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An efficient high-throughput grafting procedure for enhancing carbon fiber-to-matrix interactions in composites

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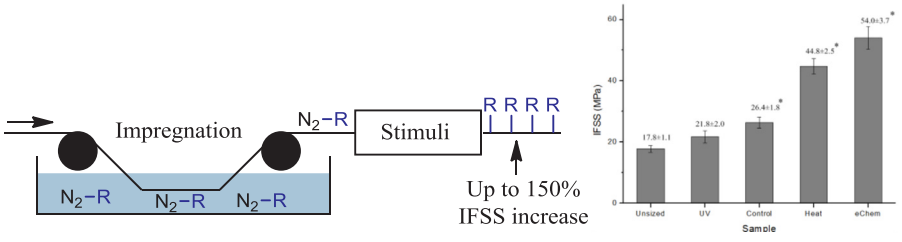
HIGHLIGHTS

- Impregnation of carbon fibers using aryl diazonium salts led to surface functionalisation.
- Interfacial shear strength improvements of up to 150% observed.
- Molecular dynamics suggests interfacial shear strength gains are via protrusion of molecules into the interphase.

GRAPHICAL ABSTRACT



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ABSTRACT

It is widely acknowledged that the integrity of the fiber-to-matrix interface inherent to carbon fiber reinforced composites has scope for improvement. One promising and highly-researched strategy is the use of surface manipulation of carbon fibers to enhance their mechanical performance under shear. The complexity of commonly used surface treatments, such as plasma and oxidative etching, Requires modification of existing manufacturing infrastructure and thus their broad adoption in a manufacturing context has been limited. Herein we show that simply impregnating the carbon fibers with aryl diazonium salts and subjecting them to external stimuli, such as mild heating (100 °C), can induce surface modification which can deliver improvements of up to 150% in interfacial shear strength (IFSS) in epoxy resins. Interrogation of the fiber-to-matrix interface using molecular dynamics simulations suggests that the surface grafted molecules imparts a 'dragging effect' though the polymer phase and that the surface concentration of these compounds is critical to enhancing IFSS. This process obviates the practical limitations of current functionalization procedures for carbon fibers and requires infrastructure that is already routinely available on fiber manufacturing lines.

1. Introduction

Carbon fiber reinforced plastics (CFRP) are commonly referred to as a material of the future as they possess a very high strength-to-weight ratio, and so have huge potential in decreasing CO_2 emissions for mass transport. A potential limitation with CFRP is that, by definition, they are mixtures of at least two materials and the interface, where the fibers and resin meet, has profound importance in the overall performance of the composite [1–5]. Typically, poor interfacial adhesion will result in fiber debonding to the resin when placed under shear forces, and has

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ramifications in other areas such as impact tolerance.

During manufacture, the fibers are subjected to an oxidative electrochemical treatment, followed by a proprietary 'sizing' which is typically an emulsion consisting of small molecular weight polymers, emulsifiers, antistatic agents and other chemical species. The role of both oxidative surface treatment and sizing of carbon fibers has been the subject of some conjecture, with conflicting findings being found between groups [6]. This topic has been debated where sizings have been claimed, in different studies, to enhance interfacial adhesion [7–9], or decrease adhesion [10–12], and similar conflicting outcomes have been reported for surface treatments [13–17].

As a potential alternative to, or in synergism with, traditional oxidative surface treatments, substantial effort has been placed on bespoke surface treatments of carbon fibers. The mystery surrounding what factors contribute to an optimal composite interface has become an area of significant interest for both academic and industrial researchers. In recent years, many reports of carbon fiber surface modification using nanomaterials in concert with chemical oxidants such as ozone, nitric acid, plasma have arisen to increase the chemical interaction between the fibers and resin [18–25]. In our previous work, we have used conventional heating, microwave heating, and electrochemical means to modify the surface of carbon fibers [22,26–32]. The majority of those studies used aryl diazonium salts, under reductive electrochemical conditions or thermally degraded, initiating covalent reaction with the graphitic fiber surface.

While all these efforts have provided critical information regarding the optimal interactions of a composite interface, their application to in-line treatments have remained a challenge, and thus their uptake into large-scale production by industry has been hampered. Typically, the addition of surface modification techniques currently explored would require the modification of carbon fiber manufacturing lines (e.g. plasma chambers, microwave heating units, etc.). Thus, a surface modification procedure, which does not require the modification of existing infrastructure, is of great interest and potential impact.

During manufacture, oxidative surface treatment is followed by fiber washing, sizing, and mild heating (~100 °C) to dry the fibers and allow for winding and collection. We have proposed that the washing and heating steps could be used as an entry point to surface modification. A major limitation of solution-based fiber functionalization is that the reactive molecule must diffuse to the surface of the fibers, and thus any reactive molecule generated in the bulk solution can degrade. In this work, we propose to circumvent this limitation by impregnating the surface of the fibers with aryl diazonium salts, then initiating the surface grafting procedure using either UV light or gentle heating (Fig. 1). Spontaneous grafting of aryl diazonium salts have also been reported previously for metals, glassy carbon electrodes, and nanotubes [33–37].

The stimuli of UV irradiation and heating were chosen for this study as they possess the benefit of being easily incorporated in an in-line manufacturing process or are part of the manufacturing process already, respectively. Therefore, the focus of this work is to demonstrate the viability of this approach applied to carbon fiber surface modification. We also seek to determine how the surface modification treatment impacts the critical performance parameters (Young's modulus, tensile strength) and their interfacial shear strength (IFSS) in an epoxy resin.

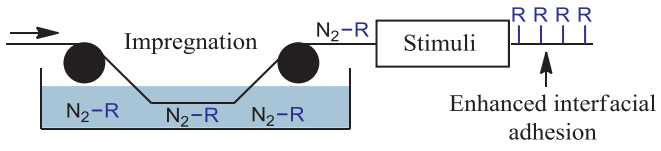

Fig. 1. Schematic representation of the functionalization approach used in this study.

2. Materials and methods

2.1. Materials

Carbon fiber samples (unsized, surface treated) were supplied by Carbon Nexus at Deakin University, Australia. All chemicals, reagents and solvents were purchased from Sigma-Aldrich Chemical Company and used as received. For the synthesis of each compound, their ^{1}H, ^{13}C, and ^{19}F spectra, molecular dynamics procedures, cyclic voltammograms, SEM, please refer to Supporting Information (SI).

2.2. X-ray photoelectron spectroscopy (XPS)

XPS analysis was performed using an AXIS Ultra-DLD spectrometer (Kratos Analytical Inc., Manchester, UK) with a monochromated Al K_α source ($h\nu$ = 1486.6 eV) at a power of 180 W (15 kV × 12 mA), a hemispherical analyser operating in the fixed transmission mode and the standard aperture (analysis area: 0.3 mm × 0.7 mm). The total pressure in the main vacuum chamber during analysis was typically below 10^{-8} mbar. For sample preparation and representation of data please refer to the SI. All analyses have been conducted to be consistent with our previous works [16–22].

2.3. Statistical analysis

A two-sample *t*-test, assuming equal variance, was used to test whether data was significantly different or not; a P-value less than 0.05 considered statistically significant.

2.4. Characterisation of control and treated carbon fibers using the Favimat + Robot

Samples were tested on a Favimat+ Robot 2 single fibre tester (Textechno H. Stein), which automatically records linear density and force extension data for individual fibres loaded into a magazine (25 samples) with a pretension weight of (~100–150 mg). Using a gauge length of 25 mm and an extension rate of 1 mm per minute, force displacement curves for 75 individual filaments were collected, and all data was normalized by linear density. As is consistent with other works in this area the ultimate tensile strength was analyzed using a 2-parameter Weibull probability (P) Eq. (1):

$$P = 1 - \exp\left[-\left(\frac{\sigma}{\sigma_0}\right)^m\right] \quad (1)$$

Here, P represents the cumulative probability of failure of a single carbon filament at an applied tensile strength. The m and σ parameters are the Weibull modulus and shape parameters, respectively, and σ_0 is the Weibull scale parameter or characteristic stress. P is determined for each point using the median rank method (2):

$$P = \frac{i = 0.3}{n + 0.4} \quad (2)$$

In (2), n = number of sample points and i is the rank. Rearrangement of the probability expression to a straight-line, allows m and σ_0 to be obtained by linear regression.

2.5. Carbon fiber electrochemical functionalisation

Carbon fiber to be functionalized (approximately 20–30 cm of tow) was prepared by affixing one end of the sample using adhesive copper tape. Electrochemical functionalization was conducted using a Metrohm Autolab Potentiostat (Kanaalweg, The Netherlands) and data processed using NOVA software (Kanaalweg, The Netherlands). A three-electrode system was employed using a Harvard Apparatus LF-2 leak free electrode (filling electrolyte 3 M KCl) half-cell and a platinum