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INVESTIGATION OF THE STRENGTH OF THERMALLY CONDITIONED BASALT AND E-GLASS FIBRES

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ABSTRACT

It is projected that the total global production of composite materials will significantly exceed 10 million tons by 2015 of which over 90% will contain glass fibre reinforcement. Traditionally most of this composite material would be directed to landfill at end of life. Thus, recycling composites has started to gain great importance due to environmental and commercial aspects. The development of an efficient process to enable cost-effective regeneration of the mechanical properties of fibre for recycling, could result in a huge decrease of landfill disposal as well as the attenuation in CO_2 emissions.

There are several processes available for recycling composites but the most technologically advanced is thermal recycling. However, during the recycling process glass fibres that are treated at temperatures in a range between 300 up to 600 °C exhibit a huge drop in strength and as a result sometimes are considered as not reusable or unsuitable for reprocessing [1]. Although basalt fibre has been available for some time, recent development in the processing and production of basalt has resulted in the availability of continuous basalt fibre in similar form to traditional glass fibre. It is often stated that basalt has better high temperature resistance compared to E-glass fibre [2,3]. If this were true then basalt fibre may show better prospects to survive an end-of-life composite thermal recycling process as a useful reinforcement.

The present work investigates and compares the changes in the mechanical properties of basalt fibres and E-Glass fibres when heat-treated to between 300 – 600 °C. Since the fibre surface plays an important role in the retained strength of brittle fibres, the investigation used fibre with similar epoxy compatible sizings in order to maximise the quality of the comparison. Results of single fibre testing of tensile strength and modulus are presented and discussed.

1 INTRODUCTION

The strength loss of E-glass fibre due to exposure to elevated temperature is a phenomenon that has been well studied in the literature [4–7]. Less prevalent are data on the strength loss of heat treated basalt fibre, although some have been published [8]. These strength loss phenomena are relevant today due to the significant quantities of fibre consumed in the manufacture of fibre reinforced composites used by industries such as automotive and wind energy. Of these, wind energy may be considered the most challenging in terms of thermal recycling and potential recovery of fibre as the epoxy resins commonly utilised require the application of relatively high temperatures for long periods of time to degrade the matrix. The recovery and reuse of the fibres in composites would, if possible, be a preferable option compared with current ‘recycling’ options (such as mechanical grinding or combusting for energy) as the fibre fraction may be considered the most valuable part of a fibre reinforced composite [9].

It is well established that the tensile failure strength of brittle materials, such as glass or basaltic fibre, is a function of the surface flaws present, following Griffith’s theory [10]. Mechanical reinforcement fibres are almost universally coated with a multi-component sizing to improve numerous processing parameters important in the formation of effective composites [11]. These

coatings can also provide a measure of protection to the fibre surface aiding in the retention of strength following fibre forming. When exposed to elevated temperatures these sizings degrade but the extent to which protection to the fibre surface is still provided will depend on the various components present in the sizing. In this investigation, both an E-glass and basaltic fibre with epoxy-compatible sizings were used to compare the effect of heat treatment on fibre tensile strength retention. Results were also compared with those produced using E-glass to which, rather than a complex multi-component sizing, either a simple single component silane coupling agent or no surface coating at all had been applied. Observations regarding the mechanical performance of the less-studied basaltic fibre in comparison to E-glass were made. Some discussion is also presented regarding possible explanations for the strength loss of brittle fibre following heat treatment.

2 EXPERIMENTAL

2.1 Materials

Owens Corning Advantex E-glass SE1500 (TYPE 30®) fibres and Technobasalt basaltic fibres were used in this investigation: both fibre types were sized with a commercial epoxy resin compatible sizing. The Advantex fibres were produced using a commercial bushing and received as single-end continuous rovings with a nominal fibre diameter of 17 μm and linear density 1200 g/km. The basalt fibres were supplied as a continuous roving with nominal diameter of 16 μm and linear density of 1200 g/km. They were sized with an epoxy-compatible sizing with designation number 76. The compositions of E-glass and basaltic fibres differ significantly, although the main component of both is silica. Compositions of basalt fibre also vary based on source of the raw materials but, in comparison with E-glass formulations, they generally contain a significantly greater proportion of iron and magnesium at the expense of silica and calcium content [12].

Additional boron-free E-glass (Advantex) fibres supplied by Owens Corning were also investigated. These fibre rovings were produced on the same pilot scale bushing and were received as 20 kg continuous single-end square edge packages. The rovings had a nominal tex of 1200 g/km and a nominal average single-fibre diameter of 17 μm. No sizing was applied to the bare fibres which had only been water sprayed using the normal cooling sprays under the bushing; these samples are referred to as water sized, unsized or bare (since it can be assumed that most water is removed during the subsequent drying step). Immediately following an identical cooling step by water spraying, the sized fibres were coated with a normal rotating cylinder sizing applicator containing a 1 % γ - aminopropyltriethoxysilane (APS) hydrolysed solution in distilled water. This silane coating process produced fibres with significantly lower weight percentage coating compared to commercially available glass fibre products. All fibre packages were subsequently dried at 105 °C for 24 hours.

For the purposes of restraining single fibres during the application of high temperature treatments a ceramic cement was required as more commonly used adhesives and glues were not effective. Glassbond Saureisen Electrotemp Cement No. 8 was selected due to its resistance to thermal shock, very high maximum operating temperature and relatively long working time available between mixing and setting.

2.2 Fibre heat treatment

Bundle heat treatment of SE1500 and basalt fibres was performed using using a CWF 1200 Carbolite electric furnace for a period of 25 minutes, after which samples were immediately removed and cooled in room temperature air. Fibres bundles were treated as-received; following heat treatment individual fibres were separated for tensile testing. A specially designed rig was used during heat treatment, preventing undesirable physical contact between any surfaces and the fibre bundles. No tensile stress was applied during heat treatment, but bundles were held sufficiently firmly that they did not sag under their own weight, leading to any bending stresses in the fibres.

Owens Corning APS only sized and bare fibres were heat treated using an alternative single fibre thermal conditioning process; individual fibres were separated prior to performing heat treatment rather than after, as in the bundle treatment procedure. The details of these contrasting treatments and their effect on retained fibre strength have been reported previously [7]. The method of mounting

single fibres on wire frames also ensured that no tensile stresses were applied to the fibres during heat treatment and, further, that any bending stresses were concentrated only at the ends. These end sections did not form part of the tested gauge length.

2.3 Tensile testing

Single fibre tensile properties were obtained according to the method described in ASTM C1557-03. The details of the procedure utilized are described comprehensively in [9]. All fibres were mounted at a gauge length of 20 mm. After each individual fibre diameter was measured by optical microscopy the samples were tested using an Instron 3342 universal testing machine equipped with a 10 N load cell. An extension rate of 0.3 mm/min was used in all cases. The average strength values at each condition are based on between 25 and 55 tensile tests. The error bars presented on all figures represent the 95 % confidence limits of the data. The statistical significance of differences in average fibre properties was assessed using the Student's t-test: a difference in properties was considered significant when the p-value was less than 0.05.

2.4 Thermo-Gravimetric Analysis (TGA)

Analysis of the mass loss of fibre with temperature was carried out using a TA Instruments Q50 Thermo-gravimetric analyser. Approximately 10 mg of material was placed in a platinum pan and heated at a rate of 10 °C/min to a maximum of 600 °C. Air was used as the furnace purge gas and nitrogen as balance purge, at rates of 60 and 40 ml/min respectively.

3 RESULTS AND DISCUSSION

3.1 Tensile strength results

The results of single fibre tensile tests on heat treated fibre bundles of Advantex SE1500 and basalt fibre are presented in Figure 1. Both epoxy-compatible fibres demonstrated room temperature strength in excess of 2 GPa, greater than 2.5 GPa for the basalt fibre.

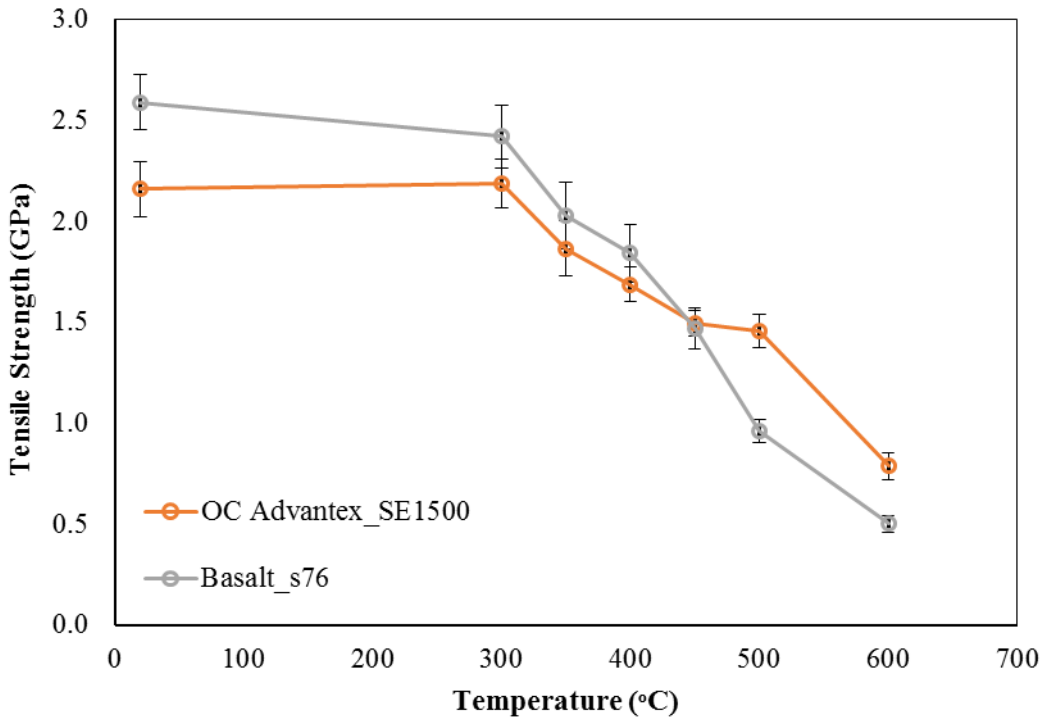

Figure 1: Tensile strengths of epoxy compatible sized Advantex E-glass fibre and basalt fibre after bundle heat treatment for 25 minutes

Following heat treatment at 300 °C this initial strength was retained, but treatment at progressively higher temperatures caused a significant decrease in average fibre tensile strength. After treatment at 400 °C between 20 – 30 % of the original strength was lost; further increase in temperature caused a continued decrease in fibre strength which was particularly severe between 500 – 600 °C. Following thermal conditioning at the maximum temperature of 600 °C strength losses of 65 and 80 % were measured for Advantex SE1500 and basalt fibre respectively.

The results for the epoxy-compatible sized fibres are presented in Figure 2 alongside data obtained using similar Advantex E-glass to which either an APS-only coating or no sizing whatsoever was applied, as outlined in 2.1. The effect of electing not to coat a fibre roving is evident; the strength of bare Advantex was significantly lower than that of the coated fibres, even when only a relatively low weight percentage (< 0.15 wt%) coating of APS was applied. No significant difference in strength was found between APS sized Advantex and basalt fibre, while the strength of Advantex SE1500 was slightly lower. Following thermal conditioning, however, the Advantex SE1500 performed better in terms of strength retention, whereas a progressive decrease in tensile strength with increasing treatment temperature was measured for APS Advantex throughout the range of temperatures investigated.

All of the treatments for which the results are presented in Figure 2 were carried out using fibre bundles from which the single fibre tensile test specimens were separated after heat treatment was performed. Using such an approach has been shown to be able to cause mechanical damage to the fibres during the separation process if their protective surface coating has been removed by, for example, high temperature thermal conditioning [7]. This explains why the strength of unsized fibre decreased significantly after treatment at 200 °C; similarly the organic fraction of APS is known to become severely degraded following treatment at 450 °C, and a corresponding large decrease in fibre strength was measured in comparison to retained strength following heat treatment at 300 °C.

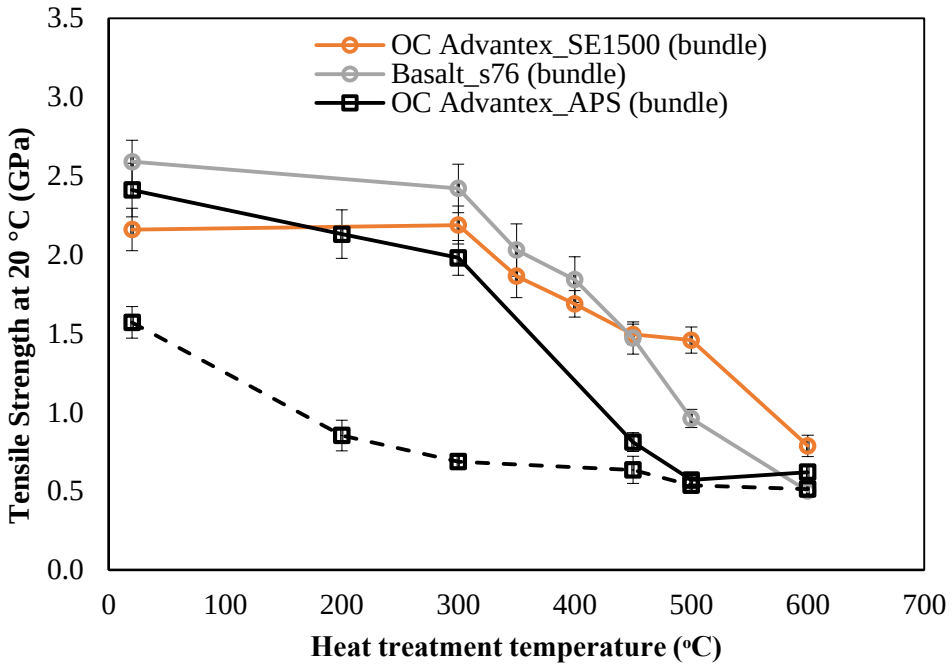

Figure 2: Tensile strengths of Advantex E-glass, basalt fibre (both epoxy compatible sizings), Advantex E-glass (APS-only sizing) and Advantex E-glass (water sized) after bundle heat treatment for 25 minutes

In contrast, both of the epoxy-compatible sized fibres used in the study demonstrated greater strength retention throughout the range of temperatures investigated, but particularly between 300 – 500 °C. It is suggested that the explanation for this relates to the sizing applied. The commercial epoxy-compatible sizing, including a silane coupling agent and additional components such as film formers, binders and anti-static agents, provides a thicker layer than silane (APS) alone. As indicated in Figure 4 the mass fraction of the fibre bundle represented by the sizing was 0.7 % for Advantex SE1500 and 1.8 % for the basalt fibre. It was clear that the presence of this multi-component sizing at the beginning of heat treatment led to significantly improved strength retention, as evidenced by the relatively low strength of bare fibre. In addition protection from surface damage at higher conditioning temperatures above 300 °C was superior. It is suggested that the difference can be attributed largely to the relative abilities of the coatings, particularly on Advantex E-glass, to protect the fibre surface from mechanically induced damage.

Evidence to support this supposition is provided in Figure 3. In this figure the tensile strength data for heat treated epoxy-sized fibre are presented alongside those obtained using APS sized Advantex treated using the alternative single fibre method, as opposed to bundle, as described in 2.2. Using the single fibre thermal conditioning procedure led to a significant increase in retained fibre strength for APS Advantex at 450 and 500 °C; approximately double the tensile strength that was retained when compared with bundle thermal conditioning (Figure 2). With the exception of 500 °C, strengths of bundle treated Advantex SE1500 and single fibre treated APS Advantex were similar. In the case of single fibre heat treatment, it has been shown that this method of treatment can minimize the degree to which mechanical handling damage of the fibre surface occurs [7]. It appears, therefore, that the epoxy-compatible sizing on Advantex SE1500 provided a degree of surface protection as a carefully controlled thermal conditioning process using single fibres separated before the application of heat. Such a conclusion is in agreement with the expectation that the strength loss with heat treatment should be similar for both Advantex formulations of glass fibre; although these may not be identical as they were manufactured at different times using different facilities.

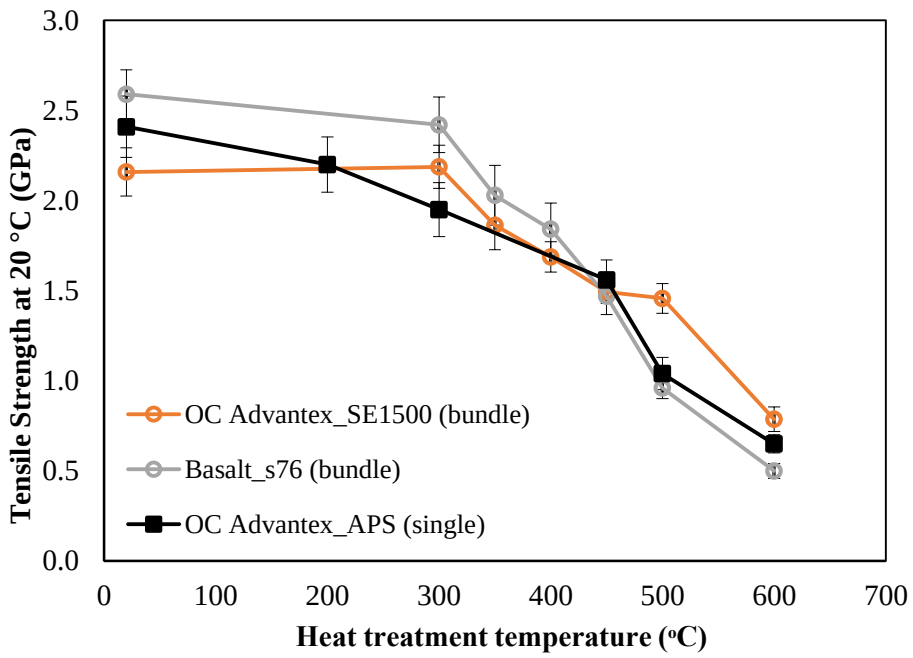

Figure 3: Tensile strengths of epoxy compatible sized Advantex E-glass fibre and basalt fibre after 25 minute bundle heat treatment, and of APS-only sized Advantex after 25 minute single fibre heat treatment

3.2 Mechanisms of strength loss in E-glass

The retained strength of both APS Advantex and basalt s76 fibre dropped most rapidly when heat treatment was performed at a temperature ≥ 450 °C. In the case of Advantex SE1500 the most significant strength loss occurred at higher temperatures in excess of 500 °C. As discussed, in the case of APS Advantex the significant strength loss over this temperature range was revealed only when heat treatment was performed on single fibres separated before the treatment was applied. This minimized surface damage to the fibres during the thermal conditioning process. It has been suggested that a fundamental process, most likely active at the fibre surface, takes place during the treatment of glass fibres to temperatures in excess of 450 °C which is responsible for the observed strength loss [6,7].

In the case of epoxy-compatible Advantex SE1500, from Figure 2 it was shown that the strength retention was significantly superior when compared to APS-only sized Advantex throughout the entire temperature range investigated, although the difference in average strengths reduced as temperature was increased. The epoxy-compatible sizing appeared to afford greater protection to the surface of glass fibres in the bundle following thermal conditioning up to 600 °C. Comparing the retained strength data of (bundle-treated) Advantex SE1500 with APS Advantex heat treated using the single fibre method, little to no significant difference in average tensile strengths was found following heat treatment, aside from a difference in strength of approximately 500 MPa which was found at 500 °C. The data in Figure 3 may be interpreted as showing that the major strength loss mechanism affecting the Advantex SE1500 during heat treatment and subsequent separation for tensile testing was the same as that fundamental mechanism causing strength loss of APS coated Advantex fibres treated carefully to minimize mechanical surface damage. The exact nature of this mechanism is still a research question of interest. Bulk changes and surface relaxation phenomena of E-glass are known to occur at elevated temperature [13,14] but a relationship, if it exists, between these and strength loss is yet to be established.

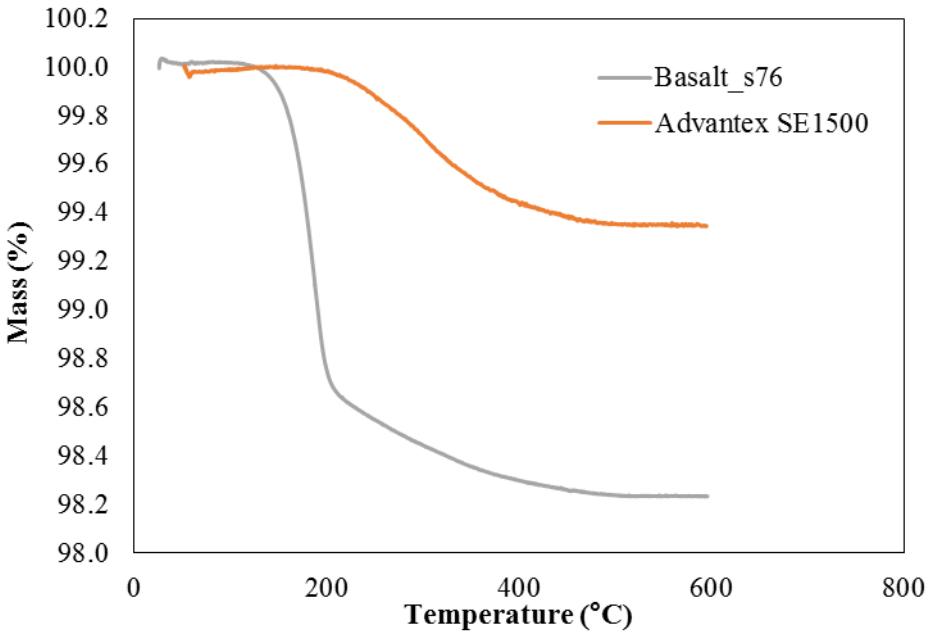

Figure 4: Mass loss of Advantex SE1500 and basalt s76 epoxy-compatible fibres as measured by TGA. Temperature ramp rate of 10 °C/min.

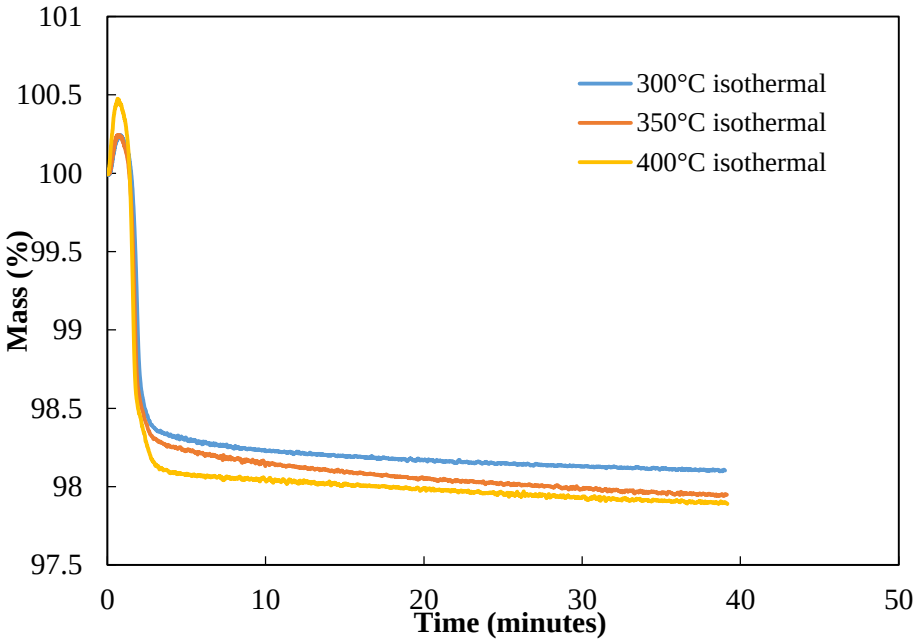

Figure 5: Mass loss of basalt s76 fibres following isothermal heating for approximately 30 minutes

3.3 Mechanisms of strength loss in basalt fibre

From the dynamic TGA data gathered it appeared that two stages of sizing degradation occurred: an initial rapid mass loss (of 1.3 %) between approximately 130 – 200 °C was followed by a second, with significantly slower rate, in which around 0.5 % of mass was volatilized between 200 – 500 °C. A greater total mass loss in excess of 2 %, however, was found during isothermal TGA measurements up to a relatively moderate 400 °C. Discrepancies in total mass loss may be explained by changes in coating thickness along the length of the fibre, although all samples were taken from a relatively small length of the roving. Further, there is a trend observed in terms of increasing mass loss with isothermal treatment temperature.

The strength retention, as shown clearly in Figure 1, does not appear to reconcile with any of the TGA data presented. Significant strength loss did not occur until conditioning was performed at 350 °C; yet after a 300 °C heat treatment it appeared from results in Figure 5 that the sizing was almost totally degraded therefore exposing the surface to possible damage mechanical damage. At 350 °C and above, strength loss progressed approximately linearly with increasing treatment temperature. This did not correspond with the onset of either the first or second stage of sizing degradation in dynamic TGA. Further, no mass loss was observed between 500 – 600 °C yet the strength loss over this 100 °C range was the most significant of those analysed. As a brittle material, basalt fibre strength is theoretically controlled by the surface flaw distribution although it is possible that failure can initiate from flaws apparently in the bulk of the fibre [15]. Results obtained did not suggest any link between the volatilization by heat of the fibre sizing and the retained strength. This was a surprising result and further study is required; for example some high resolution imaging of the fibre surface may aid in future investigations.

The behavior of basalt fibres at high temperature is somewhat more complicated than standard glasses such as E-glass. E-glass has previously been shown to undergo a thermal compaction phenomenon at elevated temperature [13,16] and the evidence showing an increase in fibre modulus presented in Figure 6 suggests that a similar effect also occurred in the heat treatment of basalt fibre. Additionally, however, evidence has been reported showing that basalt fibres also experience both oxidation and crystallization at high temperature [17,18]

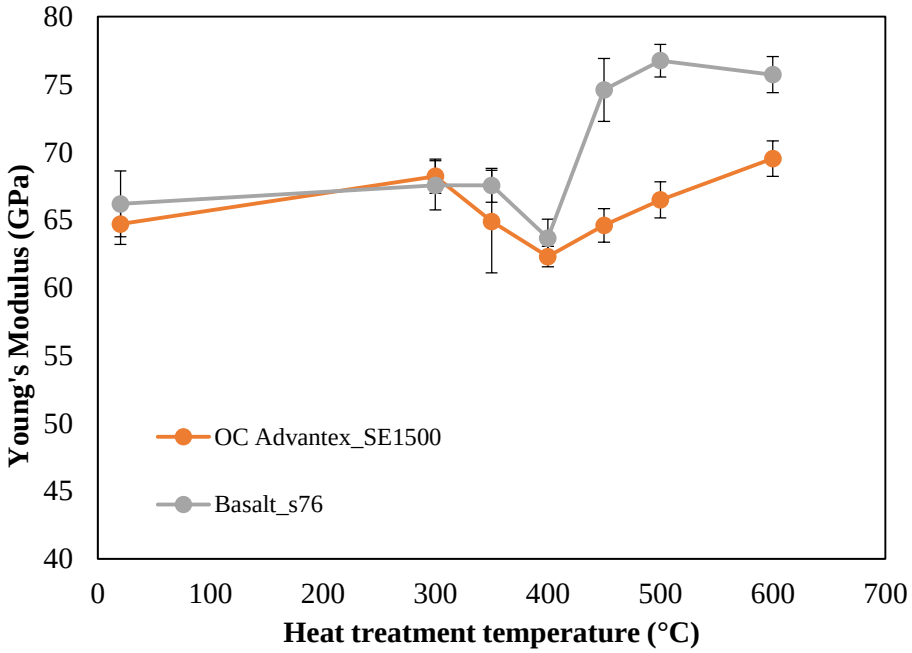

Figure 6: Young's modulus of epoxy compatible sized Advantex E-glass fibre and basalt fibre after bundle heat treatment for 25 minutes

Although it is almost certain that differences in the precise composition of the basalt fibres used in the aforementioned works and this study persist, it is nonetheless very unlikely that crystallization can help explain the observed strength loss behaviour as it tends not to commence until a temperature in excess of 800 °C is surpassed. In dynamic heating experiments using stone wool fibres, however, the oxidation of iron Fe^{2+} to Fe^{3+} was suggested to initiate between 500 – 600 °C [17,18]. A sufficient length of thermal conditioning at 500 °C may then be enough to cause oxidation of basalt fibre. A possible relationship between oxidation state and fibre tensile strength has not been studied directly. It has, however, been shown that a step change in the strength of continuous basalt fibre occurred when annealing was performed for 3 hours at greater than 500 °C [8]. It is possible that the progressive and severe loss of the strength of heat treated basalt fibre that is reported here was a product of both surface damage incurred due to manual handling following sizing degradation, as well as oxidation of the iron (Fe^{2+} to Fe^{3+}) within the fibres. It is interesting to note that oxidation is a reaction by which a loss of material will occur, and indeed a continuous but small mass loss was observed during isothermal measurements using TGA as shown in
Figure 5.

4 CONCLUSIONS

The strength loss of two epoxy-compatible sized continuous fibres – one E-glass and one of basalt composition – was measured following a 25 minute heat treatment. Retention of tensile strength was demonstrated to vary significantly between the two formulations. Basalt fibre, which has been purported to possess good resistance to temperature, was inferior to Advantex SE1500 E-glass in terms of tensile strength following treatment at 500 and 600 °C. The degradation of the epoxy-compatible sizings was investigated using TGA. From analysis of these results, and comparison with previously published data on heat treated E-glass [7], it was suggested that the SE1500 sizing provided significant protection to the fibre surface following heat treatment at temperatures up to 500 °C and therefore the strength loss measured could be attributed to a fundamental mechanism that cannot be minimized by

reducing mechanically induced damage during the heat treatment process.

Strength loss of the basalt fibres progressed approximately linearly with increasing treatment temperature between 300 – 600 °C. No correlation with the degradation of the sizing was found, which was counter to the hypothesis that exposure of the surface by sizing degradation should increase the potential of handling damage during post-heat treatment sample preparation. Some alternative suggestions for the mechanism controlling strength loss were suggested: a significant possibility requiring further investigation was progressive oxidation of the fibre, as it was observed that fibre mass loss increased with increasing temperature of isothermal analysis.

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