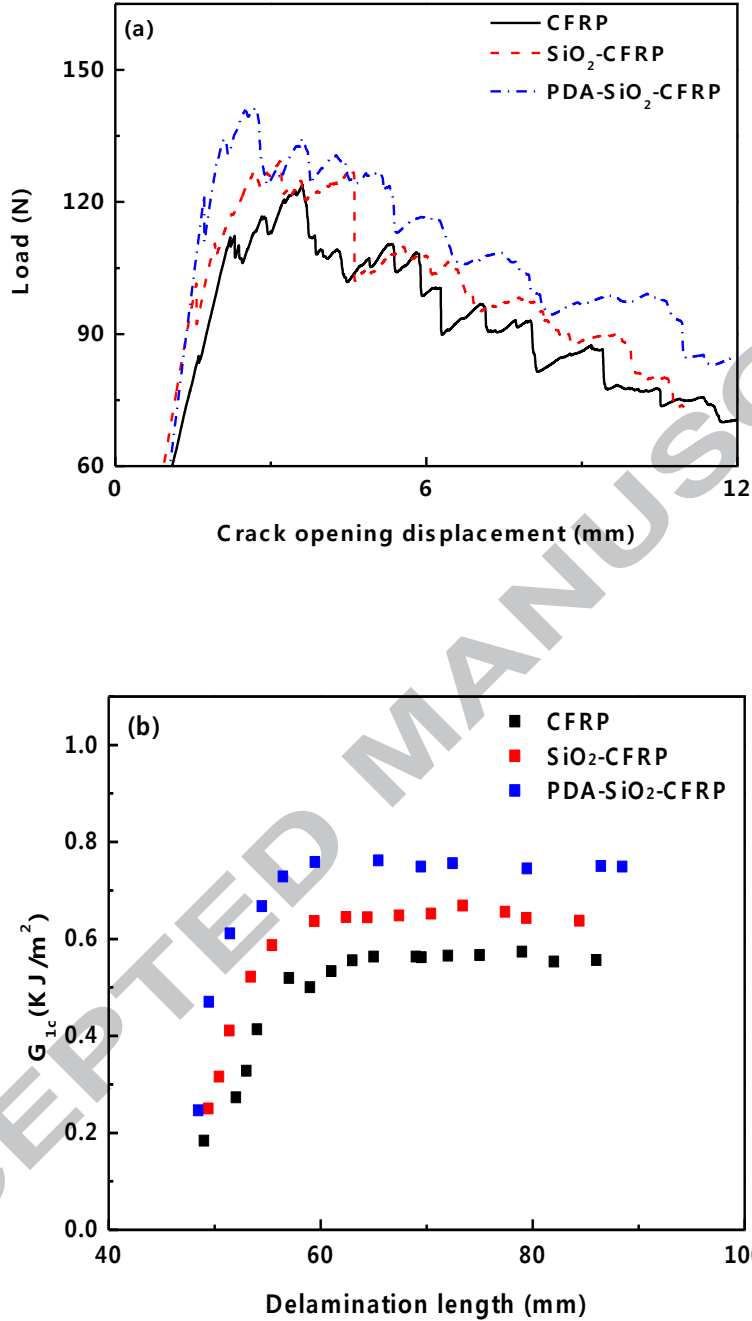


Figure 2. (a) Typical load-crack opening displacement curves obtained from Mode I interlaminar fracture toughness tests and (b) typical Mode I delamination crack growth resistance curves (R-curves) for different laminates.

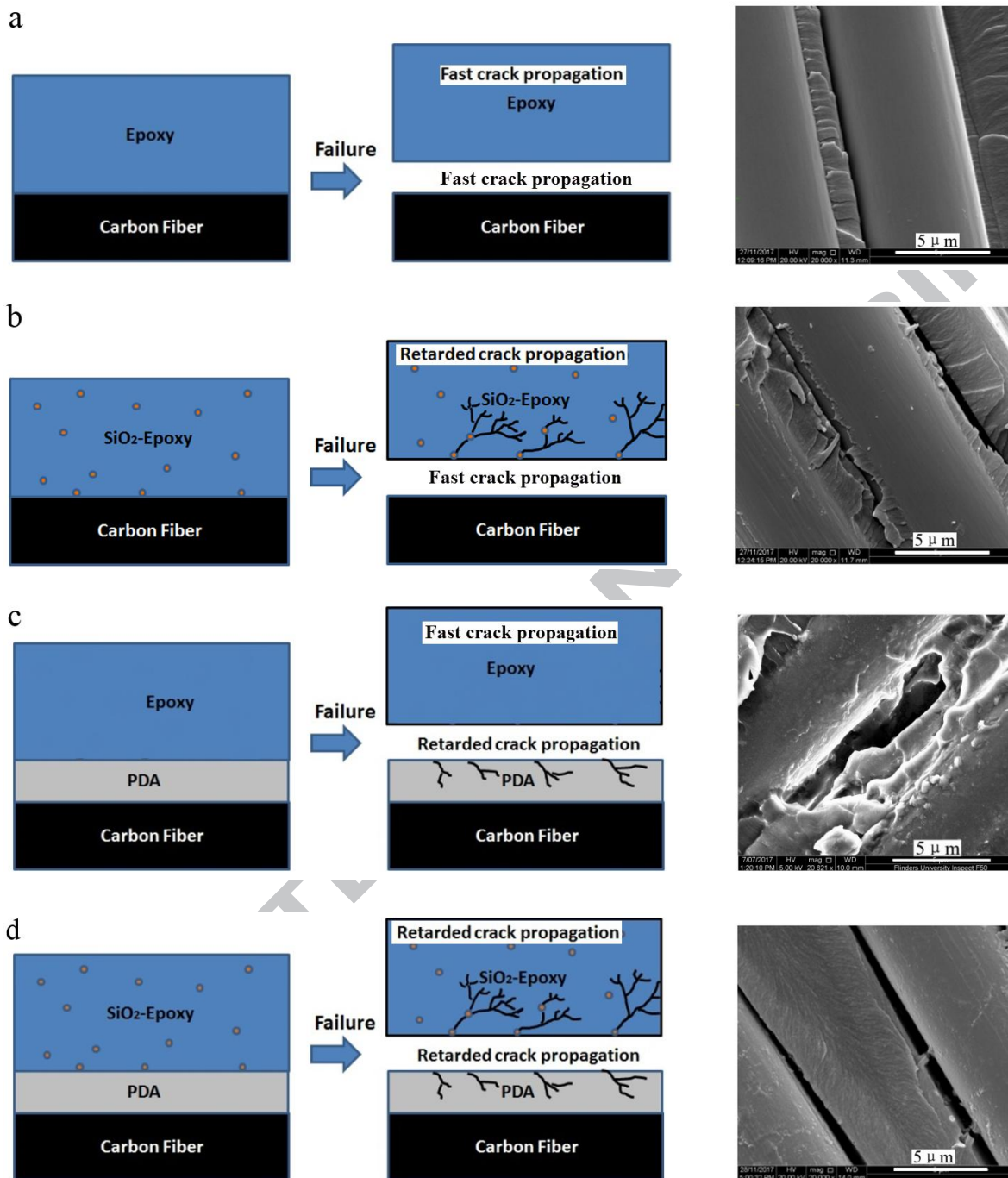


Figure 3. Schematic drawings of failure mechanism for (a) neat CFRP; (b) SiO<sub>2</sub>-CFRP; (c) PDA-CFRP and (d) PDA-SiO<sub>2</sub>-CFRP, with corresponding SEM images of the fractured surfaces after model I interlaminar fracture toughness characterizations.

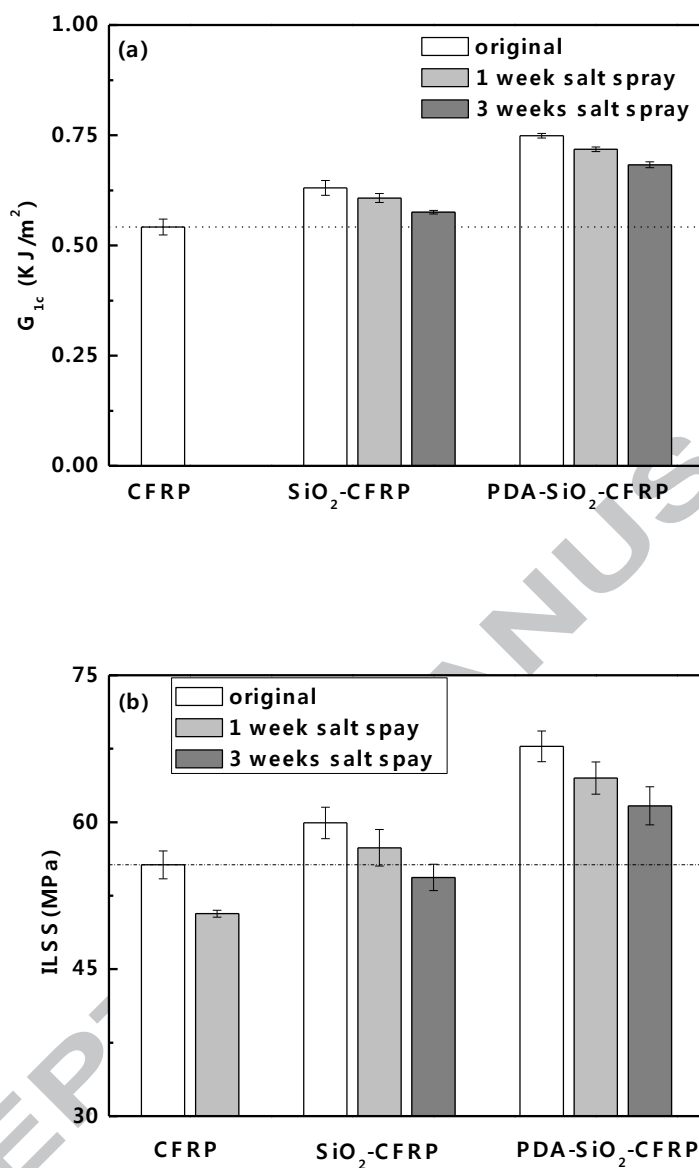


Figure 4. (a) Model I interlaminar fracture toughness and (b) interlaminar shear strength of neat CFRP, SiO<sub>2</sub>-CFRP and PDA-SiO<sub>2</sub>-CFRP laminates with different salt spray durations used to simulate marine environment effects on laminate performance.



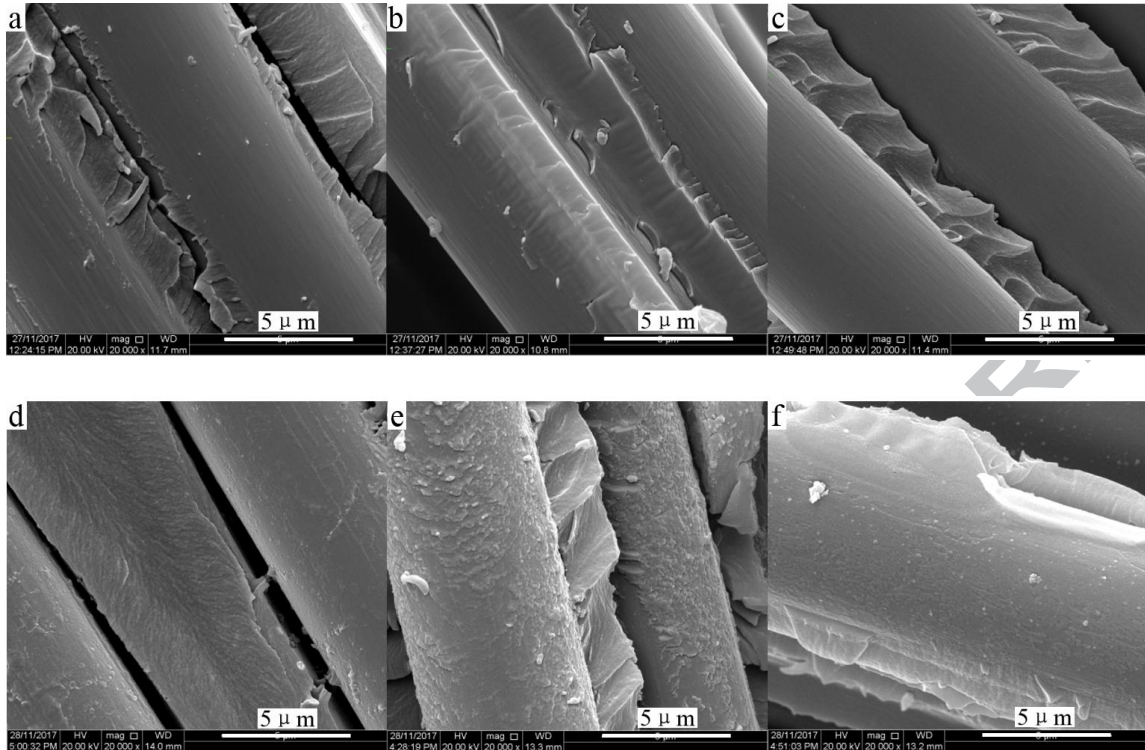


Figure 5. SEM images of fracture surfaces of (a)-(c) SiO<sub>2</sub>-CFRP and (d)-(f) PDA-SiO<sub>2</sub>-CFRP laminates (a) and (d) before salt spray testing and (b) and (e) after 1 week and (c) and (f) 3 weeks of salt spray testing.

Table 1. Selected interlaminar fracture toughness and interlaminar shear strength values with simple nanosilica enhancement on matrix or with current hybrid enhancement.

	$G_{IC}$ (KJ/m <sup>2</sup> )	Improvement (%)	Ref.
CFRP	0.54 ± 0.02	-	
2% SiO <sub>2</sub> -CFRP	0.63 ± 0.02	17	
3% PDA-2% SiO <sub>2</sub> -CFRP	0.75 ± 0.01	39	
GFRP	0.83	-	26
10% SiO <sub>2</sub> -GFRP	0.90	8	
20% SiO <sub>2</sub> GFRP	0.95	15	
CFRP	0.54	-	27
4% SiO <sub>2</sub> -CFRP	0.62	15	
6% SiO <sub>2</sub> -CFRP	0.64	19	
8% SiO <sub>2</sub> -CFRP	0.62	15	
10% SiO <sub>2</sub> -CFRP	0.62	15	
12% SiO <sub>2</sub> -CFRP	0.61	13	
CFRP	1.25	-	28
4% SiO <sub>2</sub> -CFRP	1.17	-6	
8% SiO <sub>2</sub> -CFRP	1.31	5	
8% SiO <sub>2</sub> -4% CSR-CFRP	1.52	22	
8% SiO <sub>2</sub> -8% CSR-CFRP	1.76	41	
	ILSS (MPa)	Improvement (%)	
CFRP	55.7 ± 1.4	-	
2% SiO <sub>2</sub> -CFRP	59.9 ± 1.6	8	
PDA-2% SiO <sub>2</sub> -CFRP	67.8 ± 1.6	22	
CFRP	45.5	-	29
2.5% GO-CFRP	46.0	1	
10% GO-CFRP	50.7	11	
CFRP	44.6	-	30
3% CB-CFRP	31.8	-29	
3% MWCNTs-CFRP	46.7	5	
3% GnP <sub>s</sub> -CFRP	47.5	7	

Table 2. The reduction rate of salt spray test compared to properties at 0 day of each specimen

Salt spray test		7 days	21 days
$G_{IC}$	CFRP	NA	NA
	SiO <sub>2</sub> -CFRP	-4%	-9%
	PDA-SiO <sub>2</sub> -CFRP	-4	-9%
ILSS	CFRP	-9%	NA
	SiO <sub>2</sub> -CFRP	-5%	-9%
	PDA-SiO <sub>2</sub> -CFRP	-5%	-9%

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