

Installing mixed surface chemistry on carbon fibers for maximising adhesion in epoxy and PMMA.

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Abstract: Carbon fibres were surface modified using mixed grafting solutions of methyl methacrylate and glycidyl (epoxy) methacrylate in ratios of 0:100; 25:75; 50:50; 75:25; and 100:0, respectively. When evaluated in an epoxy resin, all modified fibers showed significant improvement in fiber-to-matrix adhesion. Notably, the surface grafted polymer with blends of methyl methacrylate: glycidyl methacrylate of 0:100 and 25:75, respectively, showed a >200% improvement in adhesion, relative to control fibers. When evaluated in PMMA, again, significant adhesion improvements were observed, though fibers grafted with $\geq 25\%$ methyl methacrylate were statistically indistinguishable. This shows that by correctly tuning the surface chemistry an optimal covalent sizing can be developed for thermoplastic and thermoset resins. As an additional benefit a significant improvement in the treated fiber's tensile strength and modulus was also observed.

Keywords: Carbon Fiber; Interface; Surface Chemistry; Fiber-Matrix Adhesion.

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1. Introduction

The pursuit for ultra-stable and strength-critical components in the rapidly expanding space, automotive and aerospace industries have placed carbon fibre reinforced polymers (CFRPs) at the forefront of material research.[1-3] This is further exemplified by their growing use in emerging technologies such as in hydrogen storage, concrete reinforcement and wind-power generation. As new applications are uncovered so too is the variance in resin formulations, in many cases thermoplastics are swiftly becoming the preferred choice over epoxy thermosets. This is primarily due to thermoplastic's rapid cure cycles, ease in fabrication, low cost, mouldability and recyclable nature.[4-7]

This rising adoption of thermoplastic composites bring forth new challenges for carbon fibres, particularly due to their poor adhesion at the interfacial level - irrespective of the resin choice.[8-10] Despite this, the research on improving carbon fibre thermoplastic adhesion is growing, with several studies exploring polyether ether ketone (PEEK), polypropylene (PP), polyethersulfone (PES) and poly methylmethacrylate (PMMA) thermoplastics to name a few.[8-13]

Currently, these interfaces are designed on a case-by-case basis and depend heavily on the resin chemistry and morphology. The question remains as to whether it is possible to generate a fibre interface that binds strongly to both thermoset and thermoplastic. In doing so, it would be possible to design a fibre interface that is tailored towards a class of polymers instead of individually (i.e. Epoxies/PMMA/PES and PP/PEEK/PE).

Therefore, the focus of this work is to investigate the tailoring of multiple resins in more detail, using epoxy and PMMA as our resins of choice. As a proof of concept, PMMA was chosen due to its chemical similarities with epoxy, possessing a slightly polar ester vs slightly polar bulky bisphenol A diglycidyl ether (DGEBA) – both of which are vulnerable to hydrolysis.

Another aim of this work was to address a prevalent challenge within the literature. For epoxy resin systems, installing epoxides is a very ideal method for improving adhesion as they are capable of covalently crosslinking with the resin directly.[14-16] However, this has yet to be achieved at a sufficient level for industry scale-up, with either lengthy pretreatment times necessary to grow branched polymer chains, or through the use of ill-advised electrolytes (AlCl_3 , which reacts violently with water).

This report also builds on previous works within our group, of an electrochemical *in situ* polymerization technique that used acrylic acid to generate fibre color and reversible malleability, alongside increased adhesion in epoxy.[17-19] For these surface modification procedures, all studies have included only one monomer at a time, leading to one type of surface chemistry installed. Therefore, another focus of this work was to examine the possibility of co-polymerisation, as this would open a myriad of potential properties to be used in tailoring the fiber-matrix interface.

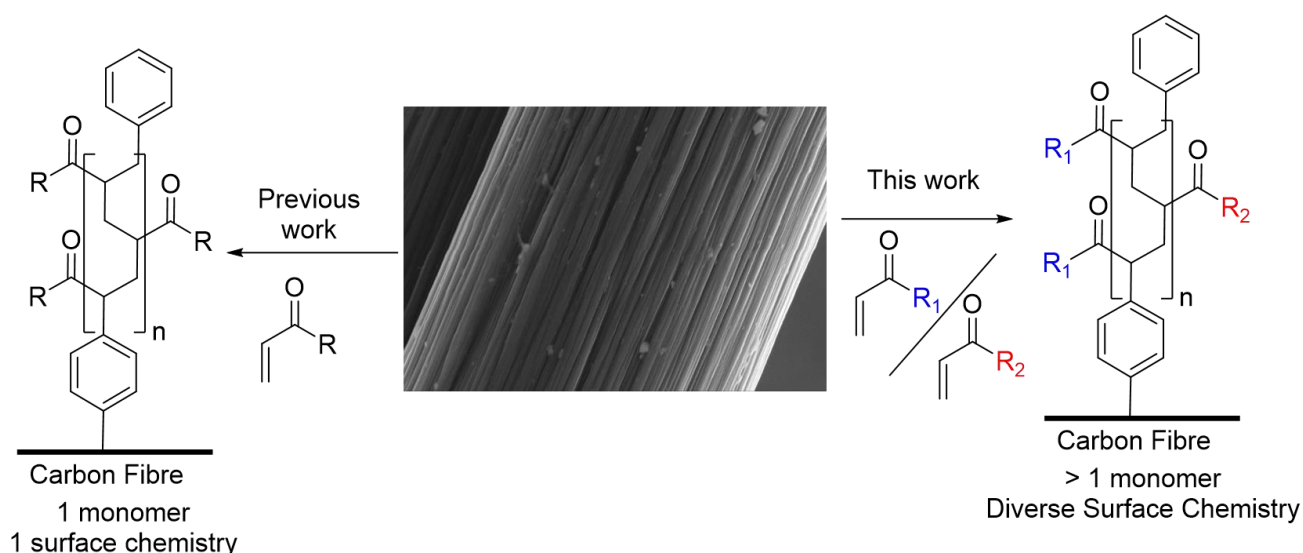


Figure 1 Overview of covalent sizing approaches, **Left:** previously reported process leading to one surface chemistry.[20, 23] **Right:** Mixed composition of surface chemistry used in this work.

Thus, the first aim of this work was to use scalable methods established in our lab to graft a glycidyl-derived polymer onto the surface of unsized carbon fibre, testing its interfacial adhesion in both epoxy thermoset and poly(methyl methacrylate) (PMMA) thermoplastic, fully characterizing these fibres. Secondly, we investigate the effect an MMA-bound polymer has on the interfacial adhesion of not only in PMMA resin – but also in epoxy thermoset. Lastly, the interfacial adhesion of hybrid polymer blends is investigated, and the effect mixtures of thermoset/thermoplastic surfaces have on adhesion is reported herein.

This hybrid epoxy/PMMA surface is achieved by utilizing electrochemically generated phenyl radicals - which are capable of rapidly grafting to the surface of carbon fibre under very mild conditions.[20] The grafting of these radicals allow for unprecedented control of the carbon fibre surface chemistry. The graft is single step and readily compliant to in-line fibre production processes that already employ electrochemical systems for oxidation baths (removing the need for electrochemical oxidation entirely).

In fact, the procedure precludes the need for a pre-treatment step entirely and generates a multifunctional surface in under an hour. Recently this was shortened to a few minutes if sacrificing the data-rich cyclic voltammetry (as employed in this study) with chronoamperometry, and is demonstrated in our previous publications.[18]

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.

2.2 *Statistical analysis*

A two-sample t-test, assuming equal variance, determined whether data was significantly different; a P-value less than 0.01 was considered statistically significant.

Statistically significant changes relative to control samples have been denoted with an asterisk (*) throughout the manuscript.

2.3 Carbon Fiber 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 counter-electrode. Experiments consisted of cycling a +1.0 V and -1.0 V vs Ag/AgCl at a scan rate of 0.01 V s^{-1} , after degassing the solvent. The electrolyte grafting mixture comprised of DMF/0.01 M H_2SO_4 (80:20, v/v), 4-nitrobenzene diazonium tetrafluoroborate (concentration of 2 mmol), as well as the corresponding monomer to a concentration of 1.0 M. After treatment, the fibers were then rinsed thoroughly with a series of organic solvents (acetone, chloroform, and ethanol), followed by drying under reduced pressure (approx. 10 mbar) for 24 hours to ensure removal of residual solvents.

2.4 Microbond test

IFSS of the functionalized carbon fibers was measured with Fibrobond device (Fibrobotics Oy, Finland) using 1N S-beam load cell.[21] Test samples were prepared with Fibrodrop setup (Fibrobotics Oy, Finland), using a computer-controlled aluminum heating element and protective N_2 atmosphere. Five fiber specimen per sample type were prepared and 20-40 PMMA droplets per fiber specimen measured.

2.5 Microscopy

Tested microbond samples were studied with Scanning Electron Microscope (field emission gun SEM, Zeiss ULTRApplus, Germany). The fibres were placed on conductive carbon tape and coated with a thin carbon coating to ensure the conductivity.

2.6 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) was conducted in an ultra-high vacuum chamber with a base pressure of a few 10^{-10} mbar. The instrument is equipped with a SPECS Phoibos 100 hemispherical analyser. A non-monochromatic X-ray source with a Mg anode (12 kV – 200 W, $K\alpha$ line with an excitation energy of 1253.6 eV) was used for irradiation. The angle between the direction to the detector and the incoming X-ray is 54.7° . Survey scans with 40 eV pass energy were performed first and followed by high-resolution scans at a pass energy of 10 eV for characterizing the chemical states of the sample surfaces including chemical composition and valence state of element. At a pass energy of 10 eV the FWHM of the Ag $3d_{5/2}$ peak is < 1 eV. The uncertainty of the peak positions is typically 0.2 eV. The fiber-shaped samples were cut into proper size and mounted in bundles with copper tape on sample holders to cover the probing area and avoid charging during measurement. Thus, a common energy correction process by calibrating the C-C sp^3 to 285.0 eV is not needed in this work.

3. Results and discussion

3.1 *Surface modification of carbon fibres with mixed monomer chemistry.*

In our previous work we have demonstrated that the introduction of aryl-amine groups to the surface of carbon fibres results in significant interfacial shear strength (IFSS) improvements. This has been attributed to the cross-linking of the surface-bound amines to the epoxy resin and to the ‘molecular drag’ of these small molecules through the polymer interphase [21, 22, 24]. In this work we have reversed the surface-bound chemistry, by growing acrylate-derived polymers, bearing a glycidyl side chain. Additionally, we were curious about the constituents of this polymer and if a ‘critical’ concentration of epoxy was required for optimal adhesion gains. Therefore, five surface grafted carbon fibres were generated using a mixture of monomers as outlined below (Figure 2). These monomers provide some structural similarities, such as the carbonyl and ester groups, but methyl(methacrylate), referred to as

Monomer 1, does not have a reactive epoxide moiety. To modify the fibers in the desired way (Figure 2) the constituents of the grafting solution monomers were varied in 25% increments, giving a total of 5 surface chemistries. It is important to note that the surface modification procedure in this work is not a living radical polymerisation in the same way that RAFT or ATRP are, and thus the sequence, grafting density, and molecular weight of polymers is random. Considering the mixed constitution of the surface grafted polymers, it was of utmost importance to characterise their physical and chemical properties to determine if any changes could be correlated to either of the grafted surface chemistries.

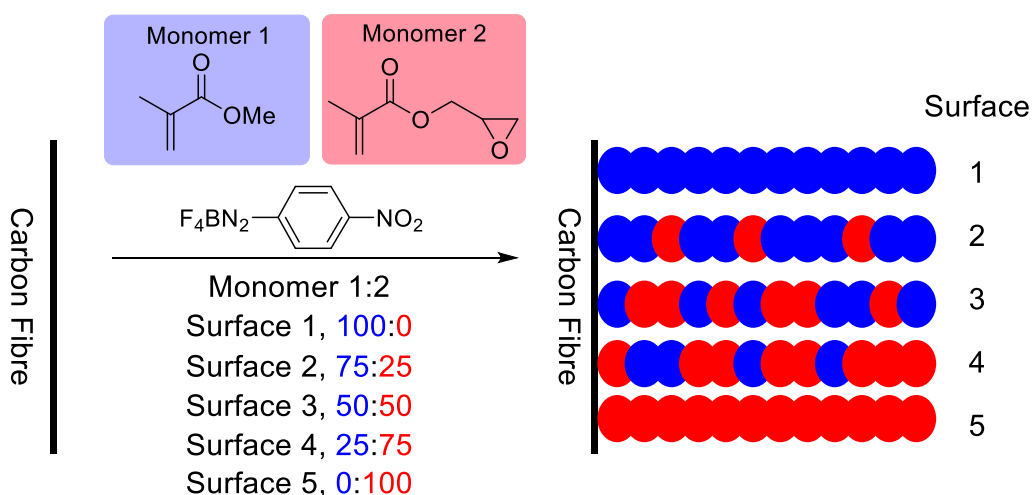


Figure 2 Electrochemical polymerization of acrylate monomers on carbon fibre to give mixed surface chemistries. Electrochemical conditions are -1 V to +1 V (vs. Ag/AgCl), 10 scans at 10 mV/sec, DMF/0.01 M H₂SO₄ (80:20, v/v).

Analysis by XPS of the fibres was undertaken to verify if the mixed polymer and its constituents could be determined (**Figure 3**). When examining the control carbon fibre (**Figure 3**) an array of carbonaceous species is observed on the surface including aromatic (C6, in red) and found at 284.4 ± 0.2 eV, [22, 23]. A second peak is found at 285.7 ± 0.2 eV and is attributed that the fraction of the aromatic C6 rings which are oxidised but where the C atoms are not bound to the functional group attached to the C6 ring. One possibility for the functional group oxidising the C6 ring is a carboxyl group (C₆H_x(COOH)_{6-x}). [24, 25] It has to

be noted that oxidation via a carboxyl group is only one option and that other oxidative functional groups could result in a similar binding energy. Through the present work we do not have information which functional groups should be assigned here. However, the oxidation of the C6 rings is consistent with the traditional view of carbon fibers being made up primarily of graphitic and turbostratic carbon.

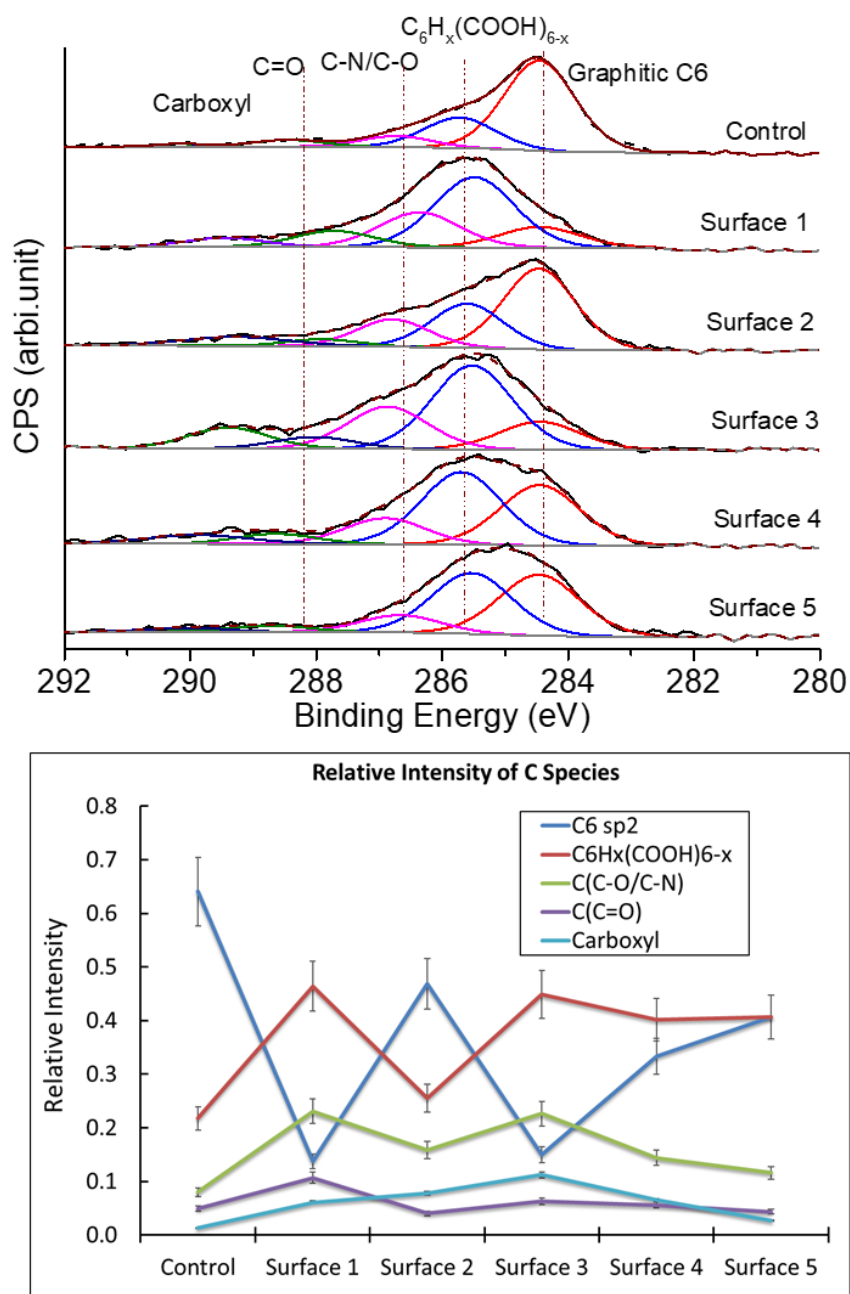


Figure 3 C1s XPS spectra, and C=O, C-O, C-C ratios for **Surfaces 1-5** and relative concentration of C species.

Adding a C-C sp³ peak to the fitting procedure and fixing the energy position at 285.0 eV is possible but the procedure is not applicable here, because such fitting requires a determined presence of C-C sp³ of correspondent relative concentration identifiable in the spectra. However, the presence of C-C sp³ is possible and could be covered to some degree by both the 284.4 and 285.7 eV peak. There are some small contributions from C-O/C-N bonds at $286.6 \pm 0.2\text{eV}$, which are presumably remnants of the initial thermal stabilization process and the poly(acrylonitrile) precursor fiber, respectively. Finally, a very small contribution to the carbon signal is that of a carboxyl (O=C-O) unit, again likely due to the introduction of oxygen during the initial stabilization process.

The C1s spectrum of surface 1 is notably changed compared to that of the control fibre, comprising an immediately larger sp³ portion of the carbon signal (**Figure 3**), and is consistent with the formation of alkane (sp³-sp³) polymer backbone on the fiber surface. Notably, the C6 signal is significantly depressed, and the carboxyl contribution (O=C-O) is more dominant, as would be expected from the polymeric ester modification of the two monomers.

The contributions for each of the following modifications, **Surfaces 2-5**, are all consistent with the expected surface chemistry, though this is most obvious for **Surface 5**, where the contribution from the C-O signal has increased. This would be due to the presence of the oxirane (epoxy) group present in the monomer.

It is worth noting that the intensity of the C6 peaks in these spectra do vary as well as the other C species, which could be due to the uncontrolled nature of this polymerization propagation and surface functionalization processes. For the changes in relative atomic ratios with respect to each surface treatment the reader is referred to the supplementary information. Additionally, the cyclic application of potential from reductive to oxidative may result in some a small amount of concomitant oxidation of the fibre surface. The rate of polymerization of each monomer is likely different based on various factors such as steric

hinderance, electronics, and diffusion. Therefore, we refer to the monomer ratio in the grafting solution, not that grafted to the fiber surface, as there may be a distinct difference between these.

The focus of this work now turned to the physical characterization of the surface modified fibres. Determining their tensile strength and tensile modulus is of critical importance as these physical values provide the innate value of this material, and any modification will (optimally) not come at the expense of either.

The surface modification procedure did not have any detrimental effect on the tensile strength or tensile modulus of the starting carbon fibres. Indeed, in all cases the surface modification had improved the tensile strength significantly, and what is more unusual, the increase was generally correlated to the amount of Monomer 2 (epoxy-containing) present in the grafting solution.

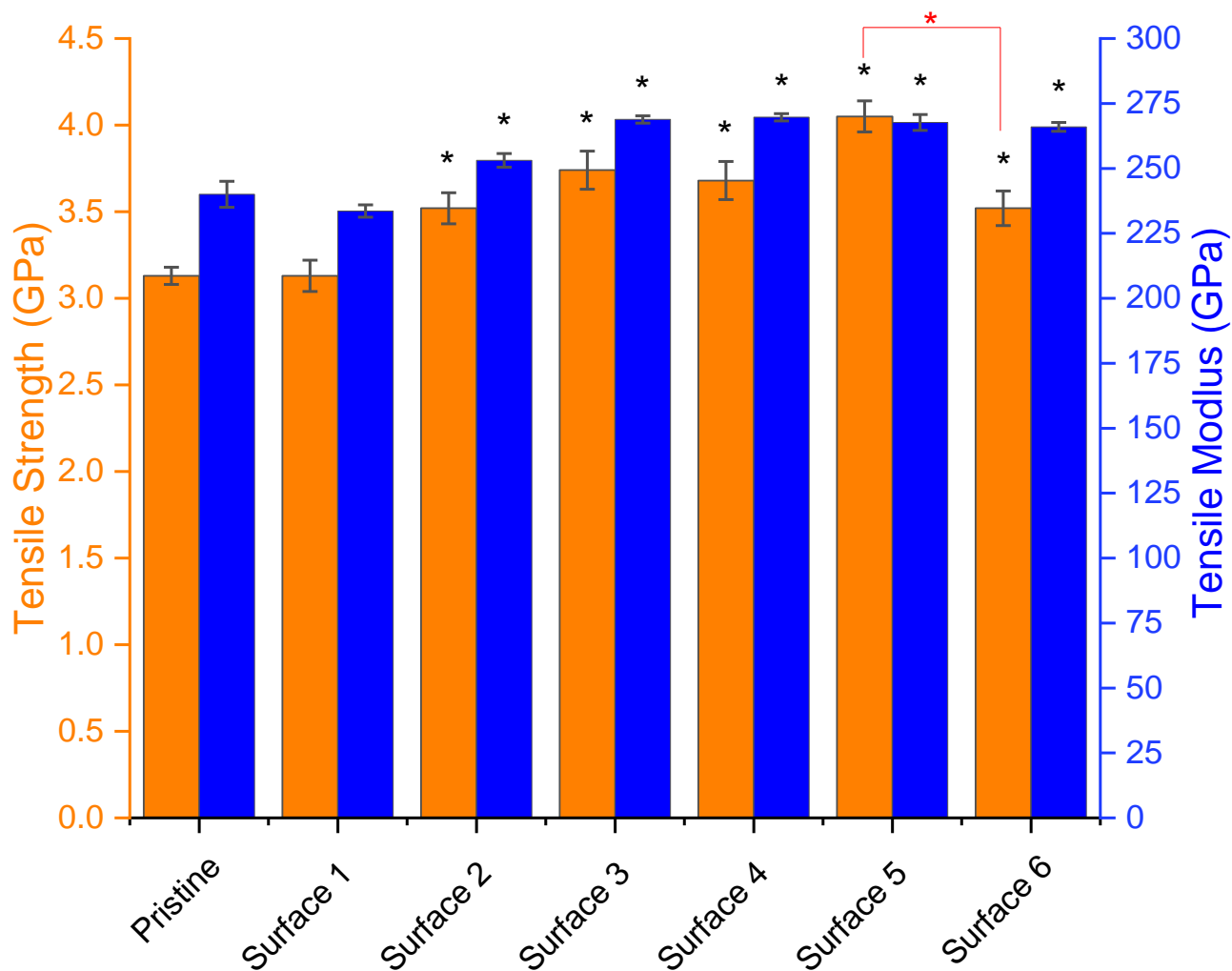


Figure 4 Tensile strength and Modulus of treated fibres *Denotes statistically significant change relative to pristine fibres ($P < 0.01$), errors shown are standard error.

The correlation of increase in tensile strength to the amount of Monomer 2 is interesting though the mechanism unclear (**Figure 4**). A similar effect was observed with the tensile modulus, with the increase seemingly correlated to the amount of Monomer 2 in the grafting solution, though this seemed to plateau earlier with surfaces containing 50%, 75%, and 100% Monomer 2 (**Surface 3, 4 & 5**, respectively) giving statistically indistinguishable tensile moduli.

In the original report of this polymerisation process the concomitant reduction of the aryl-nitro moiety was observed.[26, 27] In this instance, the reduction of the aryl-nitro group within

the polymer network would reveal the corresponding anilinic amine. This amine would be in close proximity (and high relative concentration) to the glycidyl polymer side chain, possibly leading to epoxy ring opening *in situ* (**Figure 5**). This cross-linking of the surface bound polymer would lead to a significant increase in its ability to bear load and is perhaps responsible for the increased tensile strength observed for these samples. Indeed, the increase in tensile strength is consistent with the increasing amount of glycidyl monomer.

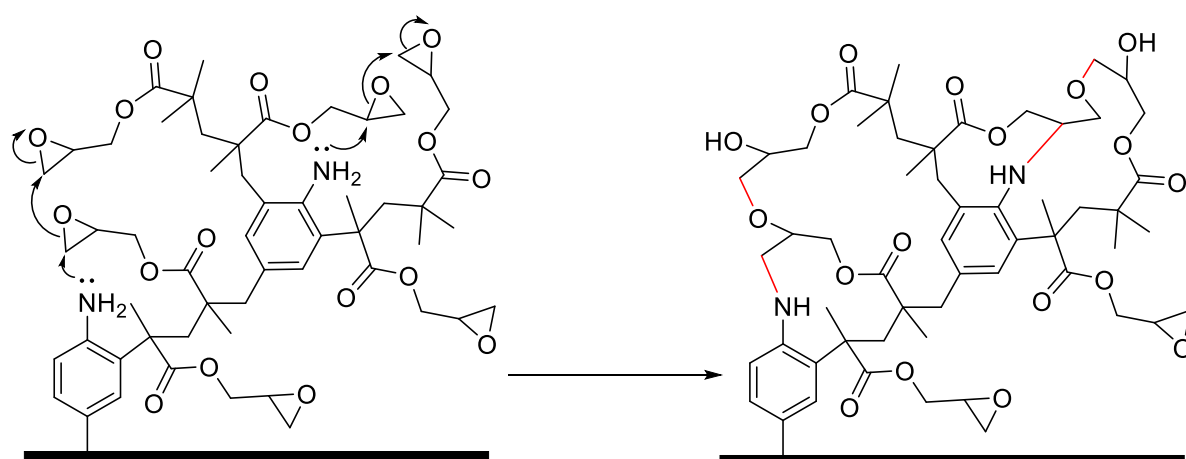


Figure 5 Schematic diagram of potential intramolecular reaction within the surface modification present for **Surface 5**. New bonds formed *via* internal cross-linking are shown in red.

To test this hypothesis, the modification process was repeated using 100% glycidyl methyl methacrylate), though mediated *via* an alternative aryldiazonium salt (**Surface 6**). The aryldiazonium salt in this instance was simply derived from aniline, and so by removing the nitro moiety removes the potential for *in situ* reduction to the amine. In that instance, the tensile strength was increased to 3.5 ± 0.1 MPa and the tensile modulus increased to 266 ± 1.7 GPa. This change is not to the same extent as observed with the aryl nitro diazonium salt for the same monomer system (**Figure 4**, statistical significance denoted by *), suggesting that that the aromatic nitro group or amine is playing a role in the strengthening of these fibres. It is important to note that this is not definitive evidence of the mechanism of tensile strength

improvement, as the kinetics of diazonium reduction, polymerisation, and branching during polymer propagation will be different in this latter instance.

The interfacial adhesion of these polymers in epoxy was also examined using the single fibre fragmentation test, as *per* our previously published reports.[28, 29] As expected, the unsized and non-surface treated carbon fibers (denoted as 'pristine' in Figure 6) possessed a very poor interfacial shear strength 20.2 ± 2.45 MPa. Growth of a covalent sizing, consisting of just methyl methacrylate (Surface 1) an immediate increase in IFSS was observed of 38.0 ± 2.3 MPa. Increasing the content of glycidyl methacrylate present in the grafting solution to 25% and 50% (**Surfaces 2** and **3**, respectively) showed minimal improvement over Surface 1, at 40.0 ± 1.4 MPa and 45.4 ± 2.3 MPa, respectively.

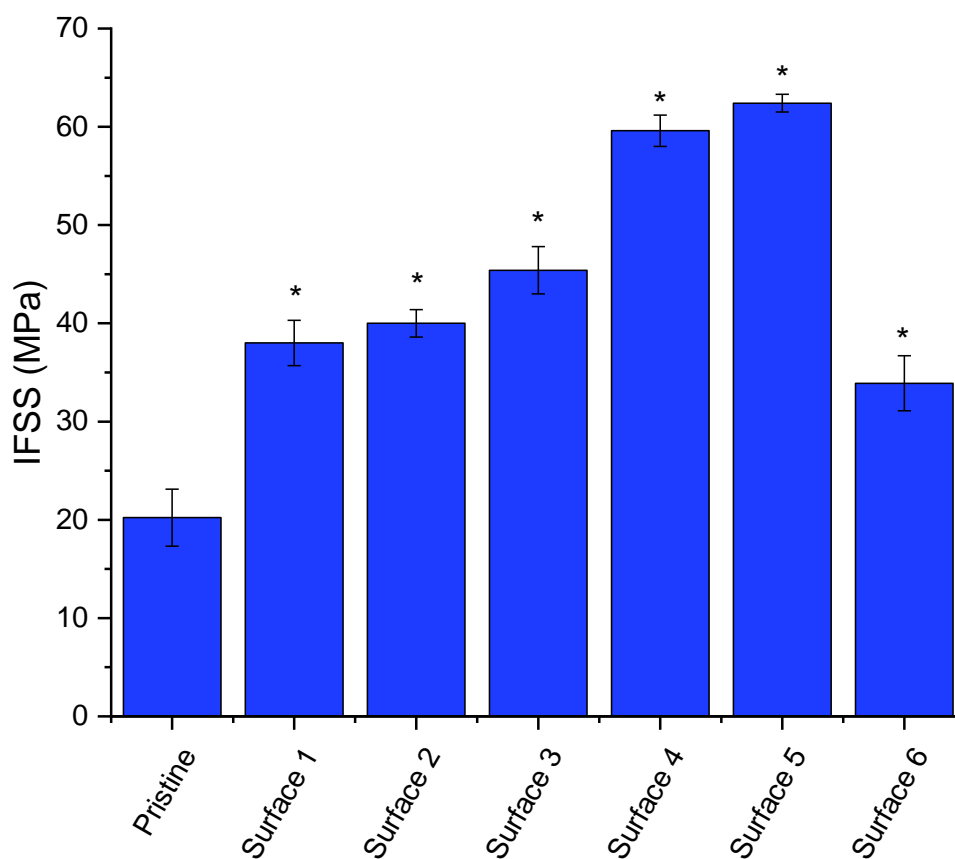


Figure 6 Interfacial shear strength of pristine and surface modified fiber in epoxy polymer using the single fiber fragmentation test; *Denotes statistically relevant changes in IFSS relative to pristine fibre ($P < 0.01$).

When increasing the surface grafting solution to 75% glycidyl methacrylate (**Surface 4**), a significant increase in IFSS was found in the specimens, relative to both the pristine fiber and the previous 3 examined surface chemistries. The IFSS of 59.6 ± 1.6 MPa, represents a 228% relative increase compared to the pristine samples and almost a 100% increase compared to Surface 1. A similar observation was made for **Surface 5**, an IFSS of 62.4 ± 0.9 MPa, which was statistically indistinguishable from **Surface 4**. This suggests that there is a point at which the surface bound polymer and the matrix become 'compatible', which correlates to the inclusion of the glycidyl methacrylate monomer into the surface grafted material. This makes sense as the resin, prior to cure, is also epoxy monomers and thus miscibility is likely high. Additionally, as outlined in **Figure 5** (above) the latent presence of amines throughout the surface bound polymer network may react with the resin as well, providing a covalent tether from the fibre to the resin. Though, as the nitrophenyl initiator is used in the same concentrations across all samples, this effect, to a degree, would also have to be a function of surface grafted polymer-resin monomer miscibility. For example, **Surface 1** and **Surface 5** possess the same quantity of an aromatic nitro/amine groups, though the inability of the largely PMMA-derived surface bound polymer to mix with the epoxy monomers facilitating access to those reactive amines to allow ring opening reactions is likely responsible for the moderate increase in IFSS. The absence of the nitro moiety, as in **Surface 6**, showed a significant reduction in IFSS (33.9 ± 2.8 MPa) relative to **Surface 5**, and was much closer to the pure PMAA grafted fibres, **Surface 2**. Again, this suggests that the identity of the diazonium initiator has a profound influence on the interfacial performance in these systems. This interpenetration of surface bound polymer and molecular entanglement has been examined in our previous reports both experimentally,[30] and using molecular dynamics simulation.[31, 32]

Notably, it is also important to consider that, as suggested by XPS, the nature and reactivity of the monomers used in this study seem to vary significantly based on the relative ratio used in the grafting solution. This may also be having an influence on the adhesion in unpredictable ways, unfortunately, due to the curved and inhomogeneous nature of carbon fibers, the quantification of polymer film thickness is not possible using typical techniques such as ellipsometry, profilometry, etc.

With these results in hand, our attention turned to the adhesion of this same grafted chemical gradient of epoxy and methyl esters but in a PMMA resin (Figure 7). Of interest was **Surface 1-3** which are primarily (or equally) composed of PMMA-derived structures and the potential for complementarity between the fibres and resin.

This adhesion was measured using an automated micro-droplet debonding instrument, able to carry out a significant number of measurements in a small amount of time.

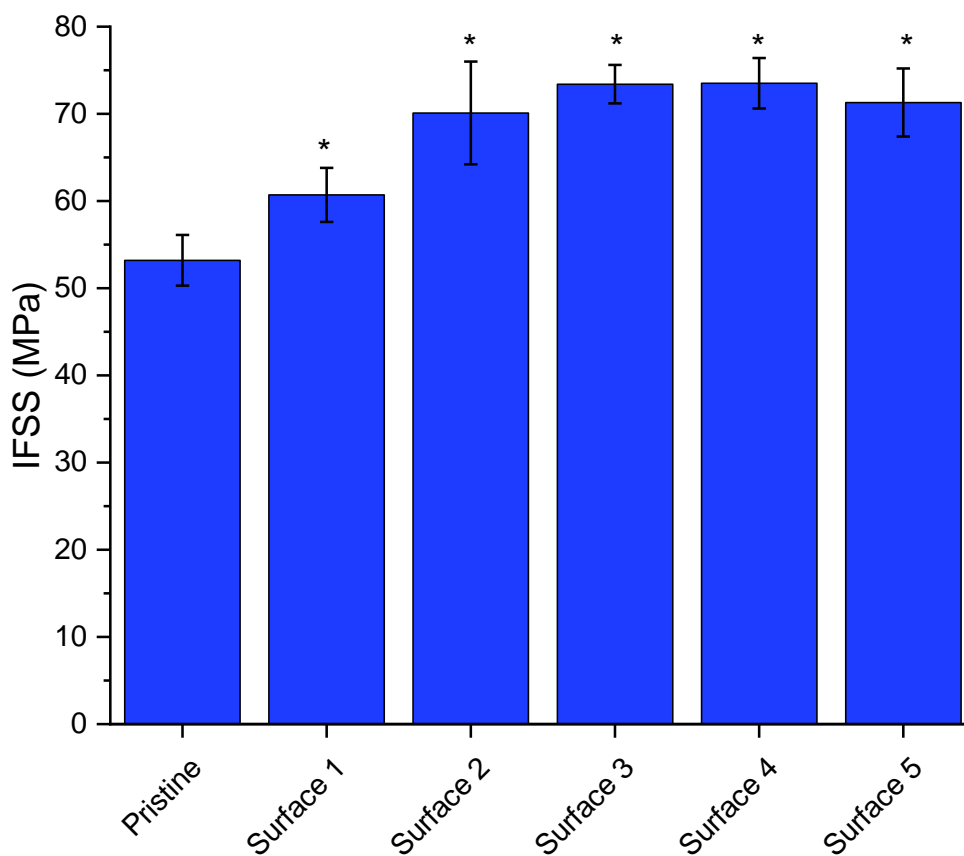


Figure 7 Interfacial shear strength of pristine and surface modified fiber in PMMA *via* micro debonding; *Denotes statistically relevant changes in IFSS relative to pristine fibre ($P < 0.01$)

The interfacial shear strength of the pristine fibre was quite high, at 53.2 ± 2.9 MPa (Figure 7). Surface 1 (100% MMA) saw a modest improvement of 14%, relative to the pristine fibres, though a much more significant increase was evident for **Surface 2**, possessing 25% of glycidyl methacrylate in the grafting solution. The IFSS improvement in this instance was 32%, relative to pristine fibre, and all subsequent formulations used in the fibre grafting solution (*i.e.* **Surfaces 3-5**, 73.4 ± 2.2 MPa, 73.5 ± 2.9 MPa, and 71.3 ± 2.7 MPa, respectively) were statistically indistinguishable from **Surface 2**. It is clear from these results that the IFSS, when determined in PMMA, reached a plateau at much earlier in the sample series, compared to that in epoxy. This would suggest that there is a complementary interaction between the PMMA matrix and the epoxy sections of the grafted polymer.

Examination by SEM of the fibres which had undergone microdebonding was consistent with the adhesion data (**Figure 7**). Here, the pristine fibres (**Figure 8**, A) show some residual PMMA on the debonded fiber surface, which is consistent with the relatively high levels of adhesion reported above.

The fibers corresponding to **Surface 1** (**Figure 8**, B) show a larger amount of residual resin on the fiber surface suggesting that, relative to the pristine sample, there was an increased degree of adhesion induced by the PMMA-like polymer grown from the carbon fiber surface. Similarly, **Surface 2** (**Figure 8**, C) shows some residual resin on the fiber surface and the longitudinal striations have been filled with the matrix signifying excellent surface-resin compatibility. When considering Surfaces 3-5 (**Figure 8**, D, E, and F, respectively) similar observations can be made with respect to the residual resin on the fiber surface. This is particularly evident for **Surfaces 4 and 5** (**Figure 8**, E and F, respectively) the former of which

shows significant sheathing of the fiber with the residual resin, while the latter displays rough protrusions from the fiber surface where resin dominated failure has occurred.

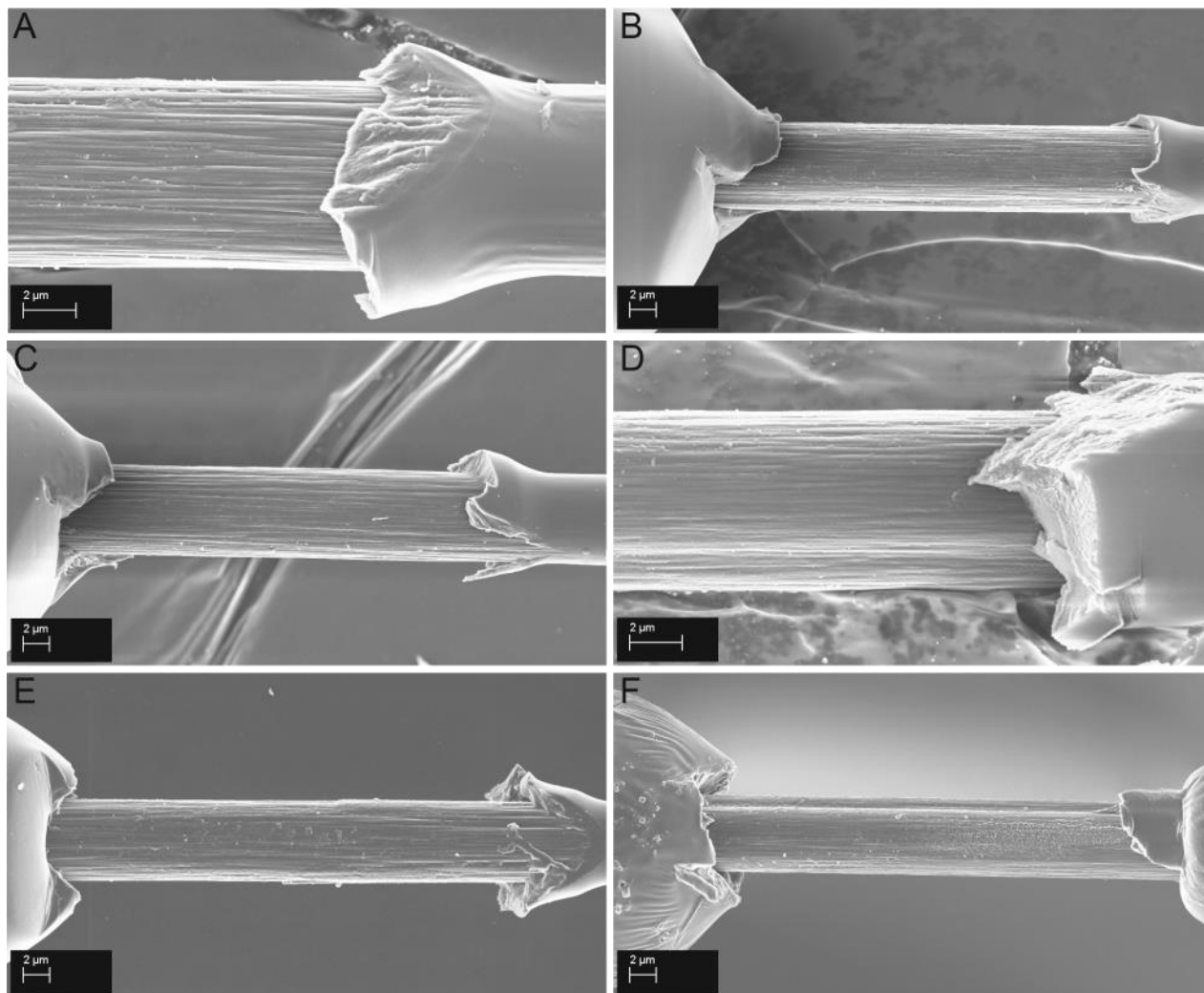


Figure 8 A: Pristine carbon fiber; **B:** Surface 1; **C:** Surface 2; **D:** Surface 3; **E:** Surface 4; **F:** Surface 5.

4. Conclusion

In conclusion, we have shown that by mixing the surface grafted material on a carbon fibre, high degrees of adhesion in multiple polymer resins may be achieved. In this case, by blending methyl methacrylate and glycidyl methacrylate we show that even by using small amounts of epoxide-containing monomer in a surface grafted material results in excellent adhesion in both epoxy and PMMA. This demonstrates that by judicious choice of surface

chemistry the adhesion for a given resin can be tuned and improved across multiple supporting polymers. Potential extension to other resins such as polyamide, polycarbonate, *etc.* are currently being undertaken and will be reported in due course.

Acknowledgements

The authors gratefully acknowledge Deakin University, this research was conducted with support from the Australian Research Council World Class Future Fibre Industry Transformation Research Hub (IH140100018), Discovery project (DP180100094), partially supported by the Office of Naval Research (N62909-18-1-2024) and the ARC Training Centre for Lightweight Automotive Structures (IC160100032). The authors also thank the Carbon Nexus Production Facility for providing fibres. The authors acknowledge the facilities, and the scientific and technical assistance, of Microscopy Australia (formerly known as AMMRF) and the Australian National Fabrication Facility (ANFF) at Flinders University.

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