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Carbon fibre surface modification facilitated by silver-catalysed radical decarboxylation

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A silver catalysed radical decarboxylation process was used to graft a copolymer (4:1; methacrylate/acrylic acid) onto short carbon fibres. Surface grafting was confirmed by XPS, SEM and TGA, suggesting that the polymer accounted for 10% of the modified materials mass. Incorporation of these surface enhanced carbon fibres into an epoxy resin gave composites demonstrating an increase in ductility and a clear change in failure mode from adhesive, at the fibre-matrix interface, to cohesive, within the matrix polymer itself.

The development of lighter and stronger materials has been a key enabler for advancing civilisations, providing benefits from stronger tools to lighter armour. The need for such materials is still high in modern times, to enhance fuel economy, transport of materials, and to make strong, light, and safe structures. Carbon fibre composites are the immediate 'go to' material when light weight and high performance are required. Being composites of two or more dissimilar materials, composites form the basis of many natural and man-made high performance structures.¹

Of critical importance to the overall performance of the composite is the interface between the constituent materials. In this instance the strong and stiff carbon fibres, and the relatively weak and ductile polymer phase. The surface chemistry of carbon fibres plays a crucial role to optimise the performance of composite materials.² The interface between the fibre and the supporting polymer is critical to transferring stress between the soft and ductile polymer and the strong and stiff carbon fibres.³⁻⁵ Indeed, it is thought that up to 80% of the potential reinforcing power of carbon fibres is lost via the formation of poor interfaces within a composite.² When the stress being experienced by the composite exceeds that of the

fibre-polymer interface, these species debond – an initial step towards catastrophic failure. During manufacture, the final step before spooling is the deposition of a 'sizing' layer.⁶ This layer is a proprietary mix of chemicals thought to include polymers, anti-static agents, etc. and is typically optimised empirically to be 'compatible' with the intended polymeric support in the final composite.⁷⁻¹¹

Strategies used to modify the surface of many materials include coatings, plasma, and electrochemical treatments, polydopamine layers – which may include a cation to encourage intermolecular bridging, and the grafting of polymers.^{5, 12-15} The covalent attachment of a polymer to a material surface can either be done via a 'grafting to' or 'grafting from' approach, being the attachment of a pre-made polymer to a surface or the sequential growth of a polymer from the surface, respectively. The attachment of covalent sizing in recent years, that is sizings that are grafted to the fibre, has become popular to influence the handling and malleability of the fibres in addition to enhancing adhesion.¹⁶⁻¹⁸

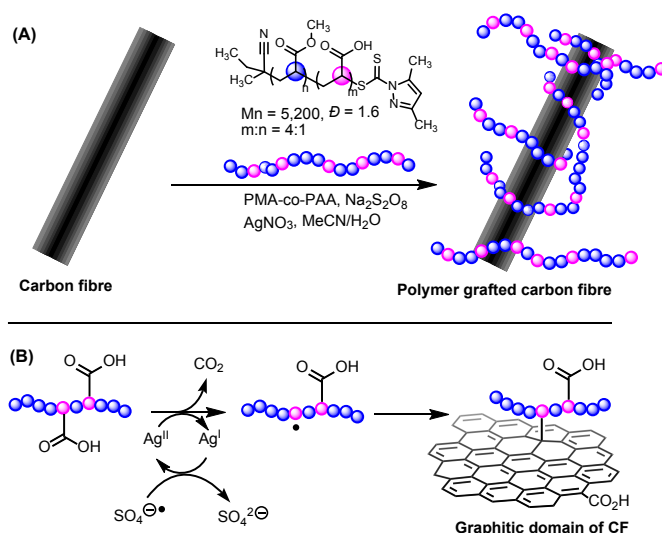


Figure 1 – (A) Grafting of PMA-co-PAA to carbon fibre (B) Mechanism of grafting by radical decarboxylation.

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Electronic Supplementary Information (ESI) available: Polymer analysis and synthesis, modification procedures, composite preparation and SEM preparation is provided. See DOI: 10.1039/x0xx00000x

Each approach has its pros and cons. 'Grafting to' allows control over polymer size, shape, and properties that will be conferred to the surface, though this comes at the expense of a high grafting density due to the steric effects causing an 'exclusion zone' around the point of attachment. Similarly, 'grafting from' allows a high grafting density of the anchor molecule to the surface but less control over the final polymer generated on the surface.

In previous work, we have shown that radical decarboxylation of carboxylic acids is an effective way to initiate radical polymerisations, and to graft small molecules and polymers to graphene and carbon nanotubes.¹⁹ We hypothesised that a similar reaction could graft a copolymer of polymethylacrylate (PMA) and polyacrylic acid (PAA) to the surface of carbon fibres via radical addition to the CF graphitic domains.

A 4:1 random copolymer of PMA/PAA was synthesised via Reversible Addition Fragmentation Transfer (RAFT) polymerisation (Number average molecular mass, $M_n = 5,200$, and dispersity index $D = 1.6$). A 4:1 ratio of methyl acrylate to acrylic acid was selected as we considered it to have a high enough carboxylate content to maximise grafting to the fibre surface, while maintaining a reasonable degree of hydrophobicity (following loss of most carboxylates via radical decarboxylation) to interact with the epoxy polymer matrix. Future studies will examine this ratio (along with the type of comonomer used) to optimise both the grafting efficiency and the fibre/matrix interactions.

Varying amounts of this polymer were grafted to milled carbon fibres with sodium persulfate and catalytic AgNO_3 in 1:1 acetonitrile/water at 60 °C. We aimed to maximise the amount of polymer grafted to the fibres, while maintaining dispersible and free-flowing fibres. A 4.3:1 w/w ratio of CF to polymer proved to be ideal, as higher polymer loadings resulted in

aggregation of the fibres in solution, making them unsuitable for incorporation into a composite. SEM of the loose modified fibres (Fig 2. (A) and (B)) clearly showed modification of the carbon fibre surface, with large polymer aggregates on the fibre periphery.

The unmodified and polymer-grafted fibres were also analysed with X-ray photoelectron spectroscopy (XPS). A significant increase in the oxygen content of the functionalised fibres was observed (17.8%), compared with the unmodified fibres (5%) (Fig.2 (C)). A small amount of residual silver (<0.2%) was also observed in the functionalised fibres. No sulfur was detected in either sample, indicating that the persulfate oxidant is not introducing sulfate groups to the fibres. Deconvolution of the C1s peak of the polymer functionalised sample showed a large (17%) peak at 290 eV, a significant increase, relative to the unmodified fibres. This is consistent with the presence of a carbonyl (C=O) group and incorporation of ester and carboxylate groups on the surface of the fibre from successful polymer grafting and has been observed in other works.²⁰ Corroborating this, analysis of the high resolution O1s spectrum also suggested the strong presence of C=O and C-O bonds on the fibre surface, consistent to what would be expected with the PMA/PAA modification.²¹

With the modified fibres in hand, they were used to fabricate composite samples, being included at a 10% w/w within an epoxy polymer matrix. At this weight loading it is expected that the dispersion of even these short (200 μm) carbon fibres will influence the mechanical properties. The suspension of the short fibres in an epoxy polymer was carried out manually via hand mixing. Then the suspension poured into rectangular and dog-bone shaped moulds. These samples are suitable for evaluating flexural and tensile properties, respectively. Note

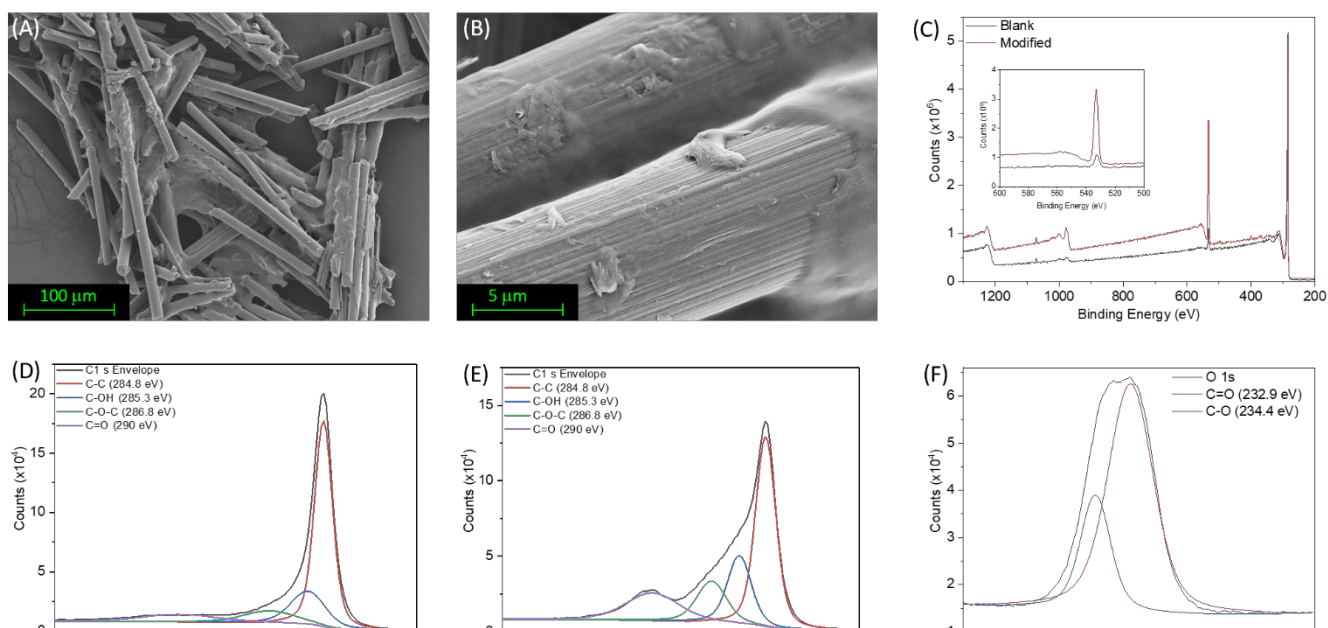


Figure 2 – (A) and (B) SEM of modified carbon fibres featuring high degree of polymer inclusion onto the surface. (C) Survey scan showing drastic increase in oxygen (inset). (D) C1s XPS analysis of control (unmodified) and (E) modified carbon fibres, showing carbon peaks consistent with the grafted polymer. (F) the high-resolution O 1s scan, highlighting peaks consistent with the surface grafted co-polymer.

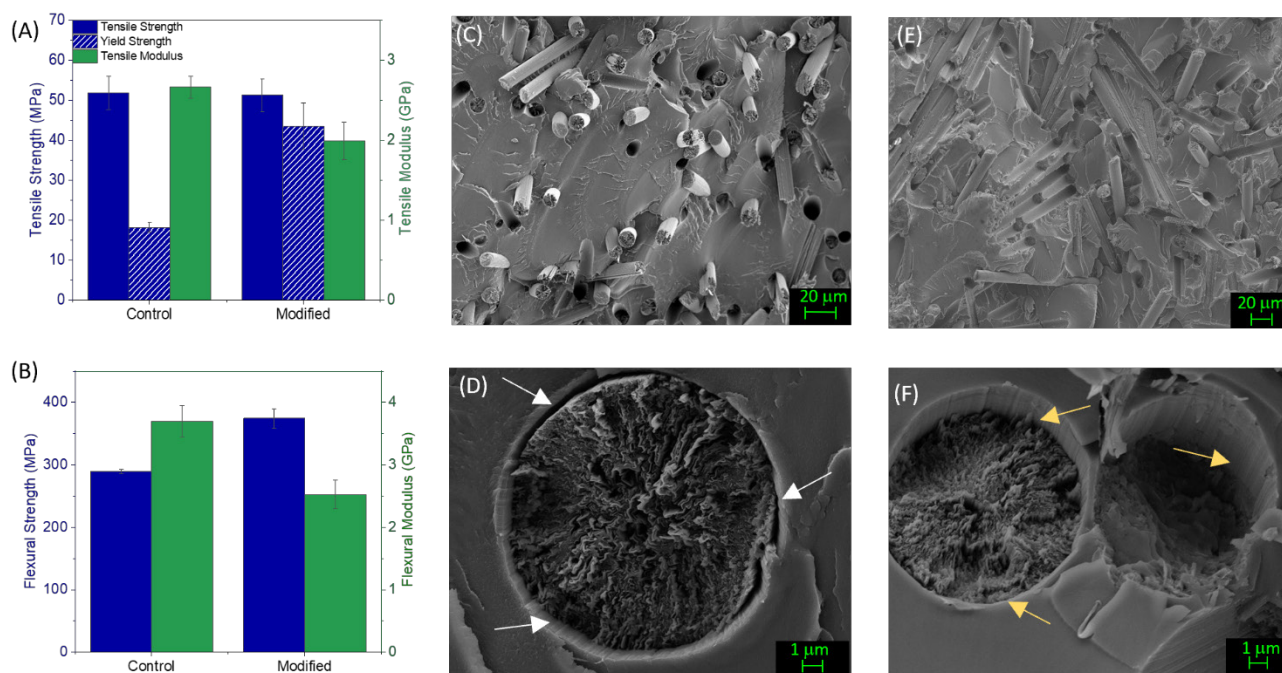


Figure 3 – (A) Tensile properties of the composites, (B) Flexural properties of the composites, (C) Low magnification SEM of fracture surfaces for control sample, (D) High magnification SEM of fracture surfaces for control sample with white arrows highlighting localised debonding of the fibre from the resin, (E) Low magnification SEM of fracture surfaces for surface modified CF sample, (F) High magnification SEM of fracture surfaces for surface modified CF sample with yellow arrows showing clear adhesion between the fibre surface and the resin, and incorporation of the resin into the cross-section of the carbon fibres.

that control samples, unmodified fibres at the same fibre loading in the epoxy polymer, were also fabricated to provide a reference point. The exploration of higher fibre weight loadings and a broader scope of physical testing is currently underway. Interestingly, samples with surface modified carbon fibre showed a significant increase in the tensile yield strength (stress at which inelastic deformation begins) compared to the control samples. However, the ultimate tensile strength (of failure) remained consistent (representative stress-strain curves are in Fig S3). This suggests that the samples with modified fibres possess a greater level of ductility than the samples with the control fibres. This is further supported by the tensile modulus (stiffness) in the samples with modified fibre compared to the control specimens. As can be seen in the stress-strain curves (Fig. S3, the slope of the curve is reduced, correlating with a less stiff and brittle material).

These changes in tensile properties (Fig. 3, (A)) would suggest the presence of a significantly softer interphase, the localised region around the carbon fibre within the polymer matrix, in the samples with surface modified fibre. This effect may result from the surface bound polymer infiltrating the interphase creating an epoxy/PMMA blend and decreasing the degree of cross-linking within the epoxy within the interphase. Similar observations have been made previously, though in a thermoplastic system, whereby the area under the stress-strain curve (an indirect indication of toughness) was increased by ~30%.²²

A softer and ductile interphase in fibre reinforced composites result in increased flexural strength, but as would be expected,

with a slight reduction in flexural modulus values (Fig. 3, (B)). This is indeed what is observed in the flexural evaluation of these materials, whereby the flexural strength is increased from 289.3 ± 3.2 MPa for the control samples, to 374.3 ± 15.5 MPa for the composites with the modified carbon fibres, while the flexural modulus decreased from 3.7 ± 0.25 GPa to 2.5 ± 0.22 GPa for the control and modified samples, respectively. It is also worth noting that the polymer grafted to the surface of the carbon fibres may not be miscible with the epoxy polymer used as the composite resin in this case. If the latter is the case, phase separation may occur at the interphase, minimising adhesion. While both are possible it is difficult to determine which (if either) of these scenarios are responsible for the observed physical data. It is the expectation that further investigations, examining a broader range of polymer constituents will be able to shed light on these subtle effects.

To ensure that the ductility observed in these specimens was due to the surface modification and not the internal debonding and slipping of the fibres within the composite, SEM of the fracture surfaces were taken (Fig. 3 (C)-(F)). The fracture surface of the specimens with control fibre showed a clear debonding of fibres from the resin matrix (Fig. 3, (D)). This is expected as the pitch-based fibres used in this work are extremely inert, with respect to the epoxy resin, leading to interface debonding due to chemical incompatibility.

In the samples containing the modified fibres no clear evidence of debonding is seen at the fracture surface (Fig. 3, (F)). Indeed, a layer of polymer is clearly adhered to the surface of the fibres,

suggesting the cohesive failure of the polymer rather than debonding at the interface.

To determine the amount of polymeric material grafted to the fibre surface and ensure it is responsible for these changes in physical properties, thermogravimetric analysis (TGA) of the unmodified fibres, the neat polymer and the modified fibres was undertaken (Fig. S4). As expected, the milled CF sample with no surface modification was thermally stable for the temperature range used (30–600 °C). The neat polymer showed significant degradation at approximately 400°C, that was mirrored by the surface modified fibre. The residual weight of the modified fibre sample (90%) suggests that the surface modification was successful and accounted for ~10% of the fibre, by weight. This represents a remarkably high grafting density as the exposed surface only contributes a small contribution of the total material mass.

These results suggest that the surface modification process dramatically affects the interphase and the performance of the corresponding composites.

In conclusion we have demonstrated a rapid, procedurally simple, and versatile means of surface modification. This method allows the grafting of well-defined polymer via a “grafting to” approach but achieves a remarkably high grafting density that is not typically seen with this approach. By modifying fibres in a stirred suspension, this method is well suited to the treatment of milled and recycled carbon fibre, and compliments existing electrochemical methods.

These modifications have immediate and significant effects on the macroscopic properties of the resulting composite materials. Considering that the parent polymer is incredibly broad in scope, as it is derived from RAFT polymerisation, this work opens new potential avenues to optimise the interface of carbon fibre composites for an array of matrices. Further investigations using higher fibre weight fractions and exploring the scope of fibre surface chemistry are currently being undertaken and will be reported in due course.

Author Contributions

Data curation: David J. Hayne, Filip Stojcevski, Bhagya Dharmasiri, Joel F. Hooper; Conceptualisation: Joel F. Hooper, Luke C. Henderson; Supervision: Luke C. Henderson, Daniel J. Eyckens; Project Administration: Joel F. Hooper, Luke C. Henderson; Writing manuscript (original and editing): All authors.

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Conflicts of interest

There are no conflicts to declare.

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