# FIBRE SIZING EFFECT ON THE ADHESION BETWEEN A CARBON FIBRE AND A REACTIVE THERMOPLASTIC POLYMER

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## ABSTRACT

The present work, part-funded as part of the Innovate UK Thermoplastic: Monomer to Automotive Parts (TMAP) project, focuses on investigating the fibre sizing effect on the degree of adhesion between carbon fibre utilised in a 3D-woven fabric, and a reactive thermoplastic polymer, with the end goal being for the material combination to be potentially utilised in the automotive sector. This paper discusses how the apparent interfacial shear strength (IFSS) is influenced by the sizing chemistry of the carbon fibre and attempt to produce, and apply, alternative sizing formulations to provide enhanced performance by re-sizing as-received fibres. For studying the IFSS value, the single fibre fragmentation technique (SFFT) was selected. The results indicated that the IFSS was strongly dependent on the sizing chemistry applied, and that the degree of adhesion observed for a thermoplastic polymer bonded to a fibre coated in a thermoplastic sizing was lesser than the equivalent epoxy combinations. It was observed that the IFSS was the largest for the industry coated fibres, with the thermoplastic sizing applied providing the largest respective IFSS. Notably it was shown that the re-sized fibres did exhibit varying IFSS values depending on the formulation, as well as the process for applying the new sizing. Whilst these IFSS values were observed to be less than those found for the industry sized fibre, observations made from the SFFT suggested that this may have been more down to the removal of the initial sizing, and re-coating process for the fibre in its 3D-woven form being inconsistent. From the results presented it is hypothesized that the new sizing formulations did provide adhesion with the reactive thermoplastic polymer, and that would further investigation and development, could provide enhanced adhesion between carbon fibre and reactive thermoplastic polymers.

## 1 INTRODUCTION

It has been well documented, within the current worldwide political and economic climate, that there is a growing need to reduce greenhouse gases and energy consumption across a number of different transport industries. The primary sector targeted is the automotive industry. From 2021, phased in from 2020, the EU fleet-wide average emission target for new cars will be 95 g $CO_2$/km. Vehicle manufacturers are now having to transition away from the internal combustion engine and all-metallic body structures of the previous century towards new battery powered multi-material structures, bonded together using a variety of different techniques.

To meet the legislated drop in emissions, reducing vehicle mass has been identified as one of the key requirements moving forward, with the subsequent reduction in fuel consumption one of the primary benefits. To achieve this necessary mass reduction, polymer composite materials have progressively begun to make up a greater proportion of vehicle body structures. Focus has been placed upon carbon fibre reinforced plastics (CFRPs) due to their high strength-to-weight ratio and capability of providing directional reinforcement where required [1]. Concurrent with this, the capability of composite materials to be recyclable has become increasingly important over the past decade, leading to the uptake of thermoplastics in applications previously reserved for thermosets. Thermoplastics traditionally have not possessed the mechanical properties to compete evenly with thermosets with a great level of investment now being placed into research to broaden understanding of how to maximise the mechanical performance of these materials.

If this performance is to be maximised, it is critical to optimise the stress transfer capability of the interfacial region, which exists between the carbon fibre and the thermoplastic polymer matrix. If this region is weak, with poor adhesion between the fibre and the matrix, then the composite will fail to reach its true potential in terms of mechanical properties. One accepted mechanically measurable value is the interfacial shear strength (IFSS), which can be influenced by several factors including the fibre surface chemistry [1–3], the chemistry of the thermoplastic polymeric system [4] and the testing temperature [5,6]. Fibre surface chemistry is primarily dictated by the sizing formulation applied to the surface of the fibre during the manufacturing process. Sizing is defined as a thin chemical coating applied to the surface of fibres during the manufacturing process in order to protect the fibres during handling and processing, as well as to promote adhesion between the fibre and the polymer matrix.

Recent literature [1] has concluded there is a relative lack of work having been completed to optimise the surface and sizing of carbon fibres for the next generation of thermoplastic polymeric systems. For example, reactive thermoplastics, such as Poly (methyl methacrylate) (PMMA) systems, designed to be processed like thermoset resins (such as resin transfer moulding), have encountered greater commercial interest. Further investigation was warranted to produce a more detailed picture. This paper focuses on an investigation into the role of the fibre sizing chemistry on the interfacial shear strength of thermoplastic CFRPs by using a single-fibre fragmentation technique (SFFT) developed to work at elevated temperature [7,8] (with statistical analysis).

## 2 EXPERIMENTAL

### 2.1 Materials

The experiments were carried out using Toray T700 SC fibres, sized initially with commercial sizings for thermoplastic systems (FOE) and epoxy systems (50C) respectively, taken from larger 3D-woven fabrics manufactured by M. Wright & Sons Ltd. The average diameter was 7 µm and the average tensile strength of the fibre was 4.9 GPa. The reactive thermoplastic resin used was an experimental formulation of the acrylic Elium® 151 resin supplied by Arkema, which was activated by using Elium® A10, and Methyl Ethyl Ketone Peroxide (MEKP). The baseline epoxy used as a comparison was Araldite LY1564/Aradur 2954 which was acquired from Huntsman and used as received.

The removal of the commercial sizing, and application of alternative sizing solutions was led by OXECO Ltd. The process for applying the sizing was altered during the course of the testing and project, based upon the feedback provided by the research team at Far-UK Ltd. The main differences which can be shared between the sample are summarised in Table 1.

For cleaning the 3D woven fabric, samples of fabric were cut to 50 cm lengths then placed in a dip bath. Enough solvent was added to the dip bath so complete cover the fabric strips. The solvent as agitated for 5 minutes before being carefully removed from the dip bath. This process was repeated 2 further times. The fabrics samples were allowed to air dry in a ventilated fume cupboard for 30 minutes before being dried at 50 °C in a convection oven for 15 minutes.

The dip coating process involved adding a mixture of carbene based polymeric crosslinker in

Dimethyl sulfoxide (DMSO) to a mixture of Poly Vinyl Acetate-co-ethylene dispersion in Ethanol. This mixture was added to a dip bath so that the volume of the bath was deeper than the respective fabric being coated. Lengths of fabric were laid into the bath and left for 5 minutes to soak before being removed at a 90° angle from one end of the dip bath. The fabric samples were allowed to air dry in a ventilated fume cupboard for 30 minutes before the coating was cured at 120 °C for 30 minutes.

For the infusion coating process, samples of fabric were laid on a polished steel plate with section of breather fabric placed at either end of the fabric measuring the same width of the fabric and 10 cm in length. Around the edge of this arrangement was applied vacuum bagging sealant tape. An input hose was placed on the breather fabric at one end and an output hose connected to a catch pot and vacuum pot applied to the other end. The fabric was sealed using vacuum bagging film. The input hose was sealed, and the setup placed under vacuum for 15 minutes to remove all air within the fabric and the system as a whole. Again, a mixture of carbene based polymeric crosslinker in Dimethyl sulfoxide (DMSO) was added to a mixture of Poly Vinyl Acetate-co-ethylene dispersion in Ethanol. The input hose was immersed in this formulation and opened to allow the formulation to be vacuum infused through the fabric. Once complete infusion had taken place the system was released from vacuum and the coated fabric samples were allowed to air dry in a ventilated fume cupboard for 30 minutes before the coating was cured at 120° C for 30 minutes.

| Code | Binder | Fabric Pre-Wash | Formulation % solids (wt/wt) | Coat Weight (wt/wt) | Coating Method |
|---|---|---|---|---|---|
| 11 | Low Viscosity Poly Vinyl Acetate Ethylene Dispersion | Acetone | 0.95% | 0.9% | Dip |
| 12 | Low Viscosity Poly Vinyl Acetate Ethylene Dispersion | 1,3-Dioxolane then Acetone | 0.95% | 0.9% | Dip |
| 13 | Low Viscosity Poly Vinyl Acetate Ethylene Dispersion | None | 0.95% | 0.8% | Dip |
| 14 | Low Viscosity Poly Vinyl Acetate Ethylene Dispersion | Acetone | 1.73% | 1.0% | Infusion |
| 16 | High Viscosity Poly Vinyl Acetate Ethylene Dispersion | Acetone | 1.71% | 1.1% | Infusion |
| 17 | High Viscosity Poly Vinyl Acetate Ethylene Dispersion | Acetone | 0.85% | 0.7% | Infusion |
| 18 | High Viscosity Poly Vinyl Acetate Ethylene Dispersion | None | 1.71% | 0.98% | Infusion |
| 19 | Low Viscosity Poly Vinyl Acetate Ethylene Dispersion | None | 2.26% | 1.12% | Infusion |

Table 1: Breakdown of different treatments applied by OXECO with respective fibre codes.

## 2.2 Sample Preparation

Preparation of the fragmentation samples began with the production of a suitable 2 mm-thick mould for securing the fibres in place and enabling the reactive Elium®-based formulation to be poured in. To achieve this a block of Polytetrafluoroethylene (PTFE) was machined via a Computer Numerical Control (CNC) milling machine to produce the 2 mm deep mould, with channels milled 1 mm down to enable placement of the carbon fibres at the mid-point. PTFE was chosen as a suitable material for the mould due to its non-stick properties, enabling the mould to be used repeatedly without the need for any release agents.

With the mould now prepared, single carbon fibres were extracted from the 3D-woven fabrics provided by M. Wright & Sons Ltd, carefully pulled taut and secured in the channels of the mould utilizing double sided tape and then vacuum bag sealing tape. Care was taken to ensure that the exposed sections of fibre to be used for the test were protected from contamination, whether through surface or human contact. With the fibres now in place, the mould was sealed against a pane of mould-released coated glass utilizing vacuum sealing tape and clamped in place to maintain the seal. The reactive Elium®-based formulation was then careful poured into a 2 mm-thick mould by utilizing a syringe. For the formulation, the mixture ratio was 100:3 Elium® 151: Elium® A10 and then 100:1.5 of the resulting mixture: catalyst (MEKP), as was recommended by Arkema. The mould was then sealed with sealing tape, and the system allowed to vitrify at room temperature, as shown in Figure 1.

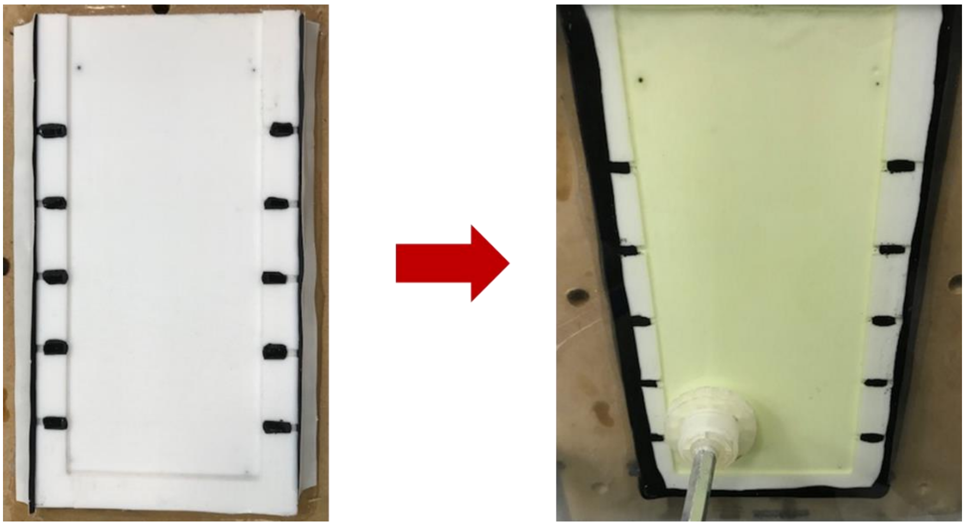

Figure 1: Mould setup utilized for curing Elium® plaques containing embedded single carbon fibres. The channels can be observed by the placement of the sealant tape.

Following vitrification, the plaque of Elium® containing the single carbon fibres was removed from the mould, carefully polished, and then machined utilizing a CNC to produce the fragmentation samples. The geometry for the samples is shown in Figure 2. The samples were then post-cured at 80°C for 4 hours.

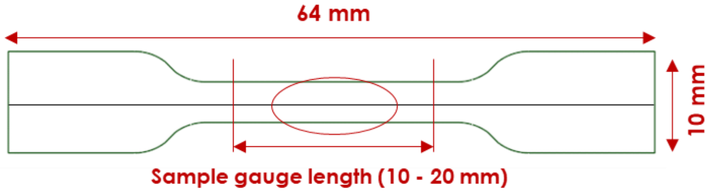

Figure 2: Geometry of SFFT samples with a thickness of 2 mm.

For consistency, the epoxy samples manufactured as a baseline comparison, with commercially epoxy-sized carbon fibres, were produced utilizing the same mould process as the Elium® samples, except with the curing process taking place under elevated temperature within an oven to achieve full degree of cure. The cure schedule utilized was 1 hour at 80 °C, followed by 2 hours at 150 °C respectively.

### 2.3 Single Fibre Fragmentation Procedure

The single fibre fragmentation test was developed by Kelly and Tyson [9], and consists of a single fibre embedded within a matrix tensile specimen. As the sample is tested under tensile conditions, the fibre, which is supposed to possess a smaller elongation-to-break than the matrix (typically between 3 to 4 times smaller), will break into multiple fragments until a saturation point is reach. The number of fragments within a defined gauge length, and as such the observed fibre length distribution, is then typically related to the degree of adhesion that exists between the fibre and matrix [7].

Kelly's approach [9] assumes that the interface between both fibre and matrix is not bonded, implying a total plastic behavior of the matrix. The shear strength of the interface is consequently constant along the fragment length. The point at the fibre cannot fragment any further into small fragments is referred to as the fibre fragmentation saturation point, with the corresponding fragment length at this point being referred to as the critical fibre length ($l_c$) which in turn can be used to calculate the apparent interfacial shear strength:

$$\overline{\tau}\,(IFSS) = \frac{r_f}{l_c}.\sigma_{f_c} \tag{1}$$

Where $r_f$ is the radius of the fibre and $\sigma_{f_c}$ is the failure strength of the fibre at the critical fibre length. The critical fibre length itself can be determined from the average fragment length given within a defined gauge length:

$$l_c = \frac{4}{3}.\bar{l} \tag{2}$$

For this investigation, for the purpose of comparing the consistency of the sizing coating applied across the length of the single fibres, two gauges lengths were specifically studied per sample. These being 10 mm and 20 mm respectively. The gauge lengths were measured on each sample following the post-curing treatment and marked on prior to testing.

Testing was conducted utilizing a Testometric M500 machine, equipped with a 1 kN load cell and specialized grips designed for testing small samples, such as for single fibre fragmentation. This setup is shown in Figure 3. In order to ensure that the samples would achieve saturation, it was necessary to test the samples at elevated temperature [7]. Carbon fibre typically has an elongation at break between 1.7 – 2%, whilst Poly (methyl methacrylate) (PMMA) systems typically have an elongation at break of around 5%, thus it was necessary to heat the samples such that the ultimate matrix strain would be at least 3 to 4 times higher than the fibre elongation at break. This was found to be the case at 50 °C [7], and as such an in-house environmental chamber was constructed by Far-UK to conduct the testing. Prior to testing the heater within the chamber was activated, and the temperature monitored via thermocouples. Once the temperature was consistent at 50 °C within the chamber, a sample would be mounted, with a thermocouple attached, and left to pre-heat. Once the sample was registered as being at 50 °C, the test would be started at a test speed of 0.5 mm/min. The process was repeated for each SFFT sample.

During the test, the force-elongation plot of the sample was observed to identify the point of saturation, with the point of fragmentations observable on the plot (as shown in Figure 3. It was observed that last fragmentation coincided commonly with the overall fracturing of the sample within the gauge length. This was not ideal when conducting analysis afterwards, thus it was decided to stop the test once the plot has been observed to level out like that shown in Figure 3, which typically suggested the sample was saturating. Following testing, each sample was analyzed using a 40X-2500X LED Digital Binocular Compound Microscope with a 3D Stage and 5MP USB Camera. A magnification of 250x was specifically used to identify and analyze the fibre fragments, with an example shown in Figure 4. To calculate $l_c$, the number of fragments between the 10 mm and 20 mm gauge length boundaries was counted, allowing for the average fragment length to be found and then used in Equation 2. $r_f$ for each fibre was measured by utilizing the image processing program ImageJ. To enable Weibull analysis, a minimum of 20 samples was tested for each fibre coating where possible.

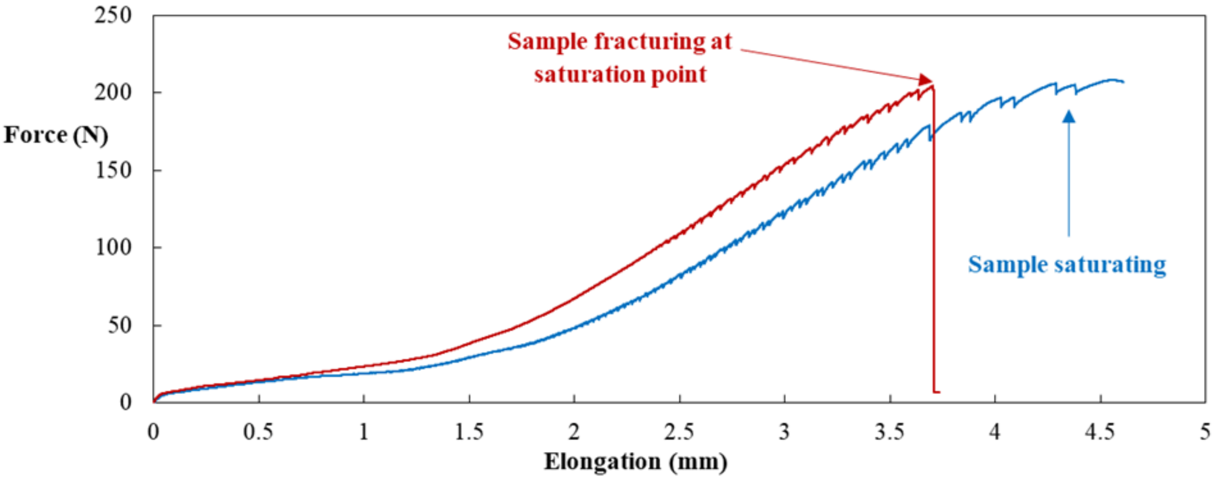

Figure 3: Force-Elongation plot for two fragmentation samples, with one having fractured at the saturation point.

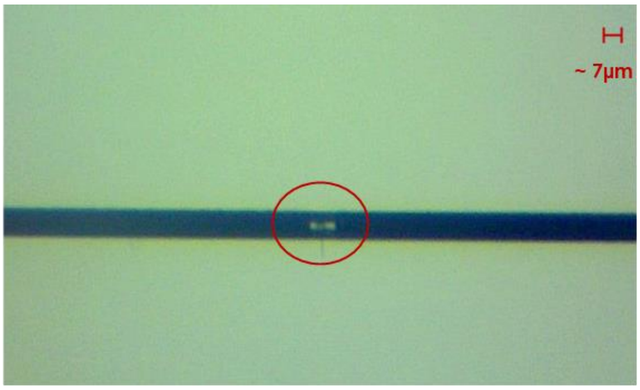

Figure 4: Image showing a fibre fragmentation within a carbon fibre whilst under 250x magnification.

## 3 RESULTS & DISCUSSION

Figures 5 and 6 display the apparent IFSS values measured for the different treated fibres studied, across both the 10 mm and 20 mm gauges. In the case of both figures, there would appear to be a significant gap between the IFSS values found for epoxy with an epoxy-compatible fibre, when compared to any of the other fibres with Elium®. This would appear to be the case for both gauge lengths studied, with overall good correlation between the two sets of data.

For Figure 5, the maximum recorded IFSS value was ~ 45.7 MPa for epoxy with an epoxy-compatible fibre, whilst the maximum IFSS recorded whilst using Elium® was found to be ~ 22.4 MPa, with the commercial thermoplastic sizing applied to the fibre. The maximum IFSS value recorded using re-treated fibres were those exposed to the F13 treatment, with a respective IFSS value of ~ 16.3 MPa. For Figure 6, the maximum recorded IFSS value was ~ 49.8 MPa for epoxy with an epoxy-compatible fibre, whilst the maximum IFSS recorded whilst using Elium® was found to be ~ 23.6 MPa, with the commercial thermoplastic sizing applied to the fibre. The maximum IFSS value recorded using re-treated fibres were those exposed to the F12 treatment, with a respective IFSS value of ~ 15.5 MPa.

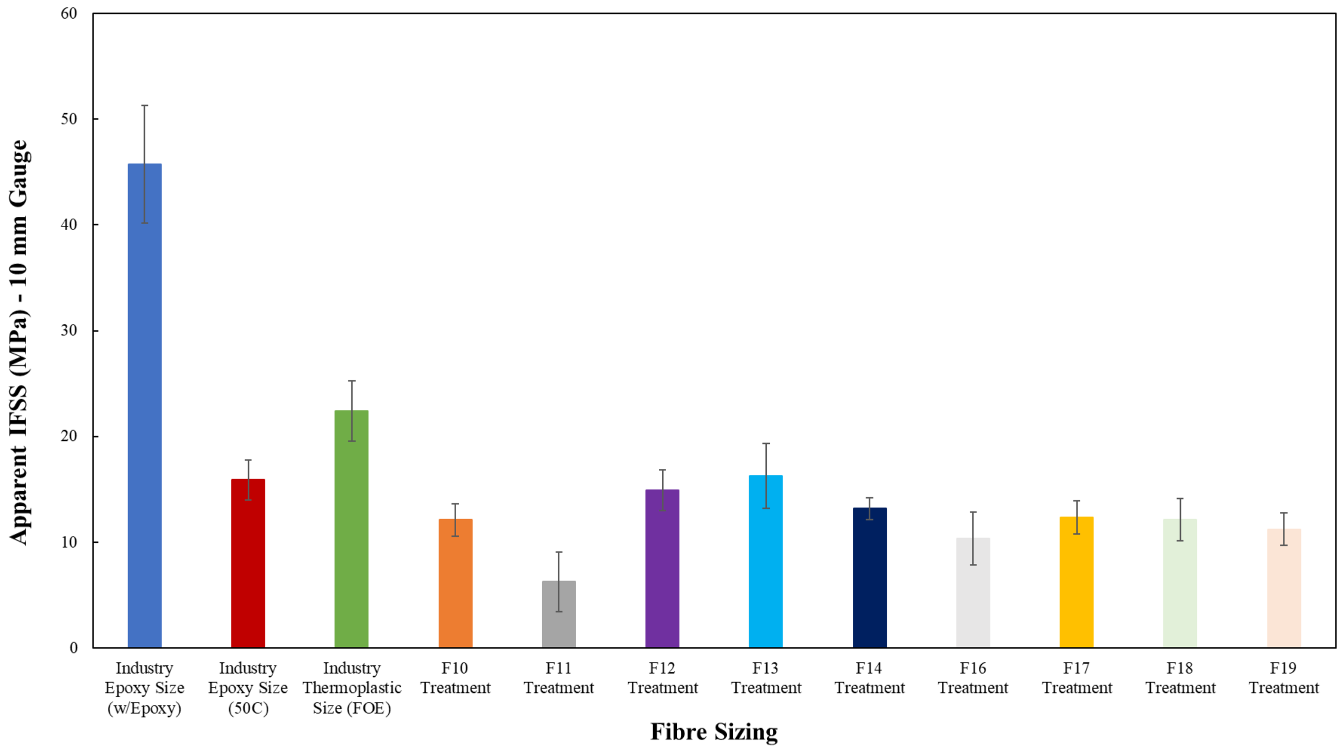

Figure 5: Comparative plot showing apparent IFSS values measured for different coated fibres embedded within epoxy or Elium® (10 mm gauge).

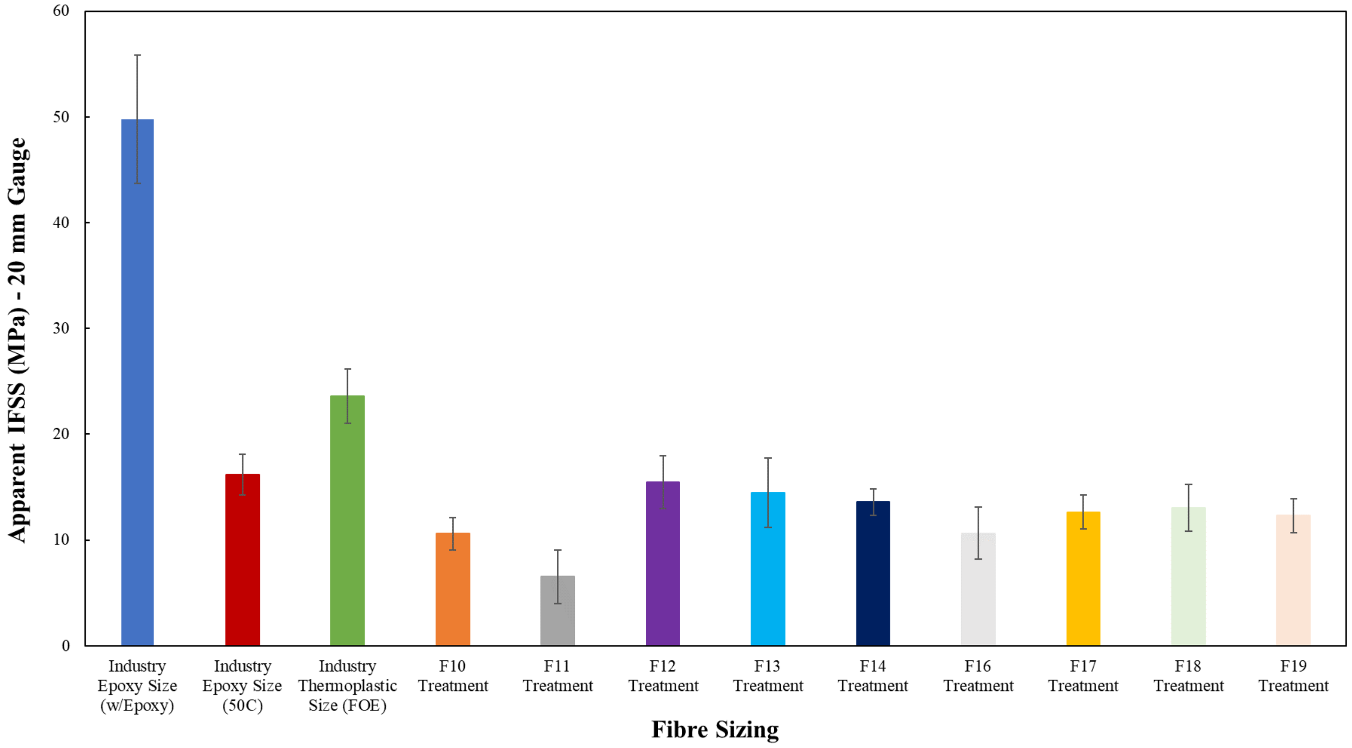

Figure 6: Comparative plot showing apparent IFSS values measured for different coated fibres embedded within epoxy or Elium® (20 mm gauge).

Across both gauge lengths, the fibres sized with a commercial thermoplastic sizing, applied during initial manufacture of the fibres, were found to possess the largest degree of adhesion with Elium®, with lesser adhesion observed for the other fibres tested. It is clear when comparing the two commercially sized fibres that the specific chemistry of the sizing still can have a notable impact on the IFSS value. In particular, past literature [1] has suggested that epoxy sizings may even be soluble in the MMA monomer of Elium®, thus the commercial epoxy sizing could be potentially dissolving during the vitrification process, and not actually contributing to the level of adhesion observed. Further analysis via Scanning Electron Microscopy (SEM) had been planned as part of the TMAP project, however this unfortunately not completed before the endpoint of the project. Further investigation is planned.

Overall, the fibres exposed to the various OXECO treatments were found to possess smaller IFSS values when compared to those measured for the commercial thermoplastic sizing. They were however found to possess comparable IFSS values to those measured when using Elium® with a commercially epoxy sized fibre. One notable observation made when investigating the OXECO treated fibres, was that fragmentations tended to be localized to one section of the gauge length, and that this was observed for both the 10 mm and 20 mm gauge lengths. This observation would suggest that the fibres were potentially inconsistently coated with the experimental sizings developed by OXECO, resulting in pockets of high adhesion on the fibre, whilst other sections presented lower areas of adhesion. The challenge of attempting to re-treat the fibre in the 3D-woven fabric form, rather than in smaller tows or separated fibres, likely played some role in this inconsistency with the sizing formulations potentially struggling to fully pierce and wet-out fibres deeper within the fabric. Again, further analysis via SEM had been planned to confirm this hypothesis but was unfortunately not completed before the endpoint of the project. The consensus across the project consortium was that the limitations observed in the IFSS values for the re-treated fibres was due to inability to apply these new sizing formulations consistently across the entire length of the fibres, rather than the chemistry of the formulation themselves. Interestingly, this observation may mirror potential current challenges arising when developing and investigating recycled fibres, given these too will be exposed to re-treatment processes which may not be as reliable as the current sizing applicators used by the fibre manufacturers.

## 4 CONCLUSIONS

The results presented in this paper show that that the IFSS was strongly dependent on the sizing chemistry applied, and that the degree of adhesion observed for a thermoplastic polymer bonded to a fibre coated in a thermoplastic sizing was lesser than the equivalent epoxy combinations. Each fibre coating tested was shown to possess different apparent IFSS values, with the differences in sizing formulation, and the procedures used to remove the commercial sizing, before then adding the new coating, shown to make a notable difference in IFSS values. Overall, it was observed that the IFSS was the largest for the industry coated fibres, with the commercial thermoplastic sizing applied providing the largest respective IFSS, as might have been expected. Whilst the IFSS values for the re-coated fibres were observed to be less than those found for the industry sized fibre, observations made from the SFFT suggested that this may have been more down to the removal of the initial sizing, and re-coating process for the fibre in its 3D-woven form being inconsistent, thus warranting further investigation. Specifically, it was found during analysis of the SFFT samples that close clusters of fragmentations would occur localised on one side of the gauge length, with none then on the other, thus suggesting inconsistent coating of the fibre.

One practical conclusion from the results presented here is that there would still appear to be significant potential for improvement in the fibre-matrix interface for thermoplastic systems. This conclusion is supported given the observation that the IFSS value for Elium® with the thermoplastic commercial fibre was still significantly less than that found for epoxy with an epoxy-compatible fibre during this study. Given past literature [1] has suggested that reactive thermoplastic systems such as Elium® may not interact with fibre sizings in the traditional manner, further investigation is warranted in order to fully understand the complex interactions occurring at the interface for these systems and allow for them to be optimised for long-term performance.

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