

A NEW METHOD TO PREPARE MORE REPRESENTATIVE COATED GLASS FIBRES FOR SCREENING AND DEVELOPMENT OF SIZINGS AT THE LABORATORY SCALE

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Abstract

Conventional laboratory scale glass fibre sizing analysis commonly involves sample preparation by dip coating, resulting in a thick size layer with a higher Loss of Ignition (LoI) than industrial sized fibres. This makes it difficult to make useful comparisons between industrial and lab-scale prepared samples when evaluating size performance. This paper presents a novel, but simple, fibre coating technique that produces a size layer similar to industrial sized samples with an average layer thickness one tenth that obtained by dip-coating. Thermogravimetric analysis and electron microscopy results show how the size layer on lab-coated fibres had a morphology much more comparable to that on industrial samples. Average size LoI could be easily controlled in a range from 1 to 5 %, compared to the 11 % obtained on samples dip coated with the same size formulation. Microbond tests results of interfacial shear strength in two different polypropylenes indicate that the lab-sized fibres exhibited comparable values to the industrial-sized fibres and enhanced values compared to the dip coated fibres. These findings highlight the considerable potential of this novel lab-scale coating technique as a viable alternative to dip coating in laboratory research, as it provides a more realistic representation of industrial-scale sizings.

1. Introduction

Glass fibre reinforcements form the backbone of the composites industry. Today glass fibre products account for more than 95% of fibre reinforcements used in the composites industry, primarily due to their highly attractive performance to price ratio. Despite their relatively low-tech image as a composite reinforcement, the production of glass fibres has evolved into a very complex technology with requirements that challenge the state of the art in materials science research and development [1,2]. Possibly the most critical component involved in the manufacture of glass fibres and their composites is the fibre size. Size is a thin surface coating of mainly organic materials applied, most often as a dilute aqueous solution or emulsion, to nearly all types of man-made fibres during their manufacture. In the case of glass fibres, sizing is probably the key component influencing the commercial success (or failure) of most reinforcement products and their composites. This is due to the major role played by the sizing in the profitability, processability, and performance of that product. Continuous reinforcement grade glass fibre could not be manufactured in a high volume, cost-effective, manner without the correct sizing formulations. Similarly, most composite production processes could not be operated in a cost-effective manner without appropriately sized glass fibres. Finally, both short-term and long-term composite performances are critically influenced by the optimization of the fibre sizing and the closely associated fibre-matrix interphase in the composite [2-7]. However, due to the lack of reliable and verifiable information on the physical and chemical nature of sizings, the generally available understanding of these complex chemical mixtures does not reflect the level of importance that they have in determining the success of any glass reinforced composite material in a specific application [7].

Despite the critical need of the composite industry to fully understand all aspects of the materials it uses, size and sizing remains a "black box" technology in composites since glass fibre producers are very reticent to reveal much information about the complex formulations they use. Consequently openly available descriptions of sizes tend to be highly generic in nature. Commercial glass fibres are often supplied with only two sizing related details. The first is the chemical "compatibility" of the sizing with a general class of matrix polymer. The second is a value for the Loss on Ignition (LoI), a measurement of the amount of size present on the fibres. This paucity of information on the physical and chemical nature of the sizing on a glass fibre product is an issue for many users of glass fibres, be they interested in quality control for manufacturing through to the fundamentals of the fibre-matrix interphase. Typically the user will be told that sizes are dilute water based emulsions or dispersions containing a complex mixture of components. These will often be described more by their generic function rather than by their chemical formulae. The primary components are the film former and the coupling agent [2-5]. The film former is designed to protect and lubricate the fibres and hold them together prior to composite processing, yet also to promote their separation and wetout when in contact with resin. The coupling agent is often said to serve primarily to bond the fibre to the matrix resin. Beyond these two major components, sizes also may include lubricating agents, antistatic agents and surfactants. A complex size formulation may contain five or more components. The interaction of these components with each other, with the fibre surface, with the matrix polymer, within a particular processing environment is extremely complex and quite inadequately researched. A number of recent reviews have highlighted some serious issues for the composites industry related to the state of play in glass fibre sizing technology [5-7]. It has been suggested that the nature of all the complex interactions involved in size formulations, size application, fibre drying, fibre wetting impregnation and composite performance are not at all fully understood, even by those with inside knowledge of size formulations. It has also been highlighted that there is virtually no information available in the open literature on what methods the manufacturers of glass fibres use to characterise their sizings and control the quality and consistency of their sized products. This problem extends to their customers who consequently have little, or no, real guidance on tools to employ for quality control of sized glass fibres, other than monitoring issues during full production processing. Even then, quality issues with sizings may only become apparent after many years in the long term performance of the final composite parts.

Notwithstanding the critical importance of size formulations to the composites industry, the enormous diversity of the applications which make use of sized glass fibre as reinforcements, coupled with the veil of industrial secrecy which covers sizing formulations have combined to hinder the development of a sound foundation to the "science" of sizing. Unlike in many other fields of materials science of a similar age the available literature on sizes, size formulations and the role of individual and combinations of size components is highly fragmented and does not form a continuous and comprehensive foundation for those outside of the glass fibre industry to build meaningful research and development programs in order to progress the knowledge base in this area. Even where research groups have been able to cooperate with glass fibre manufacturers, the knowledge generated is nearly always unsatisfactorily incomplete due to the non-disclosed information on the precise details of size formulations. Furthermore, published results are very rarely reproduced and checked by other researchers due to the non-availability of replicate glass fibre samples which have been identically manufactured and sized. This results in even this meagre amount of published information on sizings being of little help in its application to a slightly different size formulation or to assist in the reinforcement of a different polymer system. One consequence of this situation is that, while rapid and expanding progress is made in developing areas of materials science where background information is more openly available, new size development continues to be carried by an extremely small number (in proportion to the size of the composites industry) of researchers in glass fibre manufacturers' laboratories. To make matters even more challenging, these small research groups (or individuals) cannot even discuss the subject with their peers in other companies. Hence size development actually takes place in an extraordinarily isolated environment in comparison to many other fields of materials science. Having to operate in such restricted silos is highly detrimental to innovation, indeed studies on the effect of silos in large corporations have concluded that "a silo is where collaboration goes to die. The reality is that the number

one thing slowing innovation is a lack of effective cross-silo communication” [8]. Small wonder then that trial and error is still a predominant method of new size development, although nowadays the trial and error method is frequently dressed up to look more scientific by using design of experiment methods combined with statistical analysis.

From a wider perspective this situation has potentially enormous consequences for the slowing and limiting of innovation in the composites environment. Because of the lack of any comprehensive or reliable database on the science and technology of glass fibre sizings and the lack of accepted analysis and characterisation techniques and standards for sizings the number of knowledgeable researchers outside of the glass fibre producers is extremely small. This is compounded by the secrecy surrounding size formulations and the unique conditions of size application during fibre manufacture [4] and the very small concentration of the complex size mixtures in a final composite part. This situation makes it challenging for those without insider knowledge to draw any significant conclusions about whether any real progress is being made in this important area of composites science. However, there is little evidence of any real innovation in commercial glass fibre sizing development and it seems likely that the area is in near stagnation as many glass fibre products and their sizes are high up on the development S-curve, resulting in rapidly diminishing returns on effort. Indeed the glass fibre industry is on record as saying that product (i.e. sizing) development across the industry is moving at a slower pace than in the past [9].

It is well established that the pace of technology development in any scientific field is directly proportional to the level of information sharing and to the number of well-informed researchers active in the field [10-12]. While rapid and expanding progress is made in developing areas of materials science where background information is more openly available, new size development continues to be carried out by an exceedingly small number of researchers. These very limited numbers of researchers operate in an isolated and restricted environment with little or no open exchange of information. This situation seriously reduces the probability of an innovation in the field leading to a jump to a new S-curve which could bring rapid acceleration in the performance of resultant new composite products. Consequently, it seems that it is highly likely that the current overall state of size development is a serious barrier to the innovation of improved glass fibre reinforced composite materials and is something that urgently needs to be addressed on an industry-wide level. Researchers in the composite industry urgently need to acquire a better understanding of glass fibre sizings and how they can be tailored to improve composite performance. One possible way to assist this would be to develop some size screening tools which could be used in any laboratory and do not require the resource-intensive facilities of a glass fibre manufacturing plant. One of the principal roles of a glass fibre size, of importance to the end-user, is the ensuring the quality and endurance of the fibre-polymer interphase in a composite. Conventional lab-scale sizing research and development, outside of the glass fibre manufacturing companies, commonly involves sample preparation by dip coating of fibre samples in a test size formulation. Although this enables investigation of chemicals that might be used in sizing formulations, this process lacks any connection with the high speed and high shear of real-world sizing application during glass fibre manufacture. Moreover, when used with sizes containing a normal concentration of components this method usually results in an unrealistically thick size layer on the fibres with a significantly higher LoI than industrial sized fibres. This makes useful evaluation of size performance and the related composite interface performance from lab-scale prepared samples highly uncertain. Consequently, there is a pressing need for the development of a lab-scale sizing process that more closely mirrors the results of the industrial process. This paper presents a novel, but simple, fibre coating method that gives a size layer similar to industrial sized samples with an layer thickness one tenth that obtained by dip-coating.

2. Materials and Methods

2.1. Materials

Aminopropyltriethoxysilane (APS) was purchased from Sigma-Aldrich. The film former aqueous emulsion was supplied by Şişecam. A commercial E-glass fibre product (GFref) sized with a proprietary polypropylene compatible sizing was also supplied by Şişecam for comparison purposes. The fibre coating experiments were conducted using bare (water-sized) E-glass fibres taken from a large roving

supplied by Şişecam. To create 100 g of sizing S1A, 1.6 g of APS were mixed with 50 g deionized water and agitated for 10 min. Subsequently, 24.2 g of film former emulsion were added to the mixture along with deionized water, resulting in a total of 100 g of sizing with a solids concentration of 10 wt% which is also common for industrial sized fibres. Furthermore, for the dip-coated S1A a sizing dispersion with a concentration of ~2.6 wt% was prepared. This was accomplished by diluting the sizing concentration and solid content by a factor of 10. The purpose of this step was to evaluate the impact of the dip coating solution concentration on the LOI% of sized fibres. The homopolymer polypropylene (HPP) used for the microbond testing was PETOPLN EH102 and the maleic anhydride modified polypropylene (MPP) used was Polybond® 3200.

2.2. Methods

Thermal gravimetric analysis (TGA) was used to determine the Loss on Ignition of the sizing coated on to glass fibres. TGA temperature scans with a heating rate of 10 °C/min were performed using a TA Instruments Q50 TGA. The weight loss of the sized glass fibres was recorded as a function of the temperature under the air atmosphere. The LoI value was taken as the sample weight loss recorded at 500 °C. A platinum TGA pan was used for the dedicated TGA analysis. The fibre samples of around 5-15 mg were carefully positioned in the pan with fibres covering the entire surface area, ensuring good contact between fibres and pan. The structure and morphology of sized glass fibre bundles were examined using Scanning Electron Microscopy (SEM). The analysis was conducted using a Hitachi TM3000 scanning electron microscope with an accelerating voltage of 15.0 kV. All SEM samples were sputter gold coated under Argon atmosphere with an operating pressure of 0.08 mbar, 30 mA current, and a 40 s coating time. Glass fibre to polymer apparent interfacial shear strength (IFSS) was determined using the microbond test [13,14]. Sample preparation for the microbond testing was carried out following the procedure described by Nagel et al. [14]. The samples were processed at 220 °C for HPP and 200 °C for MPP for 2 h in a vacuum oven under nitrogen flow and then cooled to ambient temperature still under nitrogen flow for about 4-5 h. The droplets were examined under a Leitz Ergolux microscope (200x) and only axisymmetric droplets were chosen for the test. The fibre diameter, length of the droplet (embedded length) and droplet diameter were measured using the image processing software package ImageJ. A total of thirty samples were prepared for each batch and were subjected to microbond test using an Instron 3342 universal tensile testing machine at a rate of 0.1 mm/min using a 10 N load cell. The apparent interfacial shear strength was calculated using the standard equation.

3. Results and Discussion

Figure 1 compares typical TGA curves obtained from fibres dip coated at 10% and 1% solids compared to the industrially manufactured reference sample. Average LoI values for these three samples were 11.2%, 2.3% and 0.8% respectively. These values emphasise the comments in the Introduction that dip coating glass fibre bundles with sizings containing a normal (for commercial glass fibre production) solids content produced unacceptably high LoI values. Moreover, even by diluting the sizing solids concentration by a factor of 10 it was still not possible to reach the lower LoI levels which are typical of industrial sized fibres. Of course further reduction of the sizing solids content could eventually bring the dip coated samples LoI into an acceptable (<1%) LoI range. However, it is extremely questionable as to whether the use of such dilute sizing solutions would in any way result in a sample which is representative of an industrially manufactured sample using the same sizing ingredients. In other words, dip coating does not appear to be a useful technique to screen sizing formulations or to carry out more fundamental studies of the influence of sizing formulation on fibre-polymer adhesion.

Table 1 summarises the TGA obtained LoI values for the glass fibre sample laboratory coated with a 10% solids sizing at different process intensities along with values for the dip coated fibres and the industrially sized fibres. The laboratory coated fibres exhibit a much lower LoI compared with the dip coated fibres, and the LoI approaches that of the industry-sized fibres when the process intensity is increased. A value for the average sizing layer thickness was calculated using the LoI values, an average fibre diameter of 17 µm, and assuming a uniform sizing (density = 1 g/cc) layer distribution around the fibres. It can be seen that the developed laboratory coating technique is quite capable of producing glass fibre samples with an LoI in the same range as industrially coated fibres.

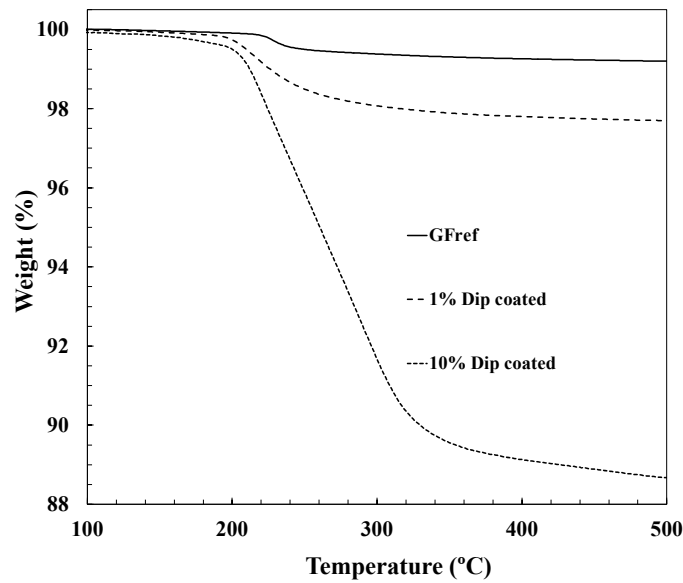


Figure 1. TGA results for dip-coated and reference glass fibres.

Table 1. Sized glass fibre LoI and calculated average size layer thickness.

Specimen type	Process intensity	LoI (%)				Size layer average thickness (nm)
		1	2	3	Average	
Dip coated	-	11.3	12	10.5	11.2	1280
S1A coated	0	6.5	6.2	5.8	6.1	685
S1A coated	0.5	4.9	4.9	6.8	5.5	618
S1A coated	1	3.8	3.5	2.9	3.4	376
S1A coated	2	2.2	3.4	2.6	2.7	302
S1A coated	5	1.5	1.4	1.4	1.4	156
S1A coated	8	1.1	1.1	1.2	1.15	125
S1A coated	10	1	1.2	1	1.0	116
GFref	-	0.9	0.8	0.7	0.8	86

Figure 2 presents typical results for weight loss (TGA) and differential weight loss (DTG) of these fibre samples. It is clear that there are major differences in the TGA results depending on the sizing technique and the laboratory coating process intensity. Given that E-glass is thermally stable in this temperature region, it is reasonable to assume that the weight changes are caused primarily by the degradation of the organic materials in the fibre sizing layer. Upon examining the TGA and DTG graphs, a distinct change in the curves becomes evident beyond a process intensity value of 0.5. It can be seen in Figure 2a that the main weight loss is observed in the temperature range of 200–350 °C. However, for process intensities higher than 0.5 the width of the degradation temperature range appears to be smaller. This can be seen more clearly in the DTG curves (Figure 2b) which appear to exhibit two overlapping thermal degradation events, a “low temperature” event peaking around 220-230 °C and a “high temperature” event peaking around 280-300 °C. It appears that once the coating process intensity exceeds 0.5 the sizing component responsible for the high temperature degradation event is reduced and eventually removed. Unfortunately, the lack of available information regarding the exact formulation of the commercial film former emulsions precludes any detailed discussion of what component may be preferentially lost during the higher speed spin coating.

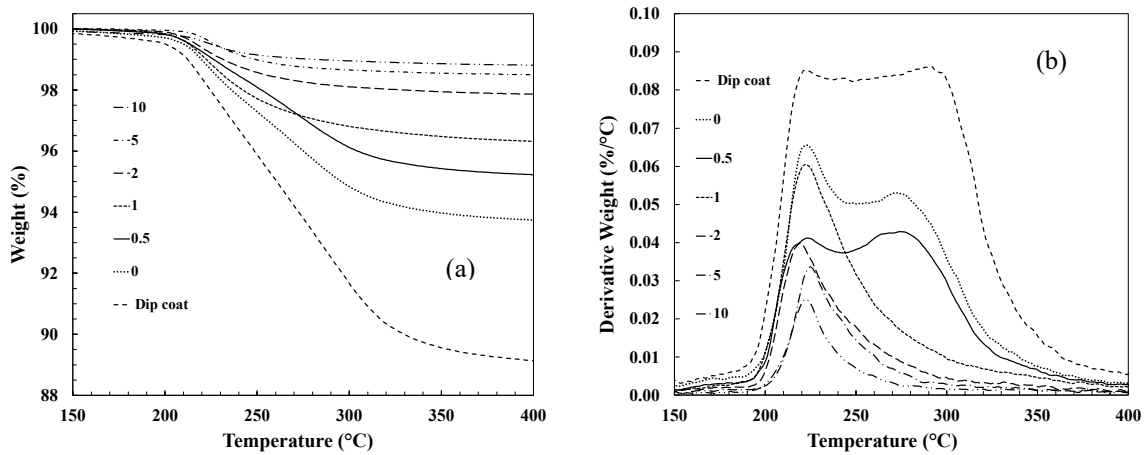


Figure 2. TGA and DTG results for S1A glass fibres coated at different process intensities.

Figure 3 compares TGA and DTG results for both the reference fibre GFref and S1A-10, bare fibre coated with size S1A using a process intensity value of 10. Both these fibre samples exhibit a single major weight loss event in the temperature range 200–300 °C, and the graphs follow a very similar pattern. The peak in the differential mass change data occurs at 225 °C, signifying the maximum rate of weight change. Thomason et al investigated the thermal degradation in air of the sizings on a range of industrial coated PP compatible glass fibre products. They reported that the majority of the weight loss between 200-300 °C which appeared to be due to degradation of the MPP film former and the aminosilane coupling agent [15]. Given that the exact formulation of the sizing on GFref is unknown and that the exact composition of the film former emulsions used in this work are also unknown due to industrial confidentiality, then the similarity in these results is notable. Thomason published a review of industrial sizing formulation patents and also noted that the same two main constituents of PP compatible sizings from different fibre manufacturers does consistently appear to be MPP and APS [4].

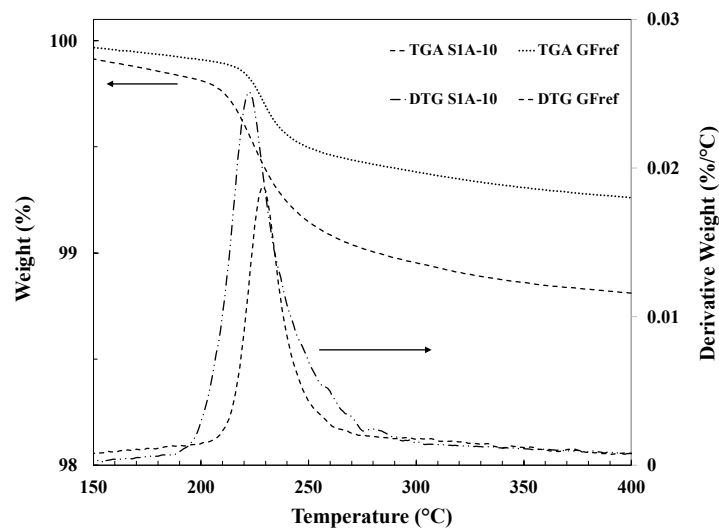


Figure 3. TGA and DTG results for GFref and S1A-10 glass fibres.

Figure 4 presents SEM images of the sized glass fibre bundles where the effects on the sizing structure on the fibre surface of the different coating methods are compared. In Figure 4a, the 10% dip-coated fibre bundle is heavily covered with sizing, rendering the fibres poorly visible as they are fully coated with a high thickness of size. More fibres are visible in the 1% dip-coated bundle in Figure 4b, which is

clearly related to the lower thickness of the size deposit. However, there is still a thick sizing coverage visible on some parts of the bundle. The micrographs in Figures 4c and 4d show that the S1A-10 lab-coated and GFref fibre bundles exhibit a similar sizing distribution pattern, with less sizing coverage in the bundle and little sign of any thick areas of sizing connecting the individual fibres.

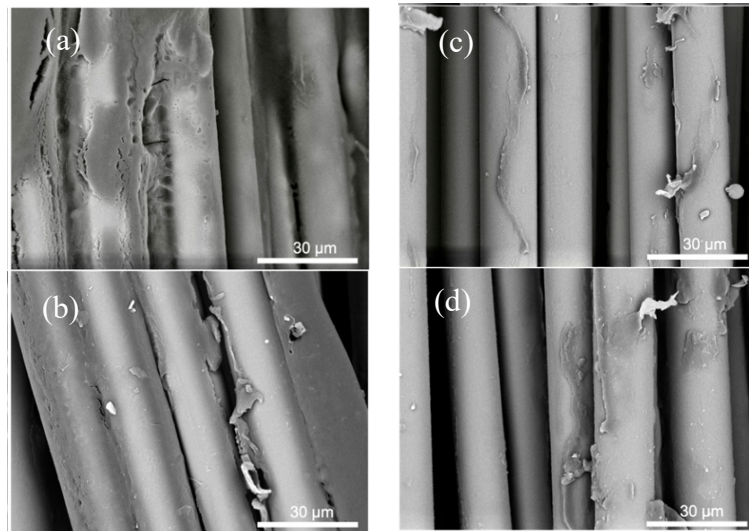


Figure 4. SEM micrographs of glass fibre bundles.

Figure 5 compares the microbond determined IFSS values for three glass fibre samples (GFref, 10% and 1% dip-coated, and S1A-10 lab-coated at process intensity 10) embedded in either HPP or MPP. It can be observed that generally the dip coated average IFSS values are lower than those of the commercial reference sample whereas the lab coated samples have higher average IFSS. However, when analysing the IFSS results of the PP matrix systems statistically, it was noted that lab-coated S1A-10 displayed a significantly (at 95% confidence level) higher IFSS compared to dip-coated fibres. No significant differences were observed between the other fibre-polymer systems.

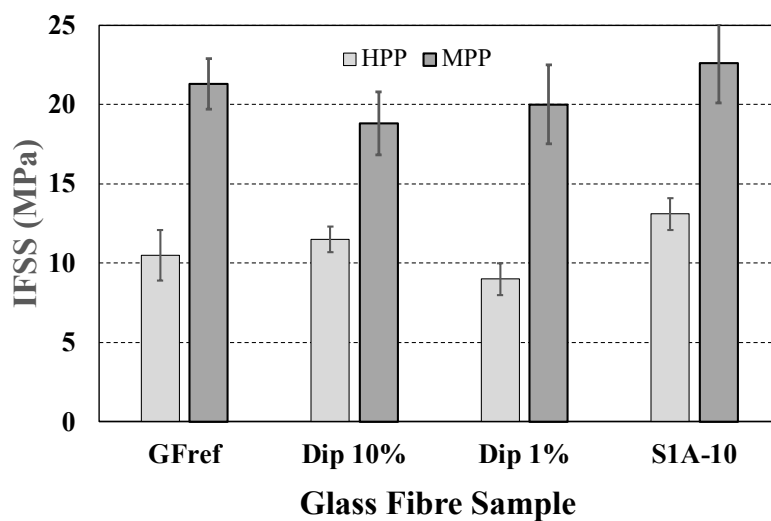


Figure 5. Microbond test results for glass fibres in two polypropylene matrices.

3. Conclusions

This study has demonstrated the feasibility of preparing small samples, suitable for micro-mechanical adhesion measurements, of sized glass fibre using a novel laboratory-based coating method. The resulting sized fibres exhibited a similar LoI and size layer thickness compared to industrially produced fibres. Moreover, this method offered the advantage of simple control of the glass fibre sample LoI in order to enable exploration of the effects of different sizing variations and thicknesses. Compared to the commonly employed dip-coating method this new laboratory scale method shows promise as it eliminates the need to alter the concentration of the sizing formulations to unreasonable levels to obtain normal LoI values. In contrast to dip-coated fibres the TGA fingerprint of the thermal degradation profile of the lab-coated sizing layer was very comparable with that of industrially produced fibres.

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