Construction and Building Materials 220 (2019) 679-689

Contents lists available at ScienceDirect

Construction and Building Materials

journal homepage: www.elsevier.com/locate/conbuildmat

UV-resistant GFRP composite using carbon nanotubes

Rahulreddy Chennareddy ^a, Hesham Tuwair ^{a,b}, Usama F. Kandil ^{a,c}, Mohamed ElGawady ^{a,d}, M.M. Reda Taha ^{a,*}

^a Department of Civil, Construction and Environmental Engineering, MSC01 1070, 1 University of New Mexico, Albuquerque, NM 87131-0001, United States ^b Department of Civil & Environmental Engineering, College of Engineering, Dhofar University, Salalah 211, Oman ^c Polymer Nanocomposite Center, Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt

^d Civil Architectural and Environmental Engineering, Missouri S&T University, 211 Butler-Carlton Hall, Rolla, MO 65409, USA

HIGHLIGHTS

• MWCNTs well-dispersed in resin prior to fabrication produce a UV-resistant GFRP.

• 0.5-1.0 wt% carboxylic functionalized MWCNTs protect GFRP against UV degradation.

• UV-resistant GFRP eliminates the need to apply UV protection paint.

ARTICLE INFO

Article history: Received 22 November 2018 Received in revised form 24 March 2019 Accepted 27 May 2019 Available online 24 June 2019

Keywords: Ultra-violet radiation Glass fibers Carbon nanotubes GFRP durability

ABSTRACT

Degradation due to exposure to ultraviolet (UV) radiation is an important durability challenge with glass fiber reinforced polymer (GFRP) composite. Design and construction guidelines of GFRP suggest using UV protection paint to prevent GFRP degradation. In this study we examine the possible use of multi-walled carbon nanotubes (MWCNTs) dispersed in epoxy matrix to produce UV-resistant GFRP composite. We suggest that MWCNTs can result in a significant improvement to UV degradation resistance in the GFRP. Direct tension tests of GFRP coupons incorporating 0.25 wt%, 0.50 wt%, and 1.0 wt% of MWCNTs show inherent stability and good resistance to UV degradation. Microstructural analysis shows the ability of MWCNTs to resist polymer backbone disassociation caused by UV radiation thus preventing UV degradation in GFRP. Scanning electron microscopy (SEM) images show MWCNTs can resist microcracking caused by UV radiation and thus improve UV degradation resistance of GFRP.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Glass fiber reinforced polymers (GFRP) composite represents an excellent material alternative for reinforcing and strengthening reinforced concrete structures because of its high strength-toweight ratio, long-term corrosion resistance, relatively low cost and ease of installation [1]. New manufacturing methods, like pultrusion and filament winding, have made it possible to use GFRP sections as frame and truss elements in FRP structures. GFRP is also used in windmill blades, airplanes and other industrial applications. GFRP is made by reinforcing polymer matrix (typically epoxy, polyester or vinyl ester) with continuous glass fibers. In this composite, the polymer matrix is the weak link and is susceptible to changes in physical properties [2]. When used in construction applications, GFRP bars and sections are prone to different types of environmental exposures including temperature, humidity, and ultraviolet (UV) radiation. It is well documented that GFRP has low resistance to UV radiation [3–6]. UV radiation experienced by the Earth's surface has a wave-

length range of 290–400 nm, which lies within the intensity known to cause bond disassociation in polymers [6,7]. The surface of the polymer degrades because of the photo-initiated oxidation that takes place due to UV exposure. This oxidation breaks the skeletal bonds in the polymers making an adverse impact on its stiffness and strength [6,8]. Currently, UV degradation of fiberreinforced polymers (FRP) is avoided by providing an additional UV protective coating, which adds to the cost of FRP materials [4]. The primary cost component comes from the need to apply then maintain the protective coating on the entire surface of the FRP materials. Labor and construction costs make the application of UV protective coating much more expensive than the cost of the coating material itself. The benefit in eliminating the need for





MIS

 ^{*} Corresponding author.
E-mail addresses: rahulreddy4@unm.edu (R. Chennareddy), htuwair@du.edu.om
(H. Tuwair), alfa_olefins@yahoo.com (U.F. Kandil), elgawadym@mst.edu
(M. ElGawady), mrtaha@unm.edu (M.M. Reda Taha).

UV protective coating is thus significant when FRP is used in construction applications, specifically in rehabilitation and retrofitting of existing concrete structures. UV protective coating acts as a selfsacrificing material degrading over time with UV exposure. Eventually, as a part of routine maintenance, UV protective coating requires reapplication. This increases maintenance costs, especially for retrofitting structures using FRP. Moreover, UV degradation is also a critical problem for offshore composite-based windmills because the UV protective coating must be reapplied using offshore platforms [9]. Karbhari et. al. reported on UV-induced damage as one of the durability challenges for FRP composites [4]. Researchers recommended creation of a polymeric matrix resin with inherent stability to UV radiation. This might eliminate the current requirements for protective coatings. Subsequently, Tcherbi-Narten et. al. fabricated woven carbon fiber epoxy nanocomposites by dispersing nano clay up to 3.00 wt% in the epoxy matrix [10]. The study showed improvement in compressive strength of composite up to 56% and reduction in UV degradation. However, nano clay could not resist the microcracking caused by UV radiation, which was evident from microstructural investigations of the exposed surface.

In similar interests to improve the mechanical behavior of polymers, carbon nanotubes (CNTs) received attention from the research community. CNTs are very strong materials that showed significantly high elastic modulus of 1000 GPa and very high tensile strength of 100 GPa when compared with high strength steel, which has 200 GPa of elastic modulus and 1.0 GPa of tensile strength [11]. Researchers showed significant improvement in polymer matrix strengths by incorporating as low as 3% by weight CNTs [13]. The challenge was to accomplish good dispersion of the CNTs, since CNTs are easily entangled. Surface functionalization, ultrasonication, and magnetic stirring were suggested as best methods to overcome the dispersion challenge, and results showed various levels of success [12,13]. Surface functionalization of CNTs accomplishes two tasks: first, it helps to uniformly disperse CNTs into the polymer matrix by causing an unbalanced charge, which helps in counteracting the Van der Waals forces. Second, functionalization can be engineered to form a strong covalent bond with the polymer chain [11,14,15]. Hence multi-walled carbon nanotubes (MWCNTs) are recognized as an efficient nanofiller for polymeric matrices to improve strength and stiffness of polymer composites.

Asmathulu et. al. developed MWCNTs/epoxy-based nanocomposite for external coating only and it showed little to no microcracking after subjecting to UV radiation [16]. Thus, incorporating MWCNTs into the polymer matrix resists the breakage of skeletal bonds and development of micro-cracks caused by photoinitiated oxidation of UV conditioning within the polymer matrix [16,17]. Additionally, MWCNTs were shown to form a dense network on the surface of the epoxy composite to protect against UV degradation. However, the above studies did not use MWCNTs epoxy matrix for fabrication of GFRP. Other UV stabilization fillers mentioned in the literature include carbon black, Dihydroxy benzophenones and benzotriazoles. These fillers, when used in the polymers, absorb the harmful UV radiation to convert into harmless infrared radiation, which is dissipated through the polymer matrix as heat [18-20]. Although numerous UV stabilizing fillers are available, when used to make the GFRP, their interaction on the mechanical properties is not known. Our previous studies showed that incorporating carboxyl functionalized MWCNTs in small amounts (below 1.00 wt% of the polymer by weight) into the polymer matrix prior to FRP fabrication improved the tensile, shear, and fatigue strengths of GFRP [21,22]. With advancements in the manufacturing methods, MWCNTs are now commercially available from different manufacturers (e.g. Cheap Tubes, Inc.,) [23]. No prior research on using MWCNTs dispersed in epoxy for fabrication of GFRP for UV stabilization has been reported.

In this study, we suggest incorporating carboxyl (COOH) functionalized MWCNTs in epoxy prior to GFRP fabrication and using this matrix to produce GFRP. As our previous studies showed that using carboxyl functionalized MWCNTs chemically react with the amine group in epoxy and the silane sizing of the glass fibers [21]. The suggested process may improve UV degradation resistance of GFRP and might eliminate the need for using UV protective coatings. We conducted mechanical characterization in the form of direct tension tests and thermomechanical characterization using a dynamic mechanical analyzer (DMA). Additionally, microstructural investigations using Fourier transformation infrared spectroscopy (FTIR) were conducted to understand the chemical change for epoxy specimens prior and subsequent to UV conditioning. Finally, the scanning electron microscopy (SEM) was used to observe surface damage of GFRP samples prior and subsequent to UV conditioning.

2. Experimental methods

2.1. Materials

The glass fibers used for fabrication of GFRP were unidirectional S2-glass fibers supplied by ACP Composites, Inc., Livermore, CA. The glass fibers are held together in 0° with a special polymeric veil fabric with low density which has the ability to dissolve into the laminate while curing. The glass fibers come in the form of a roll with a width of 300 mm. For the fabrication of GFRP laminates, a two-component epoxy system supplied by U.S. Composite, Palm Beach, FL was used. The primary component is a low viscous liquid epoxy resin 100% reactive based on Bisphenol-A containing EPOTUF[®]37-058, which is C12-C14 glycidyl ether. The second component is an epoxy-hardener consisting Aliphatic Amine EPOTUF[®]37-614. The resin to hardener mix ratio is 2:1 by weight. MWCNTs were functionalized with COOH group by 1.2% supplied by Cheap Tubes, Inc., Grafton, VT. The MWCNTs had an inner diameter of 5-10 nm and an outer diameter of 20-30 nm, specific surface area was $110 \text{ m}^2/\text{g}$ and bulk density of 0.21 g/cm^3 .

2.2. GFRP fabrication

GFRP laminates were manufactured using the vacuum assisted hand-layup technique (VAHT) with fibers in 0° direction after dispersing 0.00 wt%, 0.25 wt%, 0.50 wt% and 1.00 wt% of MWCNTs of the epoxy by weight.

The effect of dispersion on the mechanical properties was discussed and explained in the literature [13,14]. Uniform dispersion has been proven necessary to achieve improved mechanical behavior. Numerous techniques are available to achieve uniform dispersion such as high shear mixing, ultrasonication, covalent and noncovalent functionalization. In the current study, the dispersion mechanism involved mixing the desired content of MWCNTs into the epoxy resin with a mechanical stirrer at 800 RPM for 5 min; then, the mixture was placed in an ultra-sonication bath for 60 min at 40 °C to disperse the MWCNTs in the resin. Later, the mixture was mixed at 800 rpm for 120 min at 80 °C with the use of a mechanical stirrer to enable the MWCNTs to disperse uniformly into the epoxy resin. The ultrasonication and mechanical stirring allows dispersing the MWCNTs into epoxy matrix and the -COOH surface functionalization improves the dispersion process. The above technique has been reported to result in well-dispersed MWCNTs in epoxy and allow making composites with improved mechanical properties [22]. The epoxy hardener was then added to the resin-MWCNTs mixture and mixed for five minutes. SEM image of epoxy matrix incorporating 1.00 wt% MWCNTs is shown in Fig. 1 demonstrating good dispersion of MWCNTs in epoxy.



Fig. 1. SEM image showing dispersed MWCNTs in epoxy matrix. Green Arrows point to individual MWCNTs.

The epoxy prepared with the above methodology was used for fabrication of MWCNTs-GFRP using six layers of glass fiber fabric using VAHT as presented in Fig. 2. For laminate fabrication, firstly, a peel ply was applied onto a release film mounted onto a steel plate. Initially, an epoxy layer was spread on the peel ply with the help of a roller. Next, a layer of glass fiber sheet was placed on the epoxy layer and rolled using a roller to ensure proper impregnation of the epoxy. Subsequently, a layer of epoxy was poured and rolled on the previously placed glass fiber layer. Then, a new layer of glass fiber was placed and rolled to ensure the impregnation of epoxy. This process continued until 6 layers of glass fibers were pressed together. A peel ply cloth was then rolled on the layered GFRP, followed by a porous release film to ensure vacuum suction of epoxy for impregnation within the glass fibers and to ensure easy removal of excess epoxy. A breathing cloth was placed to absorb the excess epoxy and the process was completed with vacuum packaging by applying a vacuum pressure of 3 Pa for 24 h. All GFRP plates were cured in the oven for 6 h at 50 °C and then at ambient temperature for 14 days to ensure full strength gain. The VAHT technique was used for consistent production of GFRP samples. One GFRP plate for each MWCNTs concentration was fabricated using 6 layers of unidirectional S2 glass fiber fabric. All the samples for each MWCNTs concentration were randomly selected from the same plate. Of these random selected samples, five samples were subjected to UV conditioning and other five samples were not subjected to UV conditioning. The samples were cut to the desired dimensions using water jet cutting to ensure perfect cut. Enough care was taken while fabricating the plate to ensure that there are no significant misalignments and the fibers were placed at the 0-degree direction.

2.3. UV exposure

A UV chamber was constructed to meet the guidelines provided in ASTM G151 and ASTM G154 for exposing the GFRP coupons to UV radiation prior to mechanical testing [24,25]. The UV chamber was a wooden box of 698 mm length, 495 mm width and 508 mm height. A wattage intensity meter was always placed inside the chamber. Six spectral UVA 365 lamps were placed in the box (three on each side) to give the required wattage intensity and measured to be in the range of 0.77 and 0.95 W/($m^2 \cdot nm$), where ASTM specifies a $0.89 \text{ W}/(\text{m}^2 \cdot \text{nm})$ wattage intensity. The wattage intensity was constantly monitored daily to ensure the wattage is within the required range and lamps were replaced as necessary. Worldwide Specialty Lamp, Austell, GA supplied the UVA 365 lamps. In order to reflect the light onto the specimens, aluminum foil covered the interior surface of the box. The temperature inside the chamber (air temperature) was maintained at 51 °C with the use of 8 cooling fans, and the humidity was maintained at 50%. To simulate real conditions where there is a period of exposure with and without sunlight, the cycles of light and dark period (condensation) were used as is suggested by ASTM G151 and ASTM G154 to enable chemical reactions that take place in the dark period post UV exposure [24]. A light timer was used to create light cycles, such that UV exposure was 4 h and a dark period was 4 h. The coupons were conditioned continuously in repeated cycles of UV conditioning for a total time of 2,160 h. The UV chamber used in the current study is shown in Fig. 3. It is extremely difficult to make a comparison with the field condition as numerous other parameters play a role and this varies from one location to another and the type of material being tested. Therefore, ASTM G151 recommends not to compare the laboratory weathering time to the field weathering time without field experimental data. However, a study on polyester coatings suggested that 576 h of laboratory exposure of UV exposure conditions, like those reported herein, to approximately simulate 3 years of UV field exposure [26].



Fig. 2. Fabrication procedure of MWCNTs-GFRP nanocomposite.



Fig. 3. UV radiation chamber.

2.4. Test setup

Ten GFRP specimens for each MWCNTs concentration were cut into standard coupons of 12.5 mm width \times 125 mm length for mechanical testing under direct tension test. The measured thickness of the GFRP coupons was 0.85 mm ± 0.03 mm thickness. Five coupons were exposed to UV radiation as described in the UV exposure section, and the other five acted as a reference without being exposed to the UV radiation. From here on, the GFRP coupons will be designated by the MWCNTs concentration followed by the exposure condition such that if exposed to UV radiation, they will be denoted "UV" and if not exposed to UV radiation, they will be designated as unexposed, "UE". For example, a sample designated as 0.25 wt% UV corresponds to a GFRP coupon with 0.25 wt% MWCNTs concentration and was exposed to UV radiation.

The direct tension test was conducted under displacement control protocol with a displacement rate $1 \text{ mm/min using MTS}^{\oplus}$ Bionex servo hydraulic system with mechanical grips. A contact

extensometer with a gauge length of 25 mm was used to measure the strains accurately. The applied displacement, the corresponding load, and the corresponding strains were recorded throughout the test time at a sampling rate of 1 Hz. The direct tension test setup and instrumentation along with the sample dimensions is presented in Fig. 4. The tensile tests were conducted following ASTM D3039/3039 M-14 [27].

2.5. Microstructural characterization

FTIR spectroscopy was used to observe the changes in chemical bonds after UV exposure and the significance of using MWCNTs in the epoxy matrix. In the current study, a PerkinElmer Spectrum Two^M infrared spectrometer with a single reflection diamond was employed to conduct the FTIR. According to the manufacturer's specifications, the spectral range for the FTIR spectrometer is within the order of 8300–350 cm⁻¹. GFRP coupons with 0.00 wt%, 0.50 wt% and 1.00 wt% of MWCNTs were used to conduct



Fig. 4. Direct tension test experimental setup and instrumentation.

FTIR as these concentrations are representative samples to show the chemical change within the polymer matrix before and after UV exposure.

DMA tests were conducted on the epoxy samples to identify the effect of UV radiation on the glass transition temperature (T_g) of epoxy samples incorporating 0.0 wt%, 0.50 wt% and 1.00 wt% of MWCNTs before and after exposure to UV radiation. The DMA machine used in this study was Q800 DMA manufactured by TA Instruments, New Castle, DE. The DMA was conducted under 3-point bending configuration for epoxy samples with dimensions of 25 mm long × 8 mm wide × 3 mm thickness. DMA measures the viscoelastic moduli, storage and loss modulus, damping properties, and tan delta of materials as they are deformed cyclically. The tan delta peak was used to define (T_g) in the current study. A preload force of 0.05 N held at a frequency of 1 Hz from 25 °C –140 °C in 3-point bending was applied. The initial soak time was 5 min at 25 °C. The ramp rate was 3 °C /min to ensure the material was heated evenly up to 140 °C.

SEM investigation was conducted on the surface of GFRP samples before and after UV conditioning using VEGA3 TESCAN thermionic emission SEM system to observe any changes or microcracking on the GFRP samples post UV conditioning. The samples were ultra-thin sputter coated with gold/palladium (AU/ Pd) to make the sample conductive.

3. Results and discussion

3.1. Effects of UV on color of GFRP and MWCNTs-GFRP coupons

Neat GFRP with 0.00 wt% MWCNTs had a visible color change following UV exposure. The coupons, which were initially bright white in color, turned yellow-brown after exposure to UV radiation. Fig. 5. shows the color change by comparing the coupons before and after UV exposure. The chemistry of UV radiation damage is not completely understood [7]. Discoloration is related to a phenomenon well-described in the literature known as polymers' photoreactions that takes place when the polymer is subjected to UV and attributed to macromolecular changes in the polymer via chain scissions as an effect of the photo-induced degradation [7]. While it is difficult to observe discoloration of the black MWCNTs-GFRP, no visible change in color can be observed in the UV-exposed MWCNTs-GFRP as shown in Fig. 5. It is reported in the literature that carbon black enables photo-stabilization of polymers due to its high surface area and thus is used for resisting UV radiation of polymers [28,29]. It is hypothesized here that MWCNTs might have photo-stabilization effect similar or better than that reported for carbon black.

3.2. Constituent content of GFRP composite

The constituent contents of the composite material were derived following ASTM D3171 using hot furnace combustion method [30]. First, the mass and density of the composite specimen was measured. Then the composite sample is placed in a muffle furnace at 600 °C \pm 30 °C for 6 h. This process burns the epoxy matrix leaving glass fibers unaffected as a residue for which the remaining mass is determined. The fiber volume fraction was then determined using Eq. (1).

$$V_r = (M_f/M_c)(\rho_c/\rho_r) \times 100 \tag{1}$$

where M_c is the mass of the composite specimen before combustion, M_f is the mass of the glass fibers remaining after combustion, ρ_c is the density of the composite specimen, ρ_r is the density of the glass fibers and, V_r is the identified glass fiber volume fraction in the



Fig. 5. UV radiation effect on color of coupons, (a) 0.00 wt% UE; (b) 0.00 wt% UV; (c) 1.00 wt% UE; (d) 1.00 wt% UV.

composite The mechanical properties of continuous FRP composite material mainly depend on the fiber volume fraction. This is related to the fact that the elastic modulus and strength of the fiber material is orders of magnitude higher than that of the matrix. Therefore, the fiber constituent is the main load carrying element in the FRP composite. High strength and stiffness of an FRP composite material are typically accomplished be ensuring high fiber volume fraction in the composite. The fiber volume fractions for the specimens tested herein with 0.00 wt% of MWCNTs, 0.25 wt%, 0.50 wt% and 1.00 wt% MWCNTs concentrations were 47.0%, 46.5%, 45.8% and 44.6% respectively. The results confirm that all GFRP specimens with and without MWCNTs had a fiber volume fraction within 1-3% differences compared with neat GFRP. The difference in durability and mechanical behavior can only thus be attributed to the incorporation of MWCNTs and not to changes in the glass fiber volume fraction.

3.3. Effects of MWCNT on strength of unexposed GFRP coupons

The UE MWCNTs-GFRP coupons demonstrated a significant improvement in their tensile strength compared with the 0.00 wt% MWCNTs GFRP coupons as shown in Fig. 6.

The tensile strength results of GFRP coupons incorporating MWCNTs are presented in Table. 1. Comparing the results with 0.00 wt% UE coupon samples, the tensile tests showed an increase in the tensile strengths by 13%, 18% and 9% when 0.25 wt% UE, 0.50 wt% UE and 1.00 wt% UE of MWCNTs were dispersed into the epoxy matrix respectively. This improvement in strength after incorporating MWCNTs achieved a 95% confidence level with student *t*-test compared with the 0.00 wt% UE samples.

The ability of MWCNTs to alter GFRP mechanical behavior was reported before through a potential interaction between the



Table 1

Direct tension test results of GFRP coupons incorporating MWCNTs.

Tensile propert			
Sample	Strength MPa	Young's Modulus GPa	Failure Strain %
0.00wt%UE	919 ± 26	37.4 ± 2.1	2.51 ± 0.14
0.00wt%UV	829 ± 30	36.5 ± 0.9	2.23 ± 0.10
0.25wt%UE	1039 ± 58	36.8 ± 1.2	2.77 ± 0.21
0.25wt%UV	997 ± 53	37.1 ± 1.4	2.67 ± 0.15
0.50wt%UE	1084 ± 69	38.4 ± 3.0	2.80 ± 0.17
0.50wt%UV	1104 ± 94	37.5 ± 2.9	2.98 ± 0.22
1.00wt%UE	1004 ± 57	35.0 ± 0.9	2.85 ± 0.07
1.00wt%UV	1161 ± 47	36.9 ± 0.6	2.95 ± 0.21

Note: Ten GFRP specimens for each MWCNTs concentration were tested under direct tension. Five coupons were exposed to UV radiation denoted (UV) and the other five acted as a reference without being exposed to UV radiation denoted (UE).

COOH–MWCNTs and the epoxy matrix as shown schematically in Fig. 7, after Borowski et. al [31]. In addition, the functionalized MWCNTs enhanced the adhesive forces between the fiber surface and the epoxy matrix. This enhancement is attributed to the chemical reaction between the carboxylic groups and the silane sizing material located on the fiber surface as shown in Fig. 7. However, a higher concentration of MWCNTs, typically higher than 0.50 wt %, increases epoxy viscosity because of the high specific surface area of the MWCNTs [32]. Such increase in epoxy viscosity might



Fig. 7. Schematic showing the significance of COOH-MWCNTs on the epoxy-fiber bond leading to improved mechanical behavior of GFRP.



Fig. 8. Median stress-strain behavior of GFRP incorporating varying MWCNTs.

negatively affect the process of glass fibers impregnation with epoxy during GFRP fabrication. The stress-strain behavior of GFRP and MWCNTs-GFRP showed linear elastic behavior as shown in Fig. 8. The tensile modulus of elasticity of GFRP specimens incorporating varying MWCNTs contents are presented in Table. 1. Statistical analysis using Student T-Test with 95% level of confidence shows the difference in elastic modulus of the different GFRP specimens with varying MWCNTs content 0.25 wt%, 0.50 wt% and 1.00 wt% to be statistically insignificant. The absence of any significant change in the modulus of elasticity in GFRP with MWCNTs compared with neat GFRP can be attributed to the fact that all mechanical properties in the on-axis direction (0° fiber orientation) are governed by the glass fibers rather than the matrix. It is well documented in the literature that the MWCNTs can improve the elastic modulus of the composite in the matrix dominant direction i.e., 45° and 90° fiber orientations [33]. An insignificant decrease in modulus was observed for 1.00wt.%UE samples compared to the 0.00wt.%UE samples by 6%. This decrease in modulus can be attributed to the reduced quality of composite fabrication caused by the increased viscosity of epoxy matrix with 1.00 wt% of MWCNTs.

3.4. Effects of MWCNT on the strength of UV-Exposed GFRP coupons

The tensile strength results of the samples subjected to UV radiation are presented in Table. 1. The UV-exposed GFRP coupons, i.e., 0.00 wt% UV, showed a mean ultimate tensile strength of 829 MPa ± 30 MPa compared with 919 MPa ± 26 MPa for the 0.00 wt% UE samples. The tensile strength of the UV-exposed GFRP coupons showed 10% loss in their average ultimate tensile strength, which may be attributed to the significant microcracking leading to loss of fiber-epoxy bond as a result of the photodegradation. The 0.25 wt% UV coupons showed a mean tensile strength of 997 MPa ± 53 MPa compared with 1039 MPa ± 58 MPa for the corresponding UE MWCNTs-GFRP coupons representing a 4% loss in the tensile strength of the MWCNTs-GFRP after being exposed to UV radiation. Furthermore, 0.50 wt% UV coupons showed a mean strength of 1104 MPa ± 94 MPa compared tensile with 1084 MPa ± 69 MPa for the corresponding UE MWCNTs-GFRP coupons representing a 2% increase in the tensile strength of the MWCNTs-GFRP after being exposed to UV radiation. Finally, 1.00 wt% UV coupons showed a mean tensile strength of 1161 MPa ± 47 MPa compared with 1004 MPa ± 57 MPa for the corresponding UE MWCNTs-GFRP coupons, representing an 16% increase in the tensile strength of the MWCNTs-GFRP after being exposed to UV radiation. A 95% t-test confidence level was achieved for 0.00 wt% and 1.00 wt% samples when compared between the coupons before and after exposure to UV. The tensile

modulus of elasticity for GFRP samples after subjecting to UV is presented in Table. 1. UV radiation had a negligible effect on the modulus of elasticity for sample 0.00 wt% MWCNTs and 0.25 wt% MWCNTs, as the modulus of elasticity is a fiber dominant property for on-axis GFRP material. The results indicate that using MWCNTs in small concentrations as low as 0.50 wt% diminishes the strength loss of GFRP when exposed to UV radiation. The comparisons between the tensile strengths of the coupons with all MWCNTs concentrations, before and after exposure to UV radiation, are shown in Fig. 9. The ability of the UV exposure to improve the tensile strength of GFRP coupons incorporating 0.50 wt% and 1.00 wt% MWCNTs is further motivating and explained later using FTIR.

The mean strain values at failure of the MWCNTs-GFRP coupons are presented in Table 1. The strain results represent an increase in strains of the MWCNTs-GFRP coupons by 12%, 12% and 14% for 0.25 wt%, 0.50 wt%, and 1.00 wt% of MWCNTs, respectively, compared to that of the GFRP coupon samples without MWCNTs. The mean strain value at failure for the UV-exposed 0.00 wt% UV GFRP was 2.23 ± 0.10% representing a decrease in failure strain by 11% compared to that of the UE GFRP of 2.51 ± 0.14%. This can be attributed to the fact that the UV induced significant microcracking as shown later in the SEM images reduced the interfacial bond between the epoxy matrix and glass fibers causing a relatively premature failure. The 0.25 wt% UV coupons showed a mean failure strain of $2.67 \pm 0.15\%$, which indicates a 4% drop in failure strain compared with the effect of UV radiation on GFRP. The 0.50 wt% UV coupons showed a 6% increase in failure strain due to exposure to UV radiation, both exposed and unexposed coupons having a mean failure strain of 2.98 ± 0.22% and 2.80 ± 0.17%. The 1.00 wt% coupons showed a mean failure strain of $2.95 \pm 0.1\%$ indicating a negligible improvement in failure strain compared with the effect of UV radiation on GFRP. The above strain at failure results indicate that UV radiation resulted in significant reduction in failure strain of GFRP while it made no significant effect on MWCNTs-GFRP coupons as shown in Fig. 10.

3.5. Failure modes

Unexposed and exposed GFRP showed the regular broom-like failure as shown in Fig. 11. The broom-like failure of GFRP is attributed to the limited interfacial bond between glass fibers and the epoxy matrix [34,35]. However, dispersing MWCNTs into the polymeric matrix prior to producing GFRP reduced this broom-like failure as shown in Fig. 11(a). This is attributed to the ability of the MWCNTs to improve the interfacial adhesion between the epoxy matrix and the glass fibers. No significant change in the mode of failure was observed in the UV-exposed MWCNTs-GFRP showing that UV radiation did not reduce the bond strength between MWCNTs-epoxy nanocomposite and glass fibers as shown in Fig. 11 (b).

3.6. Microstructural analysis

Glass transition temperature (T_g) was derived using DMA under three-point bending configuration for the epoxy samples. Epoxy samples with 0.00 wt% UE, 0.50 wt% UE, and 1.00 wt% UE obtained the glass transition temperatures of 57 °C \pm 0.3 °C. Hence, the MWCNTs did not affect the T_g of the unexposed specimens. The samples subjected to UV radiation, i.e., 0.00 wt% UV, 0.50 wt% UV, and 1.00 wt% UV had T_g values of 56 °C, 60 °C, and 59 °C respectively. An inference can be made that a small decrease was observed in Tg when MWCNTs were not incorporated into the epoxy matrix after UV exposure. However, the epoxy samples incorporating MWCNTs showed a slight improvement in T_g after subjecting to UV exposure. This increase in T_g might be attributed to the improved crosslinking of the epoxy matrix with the energy supplied by the UV radiation. The increase in T_g in the GFRP specimens with MWCNTs after UV exposure could also be affected by the black specimens getting hotter than the white ones due to surface emissivity difference.



Fig. 9. Effect of UV radiation on tensile strength of the GFRP coupons with; (a) 0.00 wt% MWCNTs; (b) 0.25 wt% MWCNTs; (c) 0.50 wt% MWCNTs; (d) 1.00 wt% MWCNTs.



Fig. 10. Stress-strain behavior of median GFRP sample incorporating MWCNTs with and without exposure to UV radiation.



Fig. 11. Tested coupons showing similar modes of failure from significant broom to limited broom for GFRP coupons incorporation MWCNTs (a) without UV conditioning (b) after UV conditioning.

FTIR spectrographs for GFRP and MWCNTs-GFRP specimens before and after UV exposure are compared in Fig. 12. The FTIR analysis shows that all samples with and without MWCNTs display the standard epoxy peaks; the absorption bands corresponding to C-H band (2850-2930 cm-1), epoxide ring (~830 cm-1), N-H band of primary amines (1590- 1615 cm-1), O-H groups (~3350 cm-1), C-N band (1030-1115 cm-1), and ether bands $(\sim 1230 \text{ cm} - 1)$ are all apparent and have similar relative ratios to the base spectra as shown in Fig. 12. For GFRP specimens incorporating 0.50 wt% and 1.00 wt% MWCNTs, FTIR spectrographs show the C=O stretch at 1738 cm-1, indicating that an esterification reaction between the epoxy resin and the COOH group of the surface functionalized MWCNTs took place during fabrication. This shift at 1738 cm-1, due to esterification, was reported [36,37]. It was the result of direct coupling between the carboxylic groups in the MWCNTs and the hydroxyl groups in the epoxy resin.

In addition, it is important to note that all spectrographs show peaks at 1039–1100 cm⁻¹ which is attributed to ($v_{Si-O-Si}$ and v_{C-O-C}), peak at 1250–828 cm⁻¹ attributed to (δ_{C-H} in Si–CH₃), and peak at 560 cm⁻¹ attributed to ($\delta_{Si-O-Si}$) as reported [38–40]. Besides, two peaks appeared at 1590–1615 cm⁻¹ which are attributed to N-H of primary (NH₂) and secondary (>NH) amines in all GFRP composites [41]. These peaks are attributed to the chemical reaction occurred between the silane sizing material; 3-(aminopropyl) triethoxysilane (APTES); located on the glass fibers surface and carboxylic groups of MWCNTs-epoxy nanocomposite and thus improved the tensile strength of MWCNTs-GFRP compared with GFRP without UV exposure. It is important to note that a relatively high carboxyl content is present for 1.00 wt% MWCNTs. It is hypothesized that such high content of the carboxyl group might have significantly improved the polymerization process utilizing the UV radiation and thus improving the bond with carboxyl group of MWCNTs and silane sizing of the glass fibers.



Fig. 12. FTIR spectrographs: Limiting disassociation of epoxy polymer backbone via MWCNTs incorporation.

This phenomenon might have improved the strength of GFRP incorporating 1.00 wt% MWCNTs after UV exposure.

Previous studies suggested that photo-degradation generates carbonyl group (C=O) and olefinic double bond (C=C) through chain scission and hydrogen bond dissociation from the polymer backbone [42]. It can be noticed in Fig. 12 that these two absorption bands appeared at 1660 and 1738 cm-1, respectively, of the GFRP spectrograph. There is a relative higher band intensity of the C=O band at 1738 cm-1 apparent in exposed GFRP samples. However, a much weaker band intensity of the C=O at 1738 cm-1 can be observed in the FTIR spectrographs of GFRP incorporating both 0.50 wt% and 1.00 wt% MWCNTs. This indicates that the MWCNTs were able to protect epoxy and prevent its backbone disassociation typically observed with UV exposure. It is well known that carbon black is used for protecting polymers against UV radiation [43]. It has also been reported that the photostabilizing efficiency of carbon black depends mainly on its physical surface area [28,29]. Consequently, it is expected that MWCNTs would have much better photo-stabilizing efficiency because of its high surface area. This could be noticed from the lowering band intensities of both C=O and C=C groups.

SEM micrographs showing the surface of the GFRP samples are presented in Fig. 13. A grid pattern can be observed in most of the images. The peel ply cloth used in the fabrication process creates this grid pattern, and this pattern has no significance. Fig. 13(a) is the 0.00 wt% UE sample showing no signs of microcracking. After UV exposure, significant microcracking was observed (Fig. 13(b) and Fig. 13(c)) all along the sample. SEM images for multiple samples of 0.00 wt% UV showed the same pattern of microcracking. Another noticeable change is the exposure of the fibers in Fig. 13 (b) and (c) indicating a loss of epoxy matrix protection to the fibers. On the other hand, GFRP samples with 1.00 wt% MWCNTs in Fig. 13 (d) and (e) before and after UV exposure showed no signs of microcracking and no loss of epoxy matrix around the fibers. This can be attributed to the ability of MWCNTs to act as a shield by blocking UV radiation as reported by Asmatulu et. al [16]. Also, because of their high specific strength, MWCNTs creates a polymeric nanocomposite matrix that resist the microcracking. The SEM in this study did not show formation of dense MWCNTs networks after the exposure to UV radiation as reported by Petersen et. al [17].

It is, therefore, hypothesized here that MWCNTs with its relatively high carbon content might be able to protect GFRP against UV exposure similar to carbon black in addition to its ability to improve epoxy bond with glass fibers. Moreover, the carboxyl groups of MWCNTs enhance photo stabilization through its restriction effect on the movement of OH^- and H^+ ions, which are usually generated from the surrounding humidity [24]. SEM images showed no microcracking for GFRP coupons incorporating MWCNTs after being subjected to UV radiation.

The method presented herein to improve UV degradation resistance using MWCNTs can be generalized in GFRP manufacturing by dispersing MWCNTs to the polymer resin prior to fabrication of GFRP. The improved UV resistance enhances the performance of externally bonded GFRP strengthening systems, GFRP deck systems, GFRP wall panels and GFRP profiles used to make FRP frame structures [44]. Improving UV radiation resistance is a significant benefit to GFRP windmills as used in windmill blades or windmill shafts in offshore structures. The ability to eliminate UV degradation concern of GFRP composite would result in a significant



(d)

Fig. 13. SEM micrographs showing surface of GFRP (a) 0.00 wt% MWCNTs (neat) not exposed to UV (b) 0.00 wt% MWCNTs (neat) exposed to UV (c) close up of microcracks and epoxy loss of 0.00 wt% MWCNTs (neat) exposed to UV (d) 1.00 wt% MWCNTs not exposed to UV (e) 1.00 wt% MWCNTs exposed to UV.

(e)

I aDIC 2	Та	ble	2
----------	----	-----	---

Cost comparison in US\$ of fabricating GFRP with and without MWCNTs.

Material	units	unit price	Material	Neat-GFRP	1.00 wt% MWCNTs-GFRP
S2 glass fibers (12in wide)	ft.	3.00	8	24.0	24.0
Ероху	ml.	0.02	300	4.50	4.50
Vacuum bagging material	ft.	3.00	1.3	3.90	3.90
MWCNTs-COOH	gram	1.00	2.5		3.00
Total cost				32.40	35.40

Note: unit price of the materials are based on the supplier cost in 2019.

economic return [9]. It is suggested that using such small quantity of well-dispersed MWCNTs in the polymer resin during GFRP fabrication creates a new class of UV-resistant GFRP.

Finally, Table 2 presents cost analysis of fabricating GFRP with and without MWCNTs considering individual material cost. Cost analysis shows that incorporating MWCNTs (lower than 1.0 wt%) in epoxy during GFRP fabrication would result in increasing GFRP cost by \sim 10%. This increase in cost corresponds to MWCNTs material cost. It is important to note that additional one-time cost related to investment in dispersion equipment shall be considered. This is a relatively small cost increase compared with the cost associated with applying a UV protective coating to all GFRP material surfaces (including material and construction time) and maintenance of this protective coating over the life of the structure.

Using MWCNTs concentrations above 1.00 wt% has the potential of agglomerating MWCNTs leading to a non-uniform dispersion and increases the viscosity of the polymer resin. This reduces the quality of composite fabrication. Therefore, high concentrations of MWCNTs will not improve the mechanical properties of GFRP due to its negative effect on the fabrication process as a result of increased epoxy viscosity. Further research is warranted to identify the optimal MWCNTs content (between 0.50 and 1.0 wt%) to be used in industrial scale production of UVresistant GFRP using COOH-MWCNTs. The current study proves the UV radiation resistance of GFRP with carboxyl functionalized MWCNTs. Further investigations are necessary for using other type of MWCNTs (Pristine and other functional groups) to produce UVresistant GFRP.

4. Conclusions

MWCNTs well-dispersed into the epoxy matrix prior to GFRP fabrication can produce a UV-resistant GFRP composite. Of particular interest, is the improvement in tensile strength of GFRP incorporating MWCNTs when exposed to UV radiation and the correlation of this improvement with the increase in MWCNTs concentration. Such improvement in mechanical properties of GFRP

might be attributed to the improved bond of epoxy-MWNCTs to glass fibers, which might take place due to the thermal effect of UV radiation.

The experimental investigation showed that GFRP coupons not incorporating MWCNTs experienced significant drop in tensile strength when exposed to UV radiation. However, dispersing as little as 0.50 wt% MWCNTs into epoxy prior to GFRP production significantly improved the tensile strength of GFRP coupons compared with GFRP produced with neat epoxy. Dispersing MWCNTs into the polymer matrix developed a polymer nanocomposite with inherent stability to UV radiation. A relatively small amount of MWCNTS with carboxylic functionalization, i.e., 0.5-1.0 wt%, protected the GFRP against UV degradation. FTIR spectrograph showed significant bond disassociations within the epoxy matrix without MWCNTs, while coupons with MWCNTs showed lower bond disassociations specifically with newly formed chemical bonds. SEM images showed significant microcracking for GFRP without MWCNTs post UV exposure. This microcracking was absent in the samples with 1.00 wt% MWCNTs, showing the ability of MWCNTs to improve GFRP resistance to degradation due to UV radiation.

Declaration of Competing Interest

None.

Acknowledgements

The authors would like to thank the contributions of our lab manager Mr. Kenny Martinez for his immense help in conducting the experiments.

References

- [1] C. Bakis, L.C. Bank, V. Brown, E. Cosenza, J. Davalos, J. Lesko, et al., Fiberreinforced polymer composites for construction-state-of-the-art review, J. Compos. Constr. 6 (2) (2002) 73–87.
- [2] H. Tuwair, J. Volz, M. ElGawady, M. Mohamed, K. Chandrashekhara, V. Birman, Behavior of GFRP bridge deck panels infilled with polyurethane foam under various environmental exposure, Struct.: Elsevier (2016) 141–151.
- [3] H. GangaRao, P. Vijay, P. Dutta, Durability of Composites in Infrastructure, NACE Intl. Corrosion 95, (United States) Houston, TX, 1995.
- [4] V. Karbhari, J. Chin, D. Hunston, B. Benmokrane, T. Juska, R. Morgan, et al., Durability gap analysis for fiber-reinforced polymer composites in civil infrastructure, J. Compos. Constr. 7 (3) (2003) 238–247.
- [5] M.M. Shokrieh, A. Bayat, Effects of ultraviolet radiation on mechanical properties of glass/polyester composites, J. Compos. Mater. 41 (20) (2007) 2443–2455.
- [6] S. Zainuddin, M. Hosur, R. Barua, A. Kumar, S. Jeelani, Effects of ultraviolet radiation and condensation on static and dynamic compression behavior of neat and nanoclay infused epoxy/glass composites, J. Compos. Mater. 45 (18) (2011) 1901–1918.
- [7] A. Andrady, S. Hamid, X. Hu, A. Torikai, Effects of increased solar ultraviolet radiation on materials, J. Photochem. Photobiol. B: Biol. 46 (1) (1998) 96–103.
- [8] C. Giori, T. Yamauchi, Effects of ultraviolet and electron radiations on graphitereinforced polysulfone and epoxy resins, J. Appl. Polym. Sci. 29 (1) (1984) 237– 249.
- [9] H.L. Dedeurwaerder, Protecting offshore wind farm towers, J. Protective Coat. Linings. 32 (6) (2015) 24.
- [10] A. Tcherbi-Narteh, M. Hosur, S. Jeelani, Influence of nanoclay on the durability of woven carbon/epoxy composites subjected to ultraviolet radiation, Mech. Adv. Mater. Struct. 21 (3) (2014) 222–236.
- [11] P. Eklund, P. Ajayan, R. Blackmon, A.J. Hart, J. Kibng, B. Pradhan, et al., International assessment of research and development of carbon nanotube manufacturing and applications, WTEC Panel Rep. (2007).
- [12] S.A. Sydlik, J.-H. Lee, J.J. Walish, E.L. Thomas, T.M. Swager, Epoxy functionalized multi-walled carbon nanotubes for improved adhesives, Carbon 59 (2013) 109–120.
- [13] P.-C. Ma, N.A. Siddiqui, G. Marom, J.-K. Kim, Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: a review, Compos. Part A: Appl. Sci. and Manuf. 41 (10) (2010) 1345–1367.
- [14] S.G. Advani, Z. Fan, Dispersion bonding and orientation of carbon nanotubes in polymer matrices, Process. Prop. Nanocomposites (2007) 61–98.
- [15] K. Mylvaganam, L.C. Zhang, Fabrication and application of polymer composites comprising carbon nanotubes, Recent pat. on Nanotechnology. 1 (1) (2007) 59–65.

- [16] R. Asmatulu, G.A. Mahmud, C. Hille, H.E. Misak, Effects of UV degradation on surface hydrophobicity, crack, and thickness of MWCNT-based nanocomposite coatings, Prog. Org. Coat. 72 (3) (2011) 553–561.
- [17] E.J. Petersen, T. Lam, J.M. Gorham, K.C. Scott, C.J. Long, D. Stanley, et al., Methods to assess the impact of UV irradiation on the surface chemistry and structure of multiwall carbon nanotube epoxy nanocomposites, Carbon 69 (2014) 194–205.
- [18] K. Inoue, H. Takahata, T. Tanigaki, Novel UV absorbers prepared from 2, 4dihydroxybenzophenone and hexachlorocyclotriphosphazene, J. Appl. Polym. Sci. 50 (11) (1993) 1857–1862.
- [19] A.P. Kumar, D. Depan, N.S. Tomer, R.P. Singh, Nanoscale particles for polymer degradation and stabilization—trends and future perspectives, Prog. Polym. Sci. 34 (6) (2009) 479–515.
- [20] J. Parmar, R. Singh, Polymeric UV stabilizers for thermoplastics, Handbook of engineering polymeric materials, Marcel Dekker Inc./CRC Press, New York, 2000.
- [21] M. Genedy, S. Daghash, E. Soliman, M.M.R. Taha, Improving fatigue performance of GFRP composite using carbon nanotubes, Fibers 3 (1) (2015) 13–29.
- [22] E. Soliman, U. Kandil, M.R. Taha, Improved strength and toughness of carbon woven fabric composites with functionalized MWCNTs, Mater 7 (6) (2014) 4640–4657.
- [23] Cheap Tubes I. Carbon nanotube epoxy composite. 2017. URL: https://www. cheaptubes.com/contact-cheap-tubes-inc/.
- [24] G151-10 A. Standard Practice for Exposing Nonmetallic Materials in Accelerated Test Devices that Use Laboratory Light Sources. West Conshohocken, PA, USA.: ASTM International; 2010.
- [25] G154-16 A. Standard Practice for Operating Fluorescent Ultraviolet (UV) Lamp Apparatus for Exposure of Nonmetallic Materials. West Conshohocken, PA, USA.: ASTM International; 2016.
- [26] D. Santos, M.R. Costa, M.T. Santos, Performance of polyester and modified polyester coil coatings exposed in different environments with high UV radiation, Prog. Org. Coat. 58 (4) (2007) 296–302.
- [27] D3039/3039M-14 A. Standard Test Method for Tensile Properties of Polymer Matrix Composite Materials. West Conshohocken, PA, USA.: ASTM International; 2014.
- [28] Q. Shi, J. Gao, D. Zhao, S. Xu, Synergism effect between modified carbon black and organic ultraviolet absorber in polymer matrix for ultraviolet protection, J. Appl. Polym. Sci. 116 (5) (2010) 2566–2572.
- [29] A.R. Horrocks, M. Liu, UV Stabilising Synergies between Carbon Black and Hindered Light Stabilisers in Linear Low Density Polyethylene Films., in: Macromolecular Symposia, Wiley Online Library, 2003, pp. 199–220.
- [30] D3171-15 A. Standard Test Methods for Constituent Content of Composite Materials. West Conshohocken, PA, USA.: ASTM International; 2015.
- [31] E. Borowski, E. Soliman, U.F. Kandil, M.R. Taha, Interlaminar fracture toughness of CFRP laminates incorporating multi-walled carbon nanotubes, Polym 7 (6) (2015) 1020–1045.
- [32] Y.S. Song, J.R. Youn, Influence of dispersion states of carbon nanotubes on physical properties of epoxy nanocomposites, Carbon 43 (7) (2005) 1378– 1385.
- [33] E. Soliman, M. Al-Haik, M.R. Taha, On and off-axis tension behavior of fiber reinforced polymer composites incorporating multi-walled carbon nanotubes, J. Composite Mater. 46 (14) (2012) 1661–1675.
- [34] E. Greenhalgh, Failure analysis and fractography of polymer composites, Elsevier, 2009.
- [35] M.S. Kumar, K. Raghavendra, M.A. Venkataswamy, H.V. Ramachandra, Fractographic analysis of tensile failures of aerospace grade composites, Mater. Res. 15 (6) (2012) 990–997.
- [36] W.-J. Kim, S.-O. Kang, C.S. Ah, Y.-W. Lee, D.H. Ha, I.S. Choi, et al., Functionalization of shortened SWCNTs using esterification, Bull.-Korean Chem. Soc. 25 (9) (2004) 1301–1302.
- [37] W. Zou, Du Z-j, Liu Y-x, X. Yang, Li H-q, C. Zhang, Functionalization of MWNTs using polyacryloyl chloride and the properties of CNT-epoxy matrix nanocomposites, Compos. Sci. Technol. 68 (15) (2008) 3259–3264.
- [38] Ł. Byczyński, M. Dutkiewicz, H. Maciejewski, Synthesis and properties of highsolids hybrid materials obtained from epoxy functional urethanes and siloxanes, Prog. Org. Coat. 84 (2015) 59–69.
- [39] Y. Kwon, Yim B-s, Kim J-m, J. Kim, Mechanical and wetting properties of epoxy resins: Amine-containing epoxy-terminated siloxane oligomer with or without reductant, Microelectron. Reliab. 51 (4) (2011) 819–825.
- [40] S. Wang, Y. Li, X. Fei, M. Sun, C. Zhang, Y. Li, et al., Preparation of a durable superhydrophobic membrane by electrospinning poly (vinylidene fluoride) (PVDF) mixed with epoxy-siloxane modified SiO2 nanoparticles: A possible route to superhydrophobic surfaces with low water sliding angle and high water contact angle, J. Colloid Interface Sci. 359 (2) (2011) 380–388.
- [41] R.M. Pasternack, S. Rivillon Amy, Y.J. Chabal, Attachment of 3-(aminopropyl) triethoxysilane on silicon oxide surfaces: dependence on solution temperature, Langmuir 24 (22) (2008) 12963–12971.
- [42] R.S. Woo, Y. Chen, H. Zhu, J. Li, J.-K. Kim, C.K. Leung, Environmental degradation of epoxy-organoclay nanocomposites due to UV exposure Part I: Photo-degradation, Compos. Sci. Technol. 67 (15) (2007) 3448–3456.
- [43] M. Liu, A. Horrocks, Effect of carbon black on UV stability of LLDPE films under artificial weathering conditions, Polym. Degrad. Stab. 75 (3) (2002) 485–499.
- [44] J.A. Sobrino, M. Pulido, Towards advanced composite material footbridges, Struct. Eng. Intl. 12 (2) (2002) 84–86.