

## REGENERATION OF THERMALLY RECYCLED GLASS FIBRE FOR COST-EFFECTIVE COMPOSITE RECYCLING: FUNDAMENTAL STUDY OF STRENGTH LOSS OF THERMALLY CONDITIONED GLASS FIBRE

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### Abstract

*Data produced using both unsized and aminopropyltriethoxysilane (APS) coated fibre will be shown and discussed. By applying a novel method of single fibre thermal conditioning (sf-TC) it was found that retained fibre strength is, in some cases, underestimated and that the temperature range 400-500 °C is the most critical for thermally induced strength loss. This is not related to degradation of the APS surface coating, but rather is likely linked to fundamental changes occurring in the glass network or at the fibre surface.*

*X-ray Photoelectron Spectroscopy (XPS) analysis of treated fibres was performed, but it was not possible to measure any significant changes in surface chemical state. Analysis of water volatilized from unsized fibre was performed using a furnace connected to quadrupole mass spectrometer. An asymptotic minimum in volatilized water is reached between 400-500 °C.*

### 1. Introduction

The strength loss of E-glass fibres due to exposure to elevated temperature is a phenomenon that has been well studied in the past [1], [2]. It is of relevance now due to the significant quantity of glass fibre composites used in manufacturing, particularly in the automotive and wind energy industries. The recovery and reuse of the fibre reinforcement fraction from composites in terms of the production of a 'second generation' composite is a challenging proposition due to fibre strength loss. Mechanical grinding or combusting for energy and material recovery (for example in cement kilns) are current recycling options; nonetheless fibre recovery and reuse, if possible, would be a preferable option as the fibre fraction may be considered the most valuable part of a glass fibre composite [3].

Despite previous research into the phenomenon, a sufficient and full explanation for the strength loss of glass fibre has not yet been proposed. Previously posited explanations include crystallization [4] and structural relaxation [5]. Studies of sized fibre [6], [7] have concluded that degradation of this surface coating also contributes to strength loss, by exposing surface

flaws at which failure may occur according to brittle fracture theory [8]. Following Griffith's fracture theory any processes which create, or grow, surface flaws would also potentially decrease the strength of a glass fibre. Our initial single fibre tensile testing work suggested that the commonly employed method of thermally conditioning fibre in bundles may lead to erroneous assessment of retained fibre strength. Therefore a single fibre thermal conditioning procedure was developed and compared with the bundle conditioning method. The results of this study revealed that there was a critical temperature range of 400 – 500 °C where fibre strength loss was most severe. Further analyses, as outlined in 2.4, were carried out to attempt to explain the fundamental change assumed to be occurring in the glass fibre in this temperature range.

## 2. Experimental

### 2.1 Materials

Boron-free E-glass (Advantex) fibres supplied by Owens Corning Vetrotex were investigated in this study. All 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 single-fibre diameter of  $17.4 \pm 1.3 \mu\text{m}$ . No sizing was applied to the water finished 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). The sized fibres were coated with a normal rotating cylinder sizing applicator containing a 1 %  $\gamma$  – aminopropyltriethoxysilane (APS) hydrolysed solution in distilled water. All fibre packages were subsequently dried at 105 °C for 24 hours.

### 2.2 Thermal Conditioning

Thermal conditioning, or heat treatment, was carried out using a CSF1200 Carbolite electric furnace for a period of 25 minutes, after which samples were immediately removed and cooled in room temperature air. Two different procedures, bundle and single fibre, thermal conditioning were used in this work. In the former, lengths of fibre from the roving, as-received, were heat treated and once cooled single fibres were removed and mounted for tensile testing. Conversely, in the single fibre thermal conditioning process single fibres were extracted from a bundle prior to thermal conditioning. They were then attached to wire frames and heat treated in batches of approximately 30 fibres. In both cases great care was taken to avoid any contact between any surface and the fibre lengths to be tensile tested. The single fibres and fibre bundles were supported at their ends and no tensile stress was applied to them during thermal conditioning. The only difference between the two conditioning procedures is the point at which fibres are separated from the bundle, as summarised in Figure 1.

### 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 (to within  $\pm 1 \mu\text{m}$ ) 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 20 and 80 tensile tests. All tests were carried out at room temperature and approximately 50 % relative humidity.

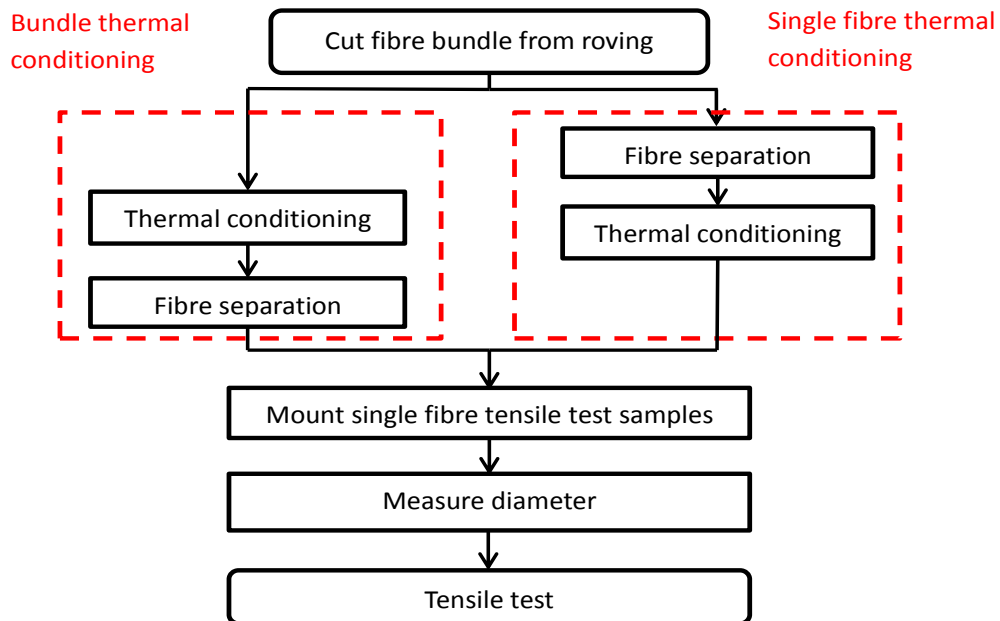


Figure 1: Simplified flowchart showing the difference between the bundle and single fibre thermal conditioning procedures

## 2.4 Chemical analysis of fibres

### 2.4.1 X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was carried out using a Thermo Scientific Theta probe instrument. A monochromated Al K $\alpha$  X-ray source with energy of 1486.6 eV was used. Untreated and bundle heat treated lengths of fibre roving were analysed using a spot size of 400  $\mu$ m. XPS spectra were taken at a take-off angle of 90° relative to the sample surface. Continuous fibre bundles were clamped in parallel beneath the analyzer using adhesive tape and a steel clamping plate. Data analysis was carried out using Avantage Data System.

### 2.4.2 Water volatilization analysis

A Hiden CATLAB<sup>TM</sup> was used to conduct thermo-chemical analysis. The CATLAB consists of a microreactor with temperature and gas flow control, coupled to a Hiden QIC-20 mass spectrometer, allowing temperature resolved identification of volatile species over the range 2 – 200 Atomic Mass Units (AMU). Samples of unsized fibre of the order of 80 mg were placed into a pre-dried quartz glass tube which was then inserted into the furnace. A ramp rate of 10 °C/min from room temperature was selected. The purge gas was helium at a flow rate of 40 ml/min.

## 3. Results and Discussion

### 3.1 Tensile strength of thermally conditioned fibre

The tensile strengths of unsized and APS sized fibres, conditioned using both the bundle and single fibre methods, are presented in Figure 2. The error bars show 95 % confidence limits.

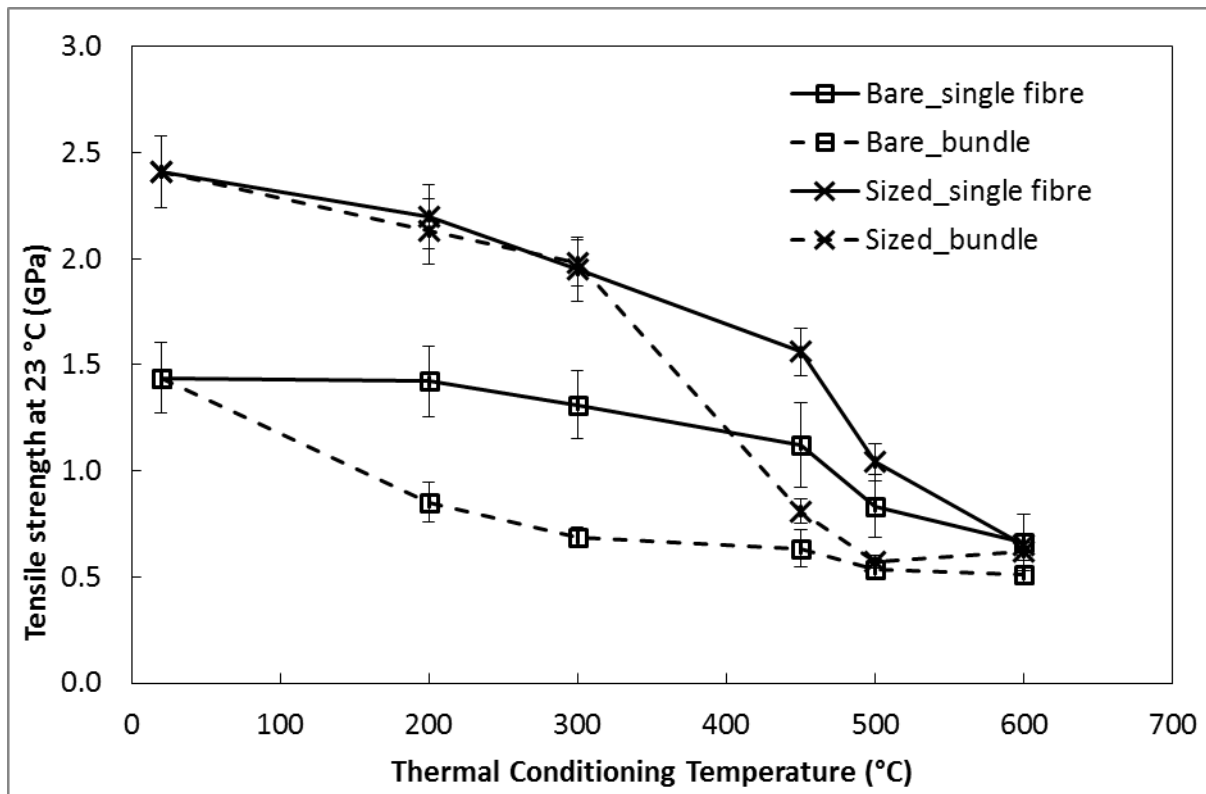


Figure 2: Tensile strengths of unsized and APS sized fibres after thermal conditioning at 200, 300, 450, 500 & 600 °C

It is evident from the results that the method of thermal conditioning employed can have a significant effect on retained fibre strength, of both unsized and APS sized fibre. The single fibre heat treatment procedure produced higher tensile strength values at temperatures between 200 – 500 °C when using unsized fibre. For APS sized fibre a significantly higher tensile strength was measured when using the single fibre method at 450 and 500 °C only.

The authors suggest that the described divergences of the data may be explained in terms of the mechanisms of damage which the fibres experience. During bundle thermal conditioning it was noted heuristically that separation of single fibres became progressively more difficult with an increase in the conditioning temperature. Fibres were easily broken despite care being taken to avoid stressing them in tension or bending. It was concluded that, even when successfully removed for testing, fibres could nonetheless have experienced some surface damage during the separation step. The authors refer to this as mechanical handling damage. The results of Figure 2 suggest that this phenomenon affects both bare and sized fibres; upon treating at 200 °C or more in the case of the former, but only when treating in excess of 300 °C in the case of the latter. This can be attributed to the protection afforded to the sized fibres by the APS coating. Glass fibre sizings have previously been shown to be thermally stable in air up to a temperature of approx. 300 °C [7].

In the case of fibres that are heat treated singly, they are removed from a bundle still in the originally manufactured state. In the case of the sized fibre, the silane surface coating is still present during this fibre separation step. During thermal conditioning and tensile testing some strength loss is observed, the degree of which increases with increasing treatment temperature. It can reasonably be assumed that this strength loss is predominantly due to a thermal damage effect alone, as great care was taken to minimize handling of the fibre and in particular the gauge length which was to be tensile tested. By studying the data in Figure 2 for both sized and bare fibre it is possible to identify the temperature range over which fibre strength loss is most severe. In both cases the data suggest that the most significant tensile strength loss occurs between approximately 400 – 500 °C.

### 3.2 XPS

Quantitative measurements were taken based on the survey scans of two samples at each condition. All samples contained significant levels of carbon-based surface contamination against which the results presented here have been corrected.

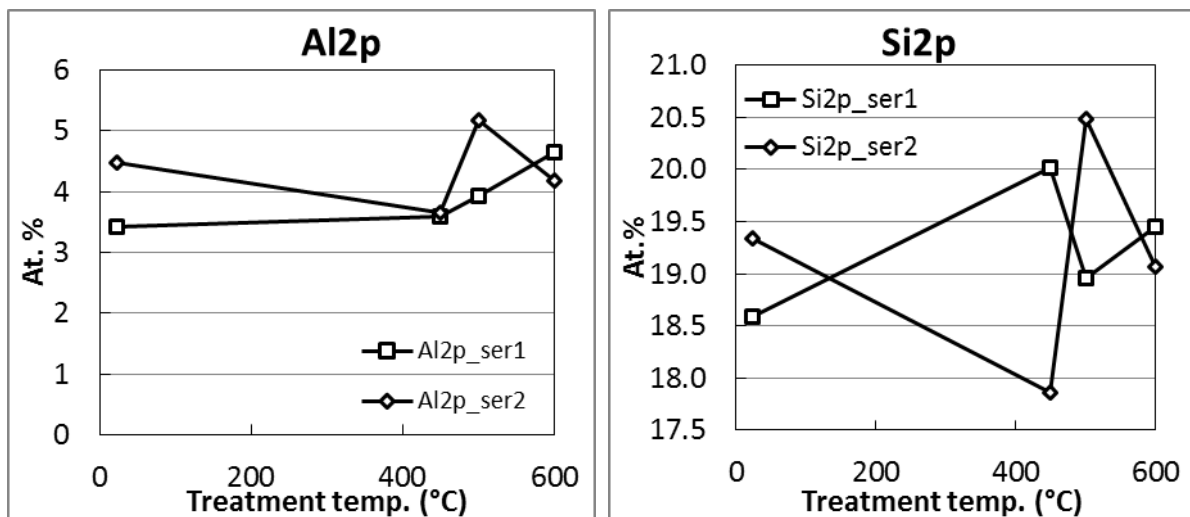


Figure 3: atomic percentage (C1s corrected) of aluminium and silicon in unsized fibre bundle samples, untreated, 450, 500 and 600 °C heat treated

The results obtained for aluminium and silicon are shown in Figure 3; they are representative of the results obtained for all other glass constituent elements such as calcium, magnesium, sodium and oxygen. The degree of variability in the data meant that no trends could be observed. Work on glass fibres of a magnesium aluminosilicate composition [10] presented evidence indicating that surface enrichment following heat treatment can occur, and an early Auger Electron Spectroscopy of the E-glass surface [11] suggested that the concentrations of aluminium and silicon varied with depth into the fibre bulk. In this study it was also noted that localized heating caused by the ion sputtering technique employed could lead to evaporation or diffusion of glass constituents. It may therefore be of interest to conduct some further analyses by XPS to confirm or deny the existence of any surface enrichment effects of glass constituent elements.

### 3.3 Water volatilization analysis

A sample of unsized glass fibre was analyzed using the system described in 2.4.2. A targeted mass spectroscopy scan at AMU 18 was performed in order to analyse the evolution of water from the sample. Results are presented in Figure 4.

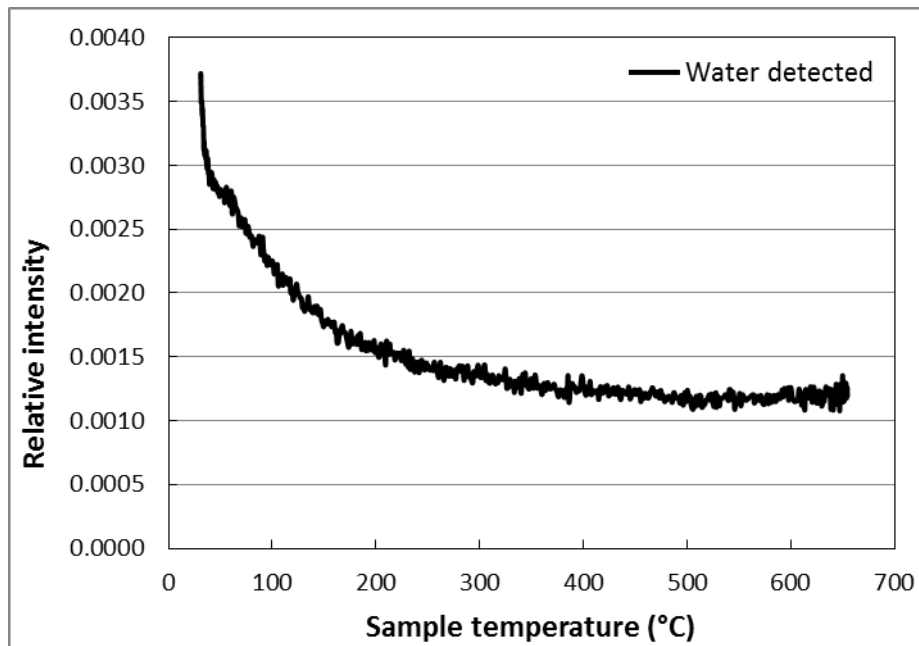


Figure 4: water volatilization curve of approx. 80 mg unsized fibre sample, 10 °C/min heating rate. Purge gas He at flow rate 40 ml/min

Between room temperature to 200 °C the relative intensity of the water signal decreased considerably, due to desorption of bound surface water. Similar results have previously been reported for both E-glass fibres, as well as silica surfaces which are often considered an analogue for more complex glass systems [12], [13]. Further water volatilization was detected in the range approx. 200 – 400 °C; while an asymptotic minimum value was reached between 400 – 500 °C. This may be related to the removal of bonded hydroxyl groups from the surface [13]. It has also been previously reported that water from within the internal structure of glass fibre may be removed following a diffusion process, upon the application of sufficient temperature [12]. Nishioka and Schramke suggested that internal water diffuses and is then removed at a temperature of 700 °C, but further that at only 300 °C so-called ‘near surface’ water may diffuse to the surface. If this were indeed the case – that volatilization of water in the range  $\geq 300$  °C is not solely from surface active phenomena such as hydroxyl group removal – it may have interesting implications.

It is known that some bulk structural rearrangement of E-glass fibre occurs during exposure to elevated temperature. A temperature range of 400 – 500 °C has shown to be critical in terms of enthalpy relaxation [5] and thermal compaction [14]. If allowed to, the fibre length will contract with time due to some global structural rearrangement, which is translated to a change in room temperature mechanical properties such as an increase in Young’s modulus. The temperature region in which the most significant structural relaxation or rearrangement takes place would also appear to be critical to fibre tensile strength loss as observed in the data in Figure 2. Furthermore, the signal for volatilized water from a bare fibre sample also approached an asymptotic minimum in the very same range. If, as has been proposed, the volatilization of water from a bare fibre sample at 400 – 500 °C is related to some diffusion of sub-surface water this process may be related to the confirmed structural rearrangement

phenomenon. It is not yet clear, however, which of these processes contribute to the loss of tensile strength. In the absence of any direct mechanical surface damage, nonetheless, a process must take place which creates surface flaws at which failure will occur, or which causes an increase in severity of pre-existing flaws.

#### 4. Conclusions

The dual effects of thermal and mechanical handling damage on the strength of thermally conditioned glass fibre have been demonstrated by application of both bundle, and the novel single fibre, thermal conditioning methods to both bare and APS coated E-glass fibre. It was possible to achieve significantly greater retained tensile strengths using the single fibre thermal conditioning procedure when treating bare fibre, and when treating sized fibre to sufficiently high temperatures that the APS coating was removed. By separating the effect of mechanical handling it was found that critical strength loss occurs in the temperature range 400 – 500 °C.

XPS analysis of heat treated unsized fibre bundles was unable to provide any evidence of consistent changes in the concentrations of glass constituent elements at the fibre surface. Volatilized water from a bare fibre sample was analysed using a coupled furnace and mass spectrometer. The results obtained may be interpreted using the conclusions drawn by other researchers [12], [13] regarding loss of surface water and surface de-hydroxylation. It was discussed that rearrangement of the glass fibre structure occurs upon exposure to elevated temperature; much like strength loss this effect is most critical between 400 to 500 °C. It is not known, however, how this phenomenon may be linked to fibre strength loss which is inextricably linked with the surface state of the fibre and its flaws. Further research is required to provide data which may aid in answering this question.

#### References

- [1] W. F. Thomas, "An investigation of the factors likely to affect the strength and properties of glass fibres," *Phys. Chem. Glas.*, vol. 1, no. 1, pp. 4–18, 1960.
- [2] N. M. Cameron, "The effect of environment and temperature on the strength of E-glass fibres. Part 2. Heating and ageing," *Glas. Technol.*, vol. 9, no. 5, pp. 212–130, 1968.
- [3] S. J. Pickering, "Recycling technologies for thermoset composite materials—current status," *Compos. Part A Appl. Sci. Manuf.*, vol. 37, no. 8, pp. 1206–1215, Aug. 2006.
- [4] M. S. Aslanova, "The Effect of Different Factors on the Mechanical Properties of Glass Fibers," *Steklo i Keramika*, vol. 17, no. 11, pp. 10–15, 1960.
- [5] M. D. Lund and Y. Yue, "Impact of Drawing Stress on the Tensile Strength of Oxide Glass Fibers," *J. Am. Ceram. Soc.*, vol. 93, no. 10, pp. 3236–3243, Oct. 2010.
- [6] S. Feih, K. Manatpon, Z. Mathys, A. G. Gibson, and A. P. Mouritz, "Strength degradation of glass fibers at high temperatures," *J. Mater. Sci.*, vol. 44, no. 2, pp. 392–400, Dec. 2008.

- [7] S. Feih, E. Boiocchi, Z. Mathys, A. G. Gibson, and A. P. Mouritz, "Mechanical properties of thermally-treated and recycled glass fibres," *Compos. Part B Eng.*, vol. 42, no. 3, pp. 350–358, Apr. 2011.
- [8] A. A. Griffith, "The Phenomena of Rupture and Flow in Solids," *Philos. Trans. R. Soc. A Math. Phys. Eng. Sci.*, vol. 221, no. 582–593, pp. 163–198, Jan. 1921.
- [9] L. Yang and J. L. Thomason, "Effect of silane coupling agent on mechanical performance of glass fibre," *J. Mater. Sci.*, vol. 48, no. 5, pp. 1947–1954, Nov. 2012.
- [10] D. B. Dorzhiev, V. E. Khazanov, and V. V Gorbachev, "Some features of the structure and strength of a magnesium aluminosilicate fiber," *Sov. J. Glas. Phys. Chem.*, vol. 15, no. 2, pp. 99–102, 1990.
- [11] J. P. Rynd and A. K. Rastogi, "Auger Electron Spectroscopy - a New Tool in the Characterization of Glass Fiber Surfaces," *Am. Ceram. Soc. Bull.*, vol. 53, no. 9, pp. 631–634, 1974.
- [12] G. M. Nishioka and J. A. Schramke, "Desorption of water from glass fibers," in *Molecular Characterization of Composite Interfaces*, 1983, pp. 387–400.
- [13] L. T. Zhuravlev, "Surface characterization of amorphous silica - a review of work from the former USSR," *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 74, pp. 71–90, 1993.
- [14] L. Yang and J. L. Thomason, "The thermal behaviour of glass fibre investigated by thermomechanical analysis," *J. Mater. Sci.*, Apr. 2013.