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Improved phosphate-based glass fiber performance achieved through acid etch/polydopamine treatment

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Abstract

Phosphate-based glass fibers (PGF) are of interest as reinforcements for degradable implants, but have seen limited application due to their rapid loss of strength when subjected to aqueous conditions. Previous studies have utilized heat treatments to improve longer term strength retention at a significant cost to initial strength. In this study, acid etching is used to recover the initial fiber strength after heat treatment and a subsequent coating of polydopamine is applied to provide longer term retention of this recovered strength. After an initial loss of strength after heat treatment (1135 -> 509 MPa), an optimized combination of acid treatment and polydopamine coating was able to recover to approximately 85% of the initial strength (969 MPa). The result was significant in comparison to acid treatment (647 MPa) or coating (688 MPa) alone. The combined acid/coating treatment was demonstrated to maintain fiber properties for at least 14 days, although the amount of polydopamine coating was observed to decrease over this period. The approach reported here is of importance as it offers the required step change in degradation performance that is needed for PGF-reinforced degradable composites.

KEYWORDS
acid treatment, annealing, coatings, mechanical properties, phosphate fibers, polydopamine

1 | INTRODUCTION

Absorbable glass fibers based on phosphates have been investigated as potential reinforcement in degradable composites for a considerable period, with patents dating from the 1980s.[1-4]

They have not yet been realized as an effective reinforcement fiber, since while presenting good fiber properties[5,6] and extremely promising initial composite properties,[7-9] they do not manage to retain their properties for sufficient time for

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practical applications in aqueous conditions. For example, failure modes switch from brittle to ductile within days of degradation in an aqueous environment, with apparent interlaminar slip and fiber pull out indicating a loss of fiber/matrix interface.[10] There has as yet been no application requirement identified for a composite material with very rapid loss of properties in water, but there may yet be use for this attribute.

The very principles that make glass fibers effective reinforcements work against a degradable version. The high strength of glass fibers and their robustness is achieved through differential cooling during production. This results
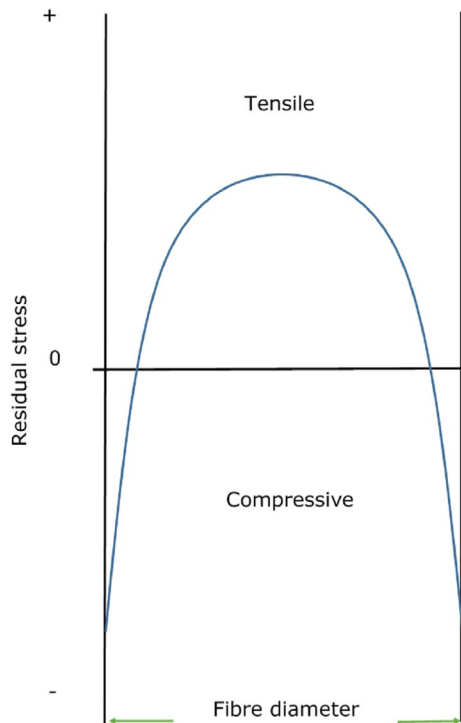
FIGURE 1 Diagrammatic illustration of the stress state across a glass fiber, with a core tensile stress and a compressive outer surface

in a tensile core providing strength and a compressive outer layer that acts to suppress flaws,[11] as illustrated in Figure 1.

However, phosphate-based glass fibers (PGF) degrade via surface erosion and, as can be seen from Figure 1, when a fiber erodes from the surface the compressive outer layer would gradually be lost and this leaves the tensile core vulnerable to catastrophic failure as soon as a flaw occurs.

Furthermore, any flaws present on the surface of the fibers are vulnerable to exacerbation by hydrolysis (which is accelerated under stress) and can act easily as points of crack propagation, causing fiber fragmentation once the crack traverses the compressive region.

This issue is exacerbated further as fibers become thinner, since composite reinforcement fibers are <30 μm and preferentially in the region of ~10 μm.[12] While the fiber properties are superior and stress transfer is improved, the larger surface area to volume ratio also increases overall degradation rates and reduces the absolute thickness of the compressive outer layer.

It has not been possible to overcome this problem through formulation, even using some of the most durable bulk glass compositions. There might be scope in the use of highly durable formulations such as aluminum phosphates but these have not been considered as the eventual application for PGF-reinforced composites has usually been focused toward medical applications, where the use of aluminum is not appropriate.[13]

Some limited improvement has been achieved through using manufacturing techniques such as in situ polymerization,[14] likely through an improved fiber wetting and minimization of voids that could retain water near the fiber surface.

There is also a large body of work around the use of chemical surface modifiers to improve the fiber/matrix interface, but this has also been of limited success.[15–17]

Thermal annealing of the PGF has shown promise, whereby the residual stresses are relieved. This reduces the stress-driven hydrolysis and smoothes the tension/compression profile across the fiber. Degradation rates have been considerably reduced as a result of this heat treatment[18] and the mode of degradation is seen to change. As-produced fibers degrade through a sloughing of the surface, via a combination of radial and axial cracks. With annealed fibers, this behavior has been observed to be either significantly reduced[19] or the behavior is changed entirely to surface/pitting erosion.[20] The difference in behavior may be related to the effectiveness of annealing.

However, as is well-known, heat treatment of glass fibers causes a significant loss of strength through the creation of surface flaws[21] and with the removal of surface compression through relaxation, these flaws are free to expand and form cracks. Interestingly, with PGF this loss in strength can be seen to recover over time to some degree,[6,19,22] presumably by this flawed surface being dissolved away. This has not greatly improved the composite results, however, as the lost surface still means a loss of the fiber matrix interface.

This study considers an approach to utilize the benefits of annealing PGF by deliberately accelerating the surface dissolution. In doing so a low stress fiber with a pristine surface can be provided for incorporation into a composite. Since the fresh surface will not fully benefit from the presence of a protective compressive outer layer, this treatment was also combined with a surface coating. The process involved etching with a solution of hydrochloric acid, followed immediately by a polydopamine coating, without allowing the fiber to dry (and thereby avoiding any surface tension-driven damage). Such an approach could be applied as a continuous process and incorporated into manufacturing relatively simply. Polydopamine was selected as catechols have been demonstrated to attach well on inorganic surfaces, provide adhesion in an aqueous environment and show promise in biomaterials applications.[23–25] Furthermore, it forms a very thin coating (10's of nm[25]) and so should provide a very small contribution to the interphase region between fiber and matrix in a composite. Thick coatings of polymers can have a substantial contribution to interphase regions, which significantly affects the macroscopic mechanical properties of a fiber-reinforced composite.[26]

As part of the study a simple shelf-life assessment was performed by storing the fibers for 9 months. The optimum
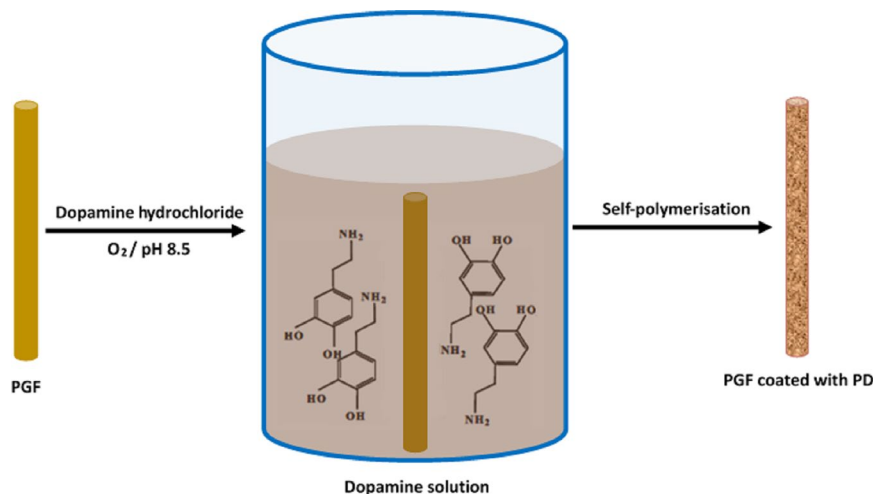
FIGURE 2 Schematic illustration of the polydopamine coating process applied after acid etching. Fibers are immersed in a solution of dopamine at pH 8.5 for 6 h

coating system was also assessed by resistance to degradation in water at 37°C, in comparison to the as received and annealed fiber.

2 | EXPERIMENTAL PROCEDURE

Fibers used in this study were produced by Sinoma Co. Ltd. using pilot scale production facilities. The fiber composition was 48 mol% P_2O_5, 12 mol% B_2O_3, 14 mol% CaO, 20 mol% MgO, 1 mol% Na_2O, and 5 mol% Fe_2O_3. Details of the properties of this glass composition have been published previously.[27] During drawing the fiber was coated with a proprietary water soluble epoxy to provide a protective outer coating.

Annealing was performed at 550°C (T_g + 10°C) for 90 minutes, followed by slow cooling. Acid etching was performed at room temperature using *ca.* 6 mol/L solution of hydrochloric acid (37% concentrated acid mixed 50/50 with deionized water) for different periods of time; 0, 5, 10, 15, and 20 minutes. After the prescribed etching period, the fibers were then rinsed with deionized water. Application of a polydopamine coating was performed directly after the rinse, before drying, following the process introduced by Lee et al[25] The process is shown schematically in Figure 2. The fibers were placed into a solution of 2 mg/mL dopamine hydrochloride (Sigma Aldrich) and 10 mmol/L tris buffer (Sigma Aldrich) in water (pH ~ 8.5) for 6 hours. After coating the fibers were rinsed with deionized water and dried at 50°C overnight. Based on the information provided by Lee,[25] it was anticipated that this treatment would form a coating approximately 30 nm thick on the fiber surfaces. An obvious color change is observed after coating.

For storage assessment, the fibers were kept in a plastic sample bag in a room maintained at ~20°C and ~40%

humidity for approximately 9 months. The annealed (AN) and optimum (10 minutes) acid treated/coated samples (AN/PD) were retested after this time period. In order to assess the efficacy of the coating in the early stages of exposure to water, the as received (AR), AN, and AN/PD fiber sets were also subjected to degradation tests in deionized water at 37°C for 14 days. The degradation medium (water) was changed at the 7 day time point. Based on previous studies,[19,20] 14 days was anticipated to be sufficient time to observe significant differences in the fiber degradation behavior.

Fiber testing was performed on a LEX-810 single filament tensile testing setup (Diastron, Andover) using a 2000 N load cell, a gage length of 25 mm and a testing speed of 1 mm/min. Analysis of the samples was based on the BS ISO 11 566 carbon filament testing standard, using the indicated method for selecting strain limits to calculate modulus. Diameters of the fibers were measured individually at the point of testing using a Mitutoyo LSM6200 laser scan micrometer (Mitutoyo, Kawasaki, Japan), calibrated using PGF of known diameter as determined by SEM. The error in diameter measurement was taken to be ± 0.3 μm. Minitab software was used to calculate Weibull values and to perform statistical comparison via ANOVA using a 95% CI and Tukey comparison.

SEM was performed using an XL30 SEM (Philips) at 20 kV accelerating voltage and 20 mm working distance. The fibers were mounted on adhesive carbon tabs and then coated with platinum for 90 seconds at 2.2 kV using a Polaron SC7640 coater (Quorum Technologies). Images were recorded using magnifications between ×1000 and ×16000. The images presented in the results section are at a magnification of ×4000.

X-ray Photoelectron Spectroscopy was conducted using a VG ESCALab Mark II X-ray photoelectron spectrometer with a monochromatic AlK_α X-ray source. The beam incidence angle was maintained at *ca.* 30°. Survey and
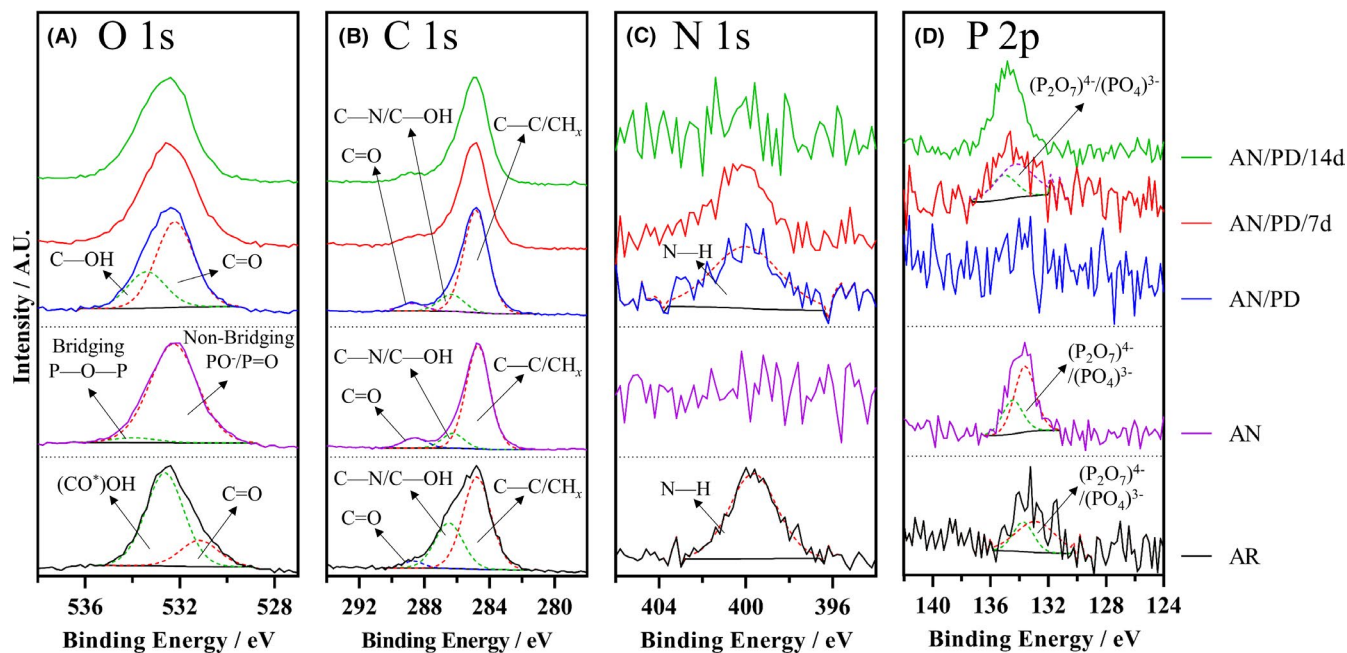
FIGURE 3　XPS analysis of as received (AR), annealed (AN), 10 min acid treated and polydopamine coated (AN/PD), as well as 7 d (AN/PD/7d) and 14 d (AN/PD/14d) degraded fibers in water at 37°C. High-resolution spectra of: A) O 1s peaks; B) C 1s peaks; C) N 1s peaks; D) P 2p peaks

high-resolution scans were conducted, with calibration being made to the adventitious C 1s spectral peak, charge corrected to 284.8 eV. Acquisition parameters were kept constant for all samples with 2 and 5 repeats for survey and high-resolution scans, respectively; dwell times of 0.2 and 0.4 seconds for survey and high-resolution scans, respectively; and a step size of 1 and 0.2 eV for survey and high-resolution scans, respectively. Survey scans were measured over a binding energy range of 0 to 1200 eV, with all scans analyzed using CasaXPS software constraining all deconvoluted peaks of the same elements to the same Full Width at Half Maximum (FWHM). For peak splitting of 2p electrons (phosphorous), a peak ratio of 1:2 was observed for 1/2:3/2 peaks.

3 | RESULTS AND DISCUSSION

Removal of the epoxy coating by the annealing process, and the presence of polydopamine after coating, were each confirmed both through XPS (Figure 3) and SEM (Figure 4). The survey spectrum and table of elemental compositions for the XPS are provided as Figure S1 and Table S1, available online. Silicon in the samples is likely related to contamination from the glass manufacturing process, where the glass batches are melted in ceramic containers.

It is clear from the XPS analysis of the as received (AR) and annealed (AN) samples that there is a shift in the deconvoluted peaks in the O 1s spectra, as well as a reduction

in the N 1s and an increase in the P 2p peak. Both the P 2p and O 1s high-resolution spectra indicate the presence of phosphate bonding, attributable to the underlying glass fibers. Overall, this demonstrates removal of the epoxy coating, which had been applied during manufacture of the fibers. Additionally, in the C 1s spectra, the contribution from the C—N bonding reduced from 31.9% to 10.8% for the AR and AN samples, respectively, further demonstrating epoxy removal.

Following polydopamine coating (AN/PD), constituent peaks of C—OH (533.6 eV; 70.1%), and C = O (532.2 eV; 29.9%) were found in the O 1s spectra, as well as a N 1s peak at ca. 400 eV, corresponding to N—H bonding. Furthermore, the deconvolution of the C 1s spectra demonstrates C—C/CHx (284.8 eV; 80.5%), C—N/C—OH (286.3 eV; 13.4%), and C = O (288.7 eV; 6.1%) bonding, which in combination the above data agree with literature studies on polydopamine formation.[28]

XPS was also conducted on the dopamine-coated fibers after 7 and 14 days of degradation in order to determine if the coating persisted. There is a clear reduction in the N 1s peak and an increase in the P 2p peak, which indicates that the coating is being lost. By the 14 day time point the polydopamine layer has reduced to a thickness below which XPS cannot detect within the noise (ca. 5 nm). Dopamine coatings are anticipated to be very thin (10s of nm)[25] and so it is possible that a very thin <5 nm layer of dopamine is still present and effective in protecting the fiber at this time point. The reduction in the amount of dopamine present is a positive factor in the long run

FIGURE 4 SEM analysis of as received (AR - top), annealed (AN - middle) and 10 min acid treated/polydopamine-coated fibers (AR/PD - bottom) subjected to degradation in water at 37°C. From left to right: 0, 7, 14 d

Degradation Time (Water; 37°C)

0 d   7 d   14 d

AR

AN

AN/PD
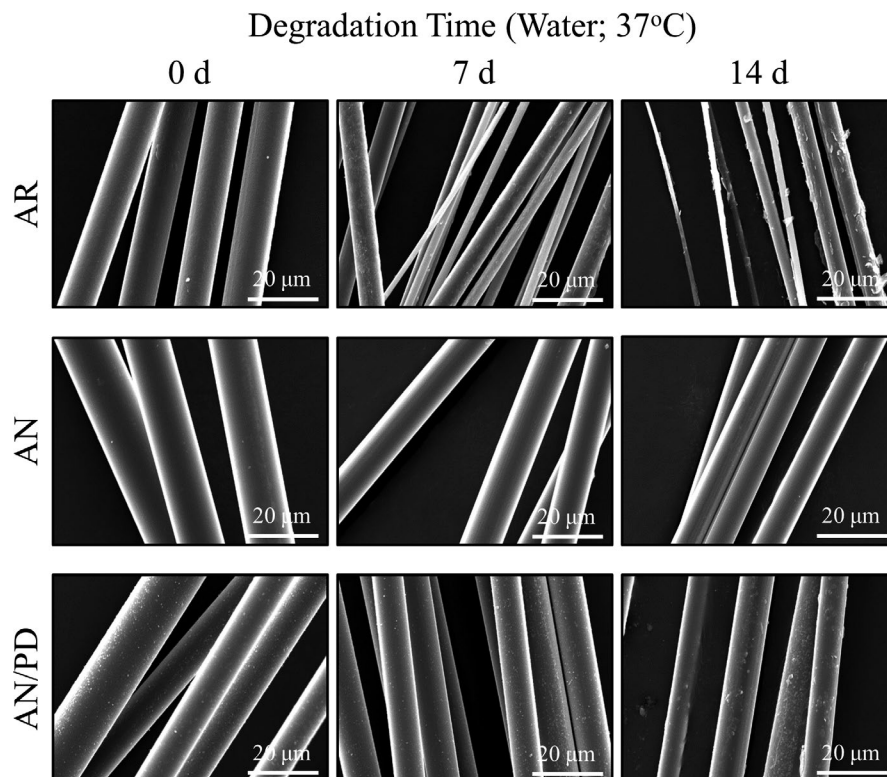
as it demonstrates that the dopamine will degrade over time and not remain as a foreign material after the rest of an implant has degraded. Although it is persisting for considerably less time that would be desirable for an implant (6 + weeks), this degradation is undertaken in an unconstrained, essentially infinite dilution case. Within a composite the degradation is constrained and must be studied in further work.

SEM images of the fibers before degradation (Figure 4, left column) supported the XPS observations, with the coated surface of the as received fiber becoming smoother post annealing and a 'speckle' of DP apparent after coating. However, there does not appear to be a significant visual change in the DP coating at 7 and 14 days. The annealed fibers also do not display a noticeable visual change over the 14 day study, but the as received fibers experience severe degradation, with significant surface peeling and loss of diameter as expected.[19]

The fiber testing data are provided in Table 1. Values of Modulus and Weibull strength are also plotted in Figure 5, showing the variation between fiber treatments. The degradation of the as received fibers was so significant that it was not possible to perform single filament testing on the 7 and 14 day samples. Individual filament data are plotted in Figures 6–8 to compare data sets.

From the data shown in Table 1, annealing caused a statistically significant increase in modulus (95% CI). Previous work has suggested a degree of fiber alignment occurs during drawing and a residual strain is known to occur in fiber drawing, as discussed in the introduction. An increase in modulus suggests that annealing has been

effective in enabling a structural relaxation and realignment.[29,30] Plotting Weibull strength against strain to failure (Figure 9) there is a linear relationship, with the exception of AR as an outlier (circled in the Figure). The fibers exhibit a flaw dependent, brittle failure mechanism and this linear relationship is indicative of a similar modulus between the samples, with the exception of AR. This further supports the effect of annealing on fiber modulus and a surface erosion degradation mechanism.

Annealing causes a significant drop in strength (Weibull 1135 -> 509 MPa), which is as expected both from burn off of the protective epoxy coating and exacerbation of surface flaws. The drop in strength and increase in modulus has been observed previously in both this and other formulations of PGF.[19,20,22]

A simple acid wash was found to be effective in recovering a degree of fiber strength (509 -> 647 MPa), likely due to removal of some flaws. Yellowing of the acid solution indicated that iron was being removed from the fiber and forming an $[Fe(III)Cl_4]-$ complex with the HCl.[31] As discussed by Bunker,[32,33] degradation of phosphate glass occurs through an initial ion exchange at the surface, whereby easily accessible ions (such as sodium) are lost. This is limited to a shallow surface effect, the depth of which is dependent on diffusion in the glass structure. Under mild conditions of pH, continued degradation of the glass occurs through the hydration and removal of entire chains of phosphate, resulting in a surface erosion mechanism. Strongly bound additives (high field strength) form bonds that are particularly resilient to

TABLE 1 Single filament tensile testing data

Sample (Code)	Diameter (µm)		Strain to fail (%)		Modulus (GPa)		Strength (MPa)				
	Mean	STERR	Mean	STERR	Mean	STERR	Median	Mean	STERR	Weibull	Weibull modulus
As received (AR)	10.9	0.3	1.7	0.1	64	1	1119	1040	52	1135	5.24
Annealed (AN)	12.1	0.4	0.61	0.02	79	1	451	475	15	509	6.28
Annealed, 0 min acid, DP	12.2	0.4	0.86	0.04	73	1	589	624	33	688	4.11
Annealed, 5 min acid	12.1	0.3	0.79	0.02	77	1	615	607	17	647	6.67
Annealed, 5 min acid, DP	11.9	0.5	1.1	0.1	76	1	804	868	52	965	3.35
Annealed, 10 min acid, PD (AN/PD)	12.0	0.5	1.2	0.1	75	1	879	886	48	969	4.61
Annealed, 15 min acid, DP	11.6	0.4	1.07	0.03	74	1	793	784	25	841	6.08
Annealed, 20 min acid, DP	14	1	1.07	0.04	69	1	692	736	27	789	6.47
AN, 9 mon shelf	12.3	0.2	0.73	0.02	77	1	548	552	13	581	9.47
AN/PD, 9 mon shelf	11.8	0.4	1.2	0.1	75	1	935	913	50	1005	4.18
AN, 9 mon shelf, 7 days water	8.7	0.2	1.38	0.03	81	1	1079	1098	37	1172	6.92
AN, 9 mon shelf, 14 days water	10.5	0.4	1.16	0.04	80	1	937	913	37	992	5.13
AN/PD, 9 mon shelf, 7 days water	10.4	0.2	1.4	0.1	75	1	980	1036	53	1137	4.07
AN/PD, 9 mon shelf, 14 days water	10.0	0.4	1.39	0.05	77	3	1075	1080	51	1175	4.70
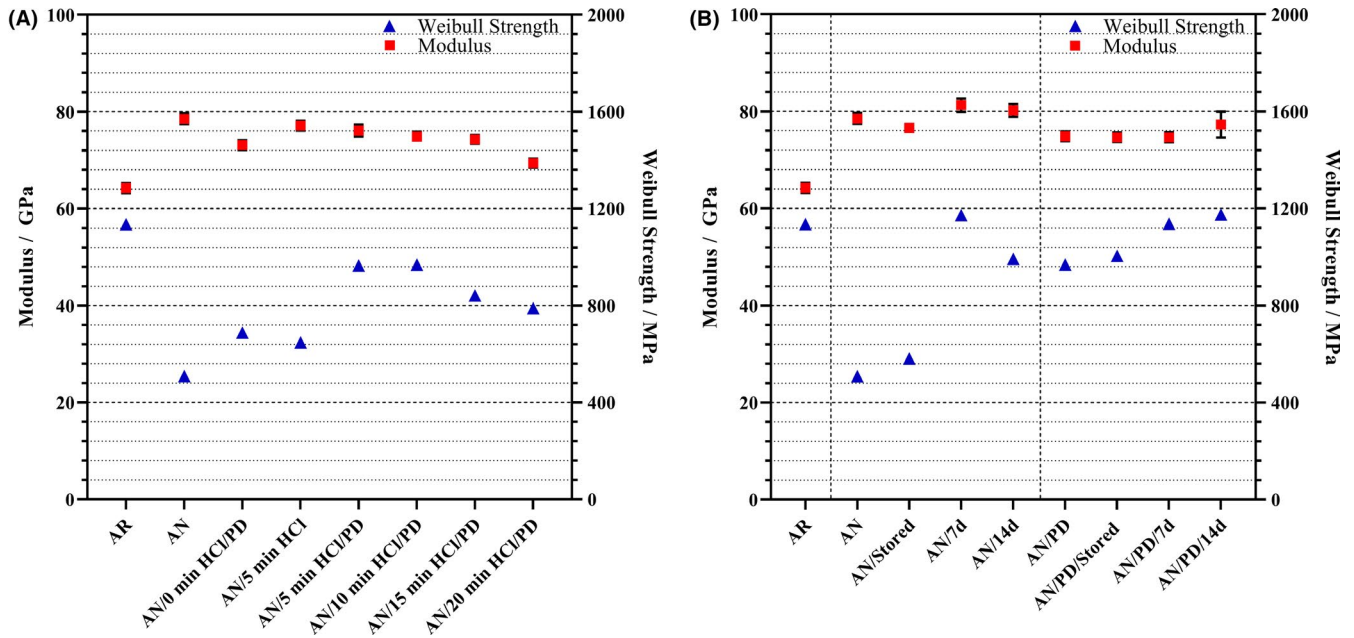
FIGURE 5 Weibull strength and modulus values plotted for each of the different fiber treatments. The graph on the left (A) shows the effect of different periods of acid treatment on the fibers. The graph on the right (B) provides a comparison of fibers after 9 mo of storage post-treatment and after subsequent degradation testing. The vertical dotted lines in B delineate the as received (AR), annealed (AN), and annealed and coated (AN/PD) fiber types. Standard errors are plotted for modulus values

FIGURE 6 Comparison of individual filament strength values for the batches of fibers subjected to the HCl acid solution for different periods of time, between 0 and 20 min. Values for each data set are plotted in ascending order to facilitate comparisons and to identify any outliers
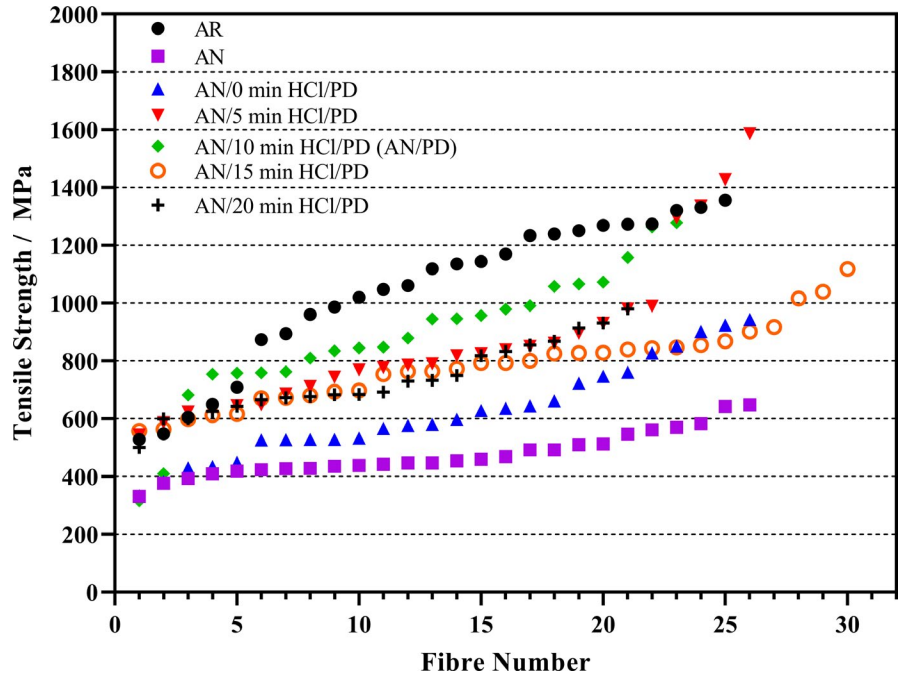

hydrolysis and can be rate limiting of the degradation. Since iron is normally strongly bound in a phosphate structure,[34] this suggests a dissolution of the full composition of the fiber rather than simply leaching of easily accessible ions from the surface.

A coating of polydopamine onto the annealed fibers also provides a modest improvement in strength (509 -> 688 MPa). Given that the coating period is 6 hours, this may

be partially due to the removal of the damaged surface of the fiber by hydrolysis, but may also relate to bridging/filling of flaws by the polydopamine coating.[35]

Use of an acid wash in conjunction with a polydopamine coating has a significant beneficial effect on the fiber strength (509 -> 969 MPa), though excessive time in acid appears to have a detrimental effect (see also Figure 6). The Weibull strength values in Table 1 for 5 and 10 minutes of acid treatment were very close
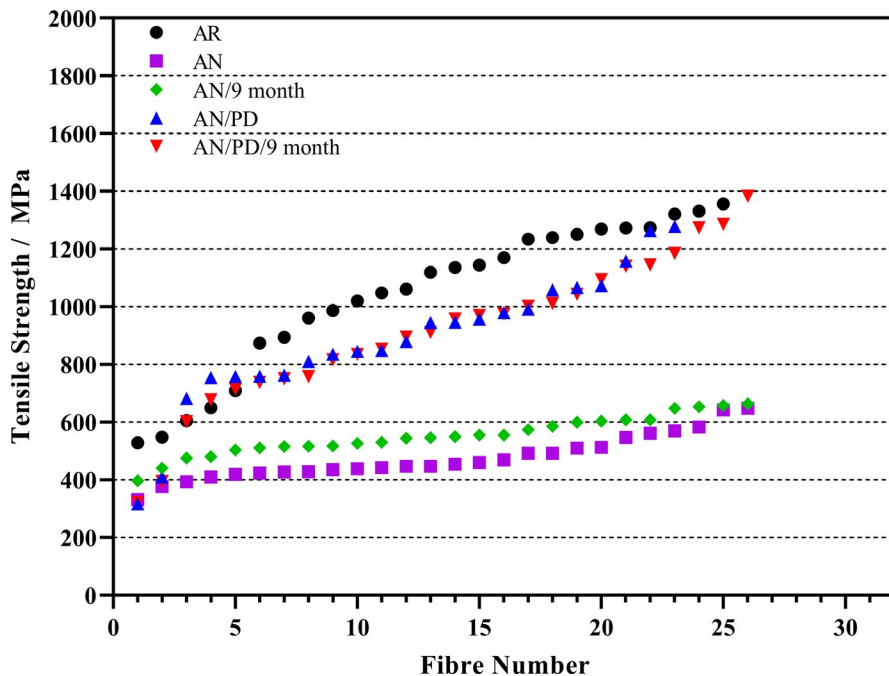
FIGURE 7 Individual filament strength values for the batches of fiber that were either annealed (AN) or annealed, washed with HCl for 10 min and coated with polydopamine (AN/PD). Comparison of the effects of shelf storage at conditions of ~20°C and 40% humidity for 9 mo. Values for each data set are plotted in ascending order to facilitate comparisons and to identify any outliers
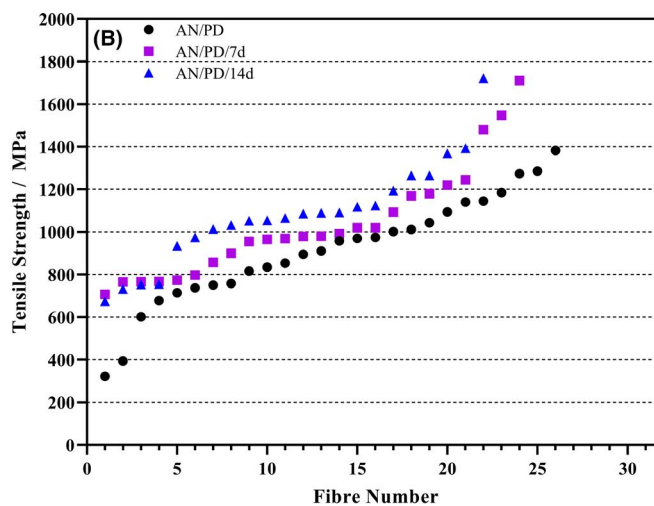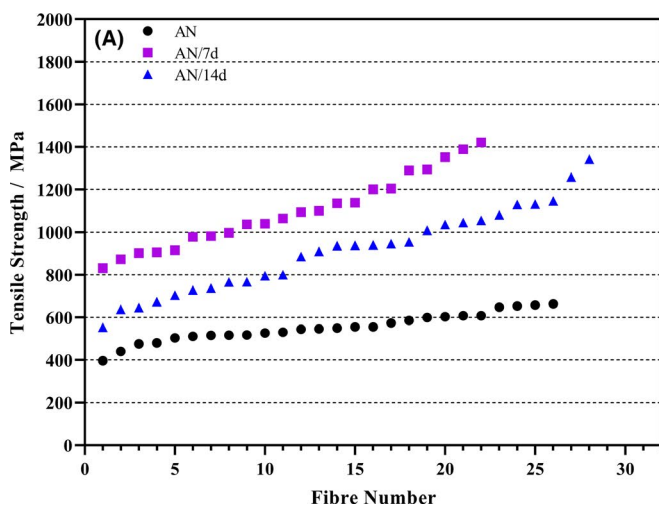
FIGURE 8 Individual filament strength values for fibers that were annealed (AN—left) with respect to fibers that were annealed, washed with HCl for 10 min and coated with polydopamine (AN/PD—right). Comparison of results for up to 14 d degradation in water at 37°C. Values for each data set are plotted in ascending order to facilitate comparisons and to identify any outliers

(965 and 969 MPa respectively). However, it can be seen in Figure 6 that the trend of individual filament properties between the 5 minutes treatment and the 15 minutes treatment were relatively similar, with the majority of the 10 minutes treatment filaments clearly higher in strength. This would suggest that the optimum is between 5 and 10 minutes and closer to 10 minutes. Thomason et al observed a similar effect in E-glass, using hydrofluoric acid as the etchant and a silane as a protective coating.[36] They dismissed the commercial potential for the process due to the need for HF but later developed another approach using alkaline etching solutions and HCl[37,38] in a process analogous to the acid/base baths

utilized for cleaning laboratory glassware. Phosphate-based fibers are resistant to HF[39] but are etched by HCl and so an acid etching approach would be much less hazardous to implement commercially for phosphates than the HF/silicate method.

Storage for 9 months does not appear to affect the properties of the acid washed/coated fibers (Figure 7). The properties for the annealed fibers are relatively similar, though appear to have improved slightly with time. It is unclear why this might be the case though the difference is statistically significant. There may be a degree of selection bias if weaker fibers are breaking before testing is possible.

FIGURE 9 Weibull strength values of all the different fiber treatments plotted against their corresponding values of strain to fail, indicating similar modulus properties for all the fiber types except the as received (AR)
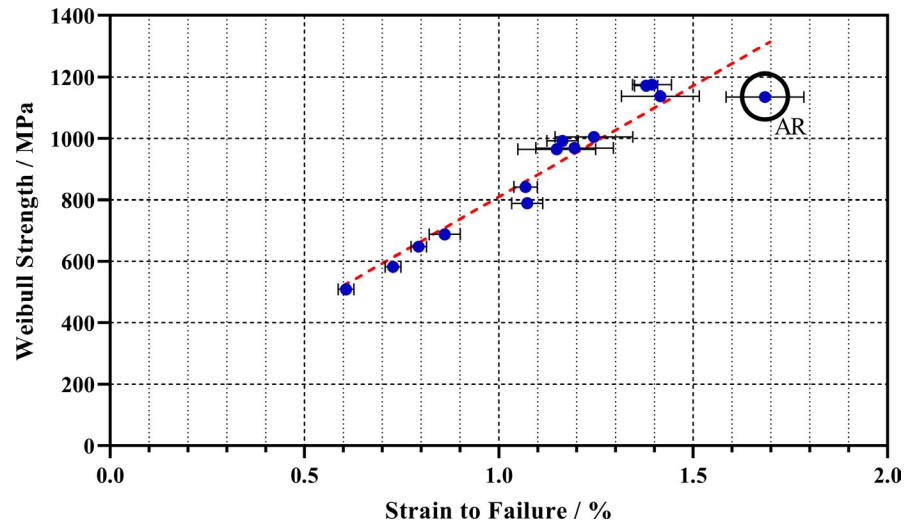
During the degradation testing, the as received fibers were severely degraded even after only 7 days, breaking into fragments too short to test. As can be seen in the SEM (Figure 4), there is significant breakdown of the fibers and loss of material with some very small diameter fibers observed. This is in keeping with previous results observed for this fiber type[19] and in composites produced using this fiber type.[8]

Of the samples that could be tested after degradation, there was no significant change in the modulus, which is as expected for a surface eroding material.

The annealed fibers appeared to recover in strength after exposure to water (Figure 8) (581 -> 1172 MPa after 7 days). As discussed in the introduction, this behavior has been observed previously and is ascribed to the removal of flaws through surface dissolution without the presence of stresses that could cause fragmentation. However, after 14 days the strength appears to have reduced again (1172 -> 992 MPa). The reason for this is unclear. The SEMs (Figure 4) indicate no apparent gross changes in the fiber, though flaws may not be visible. The difference is statistically significant and is consistently ~200 MPa across the test batch (Figure 8). Previous work on this fiber type included a longer term study of the annealed fiber with respect to the as received fiber. Although the absolute values of strength differ, a similar trend in the result was observed over the first two weeks, with an initial recovery in strength followed by the beginning of a longer term drop off. There was also little evidence of surface damage after 14 days.[19]

The acid washed/coated filaments appeared to maintain strength after 7 and 14 days of degradation (0 days 992 MPa, 7 days 1137 MPa, 14 days 1175 MPa), within the errors of measurement. The similarity in the observed strength values between AN fibers after 7 days in water and the AN/PD fibers would indicate that the 10 minutes acid wash treatment has a similar effect to 7 days in water at 37°C, a time factor of ~10^3. It suggests that an acid free, more environmentally friendly treatment might be applied with just water. However, the length of the process is likely to be impractical for industrial applications.

4 | CONCLUSIONS

This study supports and confirms the finding that without some form of post treatment, fibers of this type degrade rapidly. It demonstrated that the use of annealing causes a significant drop in strength that initially recovers after a period of degradation, but that this recovery does not persist. Furthermore, it was demonstrated that the use of an acid wash in combination with a polydopamine coating provides an immediate recovery of fiber strength after annealing, though not to the same level as the as received fibers. The length of time of the acid wash had a significant effect on the degree of fiber strength that was recovered and a prolonged period in acid was detrimental. The optimum time for the acid wash for this particular fiber type and treatment method was found to be 10 minutes. This treatment combined with a polydopamine coating resulted in no loss of strength after 9 months of storage. Furthermore, it provided a retention of properties for at least 14 days of degradation in water at 37°C, although the dopamine coating was observed to reduce in thickness over this period. Overall, the results are extremely promising for improving the performance of PGF-reinforced degradable composites.

and Microscale Research Centre, as well as the provision of fiber materials from Sinoma Co. Ltd.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.