Examining interfacial interactions in a range of polymers using poly(ethylene oxide) functionalized carbon fibers.

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Abstract: It is commonly assumed that a higher oxygenated content on the surface of carbon fibers will lead to high interfacial adhesion. Thus, carbon fibers are exposed to oxidizing treatments to increase surface polarity. Here, we examine the interfacial interactions of a range of thermoset and thermoplastic polymers with carbon fibers that have a grafted polyethylene oxide (PEO) chains to their surface. This provides an extremely hydrophilic surface, without potential degradation of the fiber via chemical oxidation. We find that high surface polarity does not always correlate to high interfacial adhesion; in some instances, unsized hydrophobic carbon fibers possess equal or better fiber-to-matrix adhesion than treated hydrophilic carbon fibers. The most notable example is in vinyl ester resin, in which the presence of an alkyne group, able to participate in the radical polymerization process, provides significant improvements in interfacial shear strength (IFSS) compared to a larger, and polar, PEO chain.

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#### 1. Introduction

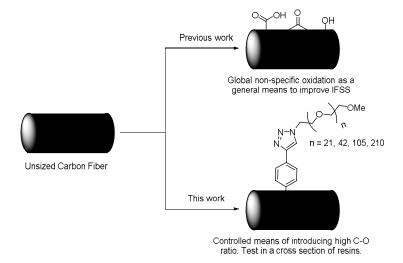
Carbon fibers have been used for decades as a means to bolster strength and stiffness of various materials, most commonly polymers. These carbon fiber reinforced polymers (CFRP) have seen exceptional uptake in light weighting applications, and thus have a large presence in the aerospace, automotive, military, and energy industries. As with all composites, which consist of at least two dissimilar materials, the junction at which these two materials meet dictates, to a large extent, the overall performance of the entire component.[1] The adhesion between fiber and matrix has been a persistent challenge in the literature for decades and, at an industrial scale, is addressed to an extent by the introduction of fiber surface treatment and sizings. The former process includes the passage of the fibers through an aqueous bath of ammonium bicarbonate, and a current is passed through the fibers, as they largely consist of graphitic carbon and are conductive.

This electrochemical process is not well understood but the general consensus is that the process removes loosely bound carbon (a potential lubricant) from the surface of the fibers, and installs some oxygen bearing functionalities such as ketones, alcohols, aldehydes, and carboxylic acid units to the surface which facilitate better fiber-matrix adhesion.[2-7] After this, the surface treated fibers are passed through an aqueous emulsion (a 'sizing') which is coated on the fiber surface. From a practical perspective, the sizing serves to bind the fibers together and assist in their handling, weaving, and processing. Though, the presence of this material on the surface of the fibers will have an effect on the final adhesion in the composite material.[8-14]

Unfortunately, the highly proprietary nature of the carbon fiber industry means that the conditions used in surface treatment (e.g. current, electrolyte concentration, duration, etc.) are not divulged to the end user. These unknowns are compounded by the application of a sizing

agent that, again, is a proprietary mixture of chemicals, presumably consisting of short polymers, emulsifiers, anti-static agents, and other components. With these (at least) two unknown processes, each of which have a multitude of unknown variables, the correlation of surface chemistry/morphology and sizing on the fiber-to-matrix adhesion is almost impossible to determine.

Despite these challenges, the area of fiber surface and interface modification for increased adhesion has seen a good deal of attention from academic and industrial research efforts.[15-20] One persistent theme, which has arisen in the literature, is that the installation of oxygenated species has a beneficial effect on fiber-to-matrix adhesion. This is typically achieved *via* global surface oxidation and often represented as interfacial shear strength (IFSS). Indeed, this oxidative approach, using techniques such as plasma, electrochemical treatment, and chemical oxidation, have resulted in adhesion improvements (**Figure 1**, Top).[8, 21-25] Improvements have occurred even in counter intuitive combinations such as increasing fiber polarity for non-polar polymers such as polypropylene.[26, 27] Though recently, our group reported the development of hydrophobic carbon fibers while simultaneously increasing interfacial adhesion, suggesting that the correlation of surface polarity and adhesion was not the complete picture.[28]



**Figure 1** Top: General oxidation techniques employed to increase oxygen content on the fiber surface, typically introducing an array of functional groups. Bottom: Surface modification with PEO polymers with a very high oxygen content, and able to use molecular entanglement.

In this work we take surface modified carbon fibers, possessing surface tethered polyethylene oxide (PEO) chains, and test their adhesion in epoxy, vinyl ester, polycarbonate, Nylon-6, and Nylon-6,6 (**Figure 1**, bottom). These fibers have a significantly high oxygen content on the surface, and are extremely polar, thus represent a unique opportunity to investigate their adhesion in a range of polymers and adhesion. Importantly, PEO polymers have been shown to be miscible in a wide variety of polymers,[29] including blends with polycarbonate,[30] polyamide[31] and polystyrene.[32] Further, PEO groups are miscible in epoxy[33, 34] and when used to chelate metal ions, have been shown to improve curing rates.[35] It is important to note that the ratio of PEO groups to polymer matrix is extremely small in this investigation, localised entirely to the interface. They are covalently bound to the fiber surface, though are able to extend and entangle with the supporting polymer matrix, especially at elevated curing temperatures.

#### 2. Materials and Methods

#### 2.1 Materials

Carbon fiber samples were manufactured by Carbon Nexus at Deakin University, Australia. They were received without sizing, and referred to throughout this manuscript as 'pristine'. All surface modifications are made using these pristine carbon fiber samples, and compared to the control, pristine sample.

Chemicals were purchased from Sigma-Aldrich Chemical Company and used without further purification.

The following polymers were used as matrix materials in order to prepare single fiber model-composites: (i) epoxy resin Epikote MGS RIM 135 from Hexion (Momentive, Columbus, GA,

USA) with Epicure Curing Agent MGS RIMH 137, (ii) polyamide 6.6 (Nylon-66) Ultramid® A34 and polyamide 6 (Nylon-6) Ultramid® B27 E 01 from BASF SE (Leverkusen, Germany) and (iii) polycarbonate (PC) LEXAN<sup>TM</sup>HF1110 from SABIC.

For microbond measurements epoxy vinyl ester resin AME<sup>TM</sup> 6001 INF-135 from Ashland (Wilmington, USA) and methylethylketoneperoxide Norox MCP-75 from United Initiators (Pullah, Germany) were used.

## 2.3 Statistical analysis

A two-sample t-test, assuming equal variance was used to determine statistical significance (P-value < 0.05) and is indicated throughout the manuscript via the use of asterisks.

## 2.4 Carbon Fiber Surface Treatment

Pristine 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 the signals processed using NOVA software. Using a three-electrode system, consisting of a reference electrode (Harvard Apparatus LF-2 leak free electrode (filling electrolyte 3 M KCl)). A platinum mesh counter-electrode was also employed for all experiments. Grafting was carried out by repeated application of a +1.0 V to -1.0 V potential (*vs* Ag/AgCl) scanning 0.02 V s<sup>-1</sup> in acetonitrile. Aryl diazonium salts were grafted at 1 mM concentration with a supporting electrolyte of tetrabutylammonium hexafluorophosphate (TBAPF<sub>6</sub>, 0.1 M). After treatment, the fibers were rinsed (acetone, chloroform, and ethanol), then dried under reduced pressure (approx. 10 mbar) for 24 hours.

The fibers in this work have been obtained via the use of click chemistry, as reported previously.[36] This is typically using reductive electrochemistry as a surface modification strategy, to attach phenylacetylene moieties as a priming layer, followed by post

functionalization (**Figure 2**). This is using copper azide-alkyne cycloaddition with poly(ethylene oxide) terminated in an azide. In this way, a series of fibers with exceptionally polar surface chemistries can be reliably accessed. We have evaluated these fibers previously in an epoxy matrix, and found that the surface density of functionalization versus polymer size and penetration to be a tradeoff. For analysis and characterization, refer to our previous works.[36]

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**Figure 2** Surface modification and post functionalization to generate PEO-surface bound carbon fibers.

In these instances, the azide terminated PEO chains that were used had an average molecular weight of 1,000 Da (n  $\approx$  21), 2,000 Da (n  $\approx$  42), 5,000 Da (n  $\approx$  105), and 10,00 Da (n  $\approx$  210), which will be referred to as **1k-PEO**, **2k-PEO**, etc.

# 2.7 Single Fiber Pull Out (SFPO) procedure and graph

For the preparation of single fiber model-composites the carbon fibers were end-embedded in a droplet of each matrix polymer using an equipment that was constructed and built up at IPF Dresden.[37] The fibers are integrated perpendicular by a computer-controlled embedding process at controlled atmosphere and temperature with a pre-selected embedding length  $l_e$ . For epoxy resin the fibers were embedded at 45°C with  $l_e$  =100  $\mu$ m followed by 1 h curing at 85 °C and 6 h at 80 °C. Nylon 6 and nylon 6.6 were heated up to 255 °C and 290 °C, respectively, to embed the fibers with  $l_e$  = 200  $\mu$ m and PC was molten at 260 °C for fiber embedding with  $l_e$  = 150  $\mu$ m. The pull-out test was carried out on a self-built pull-out apparatus with a force accuracy of 1 mN, displacement accuracy of 0.07  $\mu$ m, and loading rate of 0.01  $\mu$ m/s in ambient

conditions. Subsequent to the testing procedure, the fiber diameter  $d_f$  was measured by an optical microscope,  $l_e$  was determined by the force-displacement curve and cross-checked by SEM. For statistic reasons, at least 20 samples were tested for each fiber/matrix combination. The force-displacement curves were recorded and the maximum force  $(F_{max})$  required to pull the fibers out of the matrix was determined. A typical curve is given below (Figure 3). It can be divided in three stages that are passed through fiber pull-out. At the first stage  $(0 \le F \le F_d)$  the fiber-matrix interphase remains intact and this part of the curve is nearly linear for fiber-matrix systems whose components are considered to be linearly elastic. The fiber starts to debond though interfacial crack propagation when the external load reaches some critical value (debond force  $F_d$ ).[38] At the second stage  $(F_d \le F \le F_{max})$  the recorded force continues increasing with the displacement of the fiber end (or crack growth), because frictional load in debonded regions as added to the adhesional load from the intact part of the interphase. The crack propagation becomes instable after a peak load  $(F_{max})$  is reached and the whole embedded length fully debonds, causing a force drop from  $F_{max}$  to  $F_b$ . From this moment and until complete pull-out, the remaining force is due to frictional interaction between fiber and matrix.

The adhesion bond strength between fiber and matrix was characterized by the values of local interfacial shear strength (IFSS)  $\tau_d$  (local shear stress near the crack tip, which is required to produce debonding), that is based on the determination of the debond force  $F_d$ .

The calculation of  $\tau_d$  is based on a stress-controlled model under the assumption that  $\tau_d$  is constant during the test (i.e., independent of the crack length) using eqn (1), where  $\beta$  is the shear-lag parameter as determined by Nayfeh,[39] and  $\tau_T$  is a stress term due to thermal shrinkage, [40] which is typical to polymer composites formed at high temperatures. The model is described in detail in the literature.[38, 41]

$$\tau_d = \frac{F_d \beta}{\pi d_f} \coth(\beta l_e) + \tau_T \tanh \frac{\beta l_e}{2}$$
 (1)

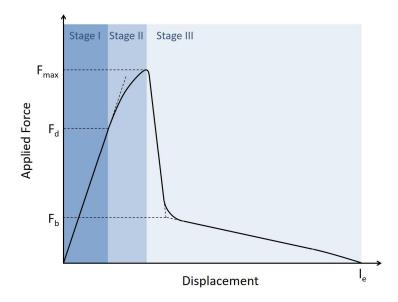


Figure 3 Typical force-displacement curve during a pull-out test.

#### 2.7 Microbond test

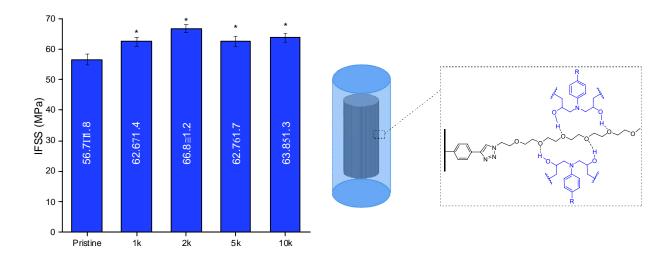
To mitigate the issue of high shrinkage of vinyl ester in the SFPO test, IFSS measurements for VE resin by the microbond methodology were done. In the microbond test, resin droplets are deposited and cured on single filaments and after curing loaded with microvise blades until the droplet detaches from the fiber surface. The maximum load required for the debonding is compared with the surface area of the fibre covered by the droplet to calculate the apparent IFSS  $\tau_{app}$ . Here, the automated debonding instrument Fibrobond® (Fibrobotics, Finland), was used. Detailed description of the device and the methodology are provided in Laurikainen *et al.* 2020.[42] As matrix material, epoxy vinylester resin was used with the mixing ration of 2.5 wt% of peroxide. Resin droplets were deposited on each fiber and a total 5 fibers were tested per sample resulting in total 196-206 data points for each fiber. The droplets were cured in nitrogen rich environment at 60 °C for 3 h, followed by 12 hours at 40 °C. The load rate was 0.008 mm/s. For each fiber, the slope of the linear regression of maximum force of individual droplets vs. embedded area was considered as the IFSS.

### 3. Results and discussion

Examination of IFSS in Epoxy, Vinyl Ester, Polycarbonate, and Nylon.

Previously, we have shown vast improvements in interfacial shear strength (IFSS) through polymer entanglement achieved by surface-bound PEO groups in epoxy resin.[36] In the present study, micromechanical IFSS evaluation is used to allow a greater variety of thermosets and thermoplastics to be explored. Initially, the single fiber pull-out (SFPO) method was used to confirm any improvements were consistent across different testing protocols.

Taking all of these functionalized fibers and conducting SFPO showed improvements in IFSS, for all samples, consistent with our previous observations. In this case, the pristine fibers gave an IFSS of 56.7±1.8 MPa, while the **1k-PEO** and **2k-PEO** modified fibers gave 62.6±1.4 MPa and 66.8±1.2 MPa, respectively. Similarly, the **5k-PEO** and **10k-PEO** gave IFSS values of 62.7±1.7 MPa and 63.8±1.3 MPa, respectively (**Figure 4, left**). In this instance the **2k-PEO** fibers showed the highest IFSS, this is likely a result of the different epoxy resin used here compared to previously (Hexion RIM135 vs. RIM985, respectively). Further to this point, the values obtained for IFSS may differ depending on the testing method used.[5] This discontinuity may be due to the area of the sample being tested (100-200 μm of fiber for SFPO vs centimeters for the single fiber fragmentation test), though it should be noted that the trends observed across different testing methods are maintained.



**Figure 4** Left: IFSS for pristine and PEO modified fibers in epoxy (RIM135) resin from the single fiber pull out test; Right: Potential interactions between the cross-linked epoxy resin and the PEO-chain tethered to the carbon fiber surface.

The presence of the extended surface-bound PEO chains within the epoxy resin serves to complement the already existing intramolecular interactions. This is due to polymer entanglement, providing anchoring of the resin to the fiber, and is enhanced through hydrogen bonding (**Figure 4**). The latter provides additional stability and miscibility of the polymers.

Examination of the fibers after SFPO by SEM shows the typical striated surface of carbon fibers, consistent with the images of the fibers prior to testing (**Figure 5**). Some debris is visible on the surface of the fibers prior to testing, and this may be due to the increased hydrophilicity imparted by the PEO groups, leading to adherence of airborne artefacts.

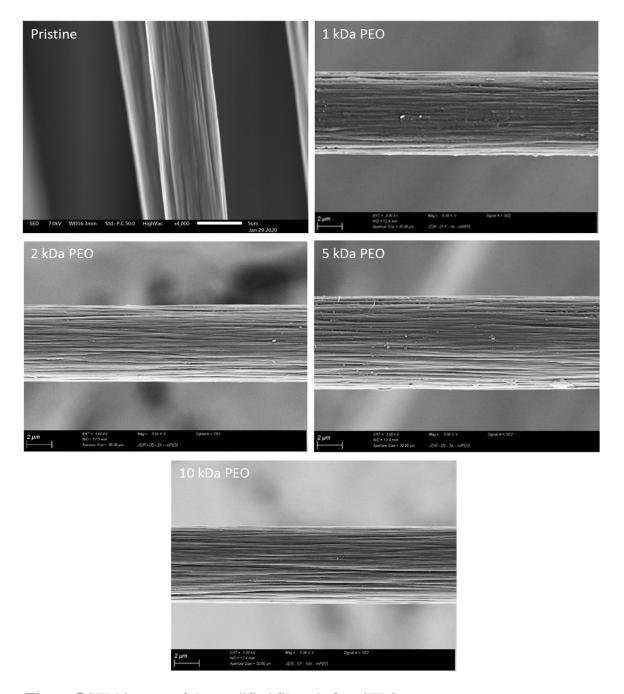
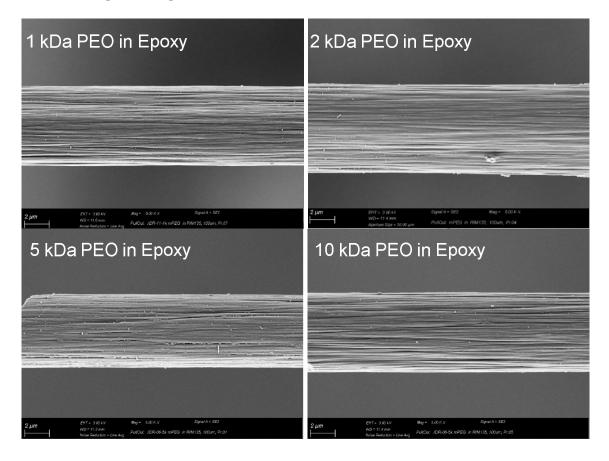


Figure 5 SEM images of the modified fibers before SFPO.

Following SFPO testing, the fibers are shown with residual epoxy polymer still adhered to the fiber surface. This is especially evident in the **5k-PEO** sample, which shows the presence of polymer between the striations on the fiber surface (**Figure 6**). This suggests that the surface of these materials is easily wet-out by the resin and mechanical interlocking is enhanced. This is complemented by the PEO chains undergoing entanglement with the cross-linked network

within the epoxy resin, and participating in hydrogen bonding from the presence of alcohols and amines (**Figure 4, right**).



**Figure 6** SEM images of the modified fibers after SFPO showing residual resin bound to the fiber surface.

In light of this, our focus shifted to nylon-6 (Ultramid B27) and nylon-6,6 (Ultramid A34) as these polyamide polymers are able to both donate (*via* the NH) and accept (*via* C=O) hydrogen bonds. While these units themselves are polar, the rest of the polymer back-bone is very lipophilic as it consists mostly of hexane-derived units (**Figure 7**). Initially we examined the use of nylon-6 as it is more polar, as suggested by the maximum water uptake (~8.5%), relative to nylon-6,6 (~5.5%), as this should be the more compatible with the poly(ethylene oxide) surface grafted groups.

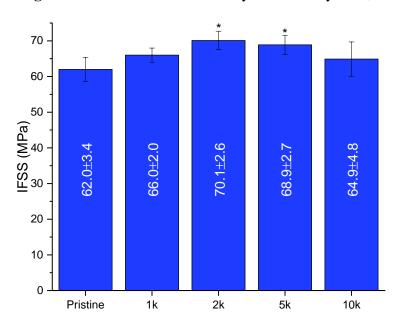
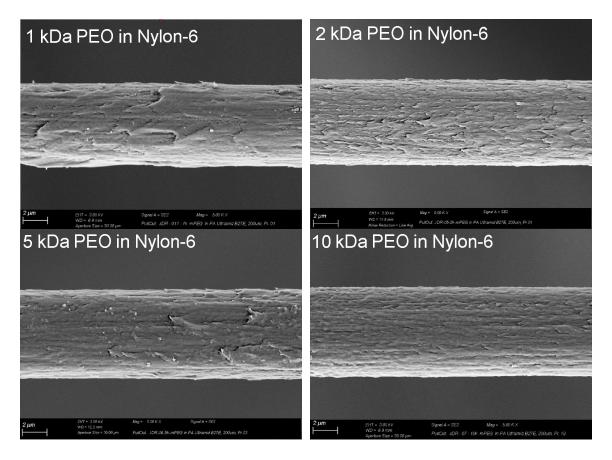


Figure 7 Chemical structures of Nylon-6 and Nylon-6,6

Figure 8 IFSS for pristine and modified fibers in Nylon-6 from SFPO test.

In this instance we examined all of the PEO functionalised fibers, all of which returned an improved IFSS. This was maximised for the **2k-PEO** functionalised fibers, though only marginally (**Figure 8**). It is worth noting that the number of fiber breakages during the SFPO test increased with the increasing molecular weight of the surface adhered polymer, suggesting that the interface was exceptionally strong. It is unlikely that this was the result of the fibers weakening after treatment as characterisation of these fibers, at a single filament level, showed no difference to the pristine sample.[36] Our assumption of a strong interfacial bond was consistent with observation of the SEM images from the functionalised fibers. In all cases, it was obvious that the polymer had adhered to the fibers exceptionally well, in most instances the underlying fiber was not visible (**Figure 9**).

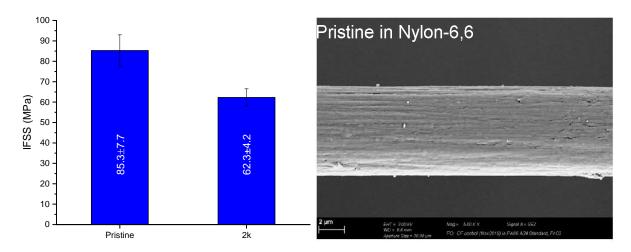


**Figure 9** SEM images of functionalized fibers after SFPO in Nylon-6, showing the ductile failure of the resin coating the carbon fibers.

While this was encouraging, no real insight was gained from these modifications, as the interface was stronger than the supporting resin, and thus no trends or key molecular interactions could be gleaned. Therefore, selecting the most promising modified fiber from the preliminary screening (**2k-PEO**), we focussed on Nylon-6,6. The goal in this instance was to reduce the compatibility of the surface-bound polymer with the resin, to reduce the IFSS and thus, potentially, reveal trends. Additionally, it was hoped that this strategy would mitigate the breaking of the functionalised fibers during pull-out.

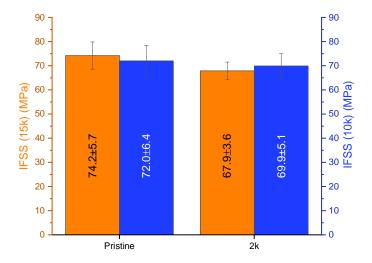
Testing the pristine fibers and those modified with **2k-PEO**, it was seen that the pristine fibers significantly outperformed the modified fiber in this instance (85.3±7.6 MPa vs. 62.0±4.2 MPa, respectively, **Figure 10**, **left**). Unfortunately, the use of unsized fibers, with no surface

treatment, appeared to be preferred to the surface modified, as revealed in the SEM, showing a thick coating of residual resin on the fibers after pull-out (**Figure 10**, **right**).



**Figure 10** Left: IFSS for both pristine and fibers functionalized with **2k-PEO** chains. Right: SEM image of the pristine fiber after SFPO showing a large degree of residual resin on the fiber surface.

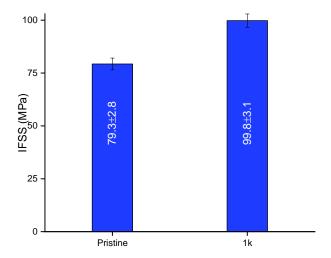
Therefore, these fibers were retested in the same Nylon-6,6 resin which had undergone thermal degradation with oleic acid present to decrease the molecular weight. In this instance, we used both 15 kDa and 10 kDa molecular weights of Nylon-6,6 for evaluating the IFSS. Unfortunately, in doing this, no difference between the pristine and modified carbon fibers (**Figure 11**) was observed in either case. Regardless of this disappointing outcome, with respect to Nylon-6,6 this serves to highlight the subtleties which can affect interfacial adhesion. Indeed, the pristine fibers which possessed very little oxygenated species on the surface were the best performing, in what is considered a polar thermoplastic polymer.



**Figure 11** IFSS resulting from degraded Nylon-6,6 (molecular weights of approx. 15 kDa and 10 kDa) in pristine and modified fiber from SFPO test.

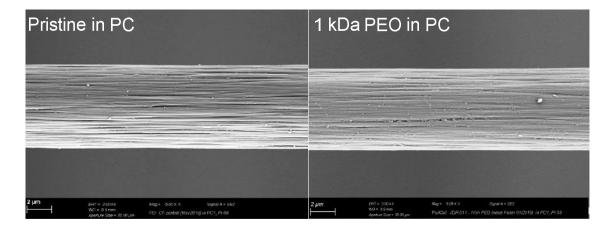
Moving forward, further investigations into IFSS effects were carried out with the **1k-PEO** functionalized fiber since these are proposed to be the most densely functionalised (from our previous findings in regard to diffusion to the surface of the carbon fiber during surface treatment, and steric hindrance with increasing molecular weight).[36] These provide the highest number of moles per unit weight for post-functionalisation and thus is the most economical. In addition, there seems to be no significant benefit in using increased molecular weight PEO groups from the earlier SFPO results.

Considering the polarity of these polymers attached to the fiber surface we wanted to examine a similarly highly oxygenated polymer with a comparable molecular backbone to the epoxy. Therefore, using polycarbonate as an example, a determination of IFSS was carried out.



**Figure 12** IFSS of pristine and **1k-PEO** modified carbon fibers in polycarbonate from SFPO test.

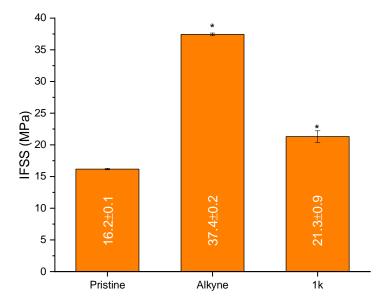
A statistically significant improvement in IFSS was observed with the **1k-PEO** functionalised fibers of 26% (**Figure 12**), relative to the pristine sample (99.8±3.1 MPa *vs.* 79.3±2. 8 MPa, respectively). It is likely that the mechanism of IFSS increase in this instance is due to polymer entanglement with the resin. Both the surface bound PEO and the polycarbonate are polar and oxygenated, thus coiling and interphase penetration are likely critical interactions. Hydrogen bonding in this instance is minimal due to neither surface bound polymer nor matrix being able to donate hydrogen bonds.



**Figure 13** SEM images of the pristine and functionalized (**1k-PEO**) after SPFO in polycarbonate resin, showing significant differences in residual resin present on the fibers.

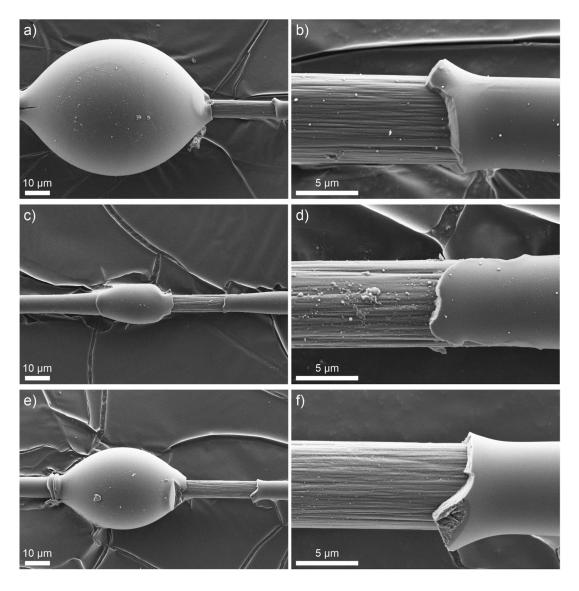
Comparison of the pristine and modified fiber surface, *via* SEM (**Figure 13**) shows residual polycarbonate resin left on the fibers. The pristine fibers show a small amount of resin speckled throughout the fiber surface, while the surface modified fibers show a great deal of resin still present. Consistent with the previous observations in epoxy above (**Figure 6**), the resin has infiltrated the striations within the fiber surface suggesting a high compatibility of these fibers with polycarbonate.

Examining IFSS in a vinyl ester (VE) resin, we chose to subject both the **1k-PEO** functionalised fiber and the alkyne-tethered precursor. As this is a new resin (in our experience) and in the interest of thoroughness we included the immediately prior chemical step in an attempt to deconvolute the effects of the surface grafted small molecule and the tethered PEO chain. In addition, the IFSS measurements for VE resin are exceptionally difficult using SFPO due to resin shrinkage during cure. Therefore, for these measurements, micro-debonding facilitated by an automated debonding instrument Fibrobond® (Fibrobotics, Finland), was used.



**Figure 14** IFSS in VE resin of the pristine, alkyne pendant and the **1k-PEO** functionalised fibers from microbond test.

Interestingly, the presence of the alkyne (carbon-carbon triple bond) enhanced the IFSS significantly, relative to both the pristine fiber and the **1k-PEO** fiber (**Figure 14**). The improved interfacial adhesion was also evident from the SEM images (**Figure 15**). The pristine fiber had virtually no changes after VE matrix debonding when compared with the fiber before matrix deposition and the grooved carbon fiber surface was visible. Matrix residues were visible especially on the alkyne enhanced fiber surface, but also the **1k-PEO** fiber had less distinctive grooves suggesting improved IFSS.



**Figure 15** SEM images of the VE resin and the pristine (a-b), alkyne pendant (c-d) and the **1k-PEO** functionalised (e-f) fibers samples after the microbond test.

It is possible that the unsaturated nature of the alkyne group facilitates the participation of the surface bound acetylene moiety in the radical chain growth mechanism of the VE resin (**Figure 16**). This would provide a strong covalent interaction with the carbon fiber manifesting as an improved IFSS, 132% relative to pristine fibers (37.4±0.2 MPa *vs.* 16.1±0.1 MPa, respectively).

**Figure 16** Possible participation of the alkyne in the radical propagation of the VE resin ester formation. Incorporation of the resin with the surface bound groups are highlighted in red and bold bonds.

As an additional benefit, the resulting alkene (**Figure 16**) is also unsaturated and potentially able to interact again with the radicals present in the resin. The likely-hood of this is low considering the steric bulk, which is present from the initial reaction. It is important to note here, that despite the vast difference in size between aryl alkyne and PEO groups, covalent anchoring provides a stronger interaction than entanglement alone, as is consistent with our previous work.[36] The IFSS gains observed with the **1k-PEO** functionalised samples were still statistically significant relative to pristine fibers (21.3±0.9 MPa *vs.* 16.1±0.1 MPa, respectively), albeit in a more modest 32% increase. In a similar way to the observations made in the polycarbonate example (above) the main mechanism of IFSS improvement is likely polymer chain entanglement. However, in this case, the vinyl ester resin is able to donate

hydrogen bonds to the PEO-tethered fibers in the interphase. Though, it should be noted that the H-bond donation comes from a relatively sterically encumbered alcohol moiety between large aryl units, and thus its contribution to the IFSS gains in this instance are assumed to be minimal.

An additional variable not taken into account in this work is the potential of the hygroscopic PEO chains absorbing water from the atmosphere. It is worth noting that the global surface oxidation of carbon fibers, which is routinely carried out, would also possess an enhanced capability to adsorb moisture but this variable is seldom considered. The presence of moisture is potentially a source of complication when it comes to interfacial adhesion, the partial or total hydration of this surface tethered polymer may cause complementary interactions in some resins and not others. For example, within nature it is observed that coordinated water molecules can serve to bridge hydrogen bonds between chemical functionalities. These bridging interactions can serve to provide a large degree of stabilisation for proteins and enzymes, and thus similar scenario may be facilitated by both polar and hydrogen bond capable environments such as epoxy or vinyl ester resins.

#### 4. Conclusion

A common strategy taken in the literature to increase the IFSS of carbon fibers with any supporting polymer is to oxidise the surface of the fibers to enhance the surface polarity. In this work, we examined carbon fibers with a covalently attached polyethyleneoxide polymers, and thus are polar, in a range of resins. This showed that beneficial effects were observed in several instances, such as for epoxy, nylon-6, and polycarbonate. In nylon-6,6 the biggest enhancement of interfacial shear strength was observed for pristine (non-surface treated and unsized) carbon fiber, suggesting that the more hydrophobic surface provided complementarity with the resin. Interestingly, when examining these fibers in a vinyl ester resin, the PEO modified fibers showed a significant increase in IFSS. That improvement was dwarfed by a covalent interaction

presence of a carbon-carbon triple potentially incorporating the surface grafted molecule into the polymer network. These results show that improvements in IFSS can be related to the surface polarity of the carbon fibers, but this is not always the best avenue to take.

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