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Electrochemical surface modification of carbon fibres by grafting of amine, carboxylic and lipophilic amide groups

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ABSTRACT

The surface of carbon fibre was rapidly modified by reductive electrochemical deposition employing a range of diazonium salts. Three sets of fibre were generated possessing pendant amine, carboxylic acid, and lipophilic amide (*N*-hexyl amide) groups and the effect of these surface chemistries on interfacial shear strength (IFSS) was examined in epoxy resins. Surface grafting of the fibres was studied by X-ray photoelectron spectroscopy, and physical characterisation of the modified fibres showed that our treatments had no detrimental effects on Young's modulus and tensile strength. IFSS increases of 172% and 30% (relative to control fibres) were observed for the amine and lipophilic amide functionalised, respectively. Molecular dynamics simulations of the lipophilic amide suggests IFSS enhancement via soft-soft interactions. Surprisingly, the IFSS of fibres that exhibited carboxylic acid groups at the surface were indistinguishable from that of the untreated control fibres. When applied to polypropylene grafted with maleic anhydride, the amine grafted fibres showed a 67% increase relative to control fibres, attributed to covalent cross-linking between the fibre and maleic anhydride co-monomer.

1. Introduction

Carbon fibre reinforced plastics (CFRP) have proliferated through many industries embracing cutting edge technologies in recent times. With society's wider effort to design eco-friendly structures and reduce CO_2 emissions, we have come to rely on CFRP as a substitute for metals in a number of applications such as light weighting of mass transport vehicles [1,2]. A notable example is the Airbus A380, which is made up of more than 50% composite material and delivers a 25% reduction in fuel consumption while allowing for expanded cabin space and improved air pressure control.[1]

As demand grows for high volume/performance production of composite materials, the importance of fibre-to-resin compatibility is becoming increasingly apparent. If CFRP are to meet the demands of next generation production and performance, they must be both accessible and optimised for each application. One such area of optimisation is the interaction between the fibre surface and the composite matrix. This key juncture is where stress and load can be transferred from the bulk matrix to the reinforcing fibre, thus enhancing the essential mechanical properties such as toughness, and longitudinal and transverse strength. Poor interfacial adhesion can result in delamination or fibre pull-out – the precursor to catastrophic failure [3]. The interface between fibre and resin has long been recognised as an area of composites research that is both poorly understood and hard to engineer [4].

One of the fundamental processes of carbon fibre manufacture is the electrochemical oxidation of the fibre surface to increase roughness and the degree of oxygenation. While this treatment typically enhances wettability, it is not necessarily the best means to treat the fibre surface for all resins. In an attempt to build on that technology, there have been numerous studies that have utilised the grafting of small and large molecules to the fibre surface to

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[1] www.airbus.com, (accessed 1/11/2016).

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improve covalent crosslinking or softer chemical interactions at the fibre surface/epoxy matrix interface. Methodologies spanning from organic functionalisation, to oxidative treatments (e.g. NO_2, plasma, etc.), electrochemical deposition and polymerisation [5–11], have showed incredible potential to enhance composite performance through improved interfacial or inter-laminar shear strength. A detailed review of the latest approaches to modify the carbon fibre surface was recently published [12]. However, the application of these new surface treatment technologies rarely lend themselves to in-line carbon fibre treatment without substantial changes to infrastructure or major impedance on production volumes. Furthermore, many of the treatment methods increase the fibre/matrix interfacial strength, but detrimentally affect the single fibre strength properties by distortion of the fibre surface [13,14].

The focus of this work was to use electrochemical grafting as a means to bias the surface of carbon fibres, thus presenting vastly different functional groups to the interface of the composite (Fig. 1) and study the effect on interfacial adhesion. To highlight the effect of these chemistries, we chose the following functionalities: amine, carboxylic acid, and lipophilic amide (left to right, respectively, Fig. 1).

We believed that the amine-grafted carbon fibre would show excellent interfacial adhesion with epoxy resins due to covalent cross-linking with the surface of the fibre, as indicated by our previous works [15–21]. The rationale for using a carboxylic acid was to mimic the oxidative surface treatment of carbon fibre manufacture, as the introduction this functional group has been often claimed to assist in the cross linking of the fibre to the resin. From a chemistry perspective, the nucleophilicity of a carboxylic acid on an epoxy group is very poorly supported and it was our hope to examine this interaction, effectively in isolation. Finally, the lipophilic amide surface serves as a counter-point to the previous functionalities and provides an excellent contrast to potential acid-base interactions.

2. Materials and methods

2.1. Materials

Carbon fibre samples (unsized, electrolytically oxidised fibre) were supplied by and carbonised in-line at Carbon Nexus at Deakin University (Australia). These fibres served as the control fibre for all experiments, they were handled and treated identically to functionalised fibre. All chemicals, reagents and solvents were purchased from Sigma-Aldrich (Australia) and used as received.

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.

Bundles of fibres were suspended across a custom-designed frame attached to standard sample bars. This ensured that only the sample to be analysed was exposed to the X-ray beam and that any signal other than that originating from carbon fibres was excluded. Each specimen was analysed at a photoelectron emission angle of 0° as measured from the surface normal (corresponding to a take-off angle of 90° as measured from the sample surface). However, since the microscopic emission angle is ill-defined for fibres the XPS analysis depth may vary between 0 nm and approximately 10 nm (maximum sampling depth).

Data processing was performed using CasaXPS software version 2.3.15 (Casa Software Ltd., Teignmouth, UK). All elements present were identified from survey spectra (acquired at a pass energy of 160 eV). To obtain more detailed information about chemical structure, C 1s, O 1s and N 1s high resolution spectra were recorded at 40 eV pass energy (yielding a typical peak width for polymers of 1.0 eV). If required, these data were quantified using a Simplex algorithm in order to calculate optimised curve-fits and thus to determine the contributions from specific functional groups. The atomic concentrations of the detected elements were calculated using integral peak intensities and the sensitivity factors supplied by the manufacturer. Atomic concentrations are given relative to the total concentration of carbon as follows: the concentration of a given element X was divided by the total concentration of carbon and is presented here as the atom number ratio (or atomic ratio) X/C. This value is more robust than concentrations when comparing different samples. No charge correction of the binding energy scale was necessary since the carbon fibres were sufficiently conductive and no differential charging of the sample was observed during analysis. The accuracy associated with quantitative XPS is ca. 10%–15%. Precision (i.e. reproducibility) depends on the signal/noise ratio but is usually much better than 5%. The latter is relevant when comparing similar samples. This is consistent with our previous works [16–22].

2.3. Single fibre tensile testing and determination of IFSS

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) attached to the bottom of each carbon fibre, a minimum of 75 samples were analysed to give reasonable reliability of the data.

Linear density was recorded using a gauge length of 25 mm and a pretension of 1.6 cN/tex (nominal L.D. of 0.65 per supplier specifications). Force-displacement curves were collected at 1 mm/min using a gauge length of 25 mm and a pretension of 1.6 cN/tex. Load data was normalised by dividing by the linear density (determined individually by vibroscope) to give specific stress strain curves from which tensile strength (ultimate specific stress or tenacity) and specific modulus (elongation range 1–2%) could be determined. Since the statistical distribution of carbon fibre strengths is usually described by a weakest link model, the strengths were also

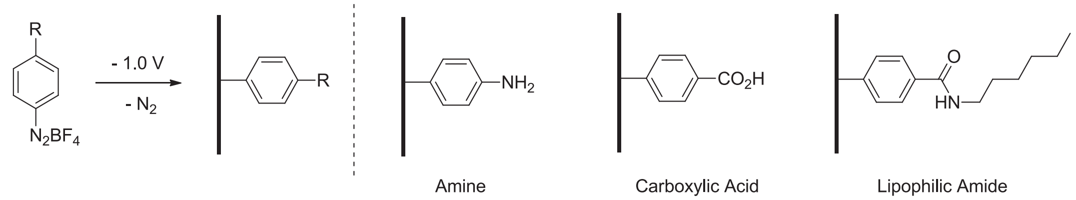

Fig. 1. Schematic of reductive electrografting of diazo salts (left) and functional groups studied in this work.