Enhancement of Mechanical Properties of FRP Composites with Silica Nanoparticles

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Abstract. To enhance the mechanical behavior of fiber-reinforced polymers (FRPs), the epoxy and vinyl ester resin modified by silica nanoparticles at 1, 2, 3, and 4 weight percent (wt%) were investigated. Tests of fracture toughness were conducted, and scanning electron microscopy (SEM) of the fracture surface was proposed to identify the toughening mechanism. In addition, impregnated fiber roving made of modified resin was studied for improvements in tensile strength and stiffness. The addition of silica nanoparticles to epoxy and vinyl ester resin resulted in various promotions in their mechanical properties. The fracture toughness and impact strength of the epoxy resin in the presence of 3 wt% nanoparticles were increased by 12% and 49%, respectively, compared with the virgin epoxy resin. Furthermore, the corresponding of the vinyl resin with 3 wt% nanoparticles were 20% and 94%. SEM of the fracture surface displayed a relatively rough surface with tortuous cracks, thereby leading to higher fracture toughness of the modified resin system. The tensile strength of the impregnated basalt fiber roving made of the modified vinyl resin was obviously improved, and results showed that 18% promotion was obtained at a particle content of 3 wt%. In addition, the modified epoxy resin had less tensile strength enhancement to basalt fiber roving. Damage mechanisms of resin with nanoparticles were analyzed and differences due to the varying nanoparticle content identified.

Keywords: Mechanical properties · Fracture toughness · Silica nanoparticles · Impregnated roving

1 Introduction

With the rapid development of marine structure, a serious problem of steel bars corrosion has gradually become prominent, and maintenance costs continue to increase [1]. Particularly, steel-reinforced concrete structures are always exposed to corrosive environments, which aggravate their deterioration. Fiber-reinforced polymer (FRP) composites have been widely used in replacing steels, due to their light weight, high strength, and high corrosion resistance [2, 3].

As common raw materials for matrices in FRP, epoxy and vinyl ester resins have a poor resistance to crack occurrence and development because their highly crosslinked structure [4]. Therefore, research on modification and performance improvement of resin

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to overcome this brittleness problem is of significant interest. Enhancing the toughness of epoxy and vinyl eater resins can be obtained by filling various materials, such as silica particles [5], rubber particles [4], nanoclay [6], and core-shell nanoparticles [7]. Among the particles mentioned above, the influence of silica nanoparticles on toughness of epoxy resin have been investigated in recent studies [8, 9]. The addition of silica nanoparticles increased the fracture toughness of resin, and the fracture toughness rose approximately linearly with the increased particle concentration [10]. The toughening mechanism was revealed by SEM that some of the nanoparticles debonded and cavitated, resulting in an increase of fracture toughness and Young's modulus of modified resin [10, 11]. In summary, as a rigid particle, silica nanoparticles can not only increase the mechanical behavior of epoxy resin, but also improve the elastic modulus, so it was selected in this study.

It should be noticed that the mechanical behavior of FRP composites can also be improved by silica nanoparticles. For instance, a 20% and 35% increase of tensile and flexural strength of carbon FRP can be achieved, respectively, at a silica nanoparticle content of 3%, which implied that matrix can dominate and influence the static mechanical properties of FRP [5]. Nevertheless, the samples in previous studies were primarily made of carbon and glass fiber. Basalt fibers are newly developed environment friendly material produced from volcanic rock [12]. Basalt FRP (BFRP) exhibits nearly 30% higher strength and modulus in a similar cost compared with glass FRP, and a better chemical stability [12, 13]. However, a low tensile strength retention of BFRP bars in alkaline solution was revealed [14], indicating that its low durability must be overcomed. Therefore, the mechanical behavior improvement of BFRP filled with silica nanoparticles is of important interest.

In this paper, the fracture toughness and impact strength of epoxy and vinyl ester resins modified by silica nanoparticles were investigated, and SEM of the fracture surface was conducted to identify the toughening mechanism. A comprehensive study of effect of nanoparticles on FRP properties is of significant interest, eapecially BFRP, which was conducted by tests of impregnated fiber roving.

2 Materials and Specimens

Two types of resin casting specimens for fracture toughness and impact tests were conducted in this study. A standard diglycidyl ether of bisphenol A epoxy resin with an epoxide equivalent weight of 196 g/eq was select, which was supplied by Zhongbo new materials, Anhui, China. Furthermore, the vinyl resin used in this study was a bisphenol-epoxy vinyl ester resin, DION 9102, supplied by Reichhold, US. Both resins were cured at a high temperature. First, the viscosity of pure epoxy/vinyl resin was reduced by heated to 60 °C for 1 h. Subsequently, resin and silica nanoparticles were mixed using a laboratory stirrer (3000 rpm) for 0.5 h at 60 °C and ultrasonic treatment for 2 h and then degassed in vacuum at -100 kPa for 2 h at 60 °C. The silica nanoparticle was purchased from Alading (China) with an average diameter of 30 nm. Four kinds of additive amount of silica nanoparticles were studied, which were 1,2,3, and 4 wt%, respectively. After the vacuum was removed, the curing agent was filled into the resin, then the epoxy and vinyl mixture was poured into a mold to cured at 168 °C and 128 °C for 2 h, respectively. After which, the cured specimens were obtained.

Furthermore, the tensile properties of FRP made of modified resins were performed by tensile tests of impregnated roving. The matrix of impregnated roving was fabricated through the same method proposed above. The fiber roving was passed through a resin bath and then stretched and fixed on a steel frame, which was placed into an oven and cured with 168 °C and 128 °C for 2 h, respectively. Figure 1 depicts the specimens of resin castings and impregnated roving.

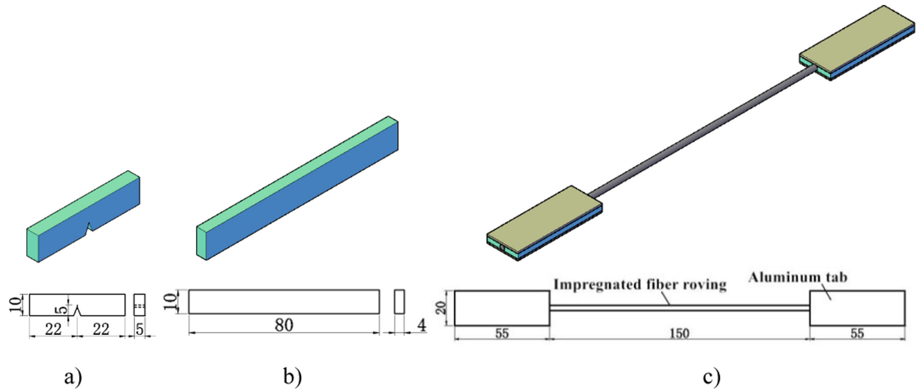


Fig. 1. Specimen geometry (dimensions in mm) a) fracture toughness samples, b) impact samples, c) impregnated roving.

3 Test Setup and Loading Procedure

Fracture tests were conducted to determine the fracture toughness of epoxy and vinyl ester resins. Based on the ASTMD5045–99, the type-A specimen was selected, which was fixed on an universal testing machine AG-X plus (SHIMADZU, Japan) and a load of 10 mm/min was applied, as shown in Fig. 2. Furthermore, unnotched specimens were used in impact tests with a chary test device TS-PIT501JA (Wance, China) according to ISO179–1:2010.

According to ISO 9163:2005, the tensile tests of the impregnated fiber roving were conducted. Prepared specimens were fixed on the universal testing machine by strengthened aluminum tab anchors, as shown in Fig. 2c. The two ends of the impregnated roving were anchored to the aluminum tabs with epoxy resin (from Sanyu, Japan) after polished with sandpaper. A load rate of 0.2 mm/min was adopted. Furthermore, an optical extrometer with an accuracy of ± 0.001 mm was carried out to measure the strain. The sensors with a gauge length of 100 mm were distributed on the surface of the impregnated roving. Ten specimens were performed for each type of specimen and at least six valid data were achieved.

a) b) c)

Fig. 2. Tests device and specimen configuration: a) fracture toughness, b) impact, c) impregnated roving.

4 Fracture Toughness Tests Results and Discussions

The formula for fracture toughness, K_{IC}, is given as follow

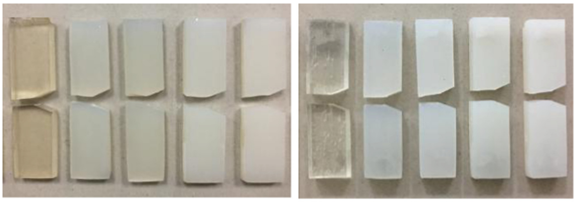
$$K_{IC} = \left(\frac{P_Q}{BW^{1/2}}\right) f\left(\frac{a}{W}\right) \tag{1}$$

Where P_Q is load, B is the thickness of specimen, W is the depth of specimen, a is the length of the pre-opening crack. Then, f(x) in Eq. 1 can be calculated as

$$f\left(\frac{a}{W}\right) = f(\tau) = 6\tau^{1/2}\frac{\left[1.99 - \tau(1-\tau)\left(2.15 - 3.93\tau + 2.7\tau^2\right)\right]}{(1+2\tau)(1-\tau)^{3/2}} \tag{2}$$

Table 1. Results of fracture toughness tests

Material code		E	E1	E2	E3	E4	V	V1	V2	V3	V4
K_{IC} (MPa·m$^{1/2}$)	Mean	2.01	2.12	2.22	2.25	2.38	1.44	1.44	1.54	1.73	1.67
	CV(%)	6.46	1.30	1.80	5.34	2.52	3.47	0.69	3.90	3.47	2.99



a) b)

Fig. 3. Failure modes of fracture toughness tests samples made of a) epoxy, b) vinyl.

K_{IC} can be obtained by substituting Eq. 2 into Eq. 1.

All the specimens of the fracture toughness tests showed the same failure mode, fracturing along the pre-opening crack, as shown in Fig. 3. Table 1 lists the fracture toughness test results from this study. The fracture toughness of epoxy resin significantly rose as silica nanoparticles content increased. For vinyl ester resin, filled with slight nanoparticles had no effect on the fracture toughness of the resin. With the content of silica nanoparticles further rose, the value of fracture toughness began to increase gradually. This indicates that the addition of silica nanoparticles allows the resin to show a better fracture behavior, as shown in Fig. 4.

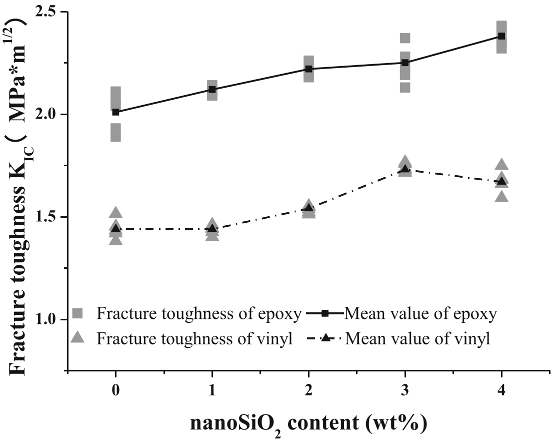
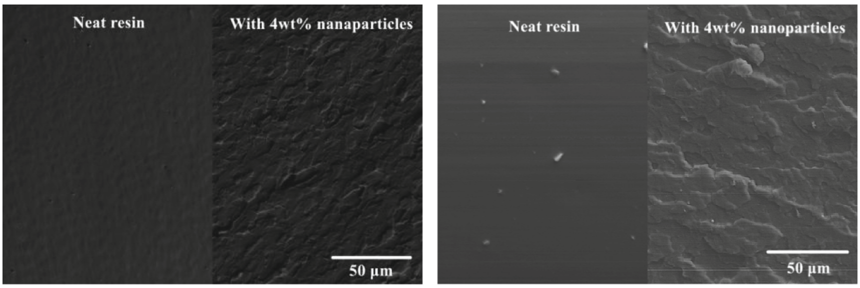


Fig. 4. Fracture toughness of nanocomposites versus weight fraction of silica nanoparticles.



a) b)

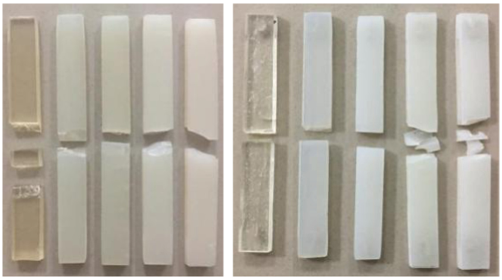
Fig. 5. SEM micrographs showing fracture surfaces of specimens made of a) epoxy, b) vinyl.

Figure 5 shows that SEM images of the fracture surfaces of the specimens without and with 4 wt% nanoparticles at a low magnification. It was clear that the fracture surface of the resin changed from a smooth plane to a rough one after the modification of the nanoparticles. The toughening mechanism can be concluded that silica nanoparticle act as a barrier in the propagation path of microcracks, which means that nano-silica has an adverse effect on the microcrack development in the resin. In order to extend, cracks have to bypass the nanoparticles by the debonding of the interface between the matrix and nanoparticles. Furthermore, cracks can also continue to extend through changing the develop direction in front of a nanoparticle. Both interface debonding and crack deflection will lead to increased fracture toughness and fracture energy. Which indicates that silica nanoparticles are beneficial to the fracture energy of epoxy and vinyl ester resins (Table 2).

5 Impact Tests Results and Discussions

Table 2. Results of impact tests.

Material code		E	E1	E2	E3	E4	V	V1	V2	V3	V4
Impact strength α_{cU} (MPa)	Mean	14.6	21.0	20.7	21.8	21.7	10.8	12.7	16.8	20.9	19.5
	CV(%)	5.48	0.95	7.25	5.50	5.07	5.56	2.36	4.17	5.74	7.18



a) b)

Fig. 6. Failure modes of impact tests samples made of a) epoxy, b) vinyl.

Calculate the Charpy impact strength of specimens, α_{cU}, using the following equation:

$$\alpha_{cU} = \frac{E_c}{h \cdot b} \times 10^3 \tag{3}$$

Where E_C is corrected energy absorbed by specimen, h is the thickness of specimen, b is the width of specimen.

Impact tests were conducted and the failure mode was plotted in Fig. 6. The specimens were ruptured from the middle, which is the position impacted by the pendulum. By observing the two curves in Fig. 7, it can be seen that silica nanoparticles had similar effect on impact strength compared with fracture toughness. The impact strength of epoxy resin increased obviously after filling in slight silica nanoparticles, and the strength

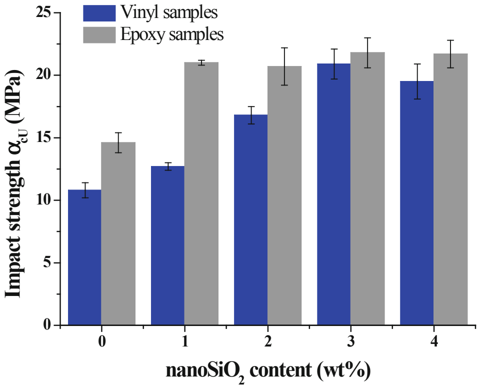
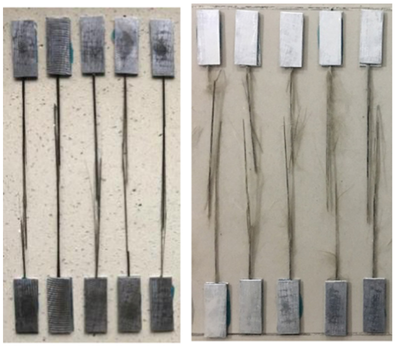


Fig. 7. Impact strength of nanocomposites versus weight fraction of silica nanoparticles.

enhancement was limited as the particle content increased. This indicates that the silica nanoparticles benefits the impact performance of epoxy resin, which can be mainly attributed to that the microcracks in the resin are restrained by the nanoparticles. Similar phenomenon can be observed in specimens made of vinyl ester resin.

6 Tensile Tests Results and Discussions



a) b)

Fig. 8. Failure modes of tensile tests of impregnated roving samples made of a) epoxy, b) vinyl.

The tensile properties of FRP made of modified resins were conducted by tensile tests of the impregnated fiber roving. Two types of specimens were carried out, which were made of: (1) epoxy resin and basalt fiber (EBR) and (2) vinyl ester resin and basalt fiber (VBR). Different failure modes of EBR and VBR specimens were obtained from the tests, as shown in Fig. 8.

The breaking stress σr is given by the equation:

$$\sigma_r = \frac{F_r \times \rho_g}{10^{-3}\rho_l} \tag{4}$$

Where F_t is breaking force, ρ_g is the density of fiber used for roving, ρ_1 is exact linear density of roving. The modulus of elasticity in tension, E_r, can be obtained from the following formula:

$$E_r = \frac{F \times \rho_g}{10^{-3}\rho_l} \times \frac{L_0}{\Delta L} \tag{5}$$

Where F is measured force corresponding to ΔL, ΔL is the elongation produced by force F, L_0 is the gauge length of extensometer (Table 3).

Table 3. Results of tensile tests of the impregnated roving

Material code		EBR					VBR				
		E	E1	E2	E3	E4	V	V1	V2	V3	V4
Breaking stress σ_r (MPa)	Mean	2443	2485	2471	2465	2464	2074	2239	2421	2456	2454
	CV(%)	4.38	5.92	3.28	4.38	5.72	4.92	7.19	4.50	4.52	2.81
Modulus of elasticity E_r (GPa)	Mean	79.4	81.2	81.7	81.6	81.0	81.3	82.0	82.2	82.7	81.4
	CV(%)	4.16	1.60	2.57	1.72	2.72	5.29	5.85	5.35	4.96	2.70

It is clear that silica nanoparticles increased breaking stress of specimens made of vinyl ester resin and that the amplitude of increase was proportional to the particle content. On the contrary, the effect of silica nanoparticles on the increase of specimens made of epoxy resin was nonlinear. To identify the contribution of modified matrices to the enhancement of breaking stress, the breaking stress enhancement of impregnated roving and impact strength of resin are compared in Fig. 9. Similar trends of the two data are observed, which implies that the tensile strength of the impregnated roving can be effected by the toughness of its matrix significantly. Therefore, it can be conclude that the toughness of the matrix is increased, so that the integrity of the FRP is guaranteed, leading to a better co-stress ability of the fibers. Additionally, the failure of FRP starts from the occurrence of cracks in the matrix. After adding silica nanoparticles in the matrix, the modified resin effectively restrained the propagation of microcracks in the matrix, resulting in the delay of FRP failure occurrence. Therefore, a higher breaking stress of impregnated roving was obtained.

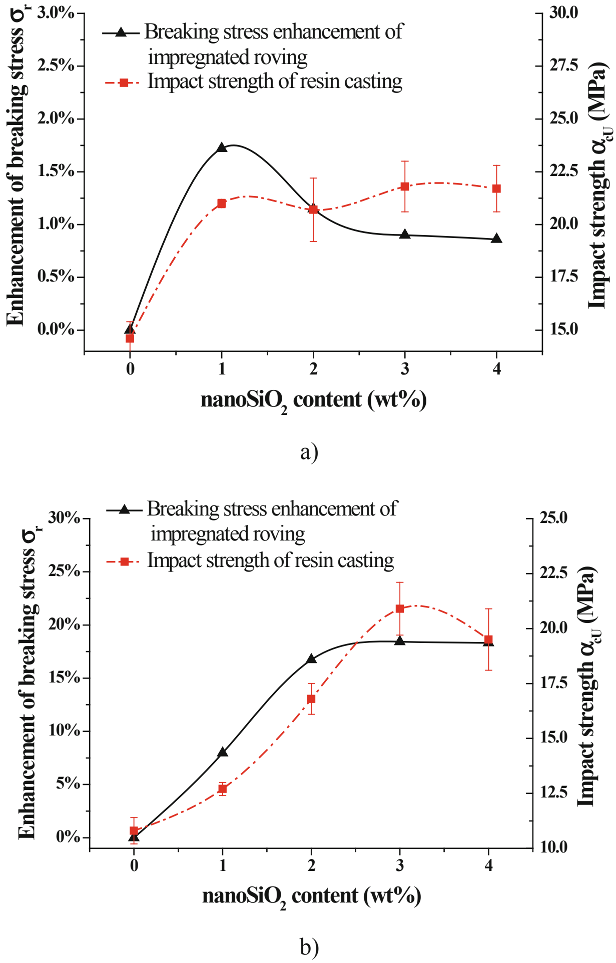


Fig. 9. Comparison of breaking stress enhancement and impact strength of samples made of a) epoxy, b) vinyl.

Figure 10b shows the elastic modulus of the impregnated roving. No distinct trends was observed. The modified resin exhibited higher elastic modulus. As the content of nanoparticle increased, the elastic modulus of the impregnated roving first rose and then fell back slightly.

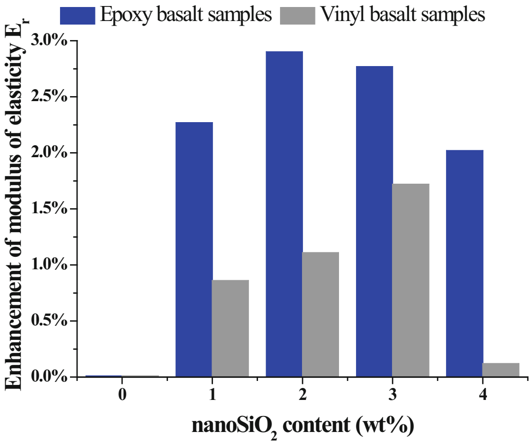


Fig. 10. Enhancement of modulus of elasticity of nanocomposites versus weight fraction of silica nanoparticles.

7 Conclusions

The beneficial effect of silica nanoparticles on fracture toughness of epoxy and vinyl ester resins under different particle contents were identified. Furthermore, the toughening mechanism was revealed by SEM of the fracture surface, indicated that the initiation and propagation of microcracks in the resin are restrained by silica nanoparticles, which was clear evidence for toughness enhancement. In addition, significant increase of impact strength were achieved for the modified resin, suggesting that silica nanoparticles can act as barriers in the develop path of microcracks. The breaking stress and elastic modulus of the impregnated roving with nanoparticles filled matrix showed a obvious enhancement, which is attributed to the improved co-stress ability of the fiber by the modified resin.

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References

1. Wu Z, Wang X, Zhao X, Noori M (2014) State-of-the-art review of FRP composites for major construction with high performance and longevity. Int J Sustainable Mater Struct Syst 1(3):201–231
2. Bakis C et al (2002) Fiber-reinforced polymer composites for construction-state-of-the-art review. J Compos Constr 6(2):73–87
3. Wu Z, Wang X, Wu G (2012) Advancement of structural safety and sustainability with basalt fiber reinforced polymers. In: Proceedings of 6th International Conference on FRP Composites in Civil Engineering (CICE), Rome, Italy, IIFC, p 29
4. Ngah SA, Taylor AC (2018) Fracture behaviour of rubber- and silica nanoparticle-toughened glass fibre composites under static and fatigue loading. Compos A 109:239–256

5. Alsaadi M, Bulut M, Erkliğ A, Jabbar A (2018) Nano-silica inclusion effects on mechanical and dynamic behavior of fiber reinforced carbon/Kevlar with epoxy resin hybrid composites. Compos B 152:169–179
6. Siddiqui NA, Woo RSC, Kim JK, Leung CCK, Munir A (2007) Mode I interlaminar fracture behavior and mechanical properties of CFRPs with nanoclay-filled epoxy matrix. Compos A 38(2):449–460
7. Liu S, Fan X, He C (2016) Improving the fracture toughness of epoxy with nanosilica-rubber core-shell nanoparticles. Compos Sci Technol 125:132–140
8. Liu HY, Wang GT, Mai YW, Zeng Y (2011) On fracture toughness of nano-particle modified epoxy. Compos B Eng 42(8):2170–2175
9. Liu H, Wang G, Mai Y (2012) Cyclic fatigue crack propagation of nanoparticle modified epoxy. Compos Sci Technol 72(13):1530–1538
10. Ngah SA, Taylor AC (2016) Toughening performance of glass fibre composites with core–shell rubber and silica nanoparticle modified matrices. Compos Part A 80:292–303
11. Vu CM, Sinh LH, Nguyen DD, Thi HV, Choi HJ (2018) Simultaneous improvement of the fracture toughness and mechanical characteristics of amine-functionalized nano/micro glass fibril reinforced epoxy resin. Polym Testing 71:200–208
12. Wang X, Shi J, Liu J, Yang L, Wu Z (2014) Creep behavior of basalt fiber reinforced polymer tendons for prestressing application. Mater Des 59(7):558–564
13. Wang X, Wu G, Wu Z, Dong Z, Xie Q (2014) Evaluation of prestressed basalt fiber and hybrid fiber reinforced polymer tendons under marine environment. Mater Des 64:721–728
14. Wang Z, Zhao X-L, Xian G, Gang W, Singh Raman RK, Al-Saadi S (2018) Effect of sustained load and seawater and sea sand concrete environment on durability of basalt- and glass-fibre reinforced polymer (B/GFRP) bars. Corros Sci 138:200–218