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Long-term moisture effects on the interfacial shear strength between surface treated carbon fiber and epoxy matrix

Bin Yu [a], Zhenyu Jiang [a,b], Jinglei Yang [a,*]

[a] School of Mechanical and Aerospace Engineering, Nanyang Technological University, Singapore 639798, Singapore
[b] School of Civil Engineering and Transportation, South China University of Technology, Guangzhou 510640, China

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ABSTRACT

In recent years, carbon fiber reinforced polymer (CFRP) composites have found increasing applications in marine and offshore area, where the CFRP components are subjected to a persistent attack of moisture. The performance degradation of composites under those critical service conditions becomes a key issue. In this work, silane coating and multiwalled carbon nanotubes were applied on carbon fibers to enhance the fiber/matrix interfacial bonding strength. The long-term effects of moisture on the interfacial shear strength (IFSS) of the composites in underwater environments, such as de-ionized water and simulated seawater, have been studied using single fiber microbond method. The silane coating and carbon nanotube-modified silane coating are found to contribute 14.5% and 26.3% increase in IFSS of the CFRP in dry air, and well maintain this improvement during a 120-day immersion test in de-ionized water and simulated seawater.

1. Introduction

Carbon fiber reinforced polymer (CFRP) composites have attracted a great amount of interest from the offshore oil industries because of their outstanding specific mechanical properties [1–4]. For example, CFRPs based composite risers integrated with titanium liner become a promising choice for offshore oil exploration and production to replace metal risers, which are completely immersed in deep seawater. It is well known that interface plays an important role in dominating the final performance of CFPRs [5]. In addition, interface also affects the hygrothermal aging behaviors of composites, and stability of interfacial region is crucial to the CFRPs' lifetime performances [6–8], especially in deep-sea application. Therefore, sufficient resistance to the negative influence from moisture attack is one of the key issues in development of CFRPs for deep-sea applications, which necessitates understanding the effects of moisture on the interfacial properties.

The mechanical degradation of CFRPs under attack of moisture is generally related to the plasticization of matrix near interphase, internal stress induced by moisture and chemical hydrolysis of the interphase [9–13]. However, the studies on long-term behavior of CFRPs in a hygrothermal environment are limited heretofore, and a reliable prediction of the long-term behavior of the CFRP components under such kind of service condition still remains a formidable task [14].

The effects of moisture on the interfacial properties of FRPs have been investigated through various tests of laminates, such as transverse tensile test [15], flexural test [16] and interlaminar shear test [17,18]. However, these macro-level characterizations are influenced to a large extent by the moisture resistance of matrix materials and the geometrical feature of composites, which may disturb the study on the properties of fiber/matrix interface [19,20].

In recent years, a few microscopic mechanical testing methods have been developed to investigate the fundamental mechanical properties of interphase between fiber and matrix, including single fiber push-out test [21–23], fiber fragmentation test [24,25], and single fiber microbond test [26–28], among which it is found that the specimens for the microbond test are more efficient to achieve a good soaking of polymer matrix and fiber/matrix interface due to the small volume of resin droplet size [19,29].

In this work, a surface treatment with silane coupling agent and carbon nanotubes (CNTs) is applied on carbon fibers in order to enhance the interfacial bonding between the fibers and epoxy matrix. The carbon fibers with deposited epoxy droplets have been immersed in de-ionized water and simulated seawater for about four months. The long-term effects of moisture on the interfacial shear strength of the CFRPs are evaluated through single fiber

* Corresponding author. Tel.: +65 67906906.
E-mail address: mjlyang@ntu.edu.sg (J. Yang).

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microbond test. The mechanisms of property degradation are explored based on the scanning electron microscopic (SEM) characterization of the fracture surfaces.

2. Experimental

2.1. Materials

Commercially available HexTow IM2C carbon fibers with an average diameter of 5.2 μm are used as the primary reinforcement. Nanocyl NC7000 multiwalled carbon nanotubes (MWCNTs) are used as the secondary reinforcement. The average diameter and length of NC7000 CNTs are 9.5 nm and 1.5 μm, respectively. The epoxy matrix, Epolam 5015 resin, is a mixture of Bisphenol F and Bisphenol A resins supplied by Axson Technologies. The Epolam 5015 hardener consists of isophoronediamine and polyoxypropylenediamine. (3-glycidyloxypropyl) trimethoxysilane coupling agent is obtained from Sigma–Aldrich. Seawater is simulated by dissolving sea salt (SIEM Trading PTE Ltd) in tap water to make a solution with a salinity of 3.5%.

2.2. Sample preparation and moisture conditioning

In this work, three composite systems with different surface treatments are compared and two moisture conditions are imposed to those composites, as listed in Table 1.

The application of silane coating is based on the fact that the (3-glycidyloxypropyl) trimethoxysilane can be hydrolyzed to produce silanol, which forms chemical bond with hydroxyl on the sizing of carbon fibers on one side [30–33]. On the other side, functional group containing epoxide group can be cross-linked with epoxy matrix under the action of hardener to produce a chemical bond. In addition, some silanol groups that do not react with the sizing on the carbon fibers can condense with themselves, forming Si–O–Si networks. By this way, the polymer matrix and carbon fibers are tightly bound to each other [34].

A mixture of ethanol and water with weight ratio of 95:5 was used as solvent for silane coupling agent. PH value of the solvent was adjusted to 5 using acetic acid, and then (3-glycidyloxypropyl) trimethoxysilane was added into the solvent to yield a 2% final concentration. The solution was ultrasonicated for about 30 min in bath sonicator to get homogeneous. The introduction of acid treated MWCNTs with loading of 0.05 wt% into the solution was achieved by ultrasonicating using a Misonix 3000 sonicator for 30 min before the aforementioned procedure. Individual carbon fiber was soaked in the prepared solution sufficiently and dried naturally. A resin droplet was then applied onto the fiber and cured in situ at room temperature for 24 h followed by the post-curing at 80 °C for 16 h [34].

Table 1
Sample codes for the composite systems with two kinds of fiber surface treatment method and immersed in the two water environments.

Sample code	Fiber surface treatment	Water
CF	Non-treated	–
SL-CF	Silane treated original CF	–
CNT/SL-CF	CNT modified silane treated original CF	–
CF-DIW	Non-treated	De-ionized water
SL-CF-DIW	Silane treated original CF	De-ionized water
CNT/SL-CF-DIW	CNT modified silane treated original CF	De-ionized water
CF-SW	Non-treated	Seawater
SL-CF-SW	Silane treated original CF	Seawater
CNT/SL-CF-SW	CNT modified silane treated original CF	Seawater

The microbond specimens were immersed in de-ionized water and simulated seawater for up to 120 days at ambient temperature.

2.3. Characterization and mechanical tests

The surface topography of fractured microbond specimen and carbon fibers was characterized by a field emission scanning electron microscope (FESEM, JEOL JSM 7600F).

Microbond tests were carried out using an in-house developed tester equipped with a 250 g force load cell. The details of the device and testing parameters can be found in our previous work [34]. The interfacial shear strength (IFSS) τ was determined using the equation below, assuming the interfacial shear stress keeps constant along the fiber:

$$\tau = \frac{F}{\pi D l} \quad (1)$$

where F is the maximum pull out force, D is the fiber diameter, l is the embedded length. For each data point, more than 20 valid testing results were collected in order to offset the scattering of the measured results.

3. Results and discussion

3.1. Surface morphology of carbon fibers and epoxy droplet

Fig. 1 shows the SEM micrographs of the carbon fibers with different treatments immersed in the two water systems. It can be seen that surfaces of as-received carbon fibers are very smooth regardless of immersion (see Fig. 1a–c). In Fig. 1c some salt from seawater deposited on the fiber surface is clearly visible. Fig. 1d–f shows much rougher fiber surface of silane treated carbon fibers. After soaking in the two kinds of water, the silane coating becomes thicker due to the diffusion of water. The salt deposit is also found on the fiber immersed in simulated seawater (Fig. 1f). Fig. 1g–i shows the morphology before and after immersion for the carbon fibers treated with MWCNT-doped silane coating. CNTs are found well dispersed on the carbon fiber surface even after immersing into de-ionized and simulated seawater for 120 days. Fig. 2a–c compares the surface morphology of epoxy droplets before and after immersing in the two water systems. In contrast to the dry sample, which looks smooth and clean (Fig. 2a), the resin droplet steeped in de-ionized water shows the wrinkled surface (Fig. 2b), whereas the resin droplet steeped in simulated seawater seems still smooth and partially covered by salt coating, as shown in Fig. 2c.

3.2. Microbond test

During the 120-day immersion tests, a few microbond specimens were took out and tested at set intervals. Fig. 3 gives the measured interfacial shear strengths for the three composite systems during the immersion test in de-ionized water and simulated seawater. The application of silane coating onto carbon fibers leads to an increase of 14.5% in IFSS of composites in dry air, from 83.8 MPa to 96.0 MPa. This improvement is ascribed to a strong chemical linkage formed between silane coating and epoxy matrix during curing process on one side. On the other side, the free silanol groups (Si–OH) of silane can react with the C–OH groups on the original sizing of carbon fibers and form Si–O–C linkage between silane coating and commercial sizing on fiber surface [34]. When MWCNTs are incorporated into the interphase, the IFSS increases 11.7% further over that of SL-CF. The additional improvement is attributed to the increased friction along interface and the restrained microcracks propagation caused by CNTs [34,35]. In