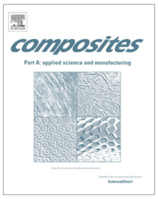
Composites: Part A 61 (2014) 201–208

Contents lists available at ScienceDirect

Composites: Part A

journal homepage: www.elsevier.com/locate/compositesa



The properties of glass fibres after conditioning at composite recycling temperatures

J.L. Thomason [*], L. Yang, R. Meier [1]

University of Strathclyde, Department of Mechanical and Aerospace Engineering, 75 Montrose Street, Glasgow G1 1XJ, United Kingdom

ARTICLE INFO

Article history:
Received 6 December 2013
Received in revised form 28 February 2014
Accepted 1 March 2014
Available online 12 March 2014

Keywords:
A. Glass fibres
B. Mechanical properties
E. Heat treatment
E. Recycling

ABSTRACT

Results are presented on E-glass fibre properties after thermal conditioning up to 600 °C. Thermal conditioning led to up to 70% strength degradation. Tensile strength and failure strain of silane-coated fibres were relatively stable up to 250 °C but exhibited a precipitous drop at higher conditioning temperatures. Unsized fibres exhibited a linear decrease in strength with increasing conditioning temperature. Little significant strength regeneration was obtained from a range of acid and silane post-treatments of heat conditioned fibres. A simple analysis of the cumulative fibre strength probability resulted in more useful understanding than the Weibull method. The modulus of both fibre types increased linearly with conditioning temperature. Evidence was found of a slow time-dependent reduction of glass fibre modulus during storage in an uncontrolled environment. The results are discussed in terms of the changes in surface coating and bulk glass structure during heat conditioning and the role of the glass fibre water content.

1. Introduction

The disposal of end-of-life composite products in an environmentally friendly manner is one of the most important challenges currently facing the industrial and academic composites community. It is projected that by 2015 the total global production of composite materials will significantly exceed 10 million tons which, at end-of-life, will occupy a volume of over 5 million cubic meters. Glass fibre reinforced composites account for more than 90% of all the fibre-reinforced composites currently produced. About 60% of this volume employs thermosetting matrix materials producing composites (GRP) that are difficult to recycle in an efficient manner. The perspectives on this issue have been recently highlighted due to the accelerating growth in the use of such composite materials in transportation and wind energy sectors [1–6]. A number of processes are available for recycling such composites [1,7]. Of these possible routes, thermal recycling is probably the most technologically advanced and has been piloted in the UK and Denmark. However, nearly all options deliver recycled fibres (which make up approximately 60% by weight of the composites) that suffer from a lack of cost competitiveness with pristine first-pass materials. A key factor in this equation is the huge drop in the performance of recycled glass fibre (80–90%) in comparison to its original state [1,7]. Consequently, recycled fibres have a very poor performance to cost ratio, and in most cases are considered unsuitable for reprocessing and reuse as a valuable reinforcement of composites. A breakthrough in this field could enable such recycled glass fibres (RGFs) to compete with pristine materials in many large volume composite applications. The development of an economically viable process for regenerating the properties of thermally recycled glass fibres would have major technological, societal, economical, environmental impacts. The reuse of these materials could result in a huge reduction in the environmental impact of the glass-fibre and composites industry where the replacement of pristine glass fibre products by RGF products would equate to a global reduction in CO_2 production of 400,000 Tons/annum from reduced melting energy requirements alone. Furthermore, such a development would also reduce the need for an annual landfill disposal of 2 million Tons of composites. These developments would clearly be in line with the growing societal and environmental pressure to reduce the use of landfill disposal, increase the reuse of valuable raw materials resources, and reduce the release of CO_2 to the atmosphere.

Processing temperatures in the production of glass fibre are significantly higher than GRP recycling temperatures. Nevertheless, earlier work has indicated that the room temperature tensile strength of glass fibre can be significantly reduced by annealing at temperature as low as 150 °C [8]. More recent studies have also confirmed that room temperature glass fibre strength can be reduced by exposure to temperatures in the 300–600 °C temperature

---

[*] Corresponding author. Tel.: +44 01415482691; fax: +44 01415525105.
E-mail address: james.thomason@strath.ac.uk (J.L. Thomason).

[1] Current address: Technische Universität München, D-85748 Garching, Germany.

http://dx.doi.org/10.1016/j.compositesa.2014.03.001
1359-835X/

range [9–12] which is typical of the many different potential GRP recycling processes. Similar behaviour has also been observed in silica and basalt reinforcement fibres [13,14]. We are currently engaged in research projects where the ultimate goal is the generation of the fundamental knowledge to enable cost-effective regeneration of the mechanical properties of glass fibres produced from thermal recycling of glass reinforced thermoset composites such as wind turbine blades. In this paper we report on the influence of thermal conditioning, at temperatures typical for GRP recycling up to 600 °C, on the properties of water sized and silane sized E-glass fibres. We also report initial results of a study on the use of acid and silane treatments on the strength of heat-treated fibres.

2. Experimental

Boron free E-glass fibres supplied by Owens Corning-Vetrotex were investigated in this work. The fibre rovings were produced on a pilot scale bushing and were received as 20 kg continuous single end square edge packages. The rovings had a nominal tex of 1200 g/m and a nominal fibre diameter of 17 μm. No sizing was applied to the water finished fibres which had only been sprayed using the normal water prepad cooling sprays under the bushing, these samples are referred to as water sized or unsized. The APS coated fibres were coated with a normal rotating cylinder sizing applicator containing a 1% volume γ-aminopropyltriethoxysilane (APS) hydrolysed solution in deionized water. All fibre packages were subsequently dried at 105 °C for 24 h. The fibres were used as received from the manufacturer. Heat treatment of both fibre types was conducted simultaneously to obtain samples with identical thermal history. 300 mm lengths of silane sized and water sized fibre strand with no visible damage were removed from the inside of the roving packages. The glass fibre strands were suspended on a specially constructed jig preventing any contact with, and therefore damage to, the fibres (see Fig. 1). Heat conditioning was carried out in a Carbolite LHT6 high temperature oven for 15 min at temperatures in the range 250–600 °C. The jig was then removed from the oven and the samples allowed to cool naturally to room temperature.

For chemical post-treatment ACS reagent 37% hydrochloric acid (HCl), APS, γ-glycidyloxypropyltrimethoxysilane (GPS) and mercaptopropyltriethoxysilane (SPS) were supplied by Sigma Aldrich in the UK. 10 v% HCl was prepared by diluting concentrated HCl with deionised water. 1% volume silane solution was prepared by mixing the silane with deionised water. APS was hydrolysed without pH adjustment, all other silanes were hydrolysed in water whose pH value had been adjusted to 5.1–5.3 prior to mixing. One silane blend was created by mixing the APS and SPS solutions in equal amounts. The solution were left for 24 h to ensure full hydrolysis. Heat treated glass fibre bundles were completely immersed in the treatment solutions, one or two hours for acid treatment, 15 min for silane solution, at room temperature and then dried in an oven at 110 °C for another 15 min.

Single fibres were meticulously separated from the glass fibre strands avoiding fibre–fibre interactions or excessive fibre bending as much as possible. Individual fibres were glued onto a card tabs with a central window cut out to matched the desired gauge length for the test. Card frames were cut from 250 g/m^2 grade card and single fibres were fixed to the card at both sides of the window using Loctite™ Gel Superglue. A Nikon Epiphot Inverted optical microscope was used at 200× magnification to obtain a digital photo of each fibre. The cross-sectional area was calculated from individual average fibre diameters measured at five points along the gauge length. During handling of the fibre in the microscope, care was taken to avoid fibre damage through contact with the microscope objective. Single fibre tensile properties were determined following ASTM C1557-03 using an Instron 3342 universal testing machine equipped with a 10 N load cell. Sample gauge length was 20 mm for both fibre types and approximately 75 fibres were tested at each condition. The tensile testing strain rate used was 1.5%/min and all the tests were carried out at room temperature and 50% relative humidity. Only the tests where the sample broke along the gauge length at a distance greater than 3 mm from the clamps were used for further data processing.

3. Results and discussion

3.1. Fibre diameter distribution

Over the course of the investigation the diameters of more than 1200 individual glass fibres were measured using optical microscopy. The results are summarised in Table 1 which reveals the relatively large distribution in fibre diameters present in commercially produced glass fibre reinforcements. Fibre diameter is an important parameter in defining the final performance of fibre reinforced composites and is related to several parameters including the internal diameter of the bushing tip, the velocity of molten glass flow, and attenuation rate [15]. For a given glass-fibre manufacturing configuration it is the variation of the molten glass flow that mainly accounts for fibre diameter distribution. The variation in the viscosity of glass melt is believed to be caused by the temperature distribution across the bushing [15]. In the case of single fibre strength and modulus these fibre diameters are used to calculate the fibre cross section. Examining the values for minimum and maximum fibre diameter in Table 1 it can be seen that using only a manufacturers nominal fibre diameter or a single average value of the distribution can lead to up to a 78% error in the value of fibre cross section. This would translate directly into errors of similar magnitude in the fibre modulus and strength. This

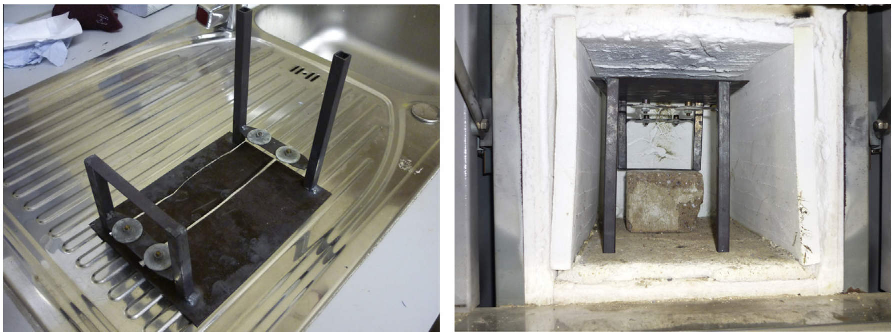


Fig. 1. Illustration of fibre suspension rig and rig positioned in furnace. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)