

# EFFECT OF THERMAL DEGRADATION OF GLASS FIBRE SIZING ON INTERFACIAL ADHESION

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## ABSTRACT

In this paper, thermal analysis, spectroscopic, and micromechanical testing methods are used to characterise the thermal degradation of a range of commercial epoxy-compatible glass fibre sizings and the effect of sizing degradation on interfacial adhesion. Thermogravimetric data indicated that around 50% of the glass fibre sizing decomposed following 300°C heat treatment and was removed almost entirely following treatment at 500°C. Spectra of thermally degraded fibre surfaces showed good correlation with TGA data, in that the intensity of bands attributable to an epoxy resin film former decreased with increasing treatment temperature and were removed completely at temperatures of 300–350°C. Recycled glass fibres recovered from end-of-life wind turbine blade material showed pristine fibre surfaces indicating good receptibility for downstream resizing processes. Reduced interfacial adhesion onset at 300–350°C and at treatment temperatures of 400°C and above was comparable to that of unsized fibres, suggesting that most of the sizing components which influence adhesion had been removed. Despite displaying interfacial adhesion properties comparable to that of unsized fibres, fibres heat treated at 400–500°C appeared to show residual oxidised sizing material that was not present in the fibres recovered from the fluidised bed.

## **1 INTRODUCTION**

Fibre-reinforced thermosetting composites are widely used in aerospace, automotive, and wind energy applications due to their light weight and excellent material properties. Consequently, the cost-effective and environmentally conscious disposal of end-of-life composites is one of the most important challenges facing the global composites industry. Recent estimates predict that by 2025 end-of-life wind turbine blades will account for as much as 35–65 thousand tonnes of composite waste in Europe alone [1]. By 2050, global accumulated wind turbine waste is predicted to be as much as 43 million tonnes. Conventional waste disposal methods, such as incineration or landfill, are already banned in several European countries. Combined with the reduced availability of landfilling sites and rising costs, such routes are unsustainable, economically unviable, and socially unacceptable. Due to these factors, there is a great need to develop viable recycling strategies and deliver a circular economy for end-of-life composite materials.

A number of composite recycling solutions have been proposed in the literature, and several of these are under development for larger scale commercial implementation. Many of these recycling processes use elevated temperatures to decompose the polymeric matrix and extract glass fibres for re-use in new applications. However, the performance of glass fibres exposed to elevated temperatures typical of thermo-oxidative recycling processes is significantly reduced due to loss of pre-existing fibre sizing and fundamental changes to flaw distribution density (and severity) on the fibre surface. The tensile strength and interfacial shear strength (IFSS) of recycled fibres are two key parameters in determining the mechanical properties of recycled composite products. While the effect of temperature of the tensile strength has been widely reported in the current literature [2], significantly fewer authors have reported on the relationship between elevated temperature processing and interfacial adhesion. Characterising the

properties of recycled glass fibres is a key step in determining suitable applications for reintroduction of these materials into new applications. If effective resizing solutions are to be developed, it is essential that the mechanism behind the thermal degradation of glass fibre sizings is understood in greater detail.

This paper reports on the effects of thermal recycling temperature on the fibre surface behaviour and interfacial adhesion to an epoxy matrix. Glass fibres sized with several commercial formulations employed in wind energy applications were exposed to elevated temperatures typical of thermal recycling processes and were characterised using thermal analysis, spectroscopic, and microbond testing.

#### 2 EXPERIMENTAL METHODS AND MATERIALS

## 2.1 Materials

Investigation of the thermal degradation of glass fibre sizings was performed on three fully sized commercial glass fibres with epoxy-compatible size formulations used in wind energy applications. Fully sized glass fibres were produced by 3B and supplied by 3B (SE1500, SE2020) and Suzlon (W2020). The fibres used in the study were of the same approximate average diameter (17.5  $\mu$ m) and nominal tex (1200 g/km).

Glass fibres were exposed to elevated temperature heat treatments representative of a thermosoxidative recycling process. Sized fibres were heat treated at 200–500°C in air atmosphere to study the effect of heat treatment and subsequent thermal degradation of glass fibre sizing. Heat treatments were performed using a Carbolite CWF1200 electric furnace. Sections of fibre bundle were removed from the larger roving and attached to a metal rig using a bolt and washer. All heat treatments were carried out for 25 min and consisted of a 10 min pre-heating step to reach the desired temperature followed by a 15 min heat treatment. The treatment time approximately reflects similar thermal recycling treatments found in the literature [3]. Individual filaments were then extracted for microbond testing. Recycled glass fibres were recovered from end-of-life wind turbine blade material using a laboratory scale fluidised bed reactor operating at 500°C [4].

The resin system used was DER 332 DGEBA epoxy resin cured with a stoichiometric (14.3 phr) amount of triethylenetetramine (TETA) tetrafunctional amine curing agent.

## 2.2 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was performed under air from 25–700°C with a heating rate of 10°C/min using a TA Instruments Q50 TGA. The weight loss of glass fibres with different sizings were recorded as a function of the temperature in air atmosphere. A baseline subtraction procedure and signal smoothing function was used to clarify thermograms with extraneous curve effects generated because of the small sample mass. Samples were analysed in triplicate. Data were analysed using TA Universal Analysis software.

#### 2.2 Fourier-Transform Infrared Spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was used to analyse the surfaces of as-received and thermally conditioned glass fibre bundles. Analysis was performed using a 4100 ExoScan FTIR fitted with a spherical diamond attenuated total reflectance (ATR) interface, adjustable probe, and benchtop docking station. Sized glass fibre bundles were placed on the sample stage and the adjustable probe was fully lowered to improve fibre contact with the crystal. Spectra were collected from ten individual points (spaced approximately 1 cm apart) along the length of 15 cm sections of each glass fibre roving. Background signal was measured after each spectral measurement and the crystal was cleaned with acetone between measurements. Analysis was performed in the 4000 to 650 cm<sup>-1</sup> range with a spectral resolution of 8 cm<sup>-1</sup> and 64 scans per sample.

#### 2.3 Microbond Testing

Individual glass fibres were isolated and aligned along the vertical axis of a card mounting template. Fibres were mounted using double-sided tape and secured with cyanoacrylate gel superglue before standing for 24 h to fully react. The resin mixture was then prepared and degassed under vacuum for 10 min to remove entrapped air. Resin was applied to individual fibres using a thin length of steel wire to produce droplets with embedded lengths in the range of  $100-180 \mu m$ . Microbond specimens were cured at  $60^{\circ}$ C for 1 h followed by  $120^{\circ}$ C for 2 h.

Apparent interfacial shear strength was measured using an in-house designed microbond jig [5]. The basic procedure for the microbond test involves a single fibre being pulled from a restrained droplet of cured matrix while measuring the force required to detach the fibre [2]. The microbond testing jig was designed around an Instron 3342 universal tensile testing machine equipped with a 10 N load cell and a microvice with adjustable shearing blades. Shearing blade horizontal movement was controlled at a resolution of 1  $\mu$ m by a pair of adjustable parallel micrometers mounted on either side of the microvice. Micrographs of cured droplets were collected using a Leitz Ergolux optical microscope at 200x magnification. Fibre diameter (D<sub>f</sub>) and embedded length (L<sub>e</sub>) were measured with ImageJ software. Microbond tests were performed at a crosshead speed of 0.1 mm/min and Instron Bluehill software was used to record crosshead displacement and applied load. Successful debonding was confirmed by in-situ observation of droplet loading using 45x magnification stereo microscopy and a live camera feed. The apparent IFSS ( $\tau_{app}$ ) was calculated using Equation 1.

$$\tau_{\rm app} = \frac{F_{\rm max}}{\pi D_{\rm f} L_{\rm e}} \tag{1}$$

Where  $F_{max}$  is the peak of the load-displacement plot generated during droplet debonding. Thirty tests were performed for each condition to obtain an average IFSS value and ensure sufficient data for a good statistical basis. Error bars shown in results are the 95% confidence limits on these averages. The microbond sample preparation and testing configuration are shown in Figure 1.



Figure 1: Microbond sample preparation and testing configuration.

#### **3 RESULTS AND DISCUSSION**

TGA thermograms of SE1500, SE2020, and W2020 glass fibres are shown in Figure 2. Epoxy-compatible glass fibre bundles appeared to remain thermally stable up to approximately 200°C after which degradation of sizing components onset. E-glass is thermally stable in this temperature region, so it is reasonable to assume that the weight changes observed are caused primarily by the

degradation of the organic components of the glass fibre sizing. Most of the mass loss occurred in the 200–400°C range and was primarily attributable to the decomposition of the polymeric film former component of the sizing, given that film former accounts for most of the sizing by weight. Further mass loss at temperatures greater than 400°C may have been due to decomposition of the coupling agent. Mass loss stabilised around 500°C, indicating that the sizing had completely degraded. TGA LOI for full sizings ranged between approximately 0.6 % and 0.8%



Figure 2: TGA mass loss temperature curves for SE1500, SE2020, and W2020 glass fibres in air.

Thermal degradation of the glass fibre sizing appeared to be a primarily single-step process, rendering the exact decomposition temperature of individual components difficult. Conversely, Petersen *et al.* have reported a clear two-step degradation process [6]. It is possible that a combination of increased sensitivity (due to the TGA-MS technique employed) and increased fibre bundle mass (approximately 100 mg) accounted for the clarity between the peaks and identification of decomposition of individual sizing components. Despite this, the authors reported that even 10 cm fibre bundles may not have been sufficient for definitive determination of sizing content due to substantial variation in the amount of sizing present along the length of the fibres.

FTIR spectra of sized glass fibre surfaces are shown in Figure 3. The 1200–800 cm<sup>-1</sup> spectral region was dominated by the strong Si-O-Si absorption from the glass fibres. A broad band corresponding to O-H and/or N-H between approximately 3600 and 3100 cm<sup>-1</sup> can be attributed to silanol and may indicate Si-OH in a coupling agent. The O-H group may also be attributable to a lubricant such as polyethylene glycol present in the sizing. A triplet with peaks at 2965, 2929, and 2875 cm<sup>-1</sup> corresponded to the C-H stretching of CH, CH<sub>2</sub>, and CH<sub>3</sub>, respectively. A peak at 1731 cm<sup>-1</sup>, assigned to C=O stretching of carbonyls, was visible in W2020 and SE2020 fibres and may be indicative of the presence of a silane coupling agent, or a DGEBA epoxy component in the sizing [7]. Peaks at 1608 and 1508 cm<sup>-1</sup> assigned to the stretching of C=C and C-C of the aromatic ring are indicative of the presence of an epoxy film former component in the sizing. Analysis of glass fibre patent literature indicates the plausibility of patent EP 2 540 683 A1 describing the sizing formulation for SE2020, a size formulation containing a silane coupling agent which is not an aminosilane, indicating that the coupling agent present is likely either GPTMMS or GPMES. The nature of the film former is specified as either epoxy or polyester resin, though compatibility with an epoxy resin matrix and the spectral bands observed would strongly indicate that the film former present is an epoxy resin. A lubricant is also included in the sizing, which may have contributed to signal in the 1731 cm<sup>-1</sup> range (due to the presence of carbonyl groups). Spectral characteristics of sized glass fibres are summarised in Table 1.



Figure 3: FTIR spectra glass fibre surfaces

Band (cm <sup>-1</sup> )	Assignment	Associated Component
3600-3100	O-H bonded to Si	Surface hydroxylation/silane/lubricant
2965, 2929, 2875	C-H stretching of CH, CH <sub>2</sub> , CH <sub>3</sub>	Epoxy film former
2929, 2875	C-H stretching of CH <sub>2</sub> , CH <sub>3</sub>	Silane/lubricant
1731	C=O stretching of carbonyl	Silane/lubricant
1608	C=C stretching of aromatic ring	Epoxy film former
1508	C-C stretching of aromatic ring	Epoxy film former
1200-800	Si-O-Si	Glass fibre

Table 1: Spectral characteristics of sized glass fibres

FTIR spectra of glass fibres after exposure to elevated temperature heat treatment are shown in Figure 4. The intensity of the broad band indicative of hydroxyl group (O-H) was reduced as temperature increased and was completely removed at 250–300°C. Reduced intensity of this band may be attributable to decomposition of a lubricant in the sizing with thermal stability lower than that of an epoxy film former or silane coupling agent. It is also possible that such a result indicates glass fibre surface dehydration and removal of initially present hydroxyl groups. The differences in initial hydroxyl group intensity, and subsequent variance in decomposition temperature, of sized glass fibres may be attributable to variability in silanol group concentrations.

The peak intensity of spectral bands attributed to an epoxy resin film former in the sizing decreased with increasing treatment temperature and were removed completely following treatment at 300–350°C. Reduction of peak intensity showed excellent correlation with TGA data that indicated that sizing mass loss in in the 200–400°C range was attributable to degradation of an epoxy film former. Reduced epoxy species concentration in the 25–200°C region observed in the spectral data is likely due to the higher sensitivity of the method compared to TGA of sized fibre bundles. A significant reduction in the concentration of epoxy species appeared to onset at a treatment temperature of 250°C.



Figure 4: FTIR spectra of heat-treated glass fibre surfaces

The triplet peaks at 2965,2929, and 2875 cm<sup>-1</sup> (also indicative of an epoxy film former) reduced in intensity at treatment temperatures exceeding 200°C and appeared to change to spectra indicative of a silane coupling agent. Silane spectra was indicated by the doublet peaks at 2929 and 2875 cm<sup>-1</sup> and peak intensity in this region appeared to increase in the 350–500°C range. Sherif *et al.* have likewise observed the disappearance of the CH, CH<sub>2</sub>, CH<sub>3</sub> triplet at 350°C and correlated the disappearance of the spectral band to either a complete removal of the glass fibre sizing or to such an extent that the amount of sizing was below the detection limit of the instrument [8].

As a general trend, the intensity of the peak at 1740 cm<sup>-1</sup> (C=O stretching of carbonyls) increased with treatment temperature to a maximum value at 400°C before reducing in intensity slightly following treatment at 500°C. This behaviour may be related to the oxidation of epoxy resins in sizing during thermal ageing [9]. Increased CH<sub>3</sub> peak intensity at 2964 cm<sup>-1</sup> may evidence chain scission and polymer decomposition [10]. It is possible that increased CH<sub>3</sub> peak intensity is related to some function of the polymeric component of the glass fibre sizing being decomposed at higher temperatures and the more strongly bound residual silane layer being exposed. It would seem plausible to suggest that increased carbonyl group peak intensity may be attributable to oxidation of the epoxy film former component in the sizing at temperatures greater than 200°C. Spectra of fibres treated at 400–500°C were comparable to those of fibres containing only a silane coupling agent, indicating that, while the polymeric film former had been completely removed, residues of degraded silane coupling agent material remained present on the glass fibre surface.

The surfaces of unsized and heated-treated (SE1500, 500°C) glass fibres are compared to those recovered from end-of-life wind blade material using a lab-scale fluidised bed reactor operating at 500°C. Surface characteristics of fluidised bed fibres were comparable to those of unsized glass fibres, indicating good receptibility for downstream resizing applications. Residues of degraded silane coupling agent material detected on the surface of thermally degraded glass fibres were not present on those of fluidised bed fibres. This is possibly due to increased local temperature in the fluidised bed caused by decomposition of polymeric component of the composite and abrasion of the sand particles. A peak at around 1408 cm<sup>-1</sup> in the fluidised bed fibres is attributable to the glass composition rather than organic species on the surface [11]. Spectral noise present in the 2400–1900 cm<sup>-1</sup> region of all samples is attributable to the instrinsic absorption of diamond due to the ATR interface used and is unrelated to spectral characteristics of the sizing or the glass fibre surface.



Figure 4: FTIR spectra of unsized, heat-treated, fluidised bed recycled glass fibre surfaces.

Microbond testing results are shown in Figure 6. IFSS data are overlaid with corresponding glass fibre sizing decomposition data determined by TGA. IFSS of epoxy-compatible glass fibres was approximately constant (within confidence limits) up to a pre-treatment temperature of 300°C even though the sizing began to degrade at around 200°C. For the SE2020 and W2020 samples, IFSS appeared to increase slightly following treatment at 200–250°C compared to the untreated baseline. Above this temperature, 350°C marked the point that apparent fibre/matrix adhesion decreased significantly before reaching a plateau at 400°C. SE2020 and W2020 sizings appeared slightly less sensitive to thermal degradation of sizing as IFSS values at the highest treatment temperatures were approximately 5 MPa greater than the value obtained for the SE1500 fibre. Samples treated at temperatures of 400–500°C showed IFSS values approximating results obtained with unsized glass fibres, indicating that most of the sizing components which influence IFSS had been removed . SE1500 fibres showed IFSS values are missing from the data set due to premature tensile failure of the weakened fibres after the 400–500°C heat treatment.



Figure 6: IFSS versus heat treatment temperature.

An alternative explanation is that there may be residual carbonised sizing material on the fibre surface, as indicated by FTIR results showing an increase in carbonyl group peak intensity at 1740 cm<sup>-1</sup>. It is possible that such a surface results in poorer interaction with the epoxy resin matrix than the hydroxyl-rich surface of water sized fibres [12]. Reduced in IFSS above 300°C showed good correlation with the weight loss of the fibre sizing at similar temperatures, suggesting that loss in IFSS is associated with a loss of the adhesion-enhancing capability of the sizing. While the film former accounts for most of the measured mass loss in the sizing, IFSS was not significantly reduced until the epoxy film former had been completely removed (300–350°C). It could be suggested that the complete removal of the film former is indeed detrimental to the chemical bonding potential of the sizing. On the other hand, no significant loss of IFSS was observed when the amount of film former present had been severely reduced at 250–300°C. It would seem possible to suggest that the loss in interfacial adhesion may be attributable to the degradation of the silane coupling agent [13,14]. While spectra of fibres treated at 500°C indicated that residues of degraded silane coupling agent material were present on the glass fibre surface, the silane coupling agent may have been degraded to an extent that the adhesion-enhancing capabilities were lost. It is also possible that interfacial adhesion was inhibited at higher treatment temperatures by the accumulation of weakly bound oxidised film former material on the glass fibre surface, evidenced by the carbonyl group growth in the spectral data. Reduced IFSS values indicate the need for regenerative post-treatments and reapplication of a relevant silane coupling agent to restore the surface functionality of the glass fibres and promote adhesion with the desired matrix material for the recycled composite product.

# 4 CONCLUSIONS

In this paper the thermal degradation of several commercial glass fibre sizings has been investigated using thermal analysis, spectroscopic, and microbond testing methods. The followings conclusions were drawn:

- Surface characterisation of fibres by FTIR showed excellent correlation with TGA data indicating that sizing mass loss in in the 200–400°C range was attributable to degradation of an epoxy film former. Fibres heat treated at 350–500°C showed residue of degraded silane coupling agent on the glass fibre surface that was not present in fibres recovered using a fluidised bed process.
- Interfacial adhesion measurements revealed an inverse relationship between IFSS and fibre treatment temperature and was concurrent with decomposition of the glass fibre sizing. Reduced IFSS appeared to onset at 300–350°C and at treatment temperatures of 400°C and above interfacial adhesion was comparable to that of unsized fibres, suggesting that most of the sizing components which influence IFSS had been removed.
- Interfacial adhesion may also have been inhibited at higher treatment temperatures by the accumulation of weakly bound oxidised film former/sizing material on the glass fibre surface corresponding to the carbonyl group growth observed in the spectra of heat-treated samples.

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