Polyester composite water uptake and organic contaminant release affected by carbon nanofiber reinforcements

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ABSTRACT: The incorporation of carbon nanofiber (CNF) into glass fiber (GF) composites is a potential route to extend polymer composite service-life and enhance mechanical properties. Under nonstatic conditions, only limited information concerning water uptake and contaminant release properties of nanocomposite materials is currently available. Polyester composites containing GF and oxidized CNF were immersed in water for 30 days under nominal pressure at 23 °C, below the polymer's glass-transition temperature. Water was analyzed and changed every three days to simulate water chemistry regeneration similar to exposures in flowing systems. Composites with oxidized CNF had greater water sorption capacity and leaching rates than CNF-free composites. The total mass of organic contaminant released correlated with the amount of water sorbed by each composite ($r^2 = 0.91$), although CNF dispersion was found to vary greatly within composites. The greatest and least contaminant release rates were found for the polyester-CNF and the polyester-GF composites, respectively. While volatile aromatic resin solvents and stabilizer compounds were detected, their concentrations declined over the 30 day exposure period. We hypothesize that the hydrophilic nature of the oxidized CNF increased the water sorption capacity of the polyester composites. Additional studies are warranted that examine the impact of this phenomenon on composite mechanical and long-term durability properties. © 2016 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43724.

INTRODUCTION

As North American buried water infrastructure pipelines continue to deteriorate, inexpensive, and corrosion resistant replacement materials are needed. Corrosion resistant fiber reinforced plastic (FRP) pipes have been used for more than 60 years for drinking water conveyance[1–3] and have a high strength to weight ratio. FRPs typically consist of a polymer matrix (i.e., polyester, epoxy, or nylon) reinforced with glass, carbon, graphite, or aramid fibers.[4–10] Incorporation of carbon nanofiber (CNF) into resins and fiber composites can further improve their mechanical properties.[11] CNF reinforcements are high aspect ratio nanofibers spanning a wide range of diameters (50–200 nm) and lengths (30–100 μm). Further, the hydrophilic nature of CNF surfaces reportedly enables easy dispersion into polar matrices. This combination of properties have been shown to improve FRP tensile strength, compression strength, Young's modulus, fracture toughness, and delamination resistance.[12–16] Many nanotechnology enhanced water infrastructure materials containing multiwall carbon nanotubes, TiO_2 and clay, have already received U.S. patents and some are being sold outside North America for potable water transport.[17–21]

Despite scientific research associated with the performance of nanocomposites, such as CNF in FRP pipes, there is little to no information regarding its influence on water/polymer interactions. It is well-known that polyester composites uptake water when immersed in deionized, tap, brackish, and salt water solutions (Table I).[22–25] Composite water sorption is important because water can degrade the polymer/fiber interface, facilitate matrix oxidation or void formation, and lead to FRP mechanical performance reductions.[26–32] Investigators have observed that GF reduces water sorption compared with resin only materials,[31,33,34] since glass fibers (GF) displace resin volume, do not

Additional Supporting Information may be found in the online version of this article.

Table I. Impact of Water Exposure on FRP Mechanical Properties: Literature Summary

Polymer matrix (reinforcement type)[Reference]	Aging condition	Result summary
u–Isophtalic polyester and vinyl ester resins (GF)[31]	DI (pH NR); 40 °C, 80 °C; 3 months	GF composites sorbed 45% to 82% less water than polyester resin only materials at 40 °C and roughly 20% less water at 80 °C. Water absorption was controlled by T_g and water temperature. Decrease in mechanical properties observed for both composites as a result of decrease in fiber-matrix interfacial adhesion.
u–Polyester resin (GF)[24]	TW (pH NR); 20 °C; 1,000 h	Water uptake measurements were conducted but not reported; Water immersion reduced creep strength by 60%.
u–Polyester resin (GF)[30]	DI (pH NR); 30 °C; (7, 14, 21) days	Water uptake measurements were not conducted; Water immersion caused delamination between fiber and matrix along with increasing bending strength, and a significant reduction in tensile strength.
Urethane and modified urethane resin (GF)[34]	Alkaline water (pH 13.4); temp NR; 6 months	GF inhibited water uptake. After 6 months aging, no reduction in tensile strength for unloaded composites was observed but tensile strength reduction was observed for the samples that were subjected to sustained load during the aging.
u–Polyester resin (GF)[25]	DI (pH NR); Room temp; 9 months	GF composite elastic modulus decreased by 2–5%; Water absorption data did not fit the Fickian diffusion model; The Lucas–Washburn capillary flow model was deemed more appropriate.
u–Polyester resin (GF)[27]	Artificial sea water (3.4–3.5% salinity) (pH NR); 30 °C; (10, 30, 60, 90, 120) days	Water uptake data were not reported; Water immersion decreased composite tensile strength and bending resistance; Material extraction was detected by an observed reduction in specimen mass during immersion.
Epoxy resin (GF, flax fiber)[33]	Water (pH NR); Room temp; (10, 20, 30, 40) days	The fiber–polymer interface was damaged due to water immersion for both reinforcement types; flax fiber reinforced composites sorbed 12 times more water than GF composites.

u, unsaturated; DI, Distilled water; TW, Tap water; NR, Not reported; Not all studies reported water pH or the ionic quality of the test water.

absorb water, and may reduce the water diffusion coefficient through the composite.[31] Although the GFs do not absorb water, secondary degradation processes can be triggered by surface reactions in the presence of water, which degrades the fiber/matrix interface resulting in loss of mechanical performance. The presence of CNF can adversely affect moisture diffusion properties in an FRP but the extent of diffusion on damage tolerance is not sufficiently quantified in the literature.

A percolated, hydrophillic CNF network has the potential to adversely affect water quality. In the presence of water, contaminants normally confined within the polymer network can diffuse into the

contact water. The diffusion rate is a function of the contaminant molecule size, polarity, concentration gradient, and temperature. The relationship between water transport through reinforced composites and the chemical leaching by the composites are a fairly well studied phenomenon.[35–37] As the composite achieves equilibrium with the surrounding water, the diffusion process can be modeled by applying one of three approaches: Fickian, Case II, and the two phase model.[38] Generally, the water uptake rate (immersion) and water loss rate (drying) are greatest (linear) during the initial exposure periods because the concentration gradients between contact water and composite are at a maximum.

From an application standpoint, the impact of a polymer composite on water quality is extremely significant, considering an estimated 60–100 year expected lifetime use of these pipelines.[39] However, on surveying water quality from 16 countries, there were only two published FRP investigations concerning water quality and both had little or no data on nanomaterial reinforced plastics.[40] FRP pipes are manufactured using three basic components namely, the resin (i.e., polyester, vinyl ester), the solvents (i.e., styrene, benzene, ethylbenzene), and the catalysts [i.e., methyl ethyl ketone peroxide (MEKP), dimethyaniline, cobalt naphthenate].[41] It has been shown that the solvents and catalysts used for composite manufacture are often environment polluting and highly carcinogenic. In the 1990s, researchers in the U.K. discovered that polyester/glass fiber (P/GF) pipe released several carcinogenic and endocrine disrupting organic contaminants into distilled water during a 24 h leaching period.[3] Several organic contaminants with and without drinking water health standards were found and included: Phthalic acid ester (26 μg/L), dimethyl phthalate (21 μg/L), benzaldehyde (4 μg/L), acetophenone (3 μg/L), styrene (0.7 μg/L), and tris(2–carboxyethyl)phosphine (3 μg/L). Other contaminants detected but not quantified were dialkoxy phthalate ester, dioctylphthalate, benzoic acid, nonanol, and 2–ethyl hexanoic acid. This 24 h test was the most experimentally quantitative effort found in the literature. In another effort, researchers in the U.S. reported that FRP well casings leached "five different contaminants into distilled water," but neither the contaminants nor experimental conditions were described.[42] No other studies were found that described either FRP contaminant leaching, the role of CNF reinforcement on material leachability, or water quality impacts caused by CNF containing composites. As real world applications of nano-FRPs are being realized, understanding the influence of nanofillers on the type and concentration of contaminants released into contact waters would highly benefit municipalities installing these solutions, standards bodies developing test methods, safety regulators, and commercial composite pipe manufacturers.

The hypotheses for this work were that GF reinforced FRP materials would uptake less water than a polyester material and CNF incorporation would not affect water uptake or leaching because of its low mass fraction in the composite. Specific objectives of these measurements were to: (1) quantify the impact of CNF on water quality and composite mass during a 30 day aging period and subsequent desiccator drying and (2) identify relationships between the contact solution quality and the composition of the composites. Several water quality characterization methods were applied to elucidate the magnitude of chemical release.

EXPERIMENTAL

Composite Fabrication

Four specimens were manufactured: Polyester only (P/O), and three composites including polyester/CNF (P/CNF), P/GF, and P/GF/CNF. Unsaturated polyester resin (Cook Composites & Polymers, Product ID: CI–1001–25), 0.005 mass fraction MEKP, eight layers of E–glass random fiber mats sized with an undisclosed silane coupling agent (Saint–Gobain Vetrotex America,

M113 random chopped strand mat) and 0.01 mass fraction of CNF (Pyrograf, PR–24 LHT, 150 nm average diameter, range of 70–200 nm diameter, 50–200 μm length, density of 1.9 g/mL) were used. Because of their high surface area, oxidized CNFs can be dispersed easily into polar polymer matrices such as epoxy, polyester and vinyl ester and show significant improvements in their mechanical properties.[43] In this study, oxidized CNFs were mixed with polyester resin and sonicated in a cold water bath for 45 min. The mixture was then degassed for 10 min and MEKP was added. P/GF and P/GF/CNF panels were manufactured with the Vacuum Assisted Resin Transfer Molding (VARTM) process.[15] P/O and P/CNF panels were cast in an open mold and allowed to cure for 12 h at room temperature. Composite thicknesses were statistically not different from one another and the surface area of each composite subjected to water immersion was ~435 cm^2. Sample thickness ranged from 2.85 to 3.40 mm.

Water Immersion and Water Quality Testing

Synthetic water (pH 6.9, 47.2 mg/L as $CaCO_3$, 23 °C) was prepared using Type I Millipore® Milli–Q water, $NaHCO_3$, and HCl. Specimens were immersed in covered glass jars filled with synthetic water (headspace free) for 30 days. Every three days, contact water was removed, characterized, and replaced with new synthetic water. The water exchanges simulated two conditions: water replenishment similar to a flowing system and water chemistry stabilization through solvated ion renewal. Water quality characterization was conducted using three replicates for each composite. The 30 day immersion period was selected to characterize short-term water quality changes caused by composite contact. The concentration gradient between the composite and contact water was reset every three days. Thus, the water uptake data does not represent a single equilibrium condition. This approach was necessary to obtain enough water sample to describe chemical leaching during the study period and the release of volatile organics. This concentration gradient "reset" approach is often used by the National Sanitation Foundation International, an organization that certifies potable water contact materials in the US.[44] While this approach enabled quantification of water quality impacts, standard water diffusion models were not applicable with the data collected in this study. Regardless, the contaminant concentration was expected to decrease over time and this trend was confirmed from our experiments.

Water quality monitoring techniques in accordance with standard methods[45] were applied to examine how the composites influenced the water chemistry. Alkalinity was determined with 0.025 N sulfuric acid and a titration end point of pH 4.5. Water pH was measured using an Accumet pH meter (Fisher Scientific; Pittsburg, PA) based on standard methods. Chemical oxygen demand (COD) concentration was measured by application of the U.S. Environmental Protection Agency ultralow range reactor digestion method. COD represents the total amount of organic contaminants present that are biodegradable as well as nonbiodegradable. Total organic carbon (TOC) concentration was determined by applying the nonpurgeable organic carbon method with a Shimadzu TOC Analyzer. Contaminant biodegradability testing was carried-out according to methods
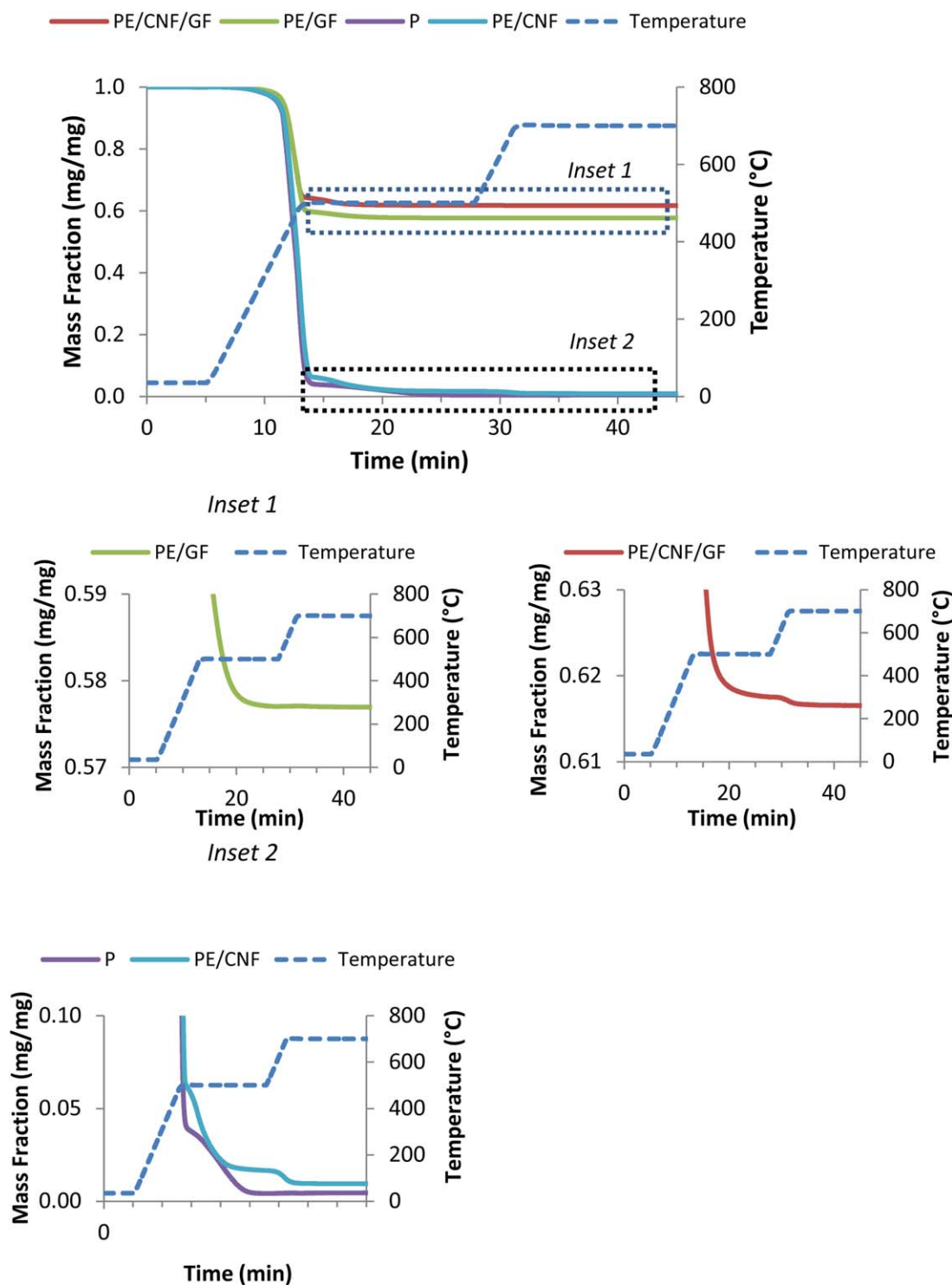
Figure 1. TGA scans for P/O, P/CNF, P/GF, and P/CNF/GF. Inset 1, left shows the loss of mass during the ramp to 700 °C for GF composites. Inset 1, right shows the loss of mass during the ramp to 700 °C for the GF composite containing CNF. Inset 2 shows the loss of mass during the ramp to 700 °C for the nonglass containing composite for matrix and nanocomposite. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

described in the SI. UV absorbance at 254 nm (UV_{254}) wavelength was recorded using a HACH DR5000 UV–Vis spectrophotometer. UV_{254} measures the quantity of sp^2 hybridized carbon and is frequently applied to gauge the level of dissolved

aromatic compounds in water. On day 3 and 30, contact waters were also characterized using solid–phase microextraction (SPME) gas chromatography–mass spectroscopy to determine if volatile organic compounds (VOCs) were leached from the

composites. A 85 µm polyacrylate coated SPME fiber was conditioned at 280 °C for 3 h before initial application of the GC port . For sampling, the fiber was exposed to the sample headspace with a 10 min adsorption time at 55 °C. Desorption was conducted in the GC injector at 220 °C for 2 min. A SPME inlet liner (splitless, 0.75 mm I.D.) was used in the injection port. The GC carrier gas was helium at a flow rate 0.65 mL/min. The GC temperature program involved a ramp from 50 to 100 °C at 10 °C/min, and was maintained for 25 min. A split/splitless injector in the splitless mode was used and held isothermally at 220 °C.

Composite Characterization

Water absorption and desorption was characterized for each composite. Absorption was measured gravimetrically during the 30 day water immersion period. Desorption was calculated during 30 days desiccator drying at room temperature. Moisture uptake and mass loss were calculated eq. (1):

$$\text{Mass Gain, Mass Loss} = \frac{M_0 - M_t}{M_0} \times 100 \qquad (1)$$

where M_o was the initial sample mass and M_t was the specimen mass at time of t.

Thermogravimetric (TGA) measurements were conducted with a Q500 instrument (TA Instruments) with an air purge flow. Three replicates were conducted to determine variability within the composites. Specimens were degraded utilizing a stepped isotherm process. In the first step, the sample was rapidly heated (<10 min) to 500 °C and held for 15 min. This action removed the majority of matrix polymer from the composite. The sample was then rapidly heated to 700 °C and held for 15 min. This process removed residual CNF material and left a residual glass in the TGA pan, for the case of glass containing composites. Thermal oxidation of raw CNFs exhibited a mass fraction loss of approximately (0.03 ± 0.01) mg/mg during the 500 °C isotherm and a final mass fraction of (0.045 ± 0.001) mg/mg (residual mass fraction) after heating to 700 °C. The presence of a stable char indicates there were noncombustible components left from the thermal degradation process. Since there is a residual char present in both the combustion of the polyester and the CNF and the void fraction of the composite was not measured, it is not possible to calculate the exact composition of the original composite. The residual char in the composite is assumed to polyester decomposition in order to calculate the apparent mass fraction of resin in each composite. The glass transition temperature (T_g) of each composite was identified using TA Instrument Q2000 differential scanning calorimeter. Temperature was ramped from 40 to 150 °C at 10 °C/min, quickly cooled to 40 °C at 20 °C/min, then reheated to 150 °C at 10 °C/min to confirm the observed T_g. Nitrogen (50 mL/min) was the applied purge gas.

For scanning electron microscopy (SEM), fractured cross section surfaces of P/CNF and P/GF/CNF were mounted onto a stainless steel stub using a highly conductive, double coated carbon tape (Ted Pella®) inside a JEOL®, JSM – 7600F (Schottky field emission), scanning electron microscope (SEM). The samples were imaged primarily using the GB-H (gentle beam) settings to counteract excessive surface charge. The SEM settings utilized

are as follows; gun voltage: 0.7–2 kV, substrate bias: 0.7–2 kV, probe currents: 20–40 pA; WD: 4–8 mm. Exposed surfaces of the P/GF/CNF samples were imaged as provided to preserve the surface details on the specimens.

Data Interpretation and Analysis

Water quality data represent a series of 3-day leaching tests with the same composite over a 30 day period. Based on this approach, the 30 day results were analyzed by two-way analysis of variance and 95% confidence interval. To interpret water quality results, each aqueous contaminant concentration (mg/L) was divided by the initial mass of resin in each composite (mg/L–mg resin), determined as the mass fraction loss at the end of the 500 °C isotherm. This enabled all water quality data to be compared on a "mg of contaminant/L of water – mg of resin" estimated basis. This method incorporates an inherent mass error of 0.01 mg/mg mass fraction in the resin. Water sorption data were converted to "mg of water sorbed/mg of resin" basis. All statistics were applied using a Type I error of 0.05. Regression analyses were conducted on each contaminant leaching data set. Regression slopes using 95% confidence intervals were applied to elucidate whether or not contaminant release rates differed between the various composites.

RESULTS AND DISCUSSION

Composite Composition

TGA showed the quantity of CNF was smaller than expected from processing (Figure 1). The instrument was able to resolve the decomposition of the CNF, but the standard deviation was 33% for the P/CNF and 57% for the P/CNF/GF. The magnitude of uncertainty is similar to the uncertainty in the residual mass fraction, which suggests the quantity of CNF in the composites is near the limit of measurement resolution or the distribution of CNF in the composites is heterogeneous. SEM was conducted on sample cross-sections to verify the distribution of CNF.

No difference was found between the glass-transition temperatures either before or after water adsorption/desorption testing. T_g values for the epoxy ranged between 64 and 72 °C (Table II). SEM images of the fractured P/CNF composite revealed large agglomerates of CNFs with diameters of a few tens of microns [Figure 2(a,b)]. These large agglomerates were found uniformly across the cross-section. Despite CNF's hydrophilic nature, the sonication process did not effectively disperse individual large aspect ratio CNFs (Supporting Information Figure 1S). Similar SEM analysis on the P/GF/CNF samples found a bimodal CNF distribution where individual CNFs were sparsely visible in the cross-sectional regions between GF layers [Figure 2(c)], while dense CNF agglomerates were found on the top surface of the VARTM processed composite [Figure 2(d)]. The dimensions of the CNFs observed in both cases agreed with manufacturer specifications of diameters and fiber lengths.

These analytical techniques suggest an inhomogeneous dispersion and a unique mass fraction and distribution of CNFs within each composite type. The surface aggregation of CNF in the GF composite likely results from the VARTM processing combined with the presence of large CNF agglomerates in the matrix. The VARTM process is a dynamic method that utilizes

Table II. Material Properties from Gravimetric, Thermal, and Mechanical Characterization

Composite	Material type			
	Polyester	P/CNF	P/GF	Polyester-GF/CNF
Resin, mass fraction	0.988 ± 0.005	0.980 ± 0.005	0.400 ± 0.032	0.368 ± 0.014
GF, mass fraction	0	0	0.600 ± 0.032	0.631 ± 0.014
CNF, mass fraction	0	0.006 ± 0.002	0	0.0007 ± 0.0004
Residual, mass fraction	0.012 ± 0.005	0.014 ± 0.008	N/A	N/A
Measured T_g, °C	67.6 ± 2.9	65.3 ± 2.1	72.0 ± 0.9	68.1 ± 1.5
Storage modulus (MPa) at 40 °C	3,592	3,499	13,837	11,853

The constituent components are based on the change in mass from TGA thermal degradation. T_g results represent mean and standard deviation values for two individual replicates on first heating. Residual for P/GF and P/GF/CNF composites at 700 °C could not be differentiated from GF. Storage modulus results were reported by Jefferson et al.[46]

the flow of a low viscosity resin to fill the GF. Since the CNFs were found to exist as large agglomerates in the P/CNF composite, it is likely these agglomerates were either filtered by the GFs or preferentially transported to the exterior surface of the composite, in particular, resin rich regions where the flow velocities are higher.

Water Absorption and Desorption Kinetics
Each material reached water saturation over the course of the 30 day exposure (Figure 3). All specimens exhibited a small mass loss of ~0.5% for P/O, P/CNF, and P/GF/CNF after desic-

cation (Supporting Information Table 1S). Observed mass loss indicated that the water diffusion coefficient calculations could not be conducted.

Composites that contained oxidized CNF sorbed more water compared to the non-CNF containing materials (Figure 3). The GF composite absorbed the least amount of water and this result is similar to what has been observed in the literature, where polyester GF composites absorbed less water than its resin-only counterparts.[31,33,34] The inclusion of GF reduced the volume of polyester resin available for water absorption.
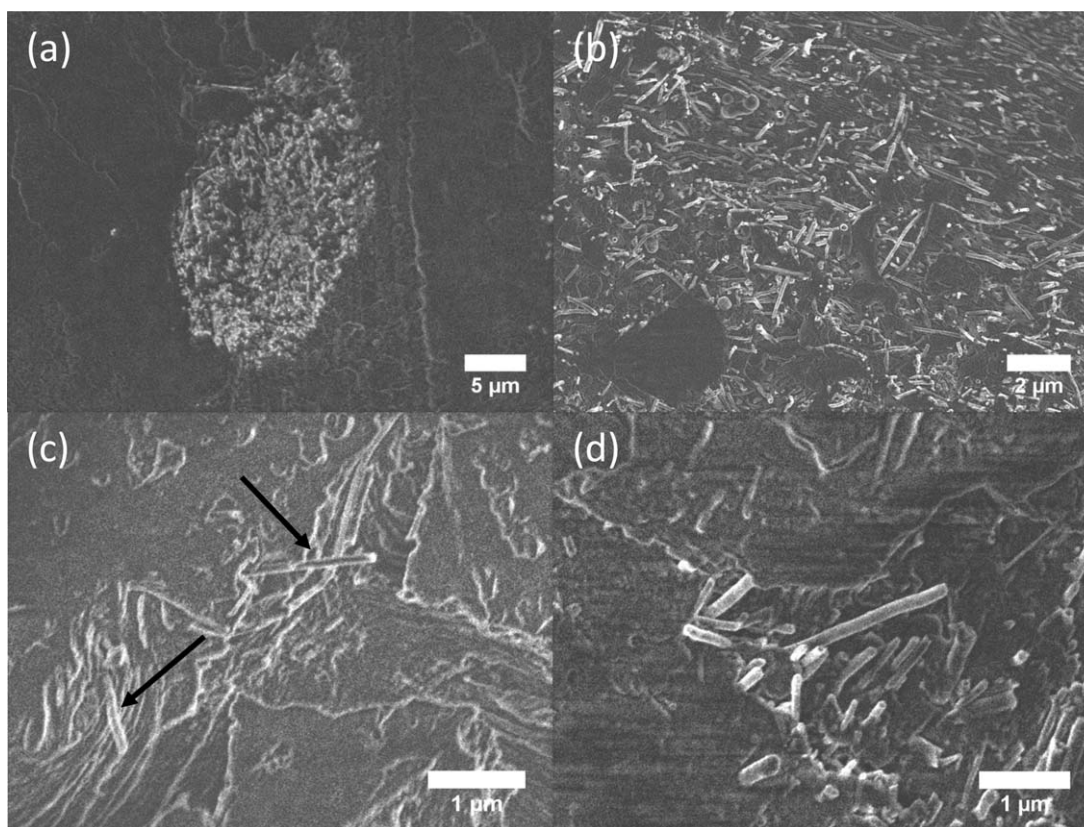

Figure 2. Representative SEM images of (a) large agglomerate of CNF in the P/CNF composite, (b) distribution of CNF within a CNF agglomerate in the P/CNF cross-section, (c) sparsely distributed CNF across the P/GF/CNF cross-section (arrows), and (d) dense agglomerate of CNF on the top surface of P/GF/CNF composite. Supplemental contains low magnification images of the P/GF/CNF top surface.
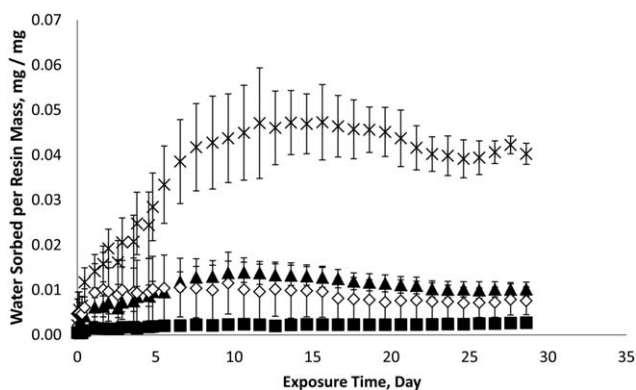
Figure 3. Moisture Content of Composites Compared on a Composite Mass of Resin Basis. Symbols represent (▲) P/O, (■) P/GF, (✳) P/CNF, and (◇) P/GF/CNF. The standard deviation of the measurement was ± 0.05 mg/mg.

Oxidized CNF also increased water absorption for the P/GF/CNF composite, but the change was not drastic as the polyester CNF composite. The hydrophilic nature of the oxidized CNFs likely contributed to the increased water sorption capacity of CNF containing materials. Other investigations indicate that incorporation of hydrophilic reinforcement fibers (i.e., vegetable, flax) increases polyester composite water sorption capacity by as much as 12 times.[23,33] When compared with the non-CNF containing materials, the initial rate of moisture uptake was greatest for the CNF materials in this study.

Impact of Composites on Water Quality

All composites released organic contaminants during the entire 30-day study period. The expected exponential decay curve for contaminant release was not observed because the exposure period consisted of a series of 3-day exposure periods; the concentration gradient was constantly reset. As a result, a diffusion model was not fit to the leaching data. Figure 4 shows the normalized leaching total organic contaminant (TOC) and COD concentrations for the four tested materials. Constituent abstraction from the polyester matrix followed a similar trend to the water absorption measurements. Contaminant concentration in the exposure water decreased monotonically after each 3-day water change. The greater mass fraction of polyester resin corresponded to a greater number of chemicals detected in the water. In both the resin and GF composites, the presence of CNF increased the rate and quantity of contaminants released.

TOC and COD leaching rates differed across composites as determined by linear regression analysis. All regression slopes were non-zero. The greatest contaminant release rate was found for P/CNF, while normalized leaching for P/O and P/GF/CNF composites were not different for COD or TOC results, similar to the moisture absorption results (Supporting Information Table 2S). The P/GF composite had the lowest contaminant release rate. GF inhibited contaminant release but CNF inclusion into the P/GF composite caused that composite to perform similar to the polyester only material. UV$_{254}$ absorbance results also showed inclusion of CNF into polymers increased contaminant release into the contact water. A small fraction of contaminants released from each material were biodegradable and this

quantity was similar across the composites tested (Supporting Information Table 3S).

Several VOCs were detected in composite contact waters that include aromatic resin solvents and stabilizer compounds (Table III). These compounds were similar to those found by previous research on leachate from fiberglass resin circuit board composites.[47] None of the aqueous contaminants reported by others were found in the present work.[3] Possible reasons for this difference could be that the other study characterized the presence of semi-volatile organic contaminants and the polyester resin formulation differed. Inclusion of CNF into composites did not impact the number of VOCs released.

A linear relationship between organic contaminant release and the amount of water sorbed by each composite was detected ($r^2 = 0.96$; Figure 5). Chemical release was likely facilitated by water diffusion into the material and subsequent contaminant extraction. The incorporation of a small quantity of oxidized CNFs into polyester composites (0.01 mass fraction) caused nanocomposites to become more susceptible to water aging than their CNF free counterparts.

A dynamic system existed during the experiment as evidenced by composite and water quality characterization results. It was
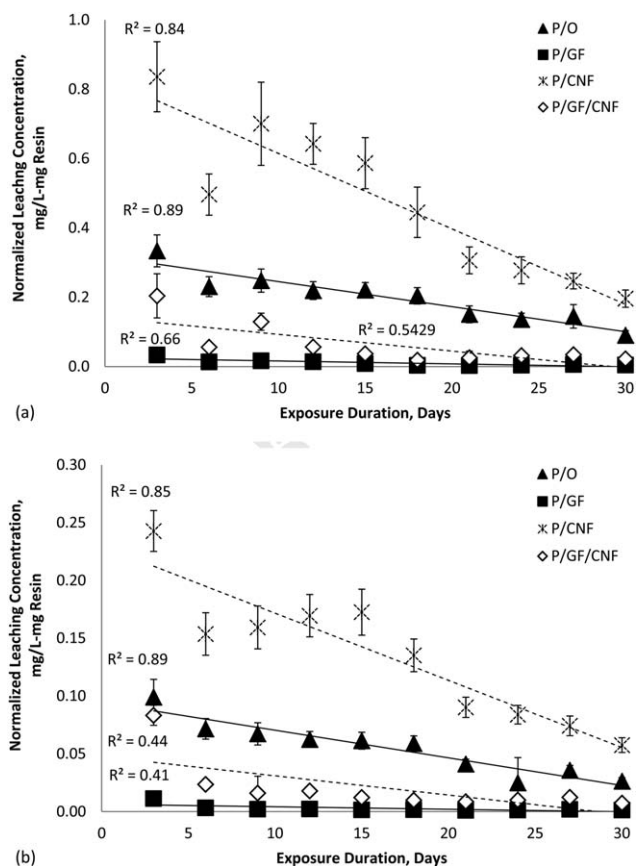

Figure 4. Water Quality Characteristics of Immersion Testing Normalized Leaching (a) COD and (b) TOC. Symbols represent (▲) P/O, (■) P/GF, (✳) P/CNF, and (◇) P/GF/CNF. The standard deviation of the measurement was ± 0.02 mg/L-mg Resin. The dashed lines represent a guide for the eye.

Table III. Volatile Organic Contaminants Detected in Contact Waters at Day 3 and Day 30

Name of compound (purpose)[c]	Day 3				Day 30			
	O	CNF	GF	GF/CNF	O	CNF	GF	GF/CNF
Styrene (resin solvent)	X	X	X	X	X	X	X	X
Ethylbenzene (resin solvent)[a]	X	X	X	X	X			
p–, o–Xylene (resin solvent)[a]	X	X	X	X	X	X		
Toluene (resin solvent)[a]	X	X	X	X				
1,2,3–TMB (stabilizer)[b]	X	X		X	X			
1,3,5–TMB (stabilizer)[b]	X	X	X	X				

[a] Suspected purpose of the contaminant.
[b] TMB = trimethylbenzene.
[c] "x" signifies the contaminant was detected as confirmed with a >93% library match.

shown that oxidized CNF caused composites to be more sensitive to water uptake compared to the CNF-free composites. Even a small magnitude of CNF in the GF composite caused a substantial change in composite water uptake. Because oxidized reinforcements are preferred to achieve better dispersion and bonding in hydrophilic matrices the impact of these materials on water sorption and mechanical properties, deserve further study. Results also indicate that a nanocomposite design strategy that limits water uptake may also limit organic contaminant leaching.

CONCLUSIONS

Results of this work have direct relevance to composite manufacturers and water infrastructure managers. Incorporation of a very small amount of oxidized CNF significantly altered water-composite interactions. Specifically, composites with CNFs sorbed more water and leached more organic contaminants than CNF-free composites. Even an addition of small oxidized CNF quantities in the GF composites caused the P/GF/CNF composites to absorb more water and release higher contaminants than the plain P/GF counterparts. While oxidized CNFs

are preferred for hydrophilic matrices, results from the present study indicate composite manufacturers should also consider their impact on composite mechanical and long-term durability properties. Greater water sorption may expedite chemically induced degradation processes. Water infrastructure managers should also consider that greater VOC leaching may be a CNF composite performance challenge that current CNF-free materials do not encounter. In addition, the additional rate of leaching from CNF containing materials is important in the context of water quality standards used to return rehabilitated pipelines to service.

Figure 5. Relationship between Total Mass of Organic Carbon Released by Each Material during the 30 Day Exposure Period and Maximum Quantity of Water Sorbed into Each Material Measured on Day 30. The figure the shows the total mass of organic carbon released per composite during the total 30 day exposure period versus the initial mass of resin per composite. Simultaneous water sorption and organics extraction occurred. Error bars (not shown) are equivalent to measurements in Figures 2 and 3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

REFERENCES

1. American National Standards Institute (ANSI)/AWWA. Standard C950–07 for Fiberglass Pressure Pipe; American National Standards Institute: Denver, CO, **2007**.

2. AWWA. M45 Fiberglass Pipe Design, 2nd ed.; AWWA: Denver, CO, **2005**.

3. Crathorne, B.; James, C. P.; Norris, M. Effect of Distribution on Organic Contaminants in Potable Water. Final Report to the Department of Environment. Water Research Centre (WRc): Birmingham, UK, **1990**.

4. GangaRao, H.; Liang, R. Advanced Fiber Reinforced Polymer Composites for Sustainable Civil Infrastructures. Proceedings of the International Symposium on Innovation & Sustainability of Structures in Civil Engineering, Xiamen University, China, **2011**.

5. GangaRao, H.; Vijay, P. V. Feasibility Review of FRP Materials for Structural Applications. Report submitted to US Army Corps of Engineers; Engineering Research & Development Center: Vicksburg, MS, USA, **2010**.
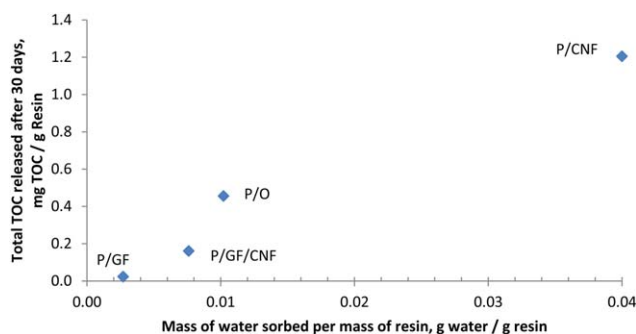
6. Ehsani, M.; Peña, C. FRP Repair of Mile–Long Pipeline with Minimum Downtime, The Northern California Pipe User's Group. Proceedings of the 18th Annual Sharing Technologies Seminar, Berkley, CA, USA, February **2010**.

7. Varga, C. S.; Miskolczi, N.; Bartha, L.; Lipoczi, G. *Mater. Des.* **2010**, *31*, 185.

8. Karbhari, V. M. Durability Data for FRP Rehabilitation Systems, Final Report. Submitted to the California Department of Transportation, Contract No. 59A0309, Sacramento, CA, USA, February **2009**.

9. Gamstedt, E. K.; Skrifvars, M.; Jacobsen, T. K.; Pyrz, R. *Compos. A* **2002**, *33*, 1239.

10. Salibi, Z. *Desalination* **2001**, *138*, 379.

11. Khanna, V.; Bakshi, B. R. *Environ. Sci. Technol.* **2009**, *43*, 2078.

12. Sahin, ÖS.; Akdemir, A.; Avci, A.; Gemi, L. *J. Reinforced Plast. Compos.* **2009**, *28*, 2957.

13. Li, B.; Wood, W.; Baker, L.; Sui, G.; Lee, C.; Zhong, W. H. *Polym. Eng. Sci.* **2010**, *50*, 1914.

14. Gou, J.; O'Braint, S.; Gu, H.; Song, G. J. *J. Nanomater.* **2006**, *32803*, 1.

15. Sadeghian, R.; Gangireddy, S.; Minaie, B.; Hsiao, K.–T. *Compos. A* **2006**, *37*, 1787.

16. Finegan, I. C.; Tibbetts, G. G.; Glasgow, D. G.; Ting, J. M.; Lake, M. L. *J. Mater. Sci.* **2003**, *38*, 3485.

17. McDonald, E.; Whelton, A. J.; Jefferson, G. A.; Nguyen, T. *Am. Soc. Mech. Eng. (ASME) Early Career Tech. J.* **2011**, 1.

18. Lee, J.; Mahendra, S.; Alvarez, P. J. J. *ACS Nano* **2010**, *4*, 3580.

19. Whelton, A. J.; Duncan, T. V.; Koontz, J.; Nguyen, T. Nanoparticle Release from Polymer Nanocomposites Used for Potable Water Infrastructure and Food Packaging: Current Progress & Beyond; Proceedings of Nanotech Conference and Exposition. Session: Nanotechnology Environment, Health & Safety, Boston, MA, USA, **2011**; Vol. *3*, p 505.

20. Jarvenkyla, J. (to Plastic Pipe) U.S. Pat. 8,470,423 B2 (**2013**).

21. Jarvenkyla, J. (to Multilayer pipe) E.P. Pat. 1,708,881 A2 (**2006**).

22. Mezghani, K. *Polym. Test.* **2012**, *31*, 76.

23. Cruz, V. C. A.; Nobrega, M. M. S.; Silva, W. P.; Carvalho, L. H.; Lima, A. G. B. *Mater. Sci. Eng. Technol.* **2011**, *42*, 979.

24. Farshad, M.; Necola, A. *Polym. Test.* **2004**, *23*, 163.

25. Czel, G.; Czigany, T. *J. Compos. Mater.* **2008**, *42*, 2815.

26. Santhosh, K.; Muniraju, M.; Shivakumar, N. D.; Munusamy, R. *J. Compos. Mater.* **2012**, *46*, 1889.

27. Gu, H. *Mater. Des.* **2009**, *30*, 1337.

28. Svetlik, S. L. An Investigation in the Hygrothermal Degradation of an E–glass/vinyl–ester Composite in Humid and Immersion Environments; Dissertation. Department of Civil Engineering, University of California San Diego, CA, USA, **2008**.

29. Visco, A. M.; Calabrese, L.; Cianciafara, P. *Compos. A* **2008**, *39*, 805.

30. Huang, G.; Sun, H. *Mater. Des.* **2007**, *28*, 1647.

31. Fraga, A. N.; Alvarez, V. A.; Vazquez, A.; Osa, O. D. L. *J. Compos. Mater.* **2003**, *37*, 1553.

32. Chateauminois, A.; Chabert, B.; Soulier, J. P.; Vincent, L. *Composites* **1993**, *24*, 547.

33. Assarar, M.; Scida, D.; Mahi, A. E. L.; Poilâne, C.; Ayad, R. *Mater. Des.* **2011**, *32*, 788.

34. Cho, E. H.; Mounts, J. L. *J. Vinyl Addit. Technol.* **2007**, *13*, 221.

35. Ghani, M. A. A.; Salleh, Z.; Hyie, K. M.; Berhan, M. N.; Taib, Y. M. D.; Bakri, M. A. I. *Procedia Engineering* **2012**, *41*, 1654.

36. Dhakal, H. N.; Zhang, Z. Y.; Richardson, M. O. W. *Compos. Sci. Technol.* **2007**, *67*, 1674.

37. Zhang, J.-H.; Mao–Sheng, Z. *J. Compos. Mater.* **2004**, *38*, 779.

38. Crank, J.; Park, J. S. Diffusion in Polymers; Academic Press: London, UK (**1968**).

39. Dunphy Guzmán, K. A.; Taylor, M. R.; Banfield, J. F. Environmental risks of nanotechnology: National Nanotechnology Initiative funding, 2000-2004, *Environ. Sci. Technol.* **2006**. *40* (5), pp 1401–1407.

40. Whelton, A. J.; Nguyen, T. *Crit. Rev. Environ. Sci. Technol.* **2013**, *43*, 679.

41. Zenko, J. R.; Wicks, W.; Jones, N. F.; Peter Pappas, S.; Wicks, D. A. Organic Coatings: Science and Technology, 3rd ed.; Wiley: Hoboken, NJ, USA, **2007**.

42. Ranney, T. A.; Parker, L. V. Susceptibility of ABS, FEP, FRE, FRP, PTFE, and PVC Well Casing to Degradation by Chemicals, Special Report 95–1. US Army Corp of Engineers, Cold Regions Research & Engineering Laboratory, Hanover, NH, USA, January **1995**.

43. Lafdi, K.; Fox, W.; Matzek, M.; Yildiz, E. *J. Nanomater.* **2008**, 1.

44. National Sanitation Foundation International Standard/American National Standards Institute. Drinking Water Treatment Units, Ann Arbor, Michigan, USA, **2007**.

45. American Public Health Association (APHA). Water Environment Federation (WEF), and American Water Works Association (AWWA), Standard Methods for the Examination of Water and Wastewater, 20th ed.; Washington DC, USA, **2012**.

46. Jefferson, J. D.; Farah, B.; Hempowicz, M. L.; Hsiao, K. T. *Compos. B* **2015**, *78*, 319.

47. Guo, J.; Jiang, Y.; Hu, X.; Xu, Z. *Environ. Sci. Technol.* **2012**, *46*, 1028.

48. Henze, H. Biological Wastewater Treatment: Principles, Modeling and Design; Cambridge University Press: London, UK, **2008**.

49. Whelton, A. J.; Salehi, M.; Tabor, M.; Donaldson, B.; Estaba, J. *J. Environ. Eng.* **2013**, *139*, 746.