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Published in:
I O P Conference Series: Materials Science and Engineering

Link to article, DOI:
10.1088/1757-899X/139/1/012040

Publication date:
2016

Document Version
Publisher's PDF, also known as Version of record

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2016 IOP Conf. Ser.: Mater. Sci. Eng. 139 012040

(http://iopscience.iop.org/1757-899X/139/1/012040)

IOP Conf. Series: Materials Science and Engineering **139** (2016) 012040 doi:10.1088/1757-899X/139/1/012040

The influence of removing sizing on strength and stiffness of conventional and high modulus E-glass fibres

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Abstract. Two types of E-glass fibres, a conventional and a high modulus where the last one in the following will be denoted as ECR-glass fibre, were investigated regarding density, diameter, stiffness and strength. The fibres were analysed as pristine and after sizing removal treatments. The sizing was removed by either burning at 565°C or soxhlet extraction with acetone. It was found that the density and the stiffness increased after removing the sizing by the two removal treatments whereas the diameter did not change significantly. The strength of the fibres decreased after burning as the sizing, protecting against water and fibre-fibre damage, had been removed. The strength of the fibres after extraction was not significantly different from the strength of the pristine fibres despite removing the sizing. This indicates that the bonded part of sizing is still protecting the glass fibre surface.

1. Introduction

There is a number of different types of glass fibres all based on silica but with different composition of additives. The silica network creates a three dimensional structure which is amorphous when the melt is rapidly cooled during manufacturing of glass fibres. Some of the additives are mixed in the melt to lower the melting temperature to around 1000°C by spoiling the native structure of silica, others are added to obtain certain bulk properties for specific usage of the fibres [1]. Aluminium, titanium, and zirconium oxides can be included in the silica tetrahedron network increasing the stability but creating charged area derived from lack of oxygen. Other oxides additives such as calcium and magnesium oxides will even out charges and hence modify the network as they are larger and have only one or two bonds to the silica network [1, 2].

E-glass fibres contain mainly aluminium and boron oxides as additives and were initially made for electical applications. They are the most used in fibre reinforced composites because of their high strength and low cost. ECR-glass fibres are a more chemically resistant version of the E-glass, but without boron oxide. Other types of glass fibres include C-, AR-, R- and S-glass fibres with different abilities and usages: corrosive acid resistance, alkali resistance used in cement and

concrete, high mechanical strength and acid corrosive resistance, and high mechanical strength and stability in environments with high temperatures and corrosion, respectively [1–3].

Manufacturing of glass fibres is almost the same for all types of fibres. The constituents are mixed and melted at high temperatures in a vessel from which the fibres are drawn through bushings. The fibres are cooled by water spray immediately after and subsequently the sizing is applied, often by passing a roll immersed in the sizing mixture. Then the fibres are gathered in strands and winded on bobbins [1, 2]. The diameter is determined by the size of the bushing holes, the melt temperature, and the draw speed [2]. The strength of the fibres is mainly determined by the glass composition but also by how quickly the melt is quenched, and surface flaws. The flaws can be divided into two types. The first type develops during manufacturing as a result of impurities or stresses induced by the quenching. The second type ocurs because of the subsequent handling, mainly fibre-fibre damages. Existing flaws will extend during tensile stress especially in moist environments ultimately leading to breakage [4, 5].

The sizing applied during manufacturing is a multicomponent surface coating with multiple functions. It is an aqueous suspension with two main elements making up around 90 wt.% of the dry components: a coupling agent and a film former [6]. The coupling agent is considered the most important as it is believed that it controls the adhesion between fibre and matrix. The film former is the protector of the surface against water attack and fibre-fibre damages [7, 8]. Furthermore the sizing is suggested to heal flaws in the glass fibre surface and also reduce the risk of new flaws to arise [9, 10]. Sized glass fibres exhibited higher strength compared to unsized fibres [11]. It has previously been shown that removing the sizing by heating increases the stiffness but at the cost of a decrease in the fibre strength [3, 12, 13]. The heating increases the dimensions and the amount of flaws in addition to the removal of the healing sizing [14].

The sizing applied during manufacturing is needed to be able to handle the fibres until usage. Removing the sizing should therefore be done right before using them e.g. in composites. Burning the fibres at high temperatures will remove all the organic material from the fibres. By extraction it is possible to remove the part of sizing that is physically adsorbed to the surface but not the bonded part. The degree of extraction depends however highly on the solvent used [6, 15–17]. The sizing removed by heat treatment and/or solvent extraction and the glass fibres before and after the sizing removal were intensively characterised [18].

In this paper commercial E-glass and ECR-glass fibres were investigated. Density, diameter, stiffness and strength were measured on pristine fibres and fibres where the sizing had been removed.

2. Methods and Materials

Two types of fibres were analysed: E-glass and ECR-glass fibres. The E-glass fibres were produced by Jushi (Chengdu, China) and the following properties was given by the manufacturer: tex number of 1200, 17 μm diameter of monofilament, moisture content $\leq$ 0.10% and sizing content in the range of 0.45-0.70 wt.%. The ECR-glass fibres were produced by Owens Corning (Brussels, Belgium) with a tex number of 1200 and a diameter of 17 μm. Soxhlet extraction with acetone of sizing from pristine glass fibres and burning pristine fibres at 565°C were reported previously [18].

Density measurements were performed using a gas pycnometer (Quantachrome Ultrapyc 1200e, England) with nitrogen gas as the displacement medium. Prior to analysis the fibres were dried at room temperature in a vacuum chamber overnight. The fibres were then cut into small pieces to fit in the sample cup and placed in the pycnometer. 2-5 grams of fibres were used. Each measurement was repeated at least eight times.

Tensile testing of single glass fibres were performed on a Favimat+ with a Robot2 from Textechno, Germany. The linear density was measured by recording the resonance oscillation of fibre vibration induced by acoustic waves, according to ASTM D 1577. The individual fibre

diameter and cross section were calculated from the linear density and the density measured by the pycnometer. The tensile test was conducted subsequently on the same fibre just used to determine the cross sectional area. 75-100 fibres were tested for each type (E-glass and ECR-glass fibres) and treatment (pristine, fibres after soxhlet extraction, and burning) with same gauge length of 40 mm and test speed of 1 mm/min.

3. Results and Discussion

The measurement of density was done three to eight times by the pycnometer until a satisfying standard deviation of less than 0.02% was obtained within three consecutive measurements. If this was not reached after the eighth measurement the data was discarded. This average density determination was repeated at least eight times. The density was determined for both glass types also after soxhlet extraction and after burning. The measured densities are shown in figure 1.

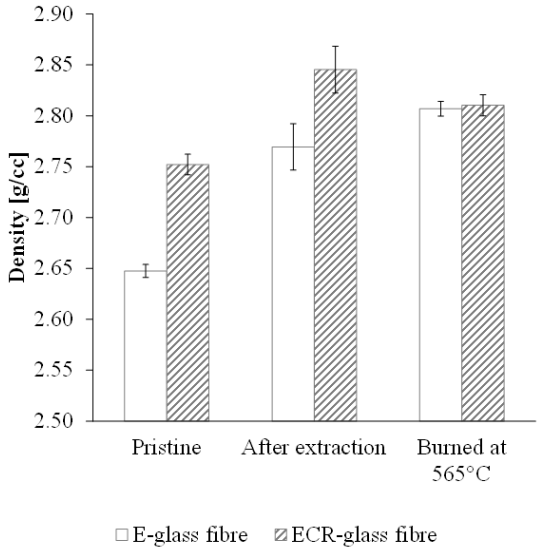

Figure 1. The densities of E-glass and ECR-glass fibres pristine and after removal of sizing by soxhlet extraction or burning at 565°C, all determined by use of a pycnometer.

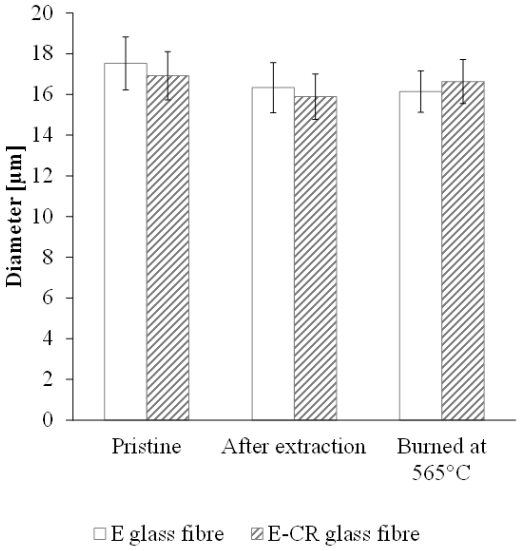

Figure 2. Diameter of the tested fibres (pristine fibres, fibres after soxhlet extraction and fibres after burning at 565°C) calculated from the linear density measured with vibroscopy.

The obtained densities of pristine E-glass and ECR-glass fibres were close to literature values of 2.58 and 2.72 g/cc, respectively [3]. The density of the glass fibres has increased after removal of sizing both by soxhlet extraction and by burning at 565°C. When estimating a density of sizing of 1 g/cc based on typical sizing components and thickness, it is reasonable that the removal of sizing is the cause of the higher density of fibres after soxhlet extraction. Extraction of the sizing is not believed to change the glass structure.

It is noticeable that the density of both E-glass and ECR-glass fibres after burning reaches the same level around 2.81 g/cc. The compositions of E-glass and ECR-glass fibres are very much alike. The main difference is that the ECR-glass is without boron oxide. Instead it contains zirconium oxide [2, 19]. Structurally they are both a random silicon oxide network with aluminium cations as a part of the network. Boron oxide is a part of the network on equal terms with silica where zirconium oxide is a intermedia along with aluminium [1]. Heating the

glass fibres to a temperature near annealing temperature could change the bulk structure of the glass fibres making them even more alike. The burned E-glass fibres have a even higher density than the fibres after soxhlet extraction. This can be explained by glass compactment where internal stresses in the glass structure are released. As a result the fibres contract yielding a higher density [13]. It was noted that the fibres after extraction were very electostatic since the antistatic agent in the sizing had been removed, but no other visible changes. The fibres after burning were much stiffer, behaved less flexible and appeared to have small bends from lying on top of other fibres while being heated, all supporting that the glass structure had changed to a more rigid network as a part of the relaxation.

The diameters of the E-glass and ECR-glass fibres were calculated in connection to the single fibre tensile testing from the linear density. The diameters are shown in figure 2. It was expected that the burned fibres had a slightly smaller diameter after the heat treatment. However, the diameter does not change significantly after heat treatment nor after soxhlet extraction. The large variation in diameter of all the fibres obstructs the possibility to observe an alteration of size and shape of the glass fibre.

Between 100 and 125 fibres of each type and treatment were tested but not all were used for the calculation of the average stiffness and strength of the fibres. Some of the data were excluded due to breakage during the linear density measurement or shortly after initiation of the tensile test, for example, if two fibres were tested simultaneously by mistake and if the fibre was sliding in the clamps during testing. Especially the burned fibres were troublesome to test as they were very fragile, so as few as 25 data points were left, whereas up to 73 data points were obtained when testing the fibres after soxhlet extraction. Stiffness was calculated based on the initial slope of the stress-strain curve in the range of 0.05-0.25% strain. The strength was calculated from the maximum force measured. The obtained values of stiffness and strength of single glass fibres as pristine fibres and after treatments are shown in figure 3 and 4, respectively.

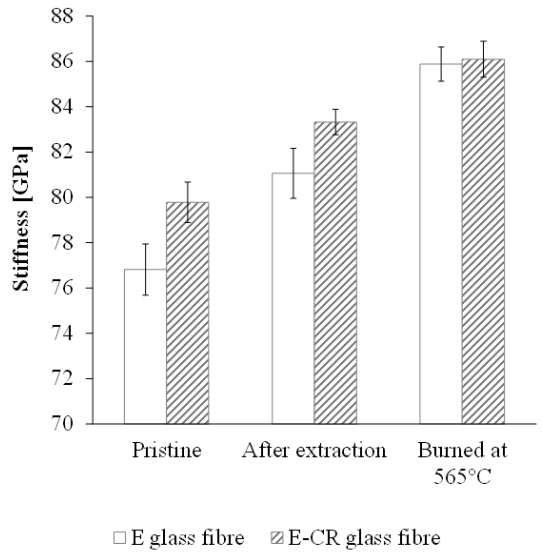

Figure 3. The stiffness of E-glass and ECR-glass fibres pristine and after removal of sizing by soxhlet extraction or burning at 565°C, obtained by single fibre tensile testing.

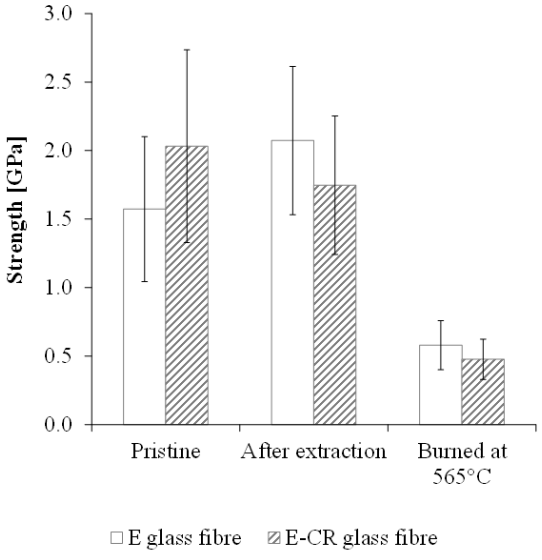

Figure 4. The strength of E-glass and ECR-glass fibres pristine and after removal of sizing by soxhlet extraction or burning at 565°C, obtained by single fibre tensile testing.

The pristine E- glass and ECR-glass fibres were found to have a stiffness of 77 GPa and 80 GPa, respectively, which are close to literature values [2, 3]. The stiffness of the fibres was found

to increase after both soxhlet extraction and heat treatment with 3-9 GPa. Similar results for heat treated glass fibres have been found in literature with the explanation that stresses induced by the rapid cooling during manufacturing are released [3, 13]. The strength of the pristine fibres are much lower than values given in literature [2, 3, 19] from which a strength of around 3 GPa was expected. The burned fibres do however still follow the decreasing tendency and have similar values as found in literature [11–13, 20]. The low strength is related to enlargement of existing surface flaws that become vulnable to attack from water [20]. The fibres after soxhlet extraction exhibit strengths close to the one obtained for the pristine fibres with no significant difference. They are however close to strengths measured on bare E-glass fibres [11]. It should be noted that a compliance correction have not been executed since only one gauge length was used. This could result in slightly lower values caused by compliance in the testing equipment [21].

4. Conclusion

The densities of E-glass and ECR-glass fibres were found to increase by 5% and 3%, respectively, when the sizing had been removed by soxhlet extraction using acetone. When removing the sizing by burning at 565°C the increase was 6% and 1%, respectively. The changes in density were related to removal of the less dense sizing and to compactment of the glass structure.

For E-glass fibres the stiffness increased from 77 GPa to 81 GPa after extracting the sizing by soxhlet and even to 86 GPa when pristine fibres were burned. Opposite was found with the strength of the fibre after burning with a decrease from 1.6 GPa to 0.6 GPa, whereas soxhlet extraction gave an increase to 2.1 GPa. ECR-glass fibres exhibit the same tendency regarding stiffness as the E-glass fibres where the pristine fibres were found to have a stiffness of 80 GPa, increasing to 83 GPa after soxhlet extraction and to 86 GPa when burned. The strength changed differently with the treatment for the ECR-glasss fibres with a large decrease after soxhlet extraction from 2.0 GPa to 1.8 GPa where burning yield a strength of 0.48 GPa.

The increase in stiffness after burning was related to relaxation of the glass structure where the decrease in strength was associated with enlargement of flaws and water attack after removal of the protective sizing. The processes behind the increase of strength when removing the sizing by extraction has not been clarified but could be related to the bonded sizing maintaining the healing effect of the surface flaws. The two types of glass fibres behaved very much alike.

Acknowledgements

This work was supported by the Danish Centre for Composite Structures and Materials for Wind Turbines (DCCSM) from the Danish Research Council for Strategic Research (grant number: 09-067212). In connection to the density measurements and tensile testing the authors would like to thank Justine Beauson and Anthony Fraisse.

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