

Research Article

## Effect of Fiber/Matrix Interface Modification on Basalt Fiber Reinforced Geopolymer Composites

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### Abstract

Continuous fiber reinforced geopolymer matrix composites offer the potential for use in structural applications at temperatures up to 700°C, while enabling the manufacture at temperatures below 100°C. Studies have investigated a variety of high temperature structural fiber reinforcements, including carbon, SiC and Al<sub>2</sub>O<sub>3</sub>. While there has been active research into various grades of Al<sub>2</sub>O<sub>3</sub> fibers, SiC is most commonly used for high temperature reinforcement of geopolymers in oxidizing environments. Both families of reinforcement are relatively expensive and are capable of use temperatures which exceed those of the geopolymer. Basalt fibers have the potential to be a good match for the geopolymer matrix, both in terms of upper use temperature and cost. In this study, Basalt fabric reinforced geopolymer composites were prepared with fibers having three different surface conditions, as-received (silane sized), cleaned, and carbon-coated, to investigate the effect of fiber-matrix interface on the mechanical properties. All specimens were fabricated, cured at 80°C and conditioned at 250°C for 5 hours to create the baseline specimens. More than half of the 70 specimens manufactured were exposed to an additional 5 hours at 650°C. Flexural



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strength, strain-to-failure and modulus were determined at ambient temperature via 4-point bend testing. The as-received and cleaned specimens showed moduli approaching theoretical predictions, indicating a strong interfacial bond, resulting in brittle failures at low loads. The carbon coating resulted in a three-fold increase in strength after the 250°C conditioning and retained a strength higher than the other specimens, even after the 650°C treatment. This strength increase did come with a reduced modulus, suggesting that the stress transfer between fiber and matrix in the carbon-coated basalt fiber reinforced geopolymer composites had also been reduced. While the carbonaceous interphase was not expected to be stable at the higher temperatures in an oxidizing environment, the results do indicate that significant Basalt fiber reinforced geopolymer strength gains are possible through the implementation of a tailored fiber/matrix interface as a crack blunting mechanism.

### **Keywords**

Basalt fiber; geopolymer; inorganic polymer matrix composite; polysialate; interface; interphase

## **1. Introduction**

Geopolymer materials are of interest due to their relatively high temperature performance capabilities while being able to be processed at temperatures below 100°C. “Geopolymer” is the term often used to refer to a class of alumina-silica based inorganic materials which are processed like a polymer and undergo polycondensation at low temperatures but resemble ceramics in the resulting structure and high temperature properties [1, 2]. The minerals that constitute this material are readily available. The name “geopolymer” was coined in 1978 during research efforts focused on the development of fire-resistant, non-toxic materials to be used in building structures [3]. This material evolved into a mineral-based binder for use as a high strength industrial cement with significantly shorter cure times than traditional Portland cements [2]. More recently there has been interest in utilizing the high-temperature resistant properties of these geopolymers and the associated low density to replace heavier metallic components in high-temperature structural applications. The ease of processing fiber reinforced composites with these inorganic polymer binders as the matrix, compared to traditional ceramic matrix composites (CMC’s), also makes them an attractive option. A geopolymer matrix composite is commonly processed to shape at temperatures below 100°C, and with a freestanding postcure performed near the planned upper use temperature, these materials offer good performance to temperatures approaching 700°C [4]. This is in contrast with more typical ceramic matrix composite (CMC) manufacturing processes which require much higher processing temperatures, usually exceeding 1,000°C [5]. In this regard, the potential exists for geopolymer matrix composite to effectively fit into the gap between the 400°C upper use temperature of organic polymer matrix materials and the more difficult to process CMC’s. While a substantial amount of research has been published on the cementitious variants of these inorganic polymers, there is less data available on fiber reinforced composites produced using the thermoset resin-like versions.

The inorganic polymer can exhibit several different structures characterized by tetrahedral aluminate and silicate units referred to as “aluminosilicates” [2]. The aluminosilicate starting precursors, the  $\text{AlO}_4$  and  $\text{SiO}_4$  tetrahedra, are found naturally in the mineral metakaolinite (nominal composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ,) by calcining kaolinite at  $700^\circ\text{C}$  to remove chemically attached water [6]. The precursors are polycondensed with alkali activators, either KOH or NaOH, to form structures which may be amorphous or semicrystalline. Three prominent structural units exist, with the base unit referred to as “sialate”, which is an abbreviation for silicon-oxo-aluminate [2, 7]:

- (1) “sialate” [-Si-O-Al-O-]
- (2) “sialate-siloxo” [-Si-O-Al-O-Si-O-]
- (3) “sialate-disiloxo” [-Si-O-Al-O-Si-O-Si-O-]

These sialate-based fragments condense together to form larger polymeric structures called polysialate (PS), polysialate-siloxo (PSS), and polysialate-disiloxo (PSDS) [8, 9]. The sialate network structure containing the  $\text{SiO}_4$  and  $\text{AlO}_4$  tetrahedra units are linked in an alternate fashion by the sharing of oxygen atoms. To balance the negative charge of  $\text{Al}^{3+}$  in IV-fold coordination, positive ions ( $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Li}^+$ ,  $\text{Ca}^{++}$ ,  $\text{Ba}^{++}$ ,  $\text{NH}_4^+$ ,  $\text{H}_3\text{O}^+$ ) must be present in the structural spaces [2, 10].

Unfortunately, these materials tend to be relatively brittle and not of great utility in engineering structural applications without the incorporation of reinforcement materials. A number of fiber reinforced geopolymer matrix composites have been described in the literature, including reinforcements of carbon fiber, silicon carbide fiber and a number of other ceramic fibers. Carbon fibers function well as a geopolymer reinforcement but tend to limit the upper use temperature, in air, of these geopolymer matrix composites due to the relatively rapid oxidation of the fiber above temperatures of  $400^\circ\text{C}$  [11, 12]. Alternatively, ceramic fibers including silicon carbide and alumina fibers have been utilized to extend the useful temperature range of the geopolymer as a structural material. Nicalon silicon carbide fibers have been shown to effectively reinforce geopolymers and maintain good properties even after extended exposure to elevated temperatures in air [13]. Fibers with a high alumina content, such as Nextel 610, have also been shown to be reasonable reinforcement candidates for geopolymers. However, due to the similarities in the material structure of the fiber and matrix, a tailored interlayer must be used to reduce the inherent bond and develop a reasonable degree of composite strength through crack blunting at the weekend fiber-matrix interface. Utilizing a tailored interfacial strength is a well recognized method of introducing a crack blunting mechanism in ceramic matrix composites, resulting in improved toughness. Monazite coatings on the Nextel fibers have been shown to be effective in increasing the strength and toughness of fiber reinforced geopolymers [14]. However, ultimately, these ceramic fibers have temperature capabilities far beyond the structural upper use temperature of the geopolymer matrix materials, and the fiber cost might be considered out of sync with that of the geopolymer. Thus, high temperature alternative reinforcement materials, with stability in air, and of moderate cost become of interest. Since the geopolymer matrix materials tend to have an upper service temperature of approximately  $700^\circ\text{C}$  before recrystallization reduces the properties, a reinforcing fiber need only maintain its performance to a similar temperature [15]. During the last decade Basalt has grown in popularity as a reinforcing fiber and has improved in quality and repeatability of properties.

Basalt fibers have shown good property retention to at least 600°C and as such, with their relatively approachable cost, seem a viable alternative to other high temperature fibers as a reinforcement for geopolymer matrix materials. The strength and modulus are similar to S-glass reinforcements, but at a price closer to E-glass. Unfortunately, there is limited information in the literature regarding the effectiveness of basalt fiber in a geopolymer matrix after thermal conditioning in air [1, 15, 16]. Three different fiber surface treatments are included to better understand the effects of interface modification, and thermal conditioning is performed in both air and a Nitrogen (N<sub>2</sub>) rich environment. Thus, this effort involves the investigation of the potential for basalt continuous fiber reinforced geopolymer matrix composites through elevated temperature aging and ambient temperature mechanical testing.

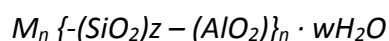
## 2. Materials and Methods

### 2.1 Materials

Continuous fiber reinforced geopolymer composites were fabricated using a Basalt woven fabric for the main study, with Nextel 610 fabric reinforcement used as the manufacturing baseline. The Nextel 610 was chosen as a baseline as the laboratory had significant previous experience in the processing and testing of this material as a reinforcement for geopolymer matrix composites. The details of the materials utilized in the current study follow, including information outlining the makeup of the specific geopolymer matrix.

#### 2.1.1 Inorganic Polymer Matrix Material

A proprietary liquid inorganic polysialate polymer resin system, referred to as MEYEB, supplied by Pyromeral Systems was used as the geopolymer matrix. The MEYEB was obtained as a liquid inorganic polymer resin. The structure of this inorganic polymer resin is PS, containing potassium ions, and is predominantly amorphous. It is a metakaolin-based, potassium balanced, polysialate glass ceramic with the ratio of Si:Al of 1:1 and proprietary proportions of K<sub>2</sub>O/SiO<sub>2</sub> and H<sub>2</sub>O/Na<sub>2</sub>O [17]. Polymerization of MEYEB is the result of a polycondensation reaction, which requires an ionic balance of the sialate network in the presence of positive alkali ions (Na<sup>+</sup>, K<sup>+</sup> and Cs<sup>+</sup>, etc.). The corresponding empirical formula for the inorganic polymer is;



where, M is the alkali cation, z is the ratio of Si:Al, n is the degree of polymerization, and w is the number of water molecules [18].

This inorganic polymer polycondenses in just a matter of minutes. The mechanical properties of the matrix appear to be directly related to the silica and alumina ratio - higher silica leads to higher strength [2, 19]. MEYEB was shipped in a cryogenic state from the manufacturer and subsequently stored at -25°C to increase the usable life. Upon removal from storage, the material has an approximate working time of 30 minutes at room temperature and a viscosity similar to many commercial high viscosity epoxies.

### 2.1.2 Basalt Reinforcement

A 220g/m<sup>2</sup> satin weave fabric with a 9 micron diameter Basalt fiber was commercially sourced [20]. This is a fabric with a nominal thickness of 0.158mm and is sized with a silane finish. Fiber modulus is reported as 89 GPa and the typical fiber strength as 3.4 GPa. Fiber density is approximately 2.65 g/cm<sup>3</sup>.

### 2.1.3 Nextel 610 Reinforcement

Nextel 610 is a fine grained  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> aerospace grade fiber. It is the highest strength variant of the Nextel fibers. While as a single phase fiber, Nextel 610 demonstrates a greater loss in strength at high temperatures than the alternative aerospace grade Nextel 720 fiber, this reduction in strength does not start until approximately 1,200°C, well above the temperatures considered in this research. The specific form of the reinforcement used is DF-11, a 370 g/m<sup>2</sup> 8-harness satin weave fabric with a nominal thickness of 0.275mm. The fabric is sized with a PVA finish. Fiber modulus is reported as 370 GPa and the typical fiber strength as 2.8 GPa. Fiber density is approximately 3.9 g/cm<sup>3</sup> [21].

## 2.2 Specimen Preparation

Laminates were prepared from Basalt fabric as well as from Nextel 610 fabric. Since the laboratory had previous experience in the preparation and evaluation of Nextel 610/MEYEB composites a limited set of these laminates were produced in parallel with the Basalt/MEYEB laminates to ensure consistency in manufacture, given the limited experience with preparation of Basalt reinforced geopolymer laminates. The Basalt fabric, which is the principal focus of this work, was treated in various ways to generate three (3) different fiber surface conditions to investigate the effect of interfacial condition on mechanical performance. Once the laminates were processed to the base condition (250°C @ 5 hours) they were cut into flexure specimens and a subset of the specimens was aged at 650°C for an additional 5 hours.

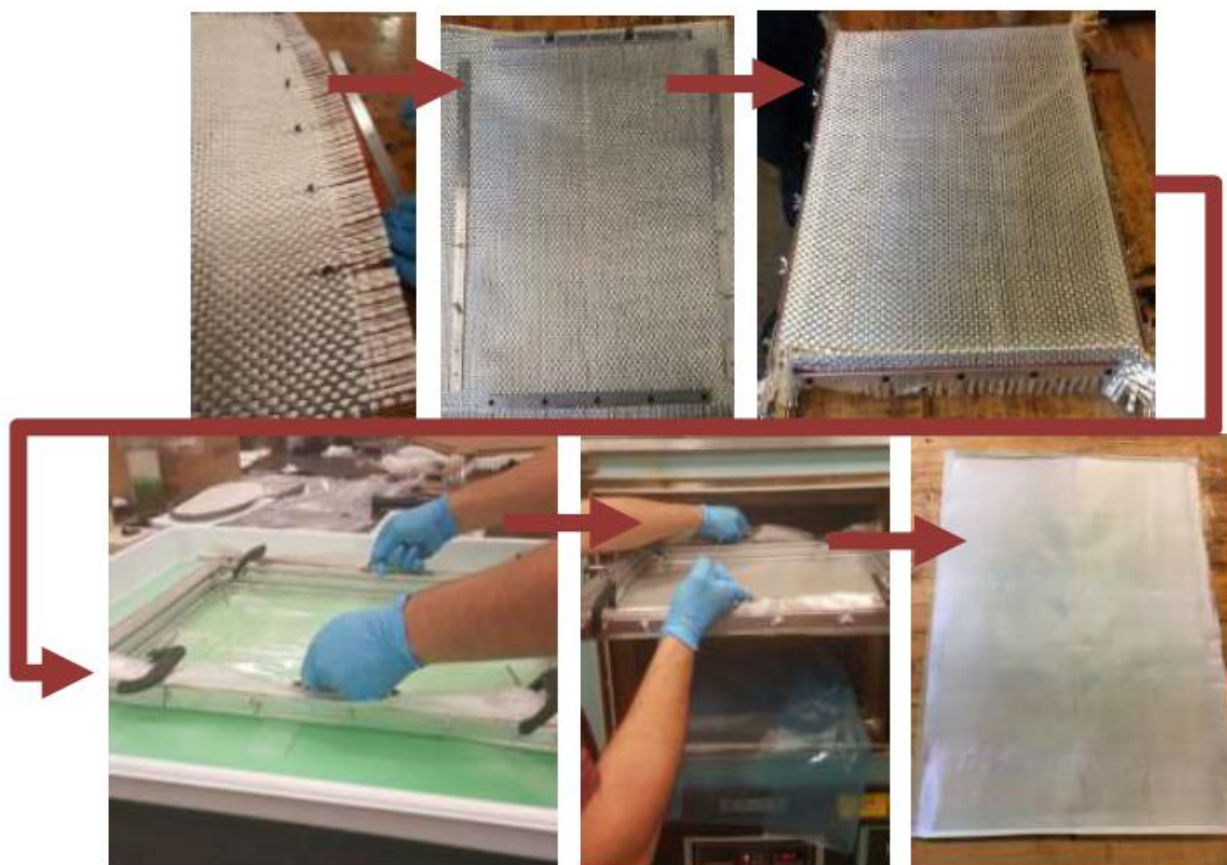
### 2.2.1 Basalt Fabric Preparation

The three (3) surface conditions utilized are, (i) sized, or in the as-received condition with the silane finish intact, (ii) cleaned through a 500°C thermal treatment in air to remove the silane finish [the temperature utilized was kept below 600°C in an attempt to minimize thermal degradation of the Basalt fiber], and (iii) carbon-coated, based on a preliminary trial application of polyvinyl alcohol (PVA), followed by conversion under nitrogen at 500°C. The two fiber surface modifications applied were based on similar successful procedures developed for Nextel fibers, but were performed at a lower temperature out of concern for thermal degradation of the Basalt fibers.

Preparation of Cleaned Fabric. "Cleaned" Basalt fabric was prepared via thermal decomposition of the factory applied silane finish. While somewhat higher temperatures would have been preferred to ensure complete decomposition, the temperature was limited to 500°C in an attempt to minimize the thermal degradation of the Basalt fiber [1, 16]. Fabric was placed in a refractory furnace, in air, and heated at a rate of 5°C/minute to 500°C, held for 1 hour, followed by slow

cooling, in the powered-off furnace, to room temperature. No visible change in the fabric was noted. The cleaned material was stored in a dry container until used in laminate preparation.

Preparation of “Carbon-Coated” Fabric. “Carbon-coated” Basalt fiber fabric was prepared via thermal decomposition of a PVA coating applied to the Basalt fabric. The basics for the process for applying a thin, uniform fiber coating were based on thin film/membrane formation descriptions in the literature [22, 23]. In preparation for PVA coating the factory supplied silane finish was first removed via thermal treatment in air, as described in the previous section. “Cleaned” fabric was stretched and attached to a dedicated frame to improve the uniformity of the applied PVA. (Figure 1) The stretched fabric and frame were dipped into a tray containing a dilute solution of Polyvinyl Alcohol (10% PVA in a mixture of equal parts 91% isopropyl alcohol and water). Fabric was dipped in the PVA solution five times and dried between each application, for 1 hour at 80°C, to form an appropriate fiber finish. This PVA modified fabric was then placed in a vacuum furnace and heated, at a rate of 5°C/minute, to 500°C where it was held for 2 hours to create a carbonaceous coating. A nitrogen-rich environment was used during the thermal decomposition.



**Figure 1** Fabric before (left) and after (right) carbon coating.

The “carbon coating” that resulted from this prototypical approach did result in a noticeable color change of the fabric, as seen in Figure 2, which shows the fabric before and after application of the carbon coating. While no assessment of the make up of the converted PVA was undertaken, the approach was based on the success of the converted PVA finishes on Nextel 610 in previous studies [24, 25]. These previous studies showed that the converted factory-applied PVA finish on



the Nextel 610 increased the relative strength of the Nextel 610 reinforced/MEYEB composite, with a small reduction in the modulus, suggesting a weakened interfacial bond and the associated strengthening mechanism/crack stopping ability. Further studies directly assessed this change in interfacial strength via individual fiber pushout and showed that this carbonaceous, converted PVA, finish did reduce the interfacial strength [26, 27].



**Figure 2** Basalt fabric before (top) and after (bottom) carbon coating.

### 2.2.2 Laminate Preparation

The laminate fabrication process is basically a “wet layup” procedure. The amount of resin is premeasured to be approximately 55% by volume, based on the amount of fabric. The MEYEB resin is mixed and applied to a sheet of fabric of sufficient size for the appropriate number of layers. Cutting of the fabric is performed after wetout to minimize fabric fraying. The fabric is cut into 90mm x 190 mm rectangles and then stacked in two symmetric halves. The fabric weave orientation is monitored to ensure that the final flexure specimens have the satin weave principal direction aligned with the specimen. One half is then “flipped” and stacked on the other half to create the symmetric wet stack-up, accounting for the different top and bottom of the weave. As soon as the laminates are wet laminated, they are placed in a vacuum bag and vacuum is applied for 10 minutes to reduce entrained air. Time under vacuum is brief to limit the removal of moisture, which is critical during the 1<sup>st</sup> stage of cure [28, 29]. Once this step is complete, the specimens are left in the sealed bag and are transferred to a heated press.

The laminates are cured in a hot press, at 80°C, for at least 3 hours under pressure, followed by an additional 21 hours at 80°C with pressure removed, but still in a sealed bag to retain moisture and enhance the cure. Aluminum caul plates are used on top and bottom of the laminates, outside the bagging material, and shims are introduced between the caul plates allowing the press only to close to dimensions that should result in a consolidated fiber volume fraction,  $V_f$ , of 50%. The caul plates and shims are also important to generate a uniform and reproducible thickness such that the flexure specimens have a minimum of taper in the thickness direction. At the end of this “moist” cure, the laminates are removed from the hot press and from the sealed bag and placed in

a drying oven at 80°C for several hours. During this stage of preliminary geopolymerization a mass loss of approximately 8% has been measured via thermogravimetric analysis (TGA) [28, 30].

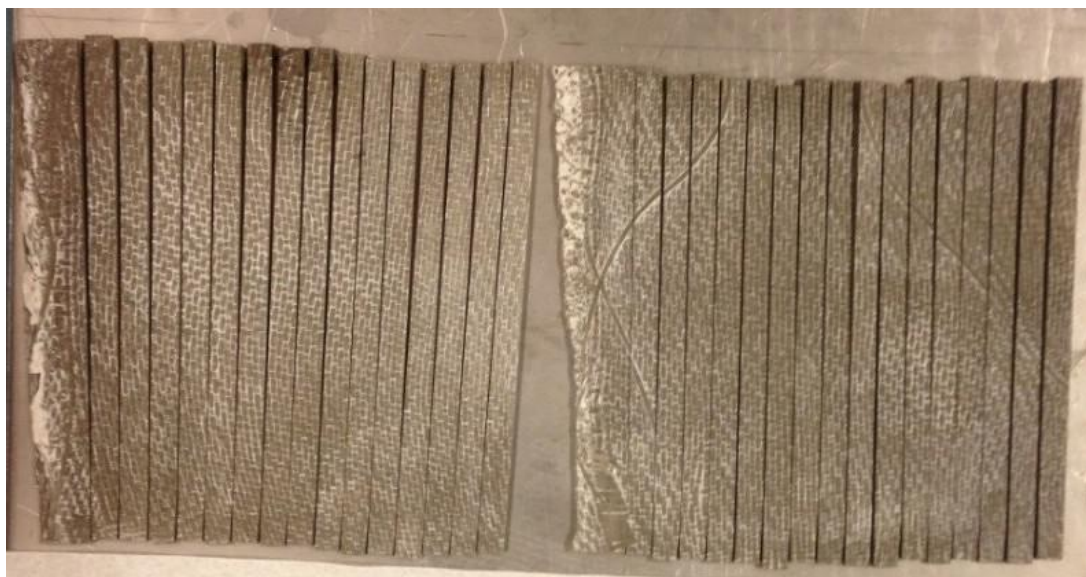
Dry 80°C laminates are processed to the baseline condition of 250°C@5hours. Specifically, laminates are heated from 80°C – 100°C at 0.5°C/minute, held at 100°C for 1 hour and then heated to 145°C at 1.0°C/minute and again held 1 hour, prior to final heating at 1.0°C/minute to 250°C. The laminates are then held at 250°C for 5 hours, followed by a slow cooldown to ambient temperature, in the furnace, powered off. This processing approach was developed during an earlier research program which focused on minimizing cure shrinkage during the processing of the neat MEYEB resin [28, 31]. Using the optimized curing limited the additional mass loss on heating to 250°C to an additional 2%. Carbon-coated fabric laminates are processed by the same method as those with cleaned fabric and with the as-received, sized fabrics.

A total of 3 Basalt fiber reinforced MEYEB laminates were produced, as follows: (i) Basalt-sized, (ii) Basalt-cleaned, and (iii) Basalt-carbon-coated. The fiber volume fractions ( $V_f$ ) were estimated by density to be approximately 48%, with the exception of the Nextel 610 demonstration panel which is approximately 51.5%  $V_f$ .

The Basalt laminates of this study are made up of 10 fabric layers. This ply count generates a nominal laminate thickness of 1.7mm. Laminates are processed in dimensions of approximately 90mm x 190mm, which allows 2 laminates to be processed simultaneously between the 200mm x 200mm hot press platens. Each of the 2 laminates processed in parallel use the same reinforcing fabric and differ only in the fabric surface treatment to ensure equal applied pressures in the two laminates.

### 2.2.3 Flexure Specimen Preparation




As detailed in the previous section, all laminates are processed to the base condition (250°C for 5 hours) prior to cutting to flexure specimen dimensions using a wet, 0.5mm thick, diamond wafering blade. The nominal beam specimen is 1.7mm thick, 5mm wide and 85mm long. 30 – 35 beam specimens are cut from each 90mm x 190mm laminate after cutting in half, to nominally 90mm x 90mm, and trimming laminate edges. The specimens are then re-dried at 100°C, in air, for at least 1 hour. As-cut examples of cleaned and sized specimens are shown in Figure 3.





**Figure 3** Basalt - 250°C treated, immediately after cutting, (Cleaned - left, Sized - right).

Heat Treatment/Thermal Conditioning. At least 10 specimens from each laminate are heat treated to an exposure temperature of 650°C for a period of 5 hours. The as received (sized) and cleaned specimens, which have been treated at baseline conditions and cut to the flexure specimen geometry, are heat treated to 650°C from ambient temperature at a rate of 5°C/minute, in air. The carbon-coated specimens are heated to 650°C at the same rate, but in a Nitrogen-rich environment to minimize the loss of the carbon interphase. During the heat treatment of the carbon-coated specimens, in Nitrogen, an additional 5 specimens of each of the other surface conditions were also thermally conditioned. These additional specimens were prepared to allow a direct comparison of the effects of the 650°C exposure in a consistent environment (N<sub>2</sub>). Further, this allows a comparison to the as received and cleaned specimens conditioned in air. The reduction to only 5 repetitions was deemed acceptable, based on prior test repeatability and the limited specimens available that had been processed to the baseline condition. Representative specimens of each treatment condition and fiber surface finish are shown in Figure 4.

	Basalt @ 250°C	Basalt @ 650°C
<b>Cleaned (Air)</b>		
<b>Cleaned (N<sub>2</sub>)</b>	<i>No specimens prepared</i>	
<b>Sized (Air)</b>		
<b>Sized (N<sub>2</sub>)</b>	<i>No specimens prepared</i>	
<b>Carbon (N<sub>2</sub>)</b>		

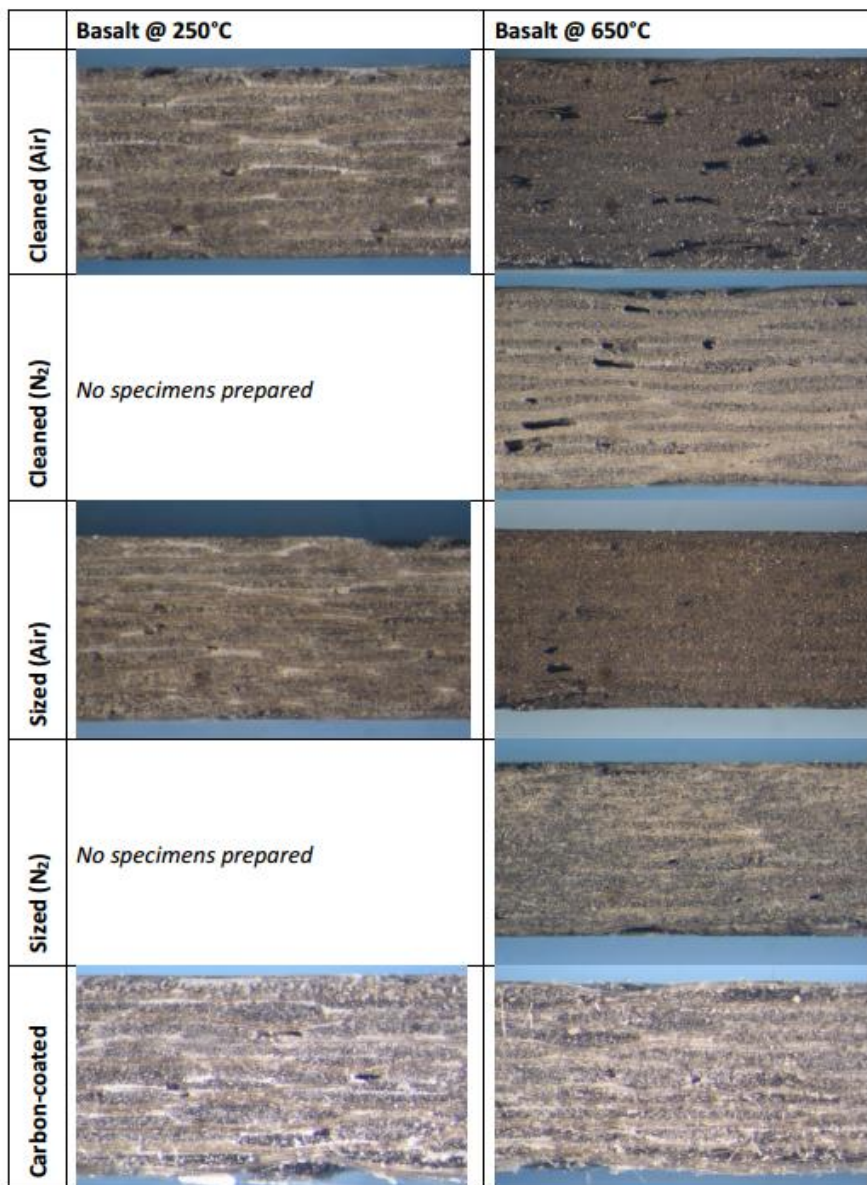
**Figure 4** Representative flexure specimens after conditioning.

Once all heat treatments were completed the specimens were measured and the dimensions documented. Specimen dimensions are recorded at three locations along the length and the average thicknesses are given in Table 1. Fiber volume fractions were determined for each specimen based on dimensions, fabric mass and constituent densities, without attempting to account for void fraction. Fiber volume fraction averages, for each set of specimens, are given in Table 1.

**Table 1** Specimen dimension and fiber volume fraction.

Heat Treatment		250°C (air)		650°C (air)		650°C (Nitrogen)	
Fabric	Fiber Surface Finish	Thickness (mm)	V <sub>f</sub> (%)	Thickness (mm)	V <sub>f</sub> (%)	Thickness (mm)	V <sub>f</sub> (%)
<b>Nextel 610</b>	cleaned	2.241 (0.056)	51.5	<i>No specimens prepared, 250°C for baseline only</i>		<i>No specimens prepared, 250°C for baseline only</i>	
<b>Basalt</b>	cleaned	1.768 (0.052)	46.1	1.954 (0.097)	41.7	2.006 (0.070)	40.6
	sized	1.691 (0.020)	48.2	1.675 (0.071)	48.7	1.770 (0.088)	46.0
	carbon-coated	1.718 (0.030)	47.4	<i>No specimens prepared, Oxidative environment</i>		1.891 (0.073)	43.1

Figure 5 shows representative specimen edges, viewed at 25X, showing the 250°C baseline panel condition on the left and, on the right, the specimens after 650°C conditioning. Swelling and a larger void population are evident after the 650°C temperature exposure. The Basalt specimens with sizing and with carbon-coating seem the most resistant to dimensional change after conditioning at 650°C. No evidence of fiber reaction with the geopolymer or dissolution in the geopolymer is present in the micrographs. These observations are consistent with other studies in the literature which have combined basalt fiber and geopolymers and investigated the behavior at elevated temperature [15, 32, 33]. Specifically, no interfacial interaction was noted by the previous authors and reduced properties, related to recrystallization of the basalt fibers, were only noted in tests performed at 800°C [15].



**Figure 5** Flexure specimens after conditioning (wetout/void) 25X.

While voids are present in all specimens, it is important to note that the micrographs clearly indicate good fiber wetting in all specimens after the 250°C cure. Tows can be seen with MEYEB wetting each of the individual fibers which is critical if concepts of interface modification are to be used to attempt to modify the performance of the composites. Void development is a result of incremental mass loss as the geopolymer is processed and by associated shrinkage that is constrained by the fibers. The combined geopolymer mass loss after the 250°C baseline heat treatment is approximately 10%, based on previous studies. TGA data from the same previous process-focused works indicate that an additional mass loss of approximately 1% occurs during the 650°C postcure step [28, 30].

### 2.3 Mechanical Testing

Mechanical testing is performed in flexure, in accordance with ASTM C1341 [34]. A 4 point, ¼ point configuration is utilized with a fully articulating test fixture. Loading is performed on an

ATS 9000 series screw driven test frame. Support and loading pin dimensions are 6.25mm diameter. A 445N load cell is utilized and a clipgauge extensometer is mounted to a “pogo-stick” to directly measure mid-span displacement. A crosshead displacement rate of 0.51mm/minute is applied throughout testing. Previous experience with fiber reinforced MEYEB bend testing suggested that a high span-to-depth ratio is required to resist interlaminar shear damage and attain acceptable flexural failures. Based on composite plate dimensions and the as-prepared laminate thickness, a span-to-depth ratio of 44:1 is utilized, based on a 75mm test span and a nominally 1.7mm laminate thickness. Specimen width is roughly 5mm and overall specimen length is 85mm. All tests are performed at ambient temperature and statistical data from each material condition is based on 10 specimens, with the exception of the additional as-received and cleaned specimens, heat treated to 650°C in Nitrogen, which each have a specimen population of 5.

### 2.3.1 Modulus Prediction

In previous studies it has been determined that the advance prediction of the modulus achievable through a simple Rule of Mixtures estimation, where perfect fiber-matrix bonding is assumed, yields an upper bound value [14, 27]. This prediction also gives a point of reference for evaluating the measured values of modulus and considering the degree of active stress transfer between the fibers and matrix.

Rule of Mixtures approximation for a crossply laminate with equal amounts of fiber in the 0° and 90° directions follows. (Note that the fabrics are not plain weave, and as such do have a slightly different fiber count in the two directions, but this detail has not been included in this prediction.)

$$E_c = \text{axial ply modulus} + \text{transverse ply modulus}$$

$$E_c = 0.5(V_f \times E_f + V_m \times E_m) + 0.5 \left( \frac{1}{\frac{V_f}{E_f} + \frac{V_m}{E_m}} \right)$$

where:

$E_c$  = composite modulus

0.5 = fraction of plies in the 0° direction and in the 90° direction

$V_f$  = fiber volume fraction

$V_m$  = matrix volume fraction

$E_f$  = fiber modulus (in this case the axial and radial fiber moduli are considered equal)

$E_m$  = matrix modulus

Using a fiber volume fraction of 48% for the Basalt fabric reinforced geopolymer samples, a  $V_f$  of 51.5% for Nextel 610 fabric reinforced geopolymer, and a modulus of 12GPa for the MEYEB geopolymer, the following laminate moduli are predicted:

Basalt/MEYEB laminate modulus: 34.7 GPa

Nextel 610/MEYEB laminate modulus: 112.7 GPa

### 3. Results and Discussion

#### 3.1 Flexure Testing

The mean and standard deviations for the measured values of the flexural strength ( $\sigma$ ), strain at flexural strength (failure  $\epsilon$ ) and modulus of elasticity in bending (E), calculated in compliance with ASTM C1341, are given in Table 2. Basalt fiber reinforced MEYEB laminate mechanical properties are presented for three (3) interphase conditions, cleaned, sized, and carbon-coated. For each interphase condition, the mechanical test results are shown for specimens conditioned at 250°C and 650°C. Nextel 610 results are given as a reference and are presented for the baseline thermal treatment (250°C) and for the cleaned interphase condition only.

**Table 2** Mechanical properties summary, mean and (standard deviation).

Heat Treatment		250°C (air)			650°C (air)			650°C (Nitrogen)		
Fabric	Fiber Surface Finish	$\sigma$ (MPa)	$\epsilon$ (%)	E (GPa)	$\sigma$ (MPa)	$\epsilon$ (%)	E (GPa)	$\sigma$ (MPa)	$\epsilon$ (%)	E (GPa)
<b>Nextel 610</b>	cleaned	322.9 (39.8)	0.32 (0.045)	110.6 (3.09)	<i>No specimens prepared</i>			<i>No specimens prepared</i>		
<b>Basalt</b>	cleaned	34.0 (5.61)	0.10 (0.013)	30.4 (1.57)	28.9 (3.09)	0.10 (0.021)	29.1 (1.76)	36.1 (5.67)	0.11 (0.015)	28.5 (1.34)
	sized	35.7 (3.60)	0.10 (0.015)	32.2 (1.81)	34.7 (4.48)	0.08 (0.015)	36.0 (2.69)	38.8 (2.44)	0.11 (0.005)	30.9 (0.98)
	carbon-coated	85.7 (5.12)	0.40 (0.030)	23.4 (0.87)	<i>No specimens prepared</i>			41.4 (2.69)	0.18 (0.013)	21.37 (1.08)

In considering the data of Table 2, it is notable that the modulus values at 250°C for the Nextel 610 and for the Basalt, cleaned and sized conditions, compare favorably with the corresponding Rule of Mixtures estimates. The sized Basalt/MEYEB modulus value is quite close to the estimated value. Considering the good consolidation shown in Figure 5, and the volume fraction matching that used for the Rule of Mixtures estimation, it would seem that the load transfer between fibers and matrix was good. This is not too different for the cleaned condition. However, the modulus in bending for the carbon-coated Basalt fiber is substantially reduced, at only 23.4 GPa versus the values above 30 GPa for the other two surface conditions. This indicates that there is a reduced load transfer from the fiber to the matrix, suggesting a weakened interface. This effect is reflected in the substantially improved strength for the carbon surface modified case, at 85.7 MPa as compared to strengths of approximately only 35 MPa for the cleaned and for the sized Basalt



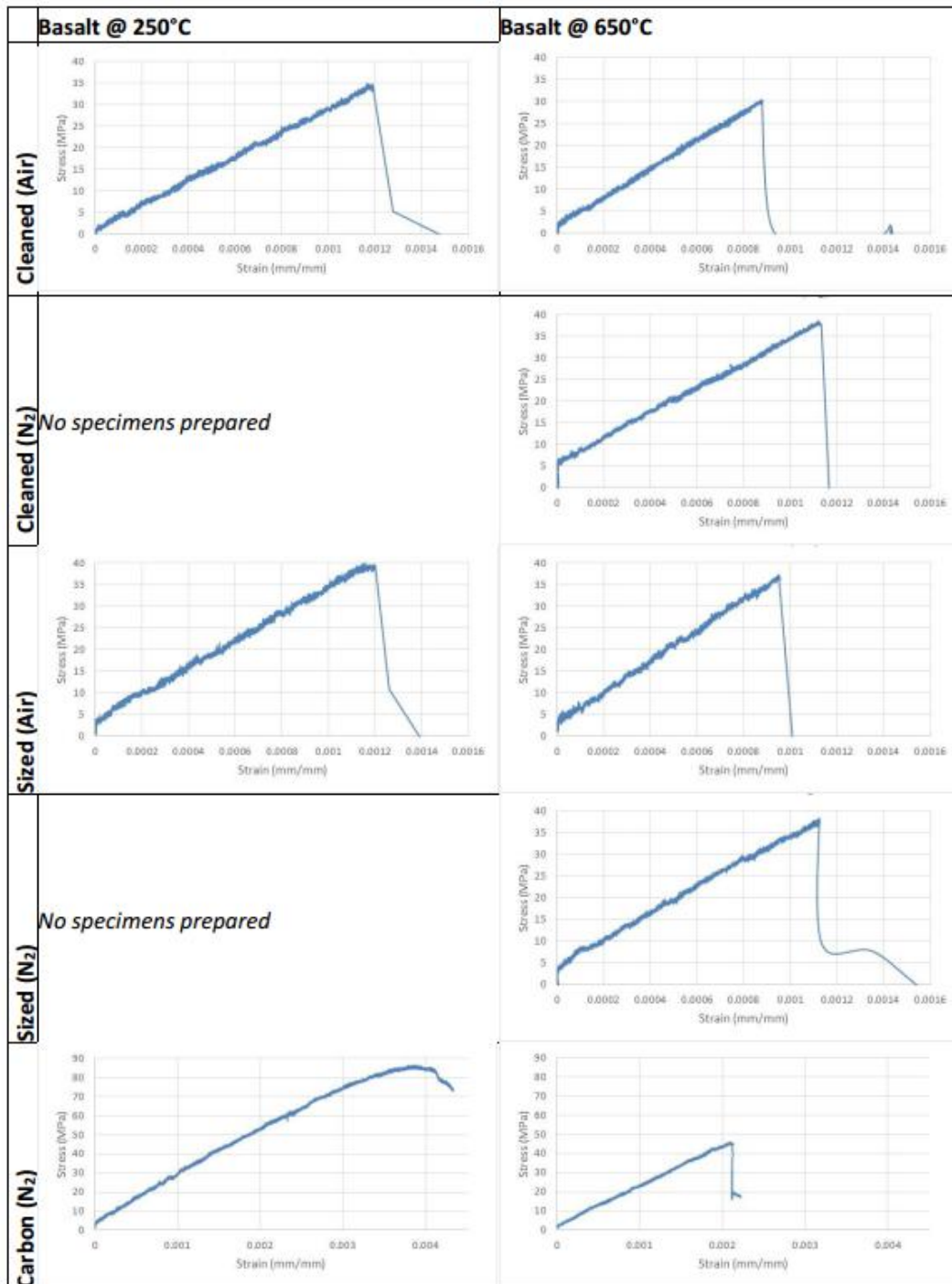
fibers, as shown in Table 2. Such an increase in strength is consistent with a tailored interfacial strength and an associated improvement in the ability to arrest crack motion.

For the two conditions, cleaned and sized, which were conditioned at 650°C in air, the differences from the 250°C conditioning were small. The average values of the flexural strength and modulus in bending were somewhat lower at 650°C for the cleaned condition; however, those differences may not be statistically significant given the values of the standard deviations listed in Table 2. For the sized condition, while the flexural strength values at 650°C and 250°C are effectively equivalent, it does seem that the modulus at 650°C has increased. This change is most likely related to the changing performance of the MEYEB resin, which does improve slightly with elevated temperature heat treatment; however, it is also possible that the interfacial strength has increased, at least to a small extent. The differences in the strains at failure for these two temperatures are not statistically significant.

For the cleaned and sized specimen conditions, after 650°C conditioning in nitrogen, changes in flexural strength and modulus in bending are again small, at best, suggesting no adverse effect of the elevated temperature heat treatment in air. However, the performance of the specimens using the carbon surface modified Basalt fibers has been affected. While the strength is still marginally better than that of the other two Basalt surface conditions heated to 650°C in nitrogen, the value of 41.4 MPa is only approximately half of the flexural strength value after treatment to 250°C. The modulus has also decreased slightly. If the source of the decreased strength was a reaction between the fiber and matrix after the 650°C conditioning, resulting in an increased bond strength, then it is also expected that the modulus would increase. Yet, this is not the result, as the measured modulus was reduced. Considering the data of Table 2, and in light of the visual information of Figure 5 and the numerical information of Table 1, which show that the specimens increase in thickness with thermal conditioning at 650°C, it would seem more likely that the increased void content was responsible for the reduced strength.

### **3.2 Representative Stress-Strain Profiles**

Stress/strain plots are shown in Figure 6. These plots are chosen to represent the typical test with a near average value of strength for each of the different fiber finishes and heat treatment conditions. The stress/strain plots for the cleaned specimens and sized specimens are linear to fracture, indicating brittle failure, independent of surface treatment, exposure temperature or environment. It is interesting to note that for the most part, the sized Basalt fiber reinforcement performs marginally better than the cleaned versions, after both 250°C and 650°C exposures. Both the geometry of the stress-strain plots and the data of Table 2 suggest that the silane-based sizing actually improves the interfacial strength in the Basalt/MEYEB composite, and that the improvement over the cleaned surface condition is retained, even after the 650°C conditioning. This is consistent with the relatively stable void content of the sized specimens independent of conditioning temperature versus the significant increase in void content noted in the cleaned specimens, as seen in Figure 5. The stress-strain plots for the cleaned and for the sized conditions look essentially the same, showing no apparent deviation from linearity to failure, whether tested after 250°C or after 650°C exposure.



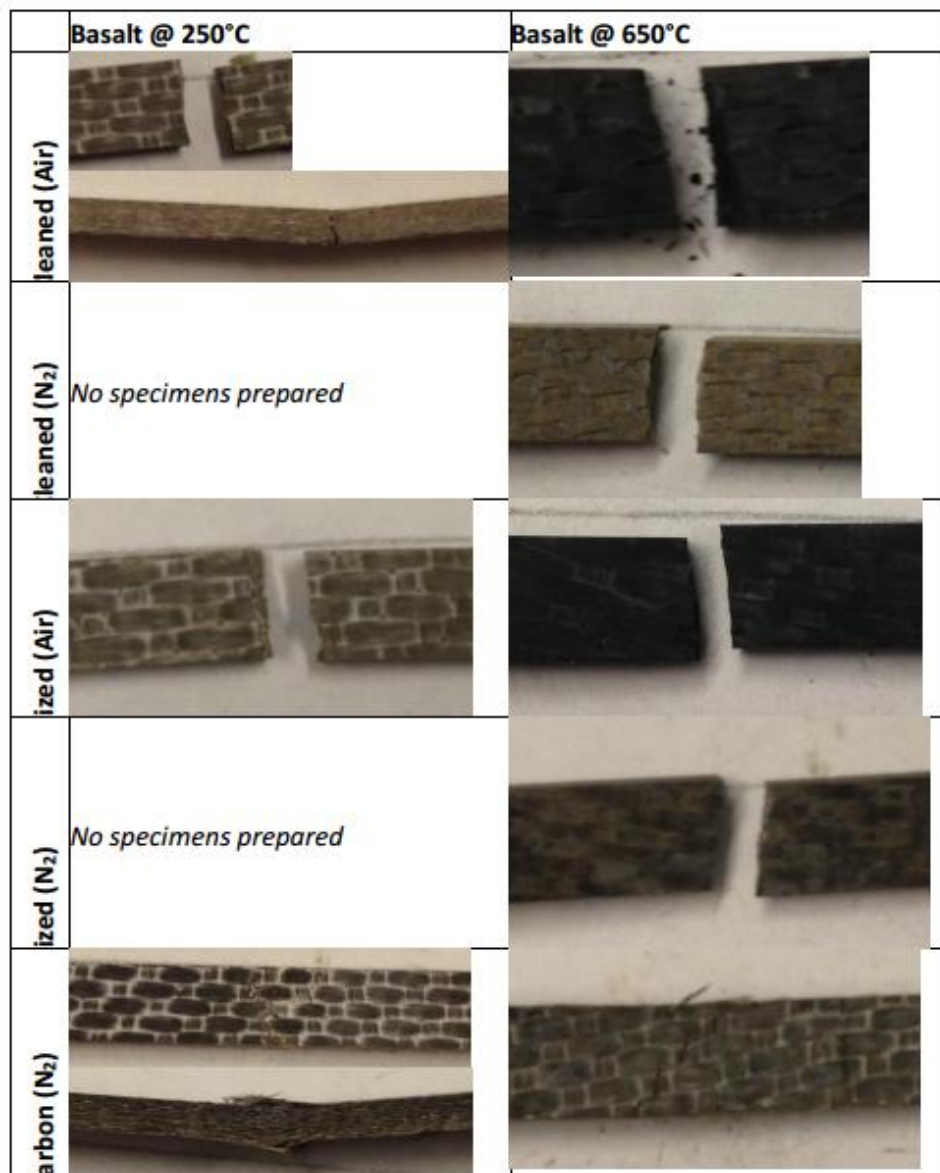
**Figure 6** Basalt/MEYEB composites – flexural stress/strain profiles.

Conversely, the carbon interface coating results in significant improvements in both strength and strain-to-failure in the Basalt/MEYEB composites. The stress/strain plots representing the carbon-coated specimens show a surprisingly large improvement in strength and strain-to-failure for the 250°C case and a lesser, but still substantial improvement after 650°C exposure. In fact, the carbon-coated Basalt charts are plotted on at a different scale than the remaining charts to capture the improvements. The non-linear shape of the 250°C exposure stress-strain curve suggests a less brittle failure, with significant damage as the maximum strength is reached and exceeded. After 650°C exposure the stress-strain plot is effectively linear to failure, but the

specimens reach a higher strain at failure given the lower measured modulus. Reviewing Table 2, a clear drop in modulus results from the carbon coating, suggesting that the improvements in strength and strain-to failure are the related to a decrease in interfacial strength.

### 3.3 Failed Specimens

Failed specimens were photographed individually; however, failure surfaces were difficult to capture and showed little additional information. Figure 7 was assembled to better show the overall failure morphologies, including the relative style of failure after conditioning at both 250°C and 650°C. The cleaned and sized specimens tested in the baseline condition (5 hrs@250°C) failed in a brittle manner resulting in two separate portions. However, none of the “carbon-coated” Basalt specimens showed catastrophic separation at failure, indicating some fiber bridging/pullout. These specimens also, in some cases, showed some upper surface compression damage and delamination.



**Figure 7** Failed conditioned specimens.

Figure 7 also shows the failed specimens which were conditioned for 5 hours at 650°C beyond the baseline temperature exposure. Here again, brittle failure is noted in most specimens, with the exception of the “carbon-coated” Basalt fiber reinforced coupons. The “carbon-coated” Basalt fiber specimens did not show complete separation on failure, indicating that some form of toughening mechanism remains active. However, no compression-side damage was noted, nor delamination, which is consistent with an improvement in properties of the MEYEB matrix material with increased temperature post-cure [29]. Since the moduli of all the “carbon-coated” Basalt fiber reinforced specimens were reduced, relative to the “sized” and “cleaned” conditions, it would seem that the carbon surface modification of the Basalt fibers results in a reduction in the interfacial shear transfer, associated with a reduced bond strength. This is consistent with the crack blocking nature of an interfacial toughening mechanism, as is the form of failure noted.

Based on the data collected and the various surface conditions investigated it is obvious that a strong interfacial bond is formed between the Basalt fiber and the geopolymer matrix in the cases without the carbon-based Basalt fiber surface modification. While this strong interfacial bond leads to good load transfer and resultant modulus values that approach the Rule of Mixtures prediction, it also results in brittle, low strength composites. It is interesting to note that the properties for these composites are little affected by the conditioning at 650°C, which suggests that the interfacial performance is also not affected. The strength increases that are noted after the 650°C conditioning are consistent with an increase in the geopolymer strength with increasing conditioning temperature which has been measured in previous research [28]. In addition, it was interesting to note that, at least within the bounds of the temperature conditioning performed, the as-received silane sized fiber performed better than the cleaned fibers. The cross-sections of Figure 5 suggest less swelling and a reduced void content for the composites produced with the sized Basalt fibers, most likely indicating enhanced wetting during fabrication versus that of the cleaned condition.

Figure 5 also shows a stable, relatively low void composite for the carbon-coated Basalt after conditioning at both 250°C and 650°C. However, for the Basalt/MEYEB composites with the carbon modified fiber surface, based on the substantial reduction in the measured modulus recorded in Table 2, a distinct effect on the interfacial bond strength was realized. The result was a 150% increase in the strength of the composite after the 250°C conditioning. After conditioning at 650°C, both strength and modulus of the composite dropped. The modulus reduction is slight and is likely related to a reduced interface performance associated with the swelling noted in Table 1. However, the reduced composite strength, which is still at least as good as that of the other composites, is most likely due to the increased strength and decreased strain-to-failure of the geopolymer matrix material which results in less delamination and compression side failure in the flexure tests [28].

Thus, it is expected that to get a good balance of strength and modulus, and to retain that balance after extended high temperature conditioning, a stable, reduced strength interphase will be required. Something other than carbon should be investigated, as the resulting 30% reduction in composite flexural modulus suggests an excessive reduction in interface strength and a need for an alternate interphase fiber coating with somewhat higher interfacial strength. Further, if the composite is to be used in an oxidizing environment, a carbon coating is not expected to be stable at elevated temperatures. For Nextel 610 these same effects were found when a carbon coating

was applied, which resulted in the investigation of Monazite fiber modifications to generate an intermediate condition, in terms of fiber/matrix interfacial strength [14, 27].

#### **4. Conclusions**

Mechanical tests of approximately 70, 4 point, flexure specimens were completed. Basalt fiber reinforcement with 3 different surface conditions, as-received with a silane sizing, cleaned and carbon-coated, in a geopolymer matrix were evaluated. Carbonaceous coatings, derived through pyrolysis of laboratory applied PVA coatings, showed positive effects on the performance of the Basalt fabric reinforced MEYEB. Strengths of the carbon-coated Basalt fiber reinforced composites, after baseline conditioning, were 85.7 MPa versus approximately 35 MPa for the alternative fiber surface treatments. The carbon surface modified Basalt fiber composite showed a reduced modulus of 23.4 GPa compared to the theoretical prediction of 35.7 GPa, which is consistent with a reduced interfacial bond strength. For Nextel 610 composites a similar result was originally seen when a carbon coating was used; however, when the Nextel 610 was coated with Monazite the modulus remained at predicted levels, but the toughness improved as well. Thus, this study does suggest that geopolymer composites reinforced with Basalt can benefit from fiber coatings/interface modification. Further, the Basalt fiber reinforced MEYEB strength did improve substantially with the fiber/matrix interface modification and demonstrated that with interface optimization Basalt fibers have potential as a lower cost, elevated temperature reinforcement for geopolymer matrix materials.

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#### **Author Contributions**

Kohl Jacobson: All mechanical testing, data reduction, preliminary draft of test results; Sam Strassler: Fiber coating process development, fabrics preparation, preliminary draft of procedure; Courtney Spalt: Laminate fabrication/process development, preliminary draft of procedure; Sara Henry: Fiber coating process development, fabrics preparation, preliminary draft of procedure; Arthur Powers: Laminate fabrication, specimen preparation and documentation, preliminary draft of procedure; Donald W. Radford development of overall experimental plan, revision of preliminary reporting, critical interpretation of results, manuscript preparation.

#### **Competing Interests**

The authors have declared that no competing interests exist.

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