



Review

Glass fibre sizing: A review

J.L. Thomason

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



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ABSTRACT

Glass fibre reinforcements form the backbone of a composites industry with a global annual production of more than 10 million tons of high performance, light-weight materials. Possibly the most critical component involved in the manufacture of glass fibres and their composites is the fibre sizing. Yet because of the intense level of secrecy surrounding size formulations there are very few people in the vast supply chain of composite materials suppliers, processors and end users who have more than a superficial understanding of glass fibre sizings. Given the importance of sizings to the continuing success and growth of the composites industry this paper reviews some of the most relevant articles from the widely dispersed literature available around glass fibre sizings. The review covers size formulation, sizing effects in fibre and composite processing, sizing and fibre performance, sizing and interphase adhesion, and sizing effects on composite performance. The conclusions highlight the fragmented nature of the knowledge base on sizings and the lack of reliable and reproducible reference materials on which to build real progress in this critical technology.

1. Introduction

Glass fibre has been particularly successful as the reinforcement of choice in the rapidly expanding fibre reinforced polymer composites market. 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. Possibly the most critical component involved in the manufacture of glass-fibres and their composites is the fibre size [1,2]. Size is a thin surface coating of mainly organic materials applied to nearly all types of man-made fibres during their manufacture. Sizing is the process of coating fibres with a size. Nevertheless, many authors use the word sizing in place of the word size which can often save confusion in the term “fibre size” not relating to the “fibre dimension”. In this review the words “size” and “sizing” will often be used interchangeably. In the case of glass fibres, sizing is probably the key component influencing the 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. Glass-fibre could not be manufactured in a high volume cost-effective manner without the correct sizing formulations, applied in the appropriate manner. 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.

Glass fibre formation involves a combination of extrusion and attenuation of molten glass as shown schematically in Fig. 1. The glass melt flows under gravity from a melting furnace via the forehearth to an array of bushings made of a platinum/rhodium alloy [3]. These bushings contain a geometric array of tipped orifices from 200 to as many as 8000. Bushing plates are heated electrically, and their temperature is precisely controlled to maintain a constant glass viscosity. The molten glass drops from the bushing tips and is rapidly attenuated into fine fibres. A fine mist of water is sprayed onto the filaments just below the bushing. This water spray is often mistaken as the primary cooling of the fibre forming process, and although the sprays do contribute to the fibre cooling, most of the heat is lost from the fibres by convection. Size is applied to freshly pulled glass fibres using a sizing applicator normally positioned approximately 1–2 m below the bushing plate. A typical recirculating sizing applicator is shown in Fig. 2 [2] and consists of a roller which sits with its lower portion in a size reservoir which is constantly recirculated, and often cooled to counteract the heating effect of the radiation from the bushing. The roller rotates at a fixed rate and picks up a layer of the size on its surface; the thickness of the layer is proportion to the rotation speed. The fibre fan comes in contact with this surface size layer and picks up a coating as it travels across a short contact distance of the roller (approximately 5–10 mm which can be seen as a dark rectangle on the fibres in Fig. 2). The amount of size

E-mail address: james.thomason@strath.ac.uk.<https://doi.org/10.1016/j.compositesa.2019.105619>

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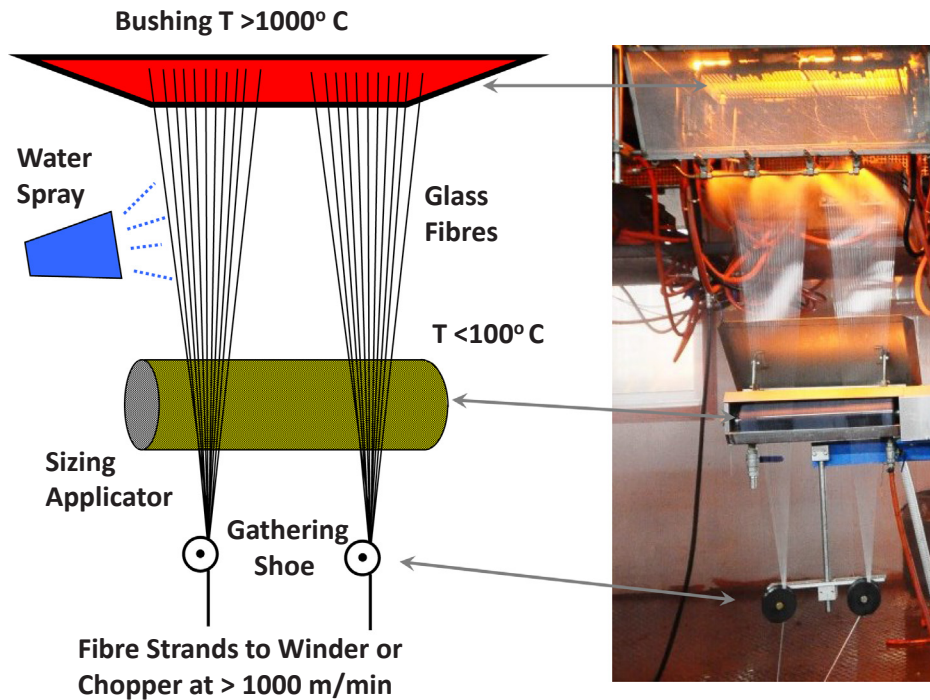


Fig. 1. Schematic and picture of a glass fibre forming position.



Fig. 2. Close up picture of a sizing applicator in glass fibre production.

picked up by the fibres is related to the thickness of the size layer on the roller. The sized fibres are then brought together to form a multi-filament strand at a gathering shoe and pass further on to a pulling device, normally a high speed winder or inline chopper.

Despite the importance of glass fibre sizes to all virtually aspects of the processing and performance of glass reinforced polymer (GRP) composites, 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. Typically the reader 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 exact chemical formulae. The primary components are the film former and the coupling agent [1–3]. 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 when in contact with resin, ensuring wetout of all the filaments. The coupling agent, almost always an alkoxy silane compound, is often said to serve primarily to bond the fibre to the matrix resin. Beyond these two major components, sizes also may include additional lubricating agents, antistatic agents and surfactants [1–3]. A complex size formulation may contain ten or more components. The interaction of these components with each other, with the fibre surface, with the matrix resin, and within a particular processing environment is extremely complex and quite inadequately researched. Given the importance of sizings to the continuing success and growth of the composites industry this work reviews some of the most relevant articles from the widely dispersed literature which is openly available around glass fibre sizings. The review is divided into sections on the formulation of glass fibre sizes, sizing in fibre and composite processing, sizing and fibre performance, sizing and interphase adhesion, and sizing and composite performance.

2. Glass fibre size formulation

Size formulations for reinforcement glass fibres will nearly always contain an organofunctional silane commonly referred to as a coupling agent [1–5]. However, these multifunctional molecules perform many roles other than just the simple fibre-matrix link that is implied by this name. Indeed, the non-coupling aspects of silanes on glass fibres are one of the areas where a much more fundamental understanding is needed in order to develop breakthrough performance composites. It is probably not an overstatement to say that organosilanes can be considered the most important class of chemicals used in the glass fibre, and consequently the composites, industry. Without these versatile molecules it is unlikely that the glass fibre reinforcement of polymers would be anywhere near as successful as it has become. One of the best-known properties of these multifunctional silane molecules is their apparent ability to promote adhesion. They have been reported to give improvements in interphase strength and hydrothermal resistance of the composite interphase [5,6]. Silane coupling agents have the general structure $[X-Si(OR)_3]$ where R is a methyl or ethyl group. When the

silane is used to treat fibres in an aqueous sizing it is first hydrolysed to a silanol. This unstable silanol can be condensed onto the fibres by the elimination of a water molecule to produce a siloxane network. Si–OH groups on the fibre surface may also participate in the process, with the result that the siloxane network becomes covalently bonded to the fibre surface. When the fibre is then used in the polymer matrix it is to reinforce, depending on the processing history and the state of any previous chemical interaction between the silane and other size components, the X groups of the silane may still be available to react with reactive functions of the polymer which can lead to a strong network bridging the fibre-polymer interphase. This interaction is intuitively accepted as being of a chemical nature when the matrix resin is thermosetting and consequently the X group on the silane has the opportunity to react with the matrix components. It is not quite so clear that chemical reactions play a major role when reinforcing high molecular weight thermoplastic polymer matrices [7–9].

Although there are very many different silane molecules available, the glass fibre industry appears to have focused its sizing products on the four silanes where the X group contains amino, epoxide, methacryloxy, or vinyl functionality [1,2,7]. Thomason's review of glass fibre sizing literature [1] showed that, of the papers reviewed, approximately 75% of them contained work on sizings containing the four silanes γ -aminopropyltriethoxysilane (APTES), γ -glycidoxypropyltrimethoxysilane (GPTMS), γ -methacryloxypropyltrimethoxysilane (MPTMS) and vinyltriethoxysilane (VTES). Of those four more than 40% of the papers contained work on aminosilane. It was suggested that it seems reasonable that this amount of research activity on APTES can be taken as an indication of its importance to the field of glass fibre sizings. In a similar exercise in a second book Thomason also analysed the usage of different silanes in the sizing formulations from the patents of the glass fibre manufacturers [2]. The results again confirmed the strong focus of sizing developers on just four basic silane types. In this case more than 90% of the size formulation patents analysed contained one of only three silanes, APTES, GPTMS, and MPTMS, with APTES by far the silane that appears most often in the size formulation patents of the major glass fibre manufacturers. APTES appears to be almost universally adopted as the coupling agent for thermoplastic compatible size; it is used as a secondary coupling agent in many polyester compatible sizes and is also being used in small amounts in some of the latest epoxy compatible sizes. MPTMS appears to be the principle coupling agent for polyester compatible sizes and GPTMS for epoxy and multicompatible sizes. Consequently, despite the enormous range of organosilane molecules which are available, the glass fibre manufacturing industry is highly dependent on the success of just three types of silane in their size formulations.

Silane coupling agents are also used widely outside of the field of fibre reinforced composite materials and consequently there is a large volume of literature available about the nature of the interaction between silanes and many different substrates. However, the application of silane containing sizing to glass fibres occurs under unique conditions which are difficult to replicate in the laboratory. Consequently, much of the available literature on the actions of silanes must be interpreted with great caution when considering silanes on glass fibres. For instance, those researchers without access to fibre forming and sizing application technology often use (polished) flat glass or "heat cleaned" glass fibres for the application of silanes or sizings in their studies. It is highly questionable whether such substrates offer appropriate and acceptable models for the highly dynamic, freshly created, surface of glass fibres to which sizing is applied within milliseconds of the fibre formation [4]. Furthermore, due to the wide availability of silanes but the lack of general knowledge of sizing formulations, many researchers have focussed on "silane only" studies on glass. Once again the extrapolation of the results of such studies to sizings on glass fibres is fraught with pitfalls, such as the questions of silane-sizing component interactions in sizing emulsions and dispersions, competitive adsorption of individual sizing components to the fibre surface, and the increased

complexity of the sizing-matrix interphase in the composite.

Film formers often make up the bulk (70–90%) of the material in a size formulation [1–3]. Film formers are chosen to be as closely compatible to the intended polymer matrix as possible and still fulfill all the other requirements of a sizing. Therefore the range of typical film former materials reflects the range of composite matrix materials. Commonly used film formers include polyvinyl acetates, polyurethanes, polyolefins, polyesters, epoxies and modified epoxies [1–3]. Emulsion-dispersion technology allows many of these high molecular weight and water insoluble materials to be applied to glass fibre surfaces. Unlike silane coupling agents, there is no *a priori* assumption that the film former, or any other size components, are chemically bound to the fibre surface. Thomason showed that hot acetone extraction removed up to 80% of the size on a range of "epoxy compatible" glass fibres [10]. It was assumed that a large fraction of these extracts must be film formers. Analysis of the extracts using elemental analysis, NMR, and Fourier-transform infrared spectroscopy (FTIR) confirmed the presence of epoxy resin, an ethoxylated compound, and a carbonyl containing compound. In terms of the film formers, Thomason's wide ranging analysis of the glass fibre manufacturers' patent literature indicates that epoxide is probably the most useful reactive group for size developers either directly as epoxy resin or in reaction with some other film forming molecules [2]. Epoxy resin appears to be used in all epoxy compatible sizes, in most multicompatible sizes, in many unsaturated polyester and vinyl ester sizes, and in certain thermoplastic compatible sizes (especially for PBT compatibility). PVA and its derivatives are commonly used in unsaturated polyester compatible sizes. Polyurethane appears to be the film former of choice for polyamide compatibility and acid modified polyolefins are found in most polypropylene compatible size formulations. Thomason's conclusions also highlighted the fact that many film formers require significant amounts of surfactants and other highly active compounds to enable the production of an emulsion or dispersion suitable for use in a size. Given that around 80% of the size solids is film former and 10–20% of that material can be emulsifier, it would appear that a significant proportion of the size solids on some glass products consists of these, frequently unknown or unnamed, processing aids. He observed that this is an area which is almost completely unexplored (by the wider composites community) and concluded that this probably merits some investigation in terms of its influence on mechanical and environmental performance of glass-reinforced composites. He also noted the high levels of "internal" cationic lubricants and "external" non-ionic lubricants present in commercial size formulations. These lubricants are essential processing aids for glass fibre and composite manufacturing. However, little systematic research has been published in terms of the influence of such lubricants on composite short- and long-term performance after they have performed their function in fibre and composite processing.

Petersen carried out a PhD research project on the analysis of glass fibre sizing with preliminary results reported in conference proceedings [11,12] and the full report in her thesis [13]. The sizings on two commercial glass fibre rovings were studied, direct roving 320 (multicompatible) from Jushi and SE1500 (epoxy compatible) from Owens Corning. The soluble and non-soluble sizing fractions were obtained from acetone extraction and loss on ignition (LOI) experiments. The soluble sizing fraction was further analysed by FTIR and TGA-MS. Similarly to previous researchers [10,14,15] it was found that between 75 and 90% of the sizing was extractable, with the Jushi size exhibiting slightly higher acetone solubility. It was not possible to distinguish unambiguously between the Jushi and the Owens Corning fibres with either FTIR or TGA-MS analysis. The observation of IR bands associated with DGEBA indicated that this epoxy resin is used as film former in both sizings. The FTIR analysis also indicated the presence of a polyethylene oxide lubricant and/or surfactant. Fibre samples were re-coated with GPTMS after acetone extraction of the original sizing. The GPTMS modified fibres displayed significant higher interfacial adhesion in comparison to the fibres with the original sizing. The authors

concluded from this that the original sizing is far from the optimal when it comes to facilitating a strong adhesion between glass fibre and matrix. This can be seen as evidence of the challenge for size developers in that they must satisfy multiple processing demands on glass fibre products as well as maximising composite performance. Guo et al. analysed the sizings on six commercial glass fibre rovings which included two unsaturated polyester and epoxy compatible; two unsaturated polyester and polyurethane compatible; and two which were multi-compatible [16]. Similar to the results of other researchers it was found that a large fraction of the sizing, in the range from 66% to 82% of the total sizing, was acetone extractable. The acetone soluble sizing fractions were characterized using NMR. The likely presence of unsaturated polyester resin was identified in all six sizing extracts. McGravey carried out his PhD research project with goal of fully characterising a common glass fibre size as well as determining the effect of the size composition on its performance [17]. Batches of vinyl acetate based film-formers were created via emulsion polymerisation from a formulation supplied by Celanese. These film-formers were then incorporated into a working glass fibre size formulation supplied by Saint Gobain Vetrotex. This contained silane, film former, lubricant, plasticizer and anti-static agent. Initial studies were undertaken to determine the location of the constituent species present in the size to produce an image of its structure. The film-former formulation was altered to produce a range of molecular weights and emulsion particle sizes. The performance of sizes produced from these film-formers was then investigated in the areas of clarity, film formation, wetting ability and strength. Alterations to the size formulation was undertaken to determine whether this produced any effect in the performance of the size over some of the same areas of investigation. Some of the main conclusions drawn from this wide-ranging, but little known, study are listed below:

- The coupling agent migrates to the glass-size interface during drying.
- A minor amount of lubricant migrates to the size-air interface during drying.
- The molecular weight of a film-former does not alter the size's ability to form a continuous film if dried under suitable conditions.
- The molecular weight and particle size of a film-former do not alter a sizes fibre wetting ability due to the large amount of water in size formulations.
- An excess of coupling agent is present in the standard size formulation.

Notwithstanding the critical importance of size formulations to the composites industry, the challenge of reviewing progress in this field is quite unique. 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 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 manufacturing 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 sizing developers, 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 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 meager amount of published information being of little help in the development of a slightly different size formulation or to assist in the reinforcement of a different polymer system. Consequently, while rapid and expanding progress is made in developing areas of materials science where

background information is more openly available, new size development is carried out by a very 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 knowledgeable peers in other companies. Hence size development actually takes place in an extraordinarily isolated environment in comparison to many other fields of materials science.

Another consequence of the highly fragmented knowledge-base on glass fibre sizes is the challenge in attempting to review the state of understanding of this important subject and evaluating whether progress is being made. A reflection of this point is the fact that it was not until recently that any major review of the available scientific literature on sizes for glass fibres had been published. In 2012 Thomason published a short book which was probably the first such review [1]. In the introduction the author highlighted a number of issues related to the secrecy surrounding sizing formulations. He summarized the problem by paraphrasing a well-known expression "never in the field of material science has so much of the success of so many applications depended on the knowledge of so few". In 2015 Thomason published a second book which reviewed the only source of openly available information on commercial size formulations, the patents of the glass fibre manufacturers [2]. This book presented the results of an analysis of more than 500 examples of patented size formulations, many of which are probably still in use in commercial glass fibre production. These were considered as forming the bulk of the patents which covered size formulations for glass fibre products for structural and semi-structural glass reinforced polymer composite applications. These included processes such as sheet moulding compounding (SMC), bulk moulding compounding (BMC), panel and gun roving, long and short fibre thermoplastic moulding compounds, pultrusion, filament winding, and woven products for resin transfer processing. Size compatibilities analysed included epoxy, polyester, vinyl ester, polyamide, polypropylene, thermoplastic polyester and other engineering polymers. The analysis of sizes is presented in such a way that formulations can easily be compared across a manufacturer's product range and also compared between different manufacturers. Thomason's book also includes a chapter discussing how patents and their associated information can be used to gain insight into which size formulations may actually be in use in glass fibre production. These two books form a unique source of information and insight into glass fibre sizings for materials scientists and developers who remain outside the glass fibre manufacturing companies' wall of secrecy. Thomason defined the principle roles of a glass fibre size, in order of importance as:

- Enabling the cost effective and efficient manufacturing of glass fibre products
- Enabling the cost effective and efficient manufacturing of composite products
- Enabling an optimized level of adhesion at the fibre-matrix interface
- Enabling optimized short and long term performance of said composite products

From even a cursory review of the available literature it would be easy to form the impression that these points are stated in the reverse order of importance given the associated volume of published research on these topics. However, the reality is that composite performance is unimportant if you are unable to manufacture the composites (cost effectively) and research and development of the manufacturing of glass fibre composites is unimportant if you are unable to manufacture the required glass fibres (cost effectively). The remainder of this review covers the relevant literature on glass fibre size and size formulations, where individual references have been loosely grouped in these four categories listed above. In order to increase the relevance of the referenced literature this review focuses principally on research papers

where the authors had access to glass fibre production and sizing technology or at least had some relevant assistance from glass fibre manufacturers in the sample preparation.

3. Sizing in fibre and composite processing

In a review of size formulation patents Thomason [2] identified that there are a number of sizing related issues with the standard glass fibre manufacturing process that have been a continued area of focus in size development. Four of these issues are

- The elimination of volatile organic compounds
- The size sling-off issue
- The migration issue
- The inline-offline chopping issue

Many size development patents have either been directly focussed on addressing these issues or at least claim to make improvements to these manufacturing related issues. From a size viewpoint most of these issues find their source in the technical and economic necessities that result in the majority of sizes currently in use being aqueous sizes, which are easy to handle but which have to be deposited on the filaments in large quantities in order to be effective. These sizes comprise a substantial amount of water (of the order of 85–95% by weight of the size) which generally results in a low viscosity “oil-in-water” emulsion which leads to glass fibre strands containing between approximately 6 to 14% by weight of water after size application. This necessitates the use of organic solvent and surfactants to emulsify certain film-forming components and also necessitates drying the glass fibre strands before they can be used as composite reinforcements. This combination of about 5–15% sizing solids with the ability of the glass strand to retain about 10% liquid sizing results in the commonly accepted range of LOI of about 0.5% to 1.5% found in most commercial glass fibre products. The two main reinforcement product forms of glass fibre manufacturing, rovings and chopped strands, involve either winding or chopping (and sometimes both) [2,3]. There are significant differences in the role of sizings in the production of continuous and chopped fibre products. Similarly the processing of these two forms of reinforcement into composites usually involves very different processing techniques which also place unique demands on the sizing. With continuous fibre products it is essential to minimise the level of fibre damage which will directly or indirectly result in broken fibres. Even a single broken fibre in a continuous production process can rapidly result in a “fuzz” build-up on equipment which can lead to an exponentially increasing number of broken fibres and result in process interruption. Consequently the lubricity and surface coverage of the sizing is critical. Drying and curing of wound glass fibre packages in hot air ovens is normally a relatively slow (12–24 h) low temperature process (100–120 °C). Once dried the fibre strand should maintain the strand integrity through the, normally continuous, transport process to the polymer impregnation stage, which is often a relatively low shear process, at which point a rapid dissolution of sizing and opening of the fibre strand to encourage excellent individual filament wet-out is desired.

Thomason [2] discussed the issue of sizing migration during drying in detail and reviewed the sizing formulation adjustments which producers have used to mitigate the problem. Migration occurs during the oven drying of wet wound roving packages. The heat from the ovens causes the moisture from the size to be driven outwardly through the package. When this occurs, some of the other size ingredients are carried along with the evaporating moisture and are deposited on the outer surfaces of the forming package. A comparison of these migration effects encountered with different sizes may be obtained by comparing the ratio of the outside LOI values with respect to the nominal LOI values within the wound package. These “migration ratios” for aqueous sizes can range in value from about four to six. In many cases the migration problem has been reluctantly lived with. Normally, the outer

wraps of a forming package are stripped away in order to partially solve the problem of uneven size concentrations on the glass strands. However, the stripping operation is costly and it also creates a waste problem. Furthermore, stripping only partially solves the problem of trying to obtain uniformly sized glass strands. The problem that still persists is at the outer faces of a roving package at the turn-around points which cannot be removed by stripping the outer wraps from the package. The deposit of size ingredients on the outer surfaces of the package may also cause discoloration, which is aesthetically unappealing. An application where the migration issue can literally appear is when such glass strands are used to produce woven products. Harinath et al. [18] stressed that sizing migration and sling-off are still an issue in glass fibre rovings currently used in the production of fabrics for wind turbine applications. The significant increase in the sizing content of the outer layers of roving packages can lead to optical effects in the appearance of fabrics produced from these rovings which show up as white lines due to Moire effect. They stated that, despite the importance of sizing, little is understood about the effect of sizing migration behaviour on the mechanical properties of glass fibre composites.

With direct chopped products the continuous sized fibres are chopped within milliseconds of the sizing application [4]. The high speed chopping process can result in significant damage to the fibres, cutting of glass fibres occurs in a “damage zone” and this causes significant loss of fibre length. Average fibre length in a chopped glass fibre bundle can be reduced by up to 33% of the nominal chop length taken from the spacing of the blades on the chopping head [19]. Protection against such chopping damage and maintaining average fibre length as much as possible is a key task of the sizing in its first second after application. The wet chopped glass fibres bundles are then normally dried in a continuous process which may involve significant mechanical agitation and quite high temperatures (> 200 °C) for a short period of time – all of which has important ramifications for the design of the sizing and its chemical and physical nature as it proceeds to the composite manufacturing stage. Here, transportation and dosing of the chopped glass bundles also normally involves significant mechanical handling, and the integrity of the glass fibre bundle is a key sizing-controlled characteristic where the early breakup of the multi-filament bundles can cause serious housekeeping issues for the processor. Finally the fibres meet the polymer matrix, commonly in a high shear environment, such as twin screw extrusion with molten thermoplastic polymer, where only the tightly bound portion of the sizing is likely to remain on the fibre surface and hence at the composite fibre–matrix interface. It is also worth noting that in older chopped fibre production processes the fibres are first wound in continuous packages and then unwound into choppers, generating a further challenge for size design where aspects of both the continuous winding and chopping processes have to be addressed.

In a patent application Vickerey et al. presented an extensive discussion of the offline (older) and inline (newer) processes for the production of chopped glass strands [20]. It was stated that chopping (and drying) the glass fibres inline lowers the manufacturing costs for products produced from the sized fibre bundles. It is further claimed that, since fibres can be chopped and dried at a much faster rate with the inventive size composition described compared to conventional offline chopping processes, manufacturing productivity is increased. Campbell has also reported on the effects on composite properties of moving from a two-step winding/drying and offline chopping process to a single inline process which involves simultaneous pulling/attenuation and chopping of wet sized fibres [21]. The high throughput, inline process, results in significant degradation of the resultant chopped glass fibre product’s performance in various matrices. The paper describes how the drop in performance has been balanced out by an increase in the efficiency of the sizing developed for use on the new process. Thomason and Kalinka reported on a novel method for measuring single fibre tensile strength (SFTS) at gauge length lengths as short as 180 µm. This enabled them to make direct measurement of the strength of short

fibres taken from nominal 4 mm chopped glass bundles [19]. Their data indicated that the values of average fibre strength in these products are significantly below the pristine glass strength value and that bundles from the inline chopping processes contained much weaker fibres than bundles from the offline chopping process with the same sizing. This is indicative of a higher level of fibre damage occurring during the inline chopping process. The inline chopped fibres also resulted in composites with significantly lower levels of mechanical performance. These results underline the importance of sizing development to the glass fibre manufacturing process and not just to the end performance of the final composite.

Wang et al. [22,23] reported on an industrial style sizing study of the development of a polypropylene compatible sizing for chopped glass fibres (Taishan Fibreglass). This pair of papers presents a typical design of experiment approach to a sizing based on a mixture of aminosilane, polypropylene (PP) and polyurethane (PU) film formers, a cationic amine salt lubricant and polyethylene glycol. The authors report how small variations in the sizing formulation affect the processing parameters of the chopped glass product such as the level of broken filaments during the fibre drawing and the amount of fibre damage during the chopping process. These parameters are balanced against the performance of injection moulded GF-PP composites such as the mechanical properties and the colour. The authors showed how the investigation of all these parameters related to the changes in the sizing which finally resulted in an optimized sizing formulation. Understanding the mechanisms contributing to the initial stage of dispersion for individual fibres from chopped bundles of sized fibres is important for optimizing process conditions and obtaining fibre composites with optimal properties. Kuroda and Scott [24] studied the initial dispersion mechanisms of chopped glass fibre bundles in a polystyrene matrix. The 4 mm long chopped bundles (408A-14C from Owens Corning) contained approximately 500 fibres, with 0.52% wt. sizing which included a "general compatibilizer". Their studies showed that under model flow conditions, bundles have two separation modes, rupture and erosion. Palmese et al. [25] reported on the effect of glass fibre sizing on the cure kinetics of vinyl ester resins. Four commercial Owens Corning S-2 glass rovings with different sizings were investigated. It was found that these fibre sizings significantly accelerate the cure of vinyl ester. A relationship between the surface energy characteristics of the fibres and the degree of cure acceleration was observed. This is in general agreement with the results of Lee and Han [26] who investigated the effects of silane-treated glass beads on the cure of polyester systems. They reported that sizing glass beads with MPTMS increased the reactivity of the glass bead-polyester system. Using the same sized S-2 fibres and vinyl ester resin systems Karbhari and Palmese also reported [27] on sizing related kinetic and flow considerations in the resin infusion of composites. They concluded that, composite behaviour is affected on a microscopic level by the formation of interphase regions that greatly affect the cure kinetics and hence the properties of the composite, which are dependent on the inter-constituent variations in local properties such as modulus and glass transition temperature (T_g). Their results also showed that fibre-sizing-resin interactions occurring during the infusion stage affected wet-out and local flow behaviour through the development of local stoichiometric imbalances.

Merhi et al. [28] investigated the correlation between the sizing formulation and the compressive behaviour of concentrated glass fibre bundle suspensions. Two glass-fibre sizing formulations on commercial glass fibre rovings were considered, one containing polyvinyl acetate (PVA) and the other containing a polyester/PVA mixture for use in SMC. An estimation of the fibre bundle bending rigidity was obtained from axial compression tests conducted on dry two-dimensional random suspensions where the forced packing was governed by the bending of fibre bundle segments between bundle-bundle contact points. This value was found to depend on the bundle sizing as well as on the interaction with solvents present in an SMC matrix. The authors stated that their results confirmed that sizing exerts a large influence on

the rheology of SMC and on the mechanical characteristics of the glass fibre rovings. Although glass fibre sizing is mainly applied using a single applicator roller positioned directly below the bushing, multiple sizing applications are also known, either through a dual roller applicator for continuous fibres or through a second sizing applicator by spraying during pelletization of chopped fibres [29,30]. Zhuang et al. [29] have reported on the application of PP compatible sizing using dual applicators. APTES coupling agent and a maleic anhydride grafted PP film (MAPP) former dispersion were applied at separate stages and with different sequences to a 204 filaments yarn. The surface properties of the sized glass fibres were studied using Atomic Force Microscopy (AFM), X-ray photoelectron spectroscopy (XPS), CAA and streaming potential (SP) analysis. Furthermore, the transverse tensile strengths of unidirectional GF-PP composites were determined. It was shown that the dual applicator produced sized yarns with lower LOI and resulted in poor fibre-matrix adhesion strength. However, applying the silane at the first sizing stage with an increased roller speed produced sized yarns with lower LOI but performance quite close to single roller sizing applicator strand.

Thomason and Adzima reviewed a number of the important parameters in the application of sizings and the use of experimental design in the formulation of commercial glass fibre sizings [4]. With regard to the process of sizing application, a simple model was developed to show that the degree of sizing pickup by a fibre bundle on the sizing applicator was dependent on parameters such as the line speed, the number of individual fibres in the bundle, and the sizing viscosity. They also showed that the wetting of freshly drawn fibres by the sizing could be strongly influenced by whether or not the fibres were dry at the point of sizing application. They pointed out that practical size development involves the design and optimization of a complex system, balancing a large number of independent variables with an even larger number of dependent variables. For this reason, many size development programmes involve experimental designs aimed at maximising the amount of information obtained on these many variables from a minimum number of lengthy and costly experiments. This was illustrated with the presentation of results from an experimental design involving a sizing consisting of a simple combination of APTES and a PU dispersion. The ratio of these two components was varied and by changing both the solids content of the sizing and the application conditions the final LOI of the products was also varied. The sizings were applied to a continuous strand containing 2000 E-glass fibres at an Owens Corning pilot facility. These fibres were chopped inline and dried inline to produce material, which was further extrusion compounded and injection moulded with polyamide-6,6 to produce composites for tensile and impact testing. Their data revealed that APTES is an important factor to composite performance and that there exists an optimum level of APTES on glass fibres for maximum composite tensile and impact strength.

Cheng et al. [31] also reported on the use of experimental design to optimise the sizing formulation applied to an E-glass fibre yarn. They used a Taguchi parameter design to obtain the optimal reduction in the number of broken filaments when processing an E-glass yarn used in a weaving process. The main variables studied were film former, lubricant, antistatic solution and emulsifier. Responses measured were fuzz levels and the frequency of rubbing resistance of each filament. The authors concluded that parameter design is an effective method for improving sizing quality. Nygard [32] used composite mechanical tests to evaluate the effects of glass fibre sizing on the quality of PP melt impregnation of two glass fibre rovings with different sizings. It was concluded that the most sensitive tests of impregnation quality were the prepreg transverse strength, compressive interlaminar double-notch shear strength and laminate transverse strength. Significant differences in the quality of fibre impregnation were observed in composites produced with the differently sized fibres. Brink and De Smet discussed the development of sizings from the materials supplier perspective [33]. They reflected on the primary roles of sizing being in fibre production,

fibre processing and then the performance of the composite interphase and emphasized the major challenge faced by sizing developers in balancing the conflicting impacts that different ingredients can have on these areas. The shelf life of a size formulation after mixing is an important parameter in the glass fibre manufacturing process. Eriksson-Scott [34] investigated the use of surfactants to stabilise trialkoxysilanes in water against self-condensation. The study compared the effects of system ageing on the films produced from by 16 different trialkoxysilane emulsions/mixtures and the respective films were evaluated by scanning electron microscopy (SEM), AFM, and electrochemical impedance spectroscopy. The reactions occurring in the emulsions were examined by following hydrolysis and condensation of silanes in water. The introduction of surfactants increased the usable time of the some trialkoxysilane emulsions to over three weeks.

4. Sizing effects on fibre performance

For high performance levels in glass fibre reinforced composites there at least three key functions that are influenced by application of sizings [1].

1. The need for a high stress transfer capability across the fibre-matrix interphase.
2. The need to maintain the highest potential level of fibre strength.
3. The need to protect the above two functions against physical, chemical, or environmental degradation.

These three functions are closely linked with the manner in which sizings interact with fibre surfaces and the manner in which this interaction combines with the protective element of the multifunctional sizings role to define the individual glass fibre strength in any particular glass and composite fibre product. The stress transfer capability of the interphase is presumed to be influenced by the ability of the silane to form bonds with the fibre surface, to enhance the wetting of the coated fibre by a liquid or molten resin, and to form links to the matrix. The glass-silane interaction this is often pictured as a condensation reaction with surface silanols and it could therefore be presumed that the bonding performance might be related to fibre surface concentration of silanols. However, silanes are known to interact with other metal oxides [5] which may also be present on the glass surface. In this respect it should be noted that there is substantial evidence in the literature that the surface composition of glass fibres can differ significantly from the bulk glass formulation [35–41]. This may complicate the use of screening results obtained on bulk glass in the development of new fibre products.

From the instant of drawing, glass fibres begin a downward spiral of declining fibre tensile strength as they first cool and then meet with both chemically and mechanically hostile environments. The reaction of the glass surface with water breaks strained Si–O–Si bonds and generates active Si–OH sites. Mechanical abrasion in the form of glass-to-glass abrasion and glass-to-production equipment contacts generates flaws. Then as the glass is dried and stored before use, water etching can increase the severity of flaws and further reduce tensile strength. Consequently, fibre strength retention may be strongly influenced by the speed and complexity with which a silane in a size can attach to the surface and form a siloxane network. Silanes are also thought to have a flaw healing ability, mitigating the usually negative effects on fibre strength of existing flaws on the fibre surface. To maintain the highest level of fibre strength sizings are designed to contribute to protection of the fibre surface against processing damage. Protection against the environmental degradation of these functions is particularly thought to be tied to reducing the ingress and action of moisture in the interphase region. Silanes have been shown to increase the hydrophobicity of surfaces although the polysiloxane networks formed by self-polymerising silanes can also contain large numbers of unreacted hydroxyl groups. The silane condensation reaction ($2\text{Si-OH} \rightarrow \text{Si-O-Si} + \text{H}_2\text{O}$)

is certainly reversible in the presence of water and the success of silanes in anti-corrosion applications may be due to the ability of these molecules to form three such bonds. These bonds would all have to be broken simultaneously for that molecule to be removed from the polysiloxane interphase network. Consequently, considerable effort has been expended on improving our understanding of glass fibre surfaces and the effects of silanes and sizing on the fibre performance, in particular on the fibre strength.

4.1. Fibre surface

Many researchers have reported that the composition of a glass fibre surface differs from that of the bulk glass formulation [35–41]. The surface compositions of E-glass fibres have been studied by Wong [35] using Auger Spectroscopy. He observed that the surface composition of E-glass fibres differed from that of the bulk glass. He reported that a typical E-glass fibre surface was low in magnesium, boron and calcium, but high in fluorine, silicon and aluminium, when compared to the bulk glass. Liu and her co-workers [36–41] have also examined the surfaces of water sized E-glass fibres using XPS. They found that aluminium tended to be enriched on E-glass fibre surface and calcium, on the other hand, was depleted relative to the bulk. Pantano et al. [42–44] have studied the surface OH concentration of glass and silica fibres and reported on the effect of boron concentration in E-glass fibres on OH surface concentration. Accessible OH surface concentrations in the range 0.5–1.4 OH/nm² were reported. The highest value was obtained with the boron-free formulation; addition of boron caused an approximate 50% reduction in the accessible surface OH concentration of these fibres. In another report Pantano et al. [45] discussed glass fibres with the nominal E-glass composition synthesized with 0, 2, 4, or 6% boron oxide. The influence of the boron oxide content on aminosilane adsorption was evaluated using XPS and SP measurements. The water adsorption capacity of the silane-treated fibres was measured using a gravimetric technique. In contrast to Liu's data reported above it was found that the presence of boron oxide enhanced the adsorption of aminosilane. However, it also greatly increased the water adsorption capacity of the silane-treated fibres. This effect of the boron oxide on water adsorption was considerably less evident in the untreated fibres. It was reported that the solubility of boron and aluminium appears to play a role in determining the chemical and physical structure of the silane layer.

Carré et al. [46] have also estimated the density of silanol groups at the surface of microscope slide glass using a contact angle measurement protocol. They measured the surface density of hydroxyl groups on microscope glass as 2.5 OH/nm². Liu et al. [41] used the same method to investigate the surface concentration of hydroxyl groups on the surface of E-glass. They determined a maximum in contact angle at a pH of 3 on polished E-glass slides in a fully hydrolysed state and after dehydroxylation for one hour at 600 °C under dry nitrogen gas. This value is in good agreement with other published values for bare E-glass obtained by Electrokinetic Analysis [47,48]. Using their values of contact angle they obtained 2.3 and 1.7 OH/nm² for their E-glass surfaces before and after heat treatment at 600 °C. Thomason [7] combined these results with molecular modelling of hydrolysed APTES molecules to show that the majority of silane molecules which react with an E-glass surface can only do so through formation of a single Si–O–Si bond. The implication of this result was that the vast majority of Si–O–Si bond formation in the silane interphase is due to silane polymerization. Thomason further showed [7] that if one aminosilane molecule reacts with each surface silanol on an E-glass fibre then a value for coverage of approximately 0.5 mg/m² of APTES is obtained. However, combining typical sizing silane concentrations with typical LOI values for glass reinforcement indicated the presence of between 4 and 12 mg/m² of aminosilane on the surface of glass reinforcements. This implies the presence of a more complex multi-layer silane interphase on the surface of commercial glass fibres.

4.2. Fibre tensile strength

Frey and Brunner highlighted the challenge for those without access to glass fibre bushing and sizing technology in developing and evaluating sizings [49]. They investigated resizing glass fibre by a dip coating process using glass fibres which had been “desized” by either solvent extraction or 600 °C thermal treatment. Although the chemical extraction process resulted in fibres which could be relatively easily resized and evaluated there always remains the uncertainty of the role of the non-extractable portion of the original sizing which confounds any analysis of the resizing materials. The only method to removal all of the organic sizing materials is by thermal methods. However, this seriously compromises the processability and performance [50,51] of the glass fibres rendering further investigation of the resized fibres virtually irrelevant. It is worth pointing out that thermal desizing only removes the organic parts of the sizing. Given the nature of the universally applied silane coupling agent it seems likely that the surface of thermally desized glass fibres will be silica rich due to the presence of thermal degraded silanes. Hence, thermally desized glass fibres are not only difficult to process and very weak; their surface is not an appropriate model for the interaction of sizings with freshly produced fibres under the bushing. Dibenedetto and Lex [52] evaluated the SFTS of silane-only sized E-glass fibres spun from a 2040 filament bushing. The silanes were applied as a solution of 5% silane and 5% water in 90% methanol. The fibres were immersed dip coated and then dried in a vacuum oven at 100 °C for 30 min. This was followed by two consecutive treatments of 1 h in boiling water and 30 min under vacuum at 100 °C. FTIR spectroscopy was used to detect any remaining silane on the glass surface after the boiling water treatment. In comparison to the unsized fibres all of the silane coatings were found to improve the tensile strength of E-glass filaments, especially at large gauge lengths.

Ahlstrom and Gerard [53] investigated the effect of various sizing materials applied to continuous unsized E-glass fibres on the SFTS. Different surface treatments were applied offline to unsized E-glass yarns (Owens Corning): APTES silane, and coated with two kinds of elastomers from MEK solution. The glass fibres were tested at six fixed gauge lengths from 3 to 80 mm at speed of 0.5 mm/min. The SFTS of the silane-treated glass fibres was higher than for the untreated fibres. This was attributed to the protection against water provided by the silane sizing. The elastomer-coated fibres exhibited the highest strength which was attributed to an improved protection and/or elimination of the weakest filaments in the strand during the treatment. Reilly and Thomason reported on an investigation of SFTS of water sized bare glass fibres (1200 tex E-glass supplied by Owens Corning) after sizing with different silanes and silane blends [54]. Fibre bundles were dip-coated in 1% aqueous silane solutions. SFTS was carried out at 20 mm gauge length and 0.3 mm/min. All silane coated fibres exhibited higher average tensile strength compared to the water sized fibres. However, none of the silane coated fibres recovered to the strength level of the reference fibres sized with APTES on a normal sizing applicator under the bushing.

Zinck et al. [55] reported on the use of mechanical characterization of glass fibres as an indirect analysis of the effect of surface treatment. The E-glass fibres investigated were taken from strands produced as water sized, APTES sized from a 1% wt. aqueous solution and two samples of differing fibre diameter and tex sized with a commercial P122 sizing. The coupling agent included in this P122 sizing formulation was also APTES at a concentration of 1% wt. along with other unspecified constituents such as a lubricant and a film former. SFTS was measured at 20 mm gauge length and 0.5 mm/min. It was stated that values of standard deviation became constant at a sample size greater than 40 tests. Results were analysed using a bimodal Weibull two parameter cumulative distribution function. The bimodal character was associated to surface and internal flaws, respectively. The APTES sized fibre had the highest average strength. Interestingly the two industrial sized samples exhibited lower average tensile strength than the water

sized fibres probably due to the extra mechanical roving process which these samples had undergone. The authors proposed a flaw healing hypothesis that sizing treatments mitigate surface defects, by diminishing separation as well as the severity of the defects. In a similar vein, Zinck et al. [56] used the same techniques to investigate the role of silane coupling agent and polymeric film former for tailoring glass fibre sizings from tensile strength measurements. E-glass fibres were produced and sized on a pilot bushing under industry-comparable processing conditions. A number of sizings including water, 0.3% aqueous APTES solution, and various silane plus film former combinations were investigated. SFTS was measured at 50 mm gauge length at a speed of 1 mm/min. The strengths of the differently sized fibres were characterized using a bimodal Weibull two parameter cumulative distribution function. The authors again interpreted their results as a sizing induced healing of surface flaws. The film former was shown to affect both the healing of initially occurring and the possibility of creating new defects. Furthermore a synergetic effect on fibre strength retention between the silane and the film former polymer was inferred from the data. In contrast Yang and Thomason studied the effect of an APTES sizing on the strength of boron free E-glass fibres. They compared the SFTS of water sized and APTES sized Advantex fibre (1200 tex supplied by Owens Corning) at five different gauge lengths [57]. They concluded that silane applied during glass fibre production results in significant fibre strength retention attributed more to a surface protection rather than a flaw healing mechanism. In the context of flaw healing Briard et al. [58] reported on a crack bridging mechanism for strengthening of flat glass. They used a microindenter to create controlled defects in the surface of soda-lime-silicate float glass plates. These were then treated with aqueous silane solutions and subjected to different drying regimes. Although single silane coatings had no effect on the strength of the indented glass, samples sized with GPTMS-APTES blends exhibited a significant increase in strength with improvements of up to 75% over the uncoated samples.

A series of papers has expanded on this hypothesis of fibre surface flaw healing by sizings and explored the use of nanoparticles in sizings to enhance the performance of alkali resistant (AR) glass and E-glass fibres. [59–62] Gao et al. [59] used over-coatings applied to sized AR-glass fibres to improve their alkali strength retention. AR-glass fibres (Nippon Electric Glass), with a sizing LOI of 0.6% wt., were further sized with styrene-butadiene based mixtures and characterized using SFTS, AFM, SP and FTIR. It was concluded that sizings and coatings on AR-glass significantly influence the tensile strength of alkali-resistant yarns, the adhesion strength with cementitious matrices and fracture energy of the composites. Gao et al. [60] also used a combination of AFM with nanoindentation, FTIR, TGA and SFTS to investigate the sizings on commercial AR-glass fibres before and after various environmental conditioning regimes. They concluded that their results showed that sizing significantly affects both the number and size of flaws on the fibre surface through a healing mechanism. They also correlated fibre tensile strength and surface roughness with Griffith fracture predictions. In another report Gao et al. [61] applied sizings containing multi-walled carbon nanotubes (MWCNTs) and/or nanoclays AR-glass and E-glass fibres. With low fractions of nanotubes (0.2% wt. in sizing), the strength of glass fibre increased by up to 70% over the unsized fibres (although no control values were reported for sized fibres without the nanotubes). A more extensive report on the same samples [62] gives more detail of the sizing formulations and the fibre production methods. The same average values of SFTS for the nanostructure sizing were reported (in the range 1.6–2.1 GPa). In this case the control values for the sized fibres (2.0 GPa) were available. Siddiqui et al. [63] reported on the tensile strength of E-glass fibres which had been coated offline with epoxy resin containing CNTs. Silane sized E-glass roving and single filaments (Hankuk Fibres) were coated continuously with a mixture of epoxy resin, curing agent and CNT (0.3–0.5% wt.). These were subsequently cured to form single fibre composites with a coating thickness of approximately 0.7 µm. These

coated single “fibres” were tested at four gauge lengths at a constant speed of 0.5 mm/min. Significant differences in average fibre strength were more apparent at the longer gauge lengths. In all cases the epoxy coating delivered higher average strengths than the silane only sized fibres. At 0.5% CNT concentration in the coating the average fibre strength was significantly lowered, at 0.3% CNT concentration the average strengths were slightly higher. This work was extended to a second type of CNT which exhibited somewhat higher level of coated fibre tensile strengths at higher CNT concentrations [64].

When considering the evidence for the “surface flaw healing” hypothesis of the effects of sizings on single fibre and strand tensile strength it is worth remembering that the final value obtained in the mechanical test is dependent on the full chemical, mechanical and environmental history of the sample. In particular the isolation of single fibres from multifilament sized fibre strands always involves a certain level of unquantified and variable mechanical handling whose effects will also vary with the degree and nature of the fibre coating. Any analysis which does not at least consider the possible consequences of these effects remains open to discussion [65]. Brown et al. [66] considered the effects of the fibre sizings on E-glass fibre bundle tensile strength in terms of flaw nucleation and growth from contact abrasion and hydrolytic degradation. E-glass fibre bundles consisting of 204 filaments sized with four commercial sizings were investigated. The sizings consisted of starch, starch and silane, starch and wax, and epoxy. Silane added to the starch chemistry was intended to protect the glass against hydrolytic damage. Wax added to the starch chemistry was proposed to reduce frictional fibre damage. Epoxy sizing was applied to enhance interfacial adhesion between the fibre bundle and an epoxy matrix. Bundle failure stress and Weibull parameters were measured at four humidity levels. The type of sizing on the glass fibres affected both the failure strength and the dependence on humidity level. The starch and silane sized bundles exhibited the highest levels of performance at all humidity levels. Gomez and Kilgour [67] compared the performance of aminosilane only sized E-glass fibres produced by offline coating of water sized glass fibres with inline coating of the same silanes on their 204 hole bushing. They showed that the design and development of silanes for use in sizing glass fibres is most realistically done by duplicating commercial sizing processes. Water sized glass fibres that were aged and then sized with a silane, contained a higher number of more severe surface flaws. In contrast, glass fibres that were sized with a silane during drawing have fewer and less severe surface flaws. In another report Gomez and Kilgour investigated a number of aminosilane-only sizings [68] for their ability to protect glass fibres from damage during production. Single fibres and fibre bundles were produced on a 204 holes glass fibre bushing from E-glass marbles, and coated online with five different aminosilanes. The SFTS of the glass fibres were found to be dependent on the chemical structure of the chosen silanes. The bonding to the glass surface and siloxane network formation increased as the number of alkoxy groups attached to silicon increased. In turn, this better protected the glass from the most severe surface flaws and increased the average strength of the fibres.

5. Sizing and interphase adhesion

Optimization of the stress transfer capability of the fibre-matrix interphase region is critical to achieving the required performance level in composite materials. The ability to transfer stress across the fibre-matrix interphase in composites is often reduced to a discussion of ‘adhesion’. This is a simple term to describe a combination of complex phenomena and there is still significant debate as to its definition and measurability. Due to its initial location on the fibre surface, sizing is a critical component in the formation and properties of the fibre-matrix interphase [4,69–71]. Much of the reported work in this area can be divided into two types of interphase related to the free and bound fractions of the sizing. One is caused by the inhomogeneous mixing of the free fraction of the sizing with the polymer matrix material. This

can result in a micrometre scale interphase with a continuously changing concentration of sizing-matrix mixture with distance from the fibre surface [10,72,73]. On a smaller scale is an interphase formed by the bound fraction of the sizing which remains as a defined nanoscale layer on the fibre surface which may or may not be mixed with other matrix components dependent on the particular composite system and processing conditions. The physical and chemical uniformity of the interphase region and its relation to the level of adhesion and consequent influence on the composite short and long term mechanical performance is a continuing region of focus for many researchers. The early history of the research and development of composite materials is dominated by the use of chemically reactive thermosetting polymers. A natural consequence of this is that much of the published work relating to adhesion and stress transfer at the fibre-matrix interphase has been grounded in the assumption that the formation of chemical bonds plays a key role. In the case of thermoplastic polymer matrices there is a substantially reduced level of chemical reaction present during composite processing. Consequently there may often be little potential for chemical bonds to develop across the interphase in these systems. Both of these aspects of sizing and interphase adhesion are explored in this section.

5.1. Silanes and interphase

It is often assumed that the silanes in glass fibre sizing condense and polymerize to form a crosslinked layer on the GF surface and that this layer persists in the composite as an interphase which may also contain some matrix components. A great deal of basic information on silanes can be obtained from Plueddemann’s book [5] and the proceedings of the “Silanes and other Coupling Agents” conference series [74–78]. There are a number of literature reviews on silanes and their role in composite materials [79–81]. Ishida [81] published a wide-ranging review of the early work on the molecular and microstructure of silane coupling agents and this is a useful reference in gaining further general insight into silane, and in particular aminosilane, gathered from a much broader perspective than just sizings on glass fibres. It is also worth noting that coupling agents based on titanates and zirconates have also been commercially developed [82], however they have seen very little application in commercial glass fibre sizings so far.

Shokoohi and Azar [83] studied the influence of silane only sizing coated onto heat cleaned chopped E-glass fibres from Cam Elyaf on the performance of injection moulded 30% fibre reinforced ABS. The silanization reaction was carried out with three different silanes, aminopropyltrimethoxysilane (APTMS), trichlorovinylsilane (TCVS) and GPTMS, for an excessively long time of 36 h at pH = 3.5 with a silane concentration 0.1% wt. of treated glass fibre. Unsurprisingly they found that untreated glass fibre had poor levels of composite performance and that application of silane improved composite properties (although notched impact performance was reduced in all cases). They stated that the TCVS gave the best performance of the three silanes studied. This was attributed to stronger fibre-matrix adhesion with this silane. Their analysis totally ignores the effects of the silanes and the 500 °C fibre heat treatment on the fibre strength and resultant reduced residual fibre length in their composites which is the likely explanation of the reduced notched impact observed with their treated fibres. Pantano et al. [45] reported on the influence on boron oxide content of E-glass fibres on their adsorption of aminosilane. Unsized glass fibres with the nominal E-glass composition were produced with 0, 2, 4, or 6% boron oxide by PPG Fibreglass using a single hole bushing. The fibres were treated offline in aminosilane solutions (1% by volume) prepared at pH 10 and pH 4. The influence of the boron oxide content on aminosilane adsorption was evaluated using XPS and SP measurements. It was reported that the solubility of boron and aluminium from the glass fibres appeared to play a role in determining the chemical and physical structure of the silane layer on these fibres. Metwalli et al. [84] reported on the surface properties and structure of mono-, di-, and tri-

aminosilane treated glass surfaces investigated using surface analytical techniques including XPS, Raman spectroscopy, AFM, and SP analysis. Glasses included two borosilicate formulations, soda-lime silicate, and synthetic fused silica. Silanization of the samples was performed by dip coating in 1% aqueous solutions of silane. Surface charge measurements indicated that aminosilanisation converts the glass surface from negative to positive potentials at neutral pH values. Higher positive streaming potential was observed for tri- compared with mono- and di-aminosilane treated glass surfaces. For all aminosilane treated glass samples, the high-resolution N 1s XPS spectra indicated a preferential orientation of the protonated amino-groups towards the glass surface whereas the free amino groups were protruding outward.

Norstrom [85] studied the effect of silane concentration on the offline deposition of various silanes onto unsized chopped E-glass fibres supplied by Ahlstrom Glassfibre. Aqueous solutions of three silanes were prepared in a range of concentrations. Both XPS and elemental analysis indicated that there were sizeable quantities of silane deposited on the surface of the E-glass fibres from the 1 and 2% silane solutions. The solution concentration, which gave the maximum amount deposited, was different for each silane tested. The same group has also reported [86] on the deposition of similar silanes from solution in ethanol onto the same fibres. Using Diffuse Reflectance Fourier Transform Infra-red (DRIFT) they showed how ureido silane deposition from ethanol results in the silane bonding in the OCH₃ down orientation, with the ureido amine functions free for reaction with the polymer matrix. Furthermore, treatment with a series of solvents having solubility parameters which matched that of the unhydrolysed silane monomer or that of the partially hydrolysed silane monomer could remove different fractions of the deposited silane and result in a certain amount of reorientation of the loosely bound physisorbed layers. XPS results were interpreted as indicating patchy silane coverage on the fibres surface. A number of other papers reporting silane deposition on the same fibres from different organic solvents are available [87–89]. Watson et al. [90] have also investigated the treatment of E-glass fibres with alternatives to the most commonly used silanes. Various authors have studied the wettability of various silane treated flat glass samples using contact angle methods and concluded that different silanes can dramatically change the wettability of glass surfaces [91,92]. Nishioka [93] used a wetting balance to investigate the interaction of organosilanes with glass fibres. Three monofunctional silanes were dip-coated multiple times onto heat cleaned E-glass fibre fabrics. The advancing and receding contact angles of different liquids on silane sized glass fibres were measured. The results indicated a gradual decrease in the polarity of the fibre surface with increasing levels of silane. A saturated surface resulted after ten coating treatments, yielding a surface whose hydrogen bond component to the work of adhesion against water was much lower than that obtained with conventional trifunctional silane treated fibre surfaces.

Kim et al. [94] examined the formation of an interphase in glass reinforced vinyl ester composites where the glass fibres had a silane only sizing. The E-glass fibres were supplied by Nitto Boseki Co. in the form of a plain-woven fabric. Two different coupling agents were used (MPTMS and GPTMS) in aqueous solutions at different concentrations acidified with acetic acid at pH 4.0. The interphase formed between these glass fibres and the polymer resin was characterized using nanoindentation and nanoscratch testing. The effective interphase thickness was measured between 0.8 and 1.5 μm depending on the type and concentration of silane agent. They observed that higher silane coupling agent concentrations resulted in a thicker interphase. Bikiaris et al. [95] reported on the use of silane coupling agent sizings in combination with modified polypropylene (PP) to influence the level of adhesion in glass fibre-PP composites. Chopped E-glass fibres from Cristaleria Espanola were heat cleaned and then coated with silane solutions (either APTMS or APTES) made in pure alcohol at 10% of the fibre weight. Unfortunately these conditions are not really similar in any way to practical glass fibre production. These fibres were used to

produce injection moulded GF-PP composites. The fibre coating was investigated using SEM and FTIR. Fibres coated with the APTMS were reported to give improved composite properties compared to those coated with the APTES. The authors interpreted their results only in terms of interfacial adhesion; they did not consider the potential effects of the fibre heat cleaning step on fibre-silane interaction, fibre strength or residual fibre length in their composites. Arora et al. [96] prepared a series of non-ionic and cationic aminohydroxysiloxanes deposited onto water sized E-glass fibres (ACI Fibreglass) from toluene and THF solution. They used DRIFT and XPS for qualitative and quantitative determination of these silane only sizings. They concluded that the non-ionic aminohydroxysiloxanes bind more effectively to the glass surface than their cationic counterparts. In their study of aminosilane only sizings on glass fibres Gomez and Kilgour [68] also tested for interfacial shear strength (IFSS) in epoxy resin. Altering the structure of the silanes increased the penetration and entanglement of the matrix with the polysiloxane interphase and thus increased the IFSS. In another report Gomez and Kilgour [67] compared the performance of aminosilane only sized glass fibres produced by offline coating of water sized glass fibres with inline coating of the same silanes on their 204 hole bushing. They showed that the design and development of silanes for use in sizing glass fibres is most realistically done by duplicating commercial sizing processes. Water sized glass fibres that were aged and then sized with a silane contained a higher number of more severe surface flaws. In contrast, glass fibres that were sized with a silane during drawing had fewer and less severe surface flaws.

Chiang et al. [97] studied the structure of APTES in aqueous solution and on heat cleaned E-glass fibres using FTIR spectroscopy. They concluded that APTES forms a multilayer on the E-glass fibre surfaces where the amino groups form intramolecular ring structures. They also suggested that the relative proportion of this structure of aminosilane probably determines the extent of interaction between this coupling agent and the resin matrix in composites. In a similar paper Naviroj et al. [98] also used FTIR to study the structure and adsorption characteristics of APTES on silica and E-glass fibres depending on pH in the range 2–12. Heat cleaned E-glass mats were dip-coated in the pH-adjusted, 1% by weight APTES solutions. They reported that the structure of the aminosilane layer on the E-glass was highly dependent on the pH of the treating solution with a maximum adsorption occurring around the natural pH 10–11. They also noted that the structure of aminosilane layer was affected by the presence of carbon dioxide when the pH range of the silane solution is between 6 and 12. Graf et al. [99] characterized MPTMS sized heat cleaned E-glass fibres using DRIFT. Quantitative information on the rates of silanol condensation and double bond reaction was derived from the results of these studies. Olmos et al. [100] studied the influence of silane only fibre sizings on the water absorption characteristics of glass reinforced epoxy composites. Commercial E-glass fibres were heat cleaned at 500 °C for 1 h, sized using 2% solutions of different aminosilanes, and then dried at 110 °C for 1 h. Three silanes were investigated providing difference in the silane silanol functionality while keeping the organic group constant. The presence of the silanized fibres appeared to induce changes in the water absorption process of the epoxy resin, decreasing the relative mass gain at equilibrium and suggesting that the glass fibre surface may induce a change in the structure of the epoxy matrix in comparison with this polymer without reinforcement. The relative amount of water absorbed by the interphase depended on the nature of the glass fibre silane sizing, with less water being absorbed the lower the functionality of the silane. Tiefenthaler and Urban [101] studied the thermal stability of a range of silane coupling agents applied to ceramic fibres using FTIR of fibres after heat treatment in air for 1 h at temperatures up to 550 °C. The thermal stability of the silane sizings were clearly shown to be dependent on the chemical structure of the silane. Shayed et al. have also recently studied the thermal stability of polysilazane coated glass fibres. They claimed that the fracture behaviour of glass fibre after heat treatment between 200 and 400 °C was changed due to the polysilazane coating [102].

Hamada et al. [103] reported on the effect of a silane interphase on interfacial strength in glass fibre epoxy composites. Heat cleaned E-glass fibres were dip-coated in sizings consisting of single and blended aminosilanes. Interfacial strength was determined using a modified single-filament test. The authors interpreted their results as showing that siloxane crosslinking of the silane interphase reduces the interfacial strength. Feresenbet et al. [104] reported on the influence of blended silane sizings on the fibre surface morphology and on glass fibre-epoxy resin interfacial shear strength. Unsized E-glass fibres (Owens Corning) were sized with solutions containing a mixture of hydrolyzed propyltrimethoxysilane (PTMS) and APTMS. AFM and ellipsometry results were used to show that the thickness of the deposited sizing films corresponded to multilayers. DRIFT analysis showed that the E-glass fibres were only partially covered at coupling agent solution concentrations lower than 45 mmol/L (approximately 1% by volume). Contact angle measurements showed an increase in the polarity of the fibre surface as the APTES component in the sizing mixture increased. Single fibre fragmentation measurements indicated that the IFSS increased as the composition of APTES increased in the sizing mixture. The authors stated that the type of silane and the composition of silane blend used in the sizing were shown to influence the adhesion between glass fibres and the epoxy matrix.

Despite the wide range of silane chemistries which have been reviewed in this section it is worth reiterating the point that the sizes used on the vast majority of reinforcement glass fibres contain one or more of just four basic silanes (APTES, GPTMS, MPTMS, VTMS) [1,2]. The organic groups on these four silanes are typical of those which might be considered for co-reacting with the range of thermosetting resins used in the composites industry. Furthermore, aminosilane versions form the largest proportion of silanes employed. Moreover, in the case of sizings for thermoplastic polymer reinforcement it is less clear that we are dealing primarily with chemical interactions. Interestingly, it has been noted that aminosilanes are used almost universally used in the formulation of thermoplastic compatible sizings [2]. Consequently any progress in the interphase region in thermoplastic composites will require an improved understanding of the role the ubiquitous aminosilane molecule.

5.2. Interphase in thermoset composites

Thomason [105,106] investigated the formation of a sizing rich interphase in glass fibre epoxy composites. He reported that the Dynamic Mechanical Analysis (DMA) loss modulus transition of the sizing on a large number of commercial glass fibre rovings ranged from $-30\text{ }^{\circ}\text{C}$ up to $65\text{ }^{\circ}\text{C}$ and that the amount of sizing not bound (acetone extractable) to the fibre surface ranged from 70% to 90% of the total sizing material. He reasoned that in a structural composite containing 80% wt. fibres, this means that the free sizing will be present at concentrations of up to 5% wt. if the sizing is homogeneously dissolved, and possibly exists in higher concentrations in an interphase around the fibre if it is not uniformly dispersed. To investigate the effect of the soluble part of the sizing on matrix properties, acetone extracted sizing from three different epoxy compatible fibres were mixed in different concentrations (up to 20% wt.) in an epoxy resin matrix formulation. After curing, the epoxy polymer glass transition temperature (T_g) determined by both Differential Scanning Calorimetry (DSC) and DMA was found to be reduced linearly by approximately $2.5\text{ }^{\circ}\text{C}$ per 1% added sizing extract from all three fibre extracts. Consequently, an interphase formed by localization of the sizing material around the fibres in a composite would be expected have a lower T_g than the bulk matrix. It was further reasoned the formation of a sizing-rich interphase would be governed by the thermodynamic and rheological properties of the coating materials and the cure kinetics of the epoxy matrix where the T_g of the sizing would clearly play a role. To test this hypothesis, composites were prepared with glass fibres whose size exhibited the highest DMA determined transition temperature ($54.2\text{ }^{\circ}\text{C}$) and an epoxy

resin system which could harden at room temperature. Two composites were prepared in an identical manner except for the initial processing temperature (either $23\text{ }^{\circ}\text{C}$ or $50\text{ }^{\circ}\text{C}$) followed by a stepwise increasing postcure up to $150\text{ }^{\circ}\text{C}$. DMA analysis of these two composites revealed that the composite initially processed at low temperatures exhibited a low temperature damping peak which was attributed to a sizing rich interphase formed around the fibres in that composite. This low temperature peak was absent in the composite initially processed at higher temperature to enhance the probability of homogeneous mixing of the sizing with the epoxy matrix. The presence of the sizing rich interphase was further confirmed in high magnification chemical images of the region around the fibres obtained by scanning SIMS. An interphase region approximately $1\text{ }\mu\text{m}$ thick was observed around the fibres in the initially low temperature processed composite.

Larson and Drzal [107] investigated the sizing-matrix interactions and the structure of the resulting interphase in a liquid composite moulding environment. A series of sized glass fibres consisting of incompatible and compatible sizings were studied in a reactive vinylester matrix system. Six sized E-glass fibres, provided by PPG Industries, had sizings which contain film formers, anti-static agents, silane coupling agents and other constituents typical of commercial sizings. Some general details of the chemical nature of these constituents were reported. Surface free energy analysis was conducted to characterize the fibre surfaces. Axial and transverse wicking rates were measured to quantify the change in total surface free energy of the fibre-matrix systems. It was concluded that the sizing surface free energy and its solubility in the matrix strongly affected the fibre-matrix interphase formation and consequently the fibre-matrix adhesion and composite shear and flexural strengths. Composites produced with fibres having soluble sizings developed an interphase which led to higher composite mechanical properties as long as the sizing did not lower the mechanical properties of the interphase below those of the matrix resin. Drown et al. [72] reported on an investigation of glass fibre sizings and their role in fibre-matrix adhesion in glass reinforced epoxy composites. They modelled the properties of the fibre-matrix interphase formed when the sizing interacts with the matrix during composite processing and fabrication by using blends of epoxy-compatible sizing with bulk matrix. E-glass tows supplied by PPG were used to manufacture GF-epoxy composites. The fibres were supplied with two sizings, water only and a commercial epoxy-compatible size. The glass fibre sizing was also supplied in bulk form and used to produce epoxy-sizing blended samples. DMA results showed that the addition of the commercial sizing caused a monotonic decrease of approximately $2.8\text{ }^{\circ}\text{C}$ per 1% added sizing extract in the T_g of the epoxy matrix. The sizing interaction with the matrix also produced a material with a higher modulus, a greater tensile strength, but a lower toughness. The composites containing the sized fibres exhibited significantly higher levels of interfacial adhesion and mechanical properties compared to those containing the unsized fibres. This study was extended by Al-Moussawi et al. [73] who investigated the potential properties of a sizing rich interphase by blending selected silanes and a sizing formulation, supplied by PPG Industries, with two stoichiometric matrices of amine-cured epoxies. The mechanical properties of the blends that could be expected to exist in a fibre-matrix interphase were shown to be substantially different from those of the bulk matrix properties. These model interphase materials had significantly lower T_g and tended to be stiffer and lower in fracture toughness than the bulk matrices.

Tanoglu et al. [14] reported on the properties of the polymeric interphase structure that remains at the fibre surface due to the glass fibre sizings in epoxy matrix composites. Epoxy compatible sized E-glass fibres were custom made for this work by Owens Corning. The sizing contained three components: DGEBA epoxy film former, triblock ethylene oxide and propylene oxide copolymer as surfactant, and GPTMS coupling agent. Using LOI and acetone extraction experiments it was determined that only 17.5% of the total 0.6% wt. sizing on these fibres was bound to the fibre and the other 82.5% was acetone

extractable. NMR analysis of the extracted sizing showed that it consisted of film former and surfactant only. The material bound to the fibre surface contained silane and surfactant but no film former. Model sizing systems were then reacted in the absence of a glass fibre surface and also subjected to acetone extraction. The non-extractable component was added, reacted in epoxy resin, and taken as a model for the interphase material in a composite. DSC and DMA were then used to characterize the T_g and flexural modulus of the model materials. The results showed that the T_g of the model interphase containing 40% wt. of the extracted sizing was reduced to about -5°C from a bulk matrix value of 155°C (which approximates to a loss in T_g of 4°C per 1% wt. sizing mixed with the matrix). The interphase flexural storage modulus at room temperature was about 50% of that of the bulk matrix. More details of these measurements were reported in a later paper from Jensen et al. [108]. The same authors also reported on a new technique to characterize the interphase properties in these composites under high strain rates [109]. They used a microindentation method based on the debonding of a fibre at displacement rates up to 3 mm/s that caused deformation of the interphase under high shear strain rates. Test results showed that the strength and energy-absorbing capability of the fibre-matrix interphase was sensitive to loading rate. This work was extended to include the influence on compatible and incompatible sizings and results were successfully correlated further with time-temperature superposition analysis of DMA results from the same composites [110].

Berg and Jones [111] investigated the role of sizing film formers, coupling agents and their blends on the formation of the interphase in glass fibre epoxy composites. The fibres used in this study were unsized E-glass fibre (Owens Corning) dip-coated with a variety of coatings based on APTES and epoxy resin sizing emulsions of low, medium and high molecular weights. A commercial epoxy sized fibre was also used as a control. XPS and SEM were used to estimate the thickness and uniformity of the sizing layer on these fibres. In an attempt to simulate possible properties of a sizing rich interphase region blends of two of the film former and matrix resin were produced. The addition of these film formers was shown to significantly change the modulus, strength and T_g of the matrix in some cases. IFSS was determined using single fibre fragmentation testing. Results showed that all sized fibres exhibited a lower interfacial strength than the unsized fibres. However, due to the high level of scatter in the results, there were no real significant differences apparent between the various sized fibres.

Gao et al. [112] also studied silane blends investigating the effects of mechanical interlocking and chemical bonding on the strength and energy absorption of the glass fibre-epoxy interphase. A series of tetraethoxysilane (TES)/GPTMS blended sizings were used to treat water-sized E-glass fibres (Advanced Glass Fibre Yarns) by dip coating. AFM and SEM analysis revealed that different sizings resulted in changes in fibre surface. The fibres sized with silane blends had significantly higher levels of surface roughness compared to the unsized and single silane sized fibres. However the IFSS measured using a microbond method did not show significant correlations with the surface roughness data. The authors stated that their results demonstrated that the creation of mechanical interlocking at the fibre-matrix interphase is a promising route to tailor the properties of composites. Chen et al. used APTES coated nano-silica particles to stabilise an emulsion of vinyl ester resin for use as a sizing film former [113]. The authors suggested that the normal chemical surfactant in film former emulsions may influence the interfacial adhesion and water resistance in composites and that nano-silica stabilized emulsions could reduce the use of such chemical surfactants. The study used E-glass fibre rovings from Taishan Glass Fibre with a sizing LOI of 0.5%. All of the nano-silica stabilized sizes were applied to unsized glass fibres (there is no indication of their source or whether they were "desized" fibres). The authors conclude that their sizings give large improvements over unsized glass. This is hardly surprising since applying any size to unsized glass will most probably lead to significant improvements. Perhaps more significantly, their nano-silica stabilized sizing offered little significant fibre or

composite performance improvement over their commercial glass fibre sample. More recently Dong et al. also studied the performance of glass fibre sized with an epoxy-based sizing containing in-situ generated silica [114]. The paper describes the preparation of an aqueous sizing based of APTES, epoxy resin film former and silica particles generated by condensation of TES. The sizings were dip-coated onto thermally desized GF rovings. Given that the authors desized for only 30 min at 400°C it seems unlikely that the original sizing was fully removed. Interphase performance was evaluated by the single fibre fragmentation test in a plasticized epoxy matrix. The sample coated with the sizing containing the silica gave a 50% higher level of IFSS compared to the desized glass fibre. However, it is noted that the IFSS base value for the desized fibre was very low at 9 MPa and there was no comparative value given for the IFSS of the commercially sized glass fibre. However, readers will be aware that much higher values of IFSS are normally obtained with a GF-epoxy system.

Plonka et al. [115] systematically investigated the effects of ageing of sized glass fibres on their adhesion to epoxy resin. Various sizings based on APTES, a cationic surfactant and either PU or epoxy film former were applied during the in-house manufacture of E-glass fibres. Five ageing conditions involving variations on time, temperature and relative humidity were applied to these fibres before testing. Surface analysis of the differently sized glass fibres revealed characteristic surface parameters and their variations upon hygrothermal ageing. Characterization of glass fibre-epoxy resin interfaces by means of the quasi-static single fibre pull-out (SFPO) and cyclic loading test showed that the interfacial strength strongly depended on the chemical nature of the fibre sizing formulation and surface roughness. The authors stated that the results of their interface characterization using SFPO and cyclic loading tests were in good agreement with the surface characterisation results. Mäder [116] has also studied the use of different sizing treatments for control of interphase properties in glass fibre epoxy composites. Six differently sized glass fibres were produced on an in-house laboratory spinning device. These included, unsized glass fibres, and combinations of film former only, APTES only, and two sizings similar to proprietary commercial sizings containing APTES and film formers. The fibre surface energy was characterized by dynamic wetting and the adhesion to epoxy resin measured using SFPO. It was concluded that wetting tests can be used to study the fibre-matrix interaction but conclusions about the resulting interphase can be drawn only in conjunction with micromechanical and macromechanical testing. Interfacial shear strength and transverse tensile strength showed the same ranking of the tested sizing treatments, whereas interlinear and compression shear strength did not reflect the expected adhesion and the interphase properties. Brodowsky et al. reported on the use of a variation on SFPO test equipment to investigate the cyclic loading of the interphase in single GF composites of epoxy and PP with different sizings [117]. The authors stated that a quantitative analysis of the hysteresis curves obtained could provide information on the interphase fatigue behaviour. Single fibre model composites were exposed to 400,000 cycles of $1.7\ \mu\text{m}$ symmetric sine load. In epoxy matrix samples, this led to only low fatigue, with the stiffness remaining high, in contrast to PP matrix samples, where fatigue due to the viscoelastic behaviour of the matrix set in.

Dwight et al. [118] studied the role of Lewis acid-base interactions at the fibre-matrix interface in glass reinforced polyester and epoxy composites. The E-glass fibres were sized with three silane coupling agents: APTES, MPTMS, GPTMS alone and with aqueous solutions of 0.5% wt. of silane coupling agent and PVA film former. Fibres were supplied by both PPG Industries and by Vetrotex Saint-Gobain. Unidirectional composites were manufactured with both polyester and epoxy matrices. Silane adsorption mechanisms and composites properties were investigated using a combination of XPS, SEM, and flow microcalorimetry. The authors concluded that the unsized basic glass fibres bonded to the acidic epoxy matrix but not the polyester. However silane coupling agents were adsorbed in patches and provided acidic

sites for interaction with the basic polyester functional groups, as well as stronger basic sites to enhance interaction with the acidic epoxy sites. Mallarino et al. [119] studied the impact of glass fibre sizing on the interphase in polycyanurate matrix composites using thermo-mechanical analysis and micro-thermal analysis. The study involved commercial D-glass fibres with an unknown sizing which was solvent extracted for analysis and found to contain mainly phthalates, long aliphatic chain compounds and PVA. Unidirectional composites were manufactured with fully sized fibres, solvent extracted fibres and heat cleaned fibres. The authors stated that analysis using iso-frequency and multifrequency DMA could differentiate between the three types of composite interphase. A decrease of T_g was observed in the composites which the authors suggested was caused by a decrease in the crosslink density of the interphase resin due to diffusion of sizing molecules into the thermoset matrix network. Dey et al. studied five S-glass fibre rovings supplied by Owens Corning which were coated with sizings produced using three different silane coupling agents and four different film formers [120]. Using the known chemical structures, the five samples were all ranked beforehand for relative reactivity and possible interactions between the fibre, the silane, the film former, and an amine-cured epoxy matrix. The microbond test was used to measure the strength and energy absorption of the interphase in these glass fibre epoxy composites. The size formulation containing an aminosilane and a polyazamide film former gave by far the highest level of interfacial shear strength. The authors further concluded that besides silanes, sizing chemistry and better wettability of film formers play a very important role in glass fibre–matrix adhesion.

Jones [121] has reviewed the formation of the interphase in thermoset matrix composites reinforced with carbon or glass fibres. The section on carbon fibre interphase reviews some useful applications of XPS and SIMS to the investigation of the interphase. The section on glass fibre focuses mainly on the structure of the 20–200 nm thick interphase formed by the polysiloxane layer bound to the glass fibre surface. Jones also reviewed some progress on the deposition of a functional sizing layer directly onto fibres using gas-phase plasma polymerization. The application of this technology to the coating of unsized E-glass fibres is described in two further papers [122,123]. Plasma polymerization [122] was used to coat E-glass fibres with an acrylic acid-octadiene copolymer at varying concentrations of acrylic acid. These fibres were then used to produce unidirectional GF-epoxy composite panels. Tensile strength and energy absorbed to failure were higher in specimens produced from plasma polymer coated fibres than from uncoated controls. The presence of a plasma polymer coating increased the composite longitudinal tensile strength by 20%. By tailoring the composition of the coating to create the optimal degree of fibre–matrix bonding the tensile strength was increased by a further 30%. In another paper [123] untreated and unsized E-glass fibre bundles were continuously coated with acrylic acid-octadiene and allylamine-octadiene plasma copolymers of various compositions to optimize the interfacial bond with the epoxy matrix. The interlaminar shear strength (ILSS) of coated GF-epoxy composites was high for the highest functional coating. However, with a coating of lower functionality, ILSS increased as the thickness of the coating decreased. Nanoindentation results showed that the reduced modulus of the allylamine plasma polymer and hence crosslink density was higher than that of the acrylic acid plasma polymer. A model was proposed whereby the epoxy matrix resin diffuses into the plasma polymer during cure to form a semi-interpenetrating network (IPN) of differing thickness, which controls interphase behaviour. The authors stated that their ILSS results demonstrated that an interphase with high shear strength and of the thickness 2–5 nm is a crucial parameter. Cech et al. [124] have reported on the use of plasma treatment for modification of the surface of glass fibres. They processed E-glass fibre bundles (Saint Gobain) with and without a commercial sizing based on MPTMS using a silane containing plasma. IFSS and ILSS of plasma processed glass fibre/polyester systems were compared with those of untreated and commercially sized fibres. The

results showed some differences between the performances of the various plasma coated fibres, however the traditionally sized glass fibres gave significantly better overall performance.

A number of authors have recently reported on adding carbon nanotubes (CNT) to glass fibre sizings in order to modify composite interphase performance. Warriar et al. [125] reported on glass fibre epoxy composites where CNTs were added to a fibre sizing formulation, in the matrix, or both. Unspecified commercially available continuous E-glass fibres were directly over-coated without the removal of the sizing by drawing the fibres through a water soluble, epoxy-compatible phenoxy-based sizing having 0.5% wt. MWCNTs and subsequent drying at 120 °C. Unidirectional GF-epoxy composites were prepared by a prepregging and lamination process. The CNT over coating of the glass fibres produced an increase of almost +10% in the matrix T_g and a significant reduction of –31% in the coefficient of thermal expansion of the composites. Additionally, the presence of CNTs in the fibre over coating resulted in an increased resistance of crack initiation fracture toughness by +10%, but a lowered crack propagation toughness of –53%. However, similar trends were observed for both instances when CNTs were introduced only in the matrix and in combination of both matrix and sizing. Godara et al. [126] investigated the IFSS in these same materials using single-fibre push-out microindentation. A large increase in IFSS (over 90%) was reported in the composite where CNTs were introduced solely in the fibre over coating. Unfortunately, in both these cases, a control experiment where the glass fibres were only over coated with the pure phenoxy sizing (in the absence of CNTs) was not considered. Consequently the authors could not exclude the possibility that phenoxy alone may have (wholly) contributed to the IFSS improvement in the system with the CNT over coated sizing. Gao et al. [127,128] have reported the use of CNT's and nanoclays in sizings applied to E-glass and AR-glass fibres. The AR-glass fibres were manufactured in-house using a sizing based on APTES and an epoxy film former. The CNT's and nanoclay were pre-dispersed in the sizings before application. Additional surface coatings were applied to the control fibres using commercial self-crosslinking styrene-butadiene copolymers. The E-glass fibres were sized with aminosilane and (MAPP) anhydride grafted PP film former dispersion containing less than 0.5% wt. nanotubes in the sizings. The effects of these coatings were investigated using AFM, SFTS and SFPO testing. The fibres with a low fraction of nanotubes or nanoclay (1% wt. in sizing) showed significant improvement in both mechanical properties and environmental corrosion resistance. Additionally, the CNT sizings appeared to increase the average interfacial adhesion between E-glass and polypropylene. Tamrakar et al. used electrophoretic deposition (EPD) to deposit CNTs onto glass fibres and investigated the effects on interphase strength in GF-epoxy composites [129]. The EPD was performed on single fibres taken from an APTES sized E-glass fabric (Thayercraft Inc.). The results of SFTS showed evidence that in all cases the CNT-coated fibres had slightly improved strength. Microbond testing results indicated that the presence of the CNTs on the fibres led to a 30% higher IFSS in an epoxy matrix. The authors stated that the increased this IFSS could be attributed to the change in surface roughness and morphology provided by the CNTs which facilitate increased levels of mechanical interlocking between the fibre and resin.

Some general conclusions which can be drawn from the presented literature include that approximately 80% or more of the sizing layer on thermoset compatible glass fibres is solvent extractable and is therefore presumably free to diffuse and dissolve into the liquid resin matrix prior to solidification. It appears that by far the greatest proportion of this soluble fraction of a sizing is represented by the film former. A number of authors have determined that the T_g of an epoxy matrix material is locally reduced by about 2–4 °C per 1% of sizing content.

5.3. Interphase in thermoplastic composites

There are significant differences in the role of sizings and the

interphase in thermoplastic matrices. Thomason and Schoolenberg [130] reported that SFPO testing of glass fibres in polypropylene (PP) showed that sizing fibres with various silane coupling agents alone did not improve IFSS relative to bare fibres. However, when fully sized commercial fibres were studied the level of glass fibre-PP IFSS varied by an order of magnitude where the silane performed in combination with other components in the sizes. Furthermore, the flexural strength of unidirectional GF-PP composites varied by a factor of two depending on the type of glass fibre size and these flexural strength results correlated well with the measured level of IFSS. The IFSS could also be correlated with the level of fibre surface coverage given by the fibre sizing as measured using XPS. Results reported by Scholtens and Brackman [131] appear to support this conclusion. Using XPS and SEM they studied the effect of the chemical nature and molecular mass of the film former on fibre-matrix adhesion inferred from 0° bending and ILSS measurements of unidirectional, continuous glass fibre reinforced PP composites. Their main conclusion was that the film former plays a crucial role in the level of fibre-matrix adhesion because it does not diffuse away from the interface into the matrix and that its effect may be larger than that of the silane. In addition, most mechanical properties of short fibre reinforced compounds improved with increasing fibre-matrix adhesion. Furthermore, confocal scanning laser microscopy demonstrated that the non-uniform topography of the sizing layers is preserved inside injection moulded parts. In contrast, Fraser et al. [132] reported on the development and use of an embedded single filament test that measures the cumulative distributions of critical fibre lengths for the evaluation of glass fibre sizings. Results were presented for a variety of E-glass fibres, surface treated with silanes (APTES and MoPTES), PVA film former and lubricants (Owens Corning and PPG), and embedded in polyamide 6, polyethylene, polypropylene, and acid-grafted polypropylene. In general, it was found that a silane, when used at sufficiently high concentration and by itself, provided the most effective surface treatment for E-glass in the above-mentioned resins, from the point of view of both the IFSS and the mechanical protection provided to the fibres by the surface coating. It is worth pointing out here that PVA is not normally considered a suitable film former for thermoplastic compatible glass fibres [2]. APTES was effective in promoting good IFSS levels even at elevated temperature with polyamide 6 and with acid-grafted polypropylene. MPPTES was effective for promoting good IFSS with high-density polyethylene. None of the silanes, sizing agents, or lubricants investigated was effective in promoting good IFSS with unmodified polypropylene.

Nygaard et al. [133] investigated the effects of sizing on the IFSS in GF-PP using fragmentation testing. E-glass fibres were supplied (IPR Dresden) with both single component sizings and complete sizings based on APTES and azidosilane coupling agents with PU and PP film formers. Some of these fibres were further solution coated with a thin layer of MAPP's with different concentrations of acid anhydride groups. Blending the MAPP into the matrix gave better results than the route of first coating the sized glass fibre with a thin layer of MAPP as IFSS was found to be highest for the systems with the MAPP pre-compounded into the PP matrix. The authors concluded that it is necessary to introduce a functionalized PP in order to enhance the bond strength between a PP matrix and an aminosilane treated glass fibre. Yue and Quek [134] studied the effect of the sizing concentration of silane coupling agent on the IFSS of E-glass-PP by SFPO testing. Single "fibres" with an average diameter of 200 μm were prepared from E-glass rods in the laboratory and were dip-coated in aminosilane solutions at different concentrations. Pull-out results indicated that a maximum in IFSS was obtained at a critical thickness of the silane layer on the treated fibre. Mäder and Freitag [135] reported that SFPO measurements revealed that, while a variety of sizings applied to the glass fibres had no influence on their IFSS with PP, the interfacial strengths were found to be significantly dependent on chemical modifications of the PP matrix. Mäder et al. [136] have also published on the relationships between fibre surface, interphase, and composite properties in glass fibre

reinforced epoxy, polypropylene and polyamide. They applied a series of model sizings to glass fibres and characterized wicking and Zeta potential, SFPO and fragmentation, and short beam shear tests. The authors concluded that contact angle and electrokinetic measurements permitted detection of differences in the surface treatment of glass fibres. An approximate correlation between the thermodynamic work of adhesion and the debonding shear strength was shown. Pull-out and fibre fragmentation gave comparable results and could be correlated to macromechanical properties such as flexural strength and ILSS. In a further paper Mäder and Pisanova [137] focussed on the characterization and design of interphases in GF-PP. They used glass fibres sized with APTES, or the same APTES sized fibre over coated with either PU or a MAPP film former dispersion. IFSS was determined by the single fibre microbond method in homopolymer PP and 2% MAPP modified PP. Composites of these materials were also produced by extrusion and injection moulding and tested for mechanical performance. Interestingly, with these two step sized fibres it was the silane-only sized fibres which exhibited the highest levels of IFSS in the micromechanical testing. However, when the same sizing combinations were applied in a "normal" one step process the IFSS values were approximately doubled. The authors stated that in this case the two mechanisms of bonding-acid-base interaction and interdiffusion were competing; however both resulted in an increase of the mechanical strength of the interphase and the composites. The one-step application of the APTES/PP-film former sizing appeared especially effective. The measured interfacial strengths correlated well with the macromechanical properties of the composites. The sizing and interphase design provided simultaneous increase in the tensile strength and the impact toughness of the composites.

Gao and Mäder [138] extended this work on a similar set of sized fibres to explore the characterisation of nanoscale property variations of the interphase in GF-PP and epoxy resin composites. They used tapping mode phase imaging and nanoindentation tests based on the atomic force microscope to study the surface topography and modulus of sized fibres as well as local mechanical property variation in the composite interphase. The authors found phase imaging AFM a highly useful tool for probing the interphase. Nanoindentation experiments detected a gradient profile in modulus across the interphase region of APTES/PU sized glass fibre reinforced epoxy composite. The interphase with APTES/PU sizing was much softer than the PP matrix, whereas the interphase with an APTES/PP sizing was apparently harder than the matrix. The interphase thickness varied between 100 and 300 nm depending on the type of sizing and matrix materials. Zhuang et al. [139] extended the work on the effects of hygrothermal ageing of sizings [115] by examining the effects of boiling water or toluene treatment on the interfacial adhesion of single glass fibres to PP. E-glass fibres were produced in-house and sized with a combination of APTES and a PP film former. The authors reported a 30% increase in IFSS, as measured by a SFPO test, with the boiling water-treated fibres. They further demonstrated that the boiling water-treated fibres had a more polar and hydrophilic surface with homogeneously distributed derivatives of the coupling agent, which they related to a higher IFSS. Zhuang et al. [140] have also reported on the use of sodium tetrafluoroborate (NaBF_4) as a sizing additive to enhance the hygrothermal durability of glass fibre reinforced PP composites. E-glass fibres were produced on an in-house bushing and sized with a mixture of APTES, a PP film former and different concentrations of NaBF_4 . These were compounded and injection moulded with PP containing 2% wt. of a MAPP polymeric coupling agent. Detailed investigations were performed on the surface properties of sized fibres and the mechanical properties of virgin and aged composites. The retention of the composite mechanical performance after hygrothermal aging at 95 $^\circ\text{C}$ in deionized water for 10 days was significantly improved by addition of NaBF_4 in the sizing. The authors related this improvement in hygrothermal durability to a small increase in fibre-matrix adhesion strength induced by the presence of NaBF_4 .

Due to the complexity of many size formulations and the high number of potential interactions in these sizes and the composite

interphase, statistical design of experiments has been in common use by commercial sizing development teams for some time. This approach enables reductions in the number of experiments required to enable statistically significant conclusions to be generated on the interactions of the many processing and formulation variables in size development [4]. Such an approach to investigate PP compatible sizing has been reported by Rausch et al. [141]. Interface related mechanical properties of unidirectional GF-PP composites made of commingled yarns were studied according to a three level, three-factor factorial design comprising APTES coupling agent and film former contents in the sizings and average fibre diameter of the E-glass fibre strand. The authors found that sizings without silane coupling agents generally delivered very poor composite mechanical performance, but no significant differences were found between the intermediate and high level of silane concentration. The film former concentration and GF diameter were negatively correlated with the interphase strength of the composites. The study illustrates well the complexity of sizing development present in even the simplest two component sizings. Jennekens et al. [142] used NMR and FTIR to study the molecular mechanisms of adhesion promotion by various aminosilane coupling agents in glass reinforced polyamide-6 model composites. They concluded that the NH_2 group of the surface-bound coupling agent, the PA-6 COOH end group and also the PA-6 amide functionalities $(-\text{NH})-(\text{CO})-$ contributed to adhesion promotion. The formation of a characteristic interphase layer was controlled by both chemical and physical interactions. The authors also stated that their results suggest that monolayer coverage of the aminopropylsilane coupling agents should lead to adhesion promotion with PA-6. However, Thomason showed [9] that commercial glass fibre products contain much more APTES than is necessary to provide monolayer coverage on the fibre surface. His calculations showed 4–12 mg/m^2 (approximately 8–24 monolayers) of aminosilane on the surface of glass reinforcements. This implies the presence of a more complex multi-layer silane interphase on the surface of these glass fibres.

Noda et al. [143] reported on the structure and molecular motion of the interface in short glass fibre reinforced polyamide (GF-PA66) composites. GF-PA66 injection moulded composites were produced using fibres which were unsized, APTES sized (low and high concentration), and an APTES-maleic anhydride film former dispersion. The fibres were described as commercially treated. The glass fibres were then extracted from the composites using phenol and studied using a variety of analytical methods. Their results revealed the presence of a strongly adhered PA66 layer on the surface of aminosilane-treated GF. It was also shown that the T_g of the PA66 layer on the fully sized glass-fibre surface was higher than that of the PA66 matrix. This was interpreted as being due to the restriction of thermal molecular motion of PA in the interphase. The authors concluded that the sizing produces a strong interfacial interaction between the glass fibre surface and the PA66 matrix with covalent bond occurring during the interphase formation. Gabet et al. used another commonly employed method for screening sizing components in their study of silane and commercial film forming agent dip-coated onto glass microscope slides [144]. The slides were first exposed to extreme surface activation by Piranha solution. Once again the difference in glass formulation and the use of extreme chemical cleaning/etching methods bring with it serious question about the applicability of any results to the case of real sizing application and interaction with E-glass fibres in production. Nevertheless the authors carried out an interesting study in polyamide compatible sizings combining APTES and GPTMS with various PU, epoxy and polyamide based commercial film formers from Michelman.

Bernet et al. [145] studied the wetting and adhesion of polyamide 12 resins on glass fibres taken from fifteen different commercial glass fibre products using CAA and single fibre IFSS measurements. Depending on the fibre sizing, variations in contact angle of up to 60° and differences in IFSS of up to 7 MPa were obtained. A strong inverse relationship between IFSS and contact angle was reported which the

authors stated was in agreement with an existing model. Bergeret [146] reported a study of the interphase in glass fibre reinforced PBT involving chopped E-glass fibres (Saint Gobain-Vetrotex International) sized with two different formulations. These consisted of an aminosilane coupling agent and two different epoxy resin film formers. The corresponding sizing solutions were also available in the study. A wide range of analytical techniques were employed to investigate the interphase around these fibres. The main feature of this study consisted of dividing the interphase into two separate regions: the fibre-sizing interphase and the sizing-matrix interphase. It was reported that between 87 and 94% of the components in these sizings were solvent extractable. Results indicated that the improvement in mechanical performance in the GF-PBT composites was due to the presence of the coupling agent and a polyfunctional epoxy film former which could react both with the coupling agent and the matrix. Mäder et al. [147] reported on an investigation of the influence of a large range of sizings on the formation of the interphase and the level of adhesion between glass fibre and cyclic butylene terephthalate (CBT). An in-house fibre spinning unit was used to produce fibres sized with various combinations of APTES, GPTMS and MPTMS coupling agents with epoxy and PU film formers. The authors used results from SFPO testing, AFM, and SP testing to conclude that the interfacial bond strength between sized glass fibres and CBT can vary depending on the nature of the sizing formulation. The greatest adhesion strength was observed with sizings based on APTES with epoxy film former.

Despite the high level of attention commonly focussed on chemical influences, such as silane coupling agents, on the level of IFSS in composites, a number of authors have commented on the role of shrinkage stresses contributing to the stress transfer capability at the fibre-matrix interphase [8,148–153]. Thermoplastic composite materials are generally shaped at elevated temperature and then cooled. Since in most cases the thermal expansion coefficients of polymers are much greater than that of the reinforcement fibres this cooling process results in compressive radial stress (σ_r) at the interface [8,152,153]. Assuming that the coefficient of static friction (β) at the interface is non-zero these compressive stresses will contribute a frictional component $\tau_f = \beta \cdot \sigma_r$ to the apparent shear strength of the interface. In the case of thermoplastic polymer matrices where there may often be little or no chemical bonding across the interphase these frictional stresses can make up a large fraction of the apparent IFSS. As a result, wetting of the fibre surface at the microscopic level may well play an important role in determining the magnitude of β and consequently the magnitude of the measured IFSS. Thomason has also pointed out [7] that, due to the chemical nature of the ingredients in many commercial sizings for glass fibre reinforcement of thermoplastic, there is statistically more opportunity for silanes (particularly aminosilane which appears to be ubiquitous in thermoplastic sizings) to react with each other, or with other sizing components, than to react with the glass fibre surface. He goes on to point out that a great proportion of the apparent interfacial strength observed in thermoplastic composites can also be explained by physical effects, in particular by the residual compressive stresses present at the interface in these composites. [8,152,153] and has presented data on the temperature dependence of interfacial strength in GF-PP composites which appears to support this hypothesis [9].

6. Sizing effects in composite performance

6.1. Epoxy composite performance

Reed reported [154] on the use of DMA to investigate the interphase in glass fibre reinforced epoxy composites. Epoxy resin composites unidirectionally reinforced with epoxy compatible sized E-glass were studied at various fibre orientation angles using a DuPont 980 DMA at a heating rate of $5^\circ\text{C}/\text{min}$. In low angle and longitudinal composite specimens the author observed an additional damping peak at higher temperatures than the resin T_g . Subsequently Thomason reported [155]

on a detailed study of this high temperature damping peak observed in DMA results from unidirectional glass reinforced epoxy composites obtained using a Du Pont 982 DMA. It was shown that this “interphase” damping peak disappeared from the damping curve when heating rates lower than 2 °C/min were employed. Further investigation showed that this additional damping peak was in fact an artefact caused by a complex interaction of the instrument, the thermal conductivity of the sample, the heating rate, and the sample modulus above T_g . Consequently, the author recommended that quantitative DMA should not be carried out at heating rates above 2 °C/min. Keusch et al. [156] investigated the influence of glass fibre sizing on the static mechanical properties and fatigue performance of glass fibre reinforced epoxy composites. E-glass fibre strands were produced on in-house fibre spinning equipment water sized and sized with five other size formulations. These were further processed into unidirectional reinforced epoxy composites which were subjected to a number of interface sensitive standard mechanical tests and compared with the tensile fatigue performance of cross ply laminates with two of the different sizings. From the macromechanical testing, only the transverse tensile strength correlated well with the micromechanical interface testing. The highest values of transverse tensile strength were achieved with a sizing consisting of aminosilane coupling agent, a PU film former, and a cationic surfactant. Untreated fibres and fibres sized with PU dispersion and cationic surfactant exhibited lower adhesion. The sizings based on polyethylene or PVA film formers gave considerably reduced adhesion performance. The best fatigue performance was obtained from composites with a good fibre-matrix interaction in both 0° and 90° layers. Keusch and Haessler [157] compared this data set with their results of DMA of the same glass reinforced epoxy resin composites. Samples were oriented in the DMA either along or transverse to the fibre direction and heated at 3 °C/min. The authors reported that the DMA flexural storage modulus of the composites with improved interfacial bonding was higher over the whole temperature range investigated. They also related that a decrease in the magnitude of $\tan \delta$ at T_g could be associated with a higher level of interfacial bonding.

More recently Mäder et al. [158] investigated sizing effects on the static and dynamic properties of glass-fibre/epoxy composites. Their E-glass fibres were manufactured in-house either as single fibres or yarns of 60 tex. Various sizings based on APTES coupling agent in combination with either PU or epoxy resin film formers were applied. Unsized reference fibres and PVA sized fibres (to simulate weak adhesion strength) were also included. Single fibre and unidirectional composite samples were prepared in combination with an epoxy resin matrix. The APTES and APTES/epoxy sized fibres exhibited the highest levels of adhesion and these results could be correlated with fatigue performance. Interestingly, in contrast to many other reports, the authors found no effect of the interface adhesion levels on the magnitude of the composite $\tan \delta$ peak at the matrix T_g . Indeed the DMA raw data from all composites revealed very little significant differences. Nevertheless, the authors presented some activation energy analysis which appeared to correlate with the IFSS data. In a series of similar papers Mallarino et al. [119,159–161] reported on sizing effects in glass fibre cyanate ester composites studied using DMA and microthermal analyses. The study involved commercial D-glass fibres with an unknown sizing which were solvent extracted for analysis and found to contain mainly phthalates, long aliphatic chains compounds and PVA. Unidirectional composites were manufactured with as received fully sized fibres, solvent (unspecified) extracted fibres and heat cleaned fibres. Unreinforced resin and resin/sizing extract mixture reference samples were also produced. Microthermal analysis indicated that the sizing and resin were partially miscible. DMA results showed that $\tan \delta$ peak at the composite matrix T_g shifted to decreasingly lower temperatures and magnitudes in order of heat cleaned, extracted and as received fibres. The authors concluded that in this system the sizing plasticises the matrix lowering the T_g by about 40 °C compared to the unreinforced polymer.

Vazquez et al. [162] reported on the application of an epoxy overcoating to glass fibres and the subsequent influence on the flexural properties of glass-fibre epoxy unidirectional composites. Commercial E-glass fibres (source Isotex, type 8204) were employed and the sizing was identified as a combination of APTES and a urethane containing film former/lubricant mixture. In the case of composites with monofunctional epoxy coated fibres, the tensile/compressive and shear stresses decreased as the coating thickness increased. However, for the composites with difunctional epoxy coated glass fibres, the tensile/compressive and shear stresses exhibited a maximum as the thickness increased. The authors stated that DMA results could be used to draw conclusions about the state of the interface bonding in these systems. In a later paper Vazquez [163] further discussed the dynamic mechanical properties of unidirectional glass fibre/epoxy composites containing similar epoxy over coated glass fibre. It was stated that composite performance could be well represented by a simple parallel-series model. Benzarti et al. [164] investigated the influence of glass fibre sizings on the transverse properties of filament wound unidirectional glass/epoxy composites. The macromechanical results were correlated with IFSS measurements obtained by a microindentation test. Experimental E-glass fibres were produced and sized with different sizings by Vetrotex International. These included bare fibres, a commercial sizing containing epoxy prepolymers, an elastomer coating, miscible but non-reactive with epoxy resins, and two sizings with a high epoxy functionality. All sizings contained fixed amounts of film former, lubricant and aminosilane. Their results revealed that the most reactive sizings promoted the highest interfacial strength and also increased the ultimate properties of laminates in transverse tension. The authors attributed this result to the crosslink density of the polymer interphase.

Thomason [165] studied the influence of the sizings on a range of different commercial glass fibres on the properties of unidirectional glass reinforced epoxy composites. Composites were prepared using fifteen different E-glass rovings in three different epoxy matrices. The interlaminar shear strength (ILSS) of these composites varied tremendously depending on the nature of the fibre sizing. Removing the sizing by heat cleaning the fibres led to a dramatic decrease in the composite interfacial strength. Furthermore, it was shown that the dependence of interfacial strength on the fibre sizing altered if the curing agent in the epoxy formulation was changed. The fibre sizing was also found to play a critical role in the retention of interfacial strength in a wet environment. Composite void content was shown to depend primarily on processing conditions and only at a secondary level on the fibre sizing. The void content of the composite was also found to have a strong influence on the ILSS. In another paper [166] this study was extended to characterize the influence of voids, the fibre sizing and the nature of the fibre-matrix interface on water absorption in glass fibre-reinforced epoxy matrix composites. It was shown that the rate of water uptake and the maximum level of water absorption in these E-glass fibre-reinforced epoxy resin composites were primarily dependent on the void content. This dependence was so strong that the presence of only 1% voids in a composite more than doubled the amount of water it absorbed. The nature of the matrix system was also found to have an effect on the water absorption properties of the composite. In particular, the epoxy resin/curing agent ratio played an important role. To a much lesser degree the fibre sizing also had some influence and thermal removal of the sizing had no apparent effect on the kinetics of water absorption despite a large detrimental effect on the interfacial strength.

Jensen and McKnight [167] investigated the tailoring of glass fibre sizing in order to enhance energy absorption in glass fibre-reinforced epoxy composites. A number of sizings based on PTMS and GPTMS coupling agents in combination with a water dispersible epoxy film former and a colloidal silica surface roughening agent were manufactured on pilot plant scale by Fibre Glass Industries. Single-end E-glass rovings were manufactured and subsequently woven into plain weave fabrics. The authors reported that their new hybrid size showed no significant differences when compared to the performance of a

structural fibre sizing. Danner et al. [168] investigated the use of a low Tg polybutadiene (PBD) and silane mixtures as E-glass fibre sizings and the resultant effects on the properties of glass-epoxy composites. Sizing mixtures were applied by solution dip-coating onto desized E-glass fabrics. Laminates were manufactured using these fabrics and epoxy resin using a vacuum assisted resin transfer moulding process. Test results showed that the use of hydroxyl terminated PBD led to a significant increase in interface shear strength, energy absorption, as well as dynamic modulus and Tg in the corresponding composites.

Korjakin et al. [169] reported on a comparative study of the interlaminar fracture toughness of epoxy resin laminates reinforced with differently sized E-glass fibres. Three different fibre sizings were considered: polyethylene treated fibres giving poor adhesion, APTES and epoxy film former treated fibres for good bond strength, and industrial fibres with a starch-oil sizing. Double cantilever beam, end notched flexure, and mixed mode flexure specimens were investigated. For the fibres treated with the silane-epoxy sizing, a value about 2.5 times higher of mode II interlaminar fracture toughness for crack initiation was obtained in comparison with the polyethylene sized fibre composite. For the composite made from the industrial fibres, a value about 2 times higher was obtained. Kessler and Bledzki [170] investigated the correlation between a number of micromechanical and macro-mechanical “interphase-relevant” tests and the impact damage resistance of glass/epoxy laminates containing three differently sized glass fibres designed and described as giving good, medium and poor adhesion (APTES coupling agents with, Epoxy, PU, PE film formers). An excellent correlation was reported between the single fibre push-out results and macroscopic laminate transverse tension and bending strength. Iglesias et al. [171] studied the effects of glass fibre silane treatments on the tensile strength of unidirectional epoxy composites. Three different aminosilanes were coated onto heat cleaned commercial E-glass fibres obtained from Vetrotex. The authors concluded that the more accessible the silane coupling agent amine groups are, the higher the interface rigidity and that an interpenetrating network mechanism in the interphase seems to be important for adhesion and therefore to the interfacial strength. Sever et al. [172] reported on heat cleaned E-glass fibres modified using different concentrations of GPTMS aqueous solutions to improve the performance of glass fibre-epoxy composites. The mechanical properties of these composites were investigated using tensile, flexural and short beam shear testing. It was found that the 0.5% GPTMS treatment provided the best mechanical properties. Feih et al. [173] studied the influence of fibre sizing on the strength and fracture toughness of glass fibre epoxy and polyester composites. Two commercial E-glass fibre products with the same fibre diameters (18 μm) but different sizings were investigated. One was multi-purpose compatible with different resin types while the second was epoxy-only compatible. Four different composite systems were manufactured using two different sizings and two matrix resins. Their crack growth resistance during crack propagation with fibre bridging in a double cantilever beam specimen loaded with end moments was measured. It was found that a strong interface provided higher transverse strength and crack initiation loads, while the weak interface exhibited higher toughness due to enhanced fibre bridging.

Peters reported on the effects of the storage conditions of sized glass fibre, with two different glass formulations, on the short-term and long-term performance of unidirectionally reinforced epoxy laminates [174]. Packages of sized glass rovings (SE1500, SE2020, W3030, 3B Fibreglass) were stored for different sets of time-temperature-humidity conditions before being processed into laminates. The interface sensitive properties of transverse tensile testing and short beam shear testing were measured for all conditions and sizings as well as a tensile-compression fatigue comparison of two commercial glass roving products. The older reference sizing (SE1500) was shown to be very sensitive to storage conditions and demonstrated a significant reduction of interfacial sensitive properties over time. The newly developed sizings demonstrated much reduced performance degradation over time in both

rovings and fabric forms for both glass fibre formulations. These were much less sensitive to temperature, and provided significantly higher initial interfacial strength. Nevertheless, composite performance degradation of sized glass fibres stored in hot and humid environments still occurred. It was suggested that this is most likely occurring at the interface of the size with the glass surface due to hydrolysis of silane, but also at the level of the silane and film formers reactive groups. It was proposed that storage under controlled moisture levels and tight packaging can help slow the process but that water will still eventually diffuse through to the size layer. In another recent paper Harinath et al. [18] stressed that sizing migration and sling-off are still an issue in glass fibre rovings currently used in the production of fabrics for wind turbine applications. They focused on the white lines, associated with sizing migration, which can appear in woven fabrics for wind turbine applications. They produced GF-epoxy laminates with and without such migration white lines and studied their effects on a wide range of mechanical properties, but interestingly they observed no significant differences due to the presence of these white lines. Nevertheless, they stated that, given the proprietary nature of the sizing composition, the impact of a given size chemistry and its migration on the fibre-matrix interphase strength cannot be generalized and should be further investigated.

Gao et al. evaluated the effect of fibre sizing and surface texture on the strength and energy absorbing capacity of E-glass fibre – epoxy laminates using a macromechanical quasi-static punch shear test and the microbond test methods [175]. Sizes consisting of blends of an epoxy film former with combinations of GPTMS and PTMS silanes were applied to single end glass fibre rovings by Fibre Glass Industries. The sizes also all contained unnamed surfactants, lubricants and anti-static agents. The size formulations varied the degree of IFSS, measured by microbond method, and modified the fibre surface texture through the incorporation of silica nanoparticles in the sizing. Microbond test results and the punch shear test results exhibited a very clear linear correlation. The incorporation of silica nanoparticles in the size yielded the highest laminate strength and specific energy absorption with the least damage volume compared to the incompatible sized fibre results. The study included one “compatible” size which would appear to be the closest to a current commercial sizing formulation. When compared with this sizing the “hybrid” nanoparticle sizing also gave a considerable lower level of performance improvement.

6.2. Polyester composite performance

Sjogrena et al. [176] reported on the effects of fibre sizing on the transverse cracking behaviour of glass fibre/vinylester cross ply laminates. Various single fibre tests were also investigated to quantify the interfacial failure characteristics of this system. The glass fibres (IPF Dresden) were treated with two different sizings. A PVA sizing was used for a weak interface (NoCA), while a combination of MPTMS coupling agent and unsaturated polyester dispersion film former was used for a stronger interface (CA). A commercial glass fibre (R25HX14 from Owens Corning) was also included. The various single fibre tests were not able to quantify the interfacial failure of CA samples as the interface never failed. Cross-ply laminates based on NoCA fibres demonstrated significant inferior transverse cracking toughness as compared with CA fibre laminates. The composites based on commercially sized glass fibre were also investigated and they performed almost as poorly as the NoCA material. The authors concluded that the high transverse cracking toughness of the CA material stemmed partly from strong interface adhesion and also from the high ductility of the interphase region. Fernberg and Berglund [177] extended this work to further investigate the effects of six different glass fibre sizing compositions on transverse cracking in vinylester and epoxy cross-ply laminates. The glass fibres and laminates were all provided by Owens Corning. MPTMS coupling agent was used in all sizing formulations combined with different polyester and epoxy film formers. Lubricants, antistatic agents

and other additives were excluded from the study. The influence of the film former on the laminate transverse cracking was found to be significant in epoxy laminates and very strong in vinylester laminates. The transverse cracking behaviour was also found to correlate with the IFSS measured by single fibre fragmentation tests. The authors proposed that the strong film former effect could be explained by a combination of improved interfacial adhesion and the plasticizing effect of the film former on the interphase region.

Hirai et al. [178] reported on the effects of silane-only sizing on the impact response of glass reinforced vinylester composites. E-glass fibre fabrics (Nitto Boseki Co) were dip-coated in aqueous solutions of either MPTMS or GPTMS coupling agents at various concentrations. Laminates were prepared by hand lay-up with these coated fabrics and an unsaturated vinylester resin. These were characterised for their instrumented impact test response. Substantial differences were noted in the shape, mode and area of damage between the front and back surfaces of impact and between the laminates with different fibre surface treatments. The authors concluded that an increase in the MPTMS concentration improved the damage resistance and damage tolerance of the laminates. Saidpour and Richardson [179] investigated the influence of sizings on the mechanical properties of unidirectional vinylester composites. E-glass fibres from PPG Fibres Ltd. were sized with a combination of coupling agent and polyester emulsion film former. The coupling agents were APTES, GPTMS, VTMS, MPTMS and PI-2 a titanate based agent, at three different concentrations. It was determined that all the coupling agents investigated were capable of significantly improving composite performance, the VTMS treatment was marginally the most effective coupling agent and the optimum coupling agent concentration was around 0.2% w/w in all cases. The APTES and PI-2 based sizings gave significantly lower levels of composite interlaminar shear strength.

Park and Kim [180] studied the effect of the sizing treatment on glass fabrics on the performance of glass reinforced polyester composites. Woven glass fabric was heat cleaned and then dip-coated with sizings based on MPTMS in combination with PVA, polyester or epoxy type film formers. Unsaturated polyester composites manufactured with these glass fabrics were characterized by short beam shear and flexural testing. The epoxy and polyester based sizing delivered significantly higher mechanical performance composites in comparison to unsized or PVA sized fibres. In a similar investigation, Park et al. [181] characterized the influence of silane coupling agents on the surface energetics of glass fibres and the mechanical properties of glass fibre-reinforced polyester composites. Using the same E-glass fabric (Hyun-Dai Fibre Co.) and processing methods, fibres sized with three silanes (MPTMS, APTES, and GPTMS) were investigated. Using contact angle measurements based on the wicking rate of test liquids, it was observed that silane treatment of glass fibre led to an increase in the fibre surface free energy, mainly due to the increase of its polar component. It was also reported that both the interlaminar shear strength and the critical stress intensity factor of the resultant composites exhibited a linear relationship with the polar component of the fibres surface free energy. The authors stated that this indicated that hydrogen bonding between the glass fibres and coupling agents plays an important role in improving the degree of adhesion at the interfaces of these composites. Lindsey et al. [182] investigated the effects of fibre sizing formulations on the mechanical properties of unidirectional reinforced glass fibre/polyester resin laminates. These laminates were manufactured using rovings on which three different sizing had been applied by Vetrotex UK Ltd. The same MPTMS coupling agent was used throughout the trials while the film former was varied between epoxy resin, unsaturated polyester or saturated polyester. Samples of the resin mixed with sizing and the unidirectional laminates were subjected to various mechanical tests before and after post-curing. The mechanical properties of unidirectional fibre reinforced laminates were shown to be influenced by the film formers in the sizing formulations. The type of film former was found to modify the matrix properties and it was suggested

that this would produce an interphase effect around the reinforcement. Evidence was presented that suggested the interphase to be a major factor in determining the in-plane shear properties of the laminates. The highest static properties were generally from the laminates with an unsaturated polyester sizing. Impact properties were maximized in the laminates produced from epoxy sized reinforcement. Post-cure resulted in increases in each of the investigated mechanical properties. The authors suggested that this arose from a combination of increased interfacial and matrix properties.

Larson et al. [183] investigated the formation of a sizing rich interphase through the use of micro-dielectrometry to study swelling and dissolution rates of glass fibre sizings in a vinylester matrix resin. Three model commercial glass fibre sizings (provided by PPG), having varying levels of solubility in the resin, were based on film formers of soluble polyester, semi-soluble PVA and insoluble polyurethane. It was shown that two distinct types of interactions, the initial resin swelling of the sizing and the dissolution of the sizing into the resin, can be monitored by micro-dielectrometry. Furthermore, an estimate of the times associated with swelling and dissolution of the sizing into the matrix resin could be made from micro-dielectric measurements. The authors concluded that their results showed that the styrene penetration of these sizing systems is only slightly dependent on the solubility of the sizing systems in the resin. Larson and Drzal [107] also investigated the effect of six different compatible and incompatible sizings on the properties of glass fibre vinylester composites. Composites produced with fibres having matrix soluble sizings developed an interphase which delivered high composite mechanical properties. An interphase did not develop in composites produced with fibres having insoluble or non-wettable sizings, yielding low composite mechanical properties. Wu et al. [48] studied the effects of silane coupling agents on the formation and structure of the interphase and the resultant effects on the performance of unidirectional glass-fibre-reinforced polyester composites. E-glass filaments were manufactured using an in-house single hole bushing (Owens Corning). These filaments were coated using methacryloxy and amino silanes with one, two, and three silanols (mono-ol, diol, and triol) to two types of glass fibres with different bulk glass compositions in a range representative of commercial reinforcements. Fibre surface analyses by angular-dependent XPS, SP analysis, and CAA measurements were used to characterize the surface coatings. The micro-indentation technique was used to evaluate fibre/matrix interfacial adhesion. The authors stated that molecular modelling, ADXPS and SP is a powerful combination for constructing detailed models of silane adsorption and bonding on glass fibre surfaces. They concluded that for composite dry strength, compatibility of the coupling agent reactive organic group with the resin is more important than chemisorption to the glass fibre. However, chemisorption of silane to the glass is essential for hot-wet durability, and the reactive organic group compatibility has a secondary influence. The decrease of composite flexural strength during hot-wet aging was caused primarily by degradation of the interphase.

Gorowara [184] reported on the effect of sizing molecular weight on interphase durability in E-glass fibre-vinylester composites. Model multi-component glass fibre sizings, with formulations based upon patent disclosures, were prepared to model the full coating packages used in commercial glass fibre manufacture. The sizings consisted of MoPTES and GPTMS silane coupling agents and either a DGEBA epoxy, an unsaturated bisphenol-A epoxy methacrylate, or a higher molecular weight unsaturated DGEBA polyester film former. The sizings were applied from a 5% wt. solids emulsion to E-glass fibres (Owens Corning) as produced in a manner consistent with commercial production. Unidirectional reinforced composites were prepared with a vinylester / styrene resin system. Interphase durability was characterized by interlaminar shear strength, before and after hydrothermal exposure. Composites made with the higher molecular weight film former polyester had 25% greater water uptake, and composites made with the fibres sized with the non-reactive silane coupling agent had a three times

greater water uptake, compared to the low molecular weight or no film former sized fibres. Variations in equilibrium water uptake for composites made of glass fibres using different silane coupling agents appeared to correlate with durability as measured using ILSS, but did not correlate within the group of fibres with the same coupling agent.

Nagae and Otsuka reported [184,186] briefly on the influence of glass fibre sizing agent on the interfacial strength and tensile strength retention of water immersed glass fibre reinforced polyester and epoxy composites. Acrylsilane was used as a coupling agent. It was shown that the rate of property loss of poly(acrylate)-sized glass fibre composites was higher than that of those containing epoxy sized fibres or unsized fibres. The authors noted that this could be correlated with values for the IFSS obtained by single fibre fragmentation testing. Matinlinna et al. [187] studied the effect of different coupling agent coatings on E-glass fibres on the flexural properties of fibre-reinforced composites. Five different silanes were coated onto heat cleaned commercial E-glass strands (Ahlstrom Glassfibre). Unidirectional composites were manufactured with an experimental bis-phenol-A-diglycidyl dimethacrylate based resin and subjected to flexural testing after various time immersed in water. The highest flexural strength, both dry and after storage in water for 6 months, was obtained for the control sample (with the original unknown sizing). Although the authors interpreted their results mainly in terms of the various silanes reactivity they did correctly note that the reaction of silanes to a heat cleaned fibre surface adds a considerable unknown to the system.

6.3. Thermoplastic composite performance

Daemen and den Besten [188] discussed the influence of glass fibre sizing on the properties of injection moulded GF-PP. They compared the mechanical performance of injection moulded homopolymer PP composites over a range of fibre contents based on chopped glass fibres coated (Silenka bv) with compatible and incompatible sizings. The use of a compatible sizing generally resulted in significant improvements in composite performance although a notable exception was the unnotched Charpy impact which was lower with the compatible sizing. These effects were interpreted in terms of an increased level of fibre-matrix interaction caused by the compatible sizing. The authors also reported on the effects of adding chemical coupling agents to the PP matrix where significant increases in composite performance could also be obtained. Hamada et al. [189] investigated the influence of the fibre sizing on the bending properties of continuous GF-PP composites. E-glass fibres were supplied by Nippon Glass Fibre Co with aminosilane coupling agent, MAPP film former, sizings. The molecular weight of the film former was varied from high to low in these experiments. According to a near infra-red analysis of the sized glass fibres, the low molecular weight PP film former showed the existence of an amide type bond with the coupling agent in the sizing. Furthermore, the low molecular weight sizing specimens gave the highest bending strength. Finally the authors concluded that there exists an optimum concentration of the PP film former in order to obtain high composite strength.

Mäder et al. [190] reported on the role of film formers in the mechanical performance of injection moulded GF-PP. They investigated in-house produced E-glass fibres sized with APTES coupling agent and either PU dispersion or PP dispersion film former. The adhesion strength determined using SFPO tests showed a strong dependence on the type of film former. Both the variation of adhesion strengths and interphase modulus determined using nanoindentation were found to correlate with the tensile strength, the Charpy impact strengths of the composites. Thomason and Schoolenberg [130] reported that the flexural strength of unidirectional GF-PP composites varied by a factor of two depending on the type of glass fibre sizing and these flexural strength results correlated well with the measured level of IFSS as determined by SFPO testing. In a study of GF-PP related more to glass fibre and composite recycling, Nagel et al. noted the loss in IFSS and composite tensile strength when the commercial chopped glass fibres

(with PP compatible sizing) were thermal conditioned above 200 °C [191]. The degradation of reinforcement performance at such relatively low temperature was attributed to the loss in functionality of the sizing due to thermal degradation. Thomason et al. [192] noted a similar effect in a large range of commercial PP compatible glass fibre products, both chopped strands and rovings, from different suppliers. When thermally conditioned between 200 and 250 °C these fibre all lost their sizing and this was associated with a total loss of adhesion ability with PP. They also noted an associated TGA measure weight loss from APTES only coated fibres in the same temperature range and suggested that, since APTES is the commonly used silane coupling agent in PP compatible sizings, the loss in reinforcement effect of the commercial fibres could be due to thermal degradation of the APTES functionality. In a similar vein Jenkins et al. reported a TGA study of thermal stability of epoxy compatible sizes on glass and basalt fibres [193] and also confirmed the degradation of APTES in the 200–300 °C temperature range [194].

Frenzel et al. [195] investigated the influence of different glass fibre sizings on the mechanical properties of unidirectional glass reinforced poly(ethylene terephthalate) (PET) laminates. E-glass fibres (IPR, Dresden) were treated with sizings including APTES coupling agent and PU and epoxy film formers. These fibres were comingled with PET yarns and used to produce unidirectional laminates. DSC results showed that the overall crystallinity and the melting behaviour of the PET matrix were not significantly influenced by the different sizings investigated. The strength performance of the composites was significantly influenced by both the presence of the silane coupling agent and the type of film former. Laminate mechanical performance was higher with the epoxy film former compared with the polyurethane.

Yun et al. [196] reported briefly on the effect of different silane coupling agents on the IFSS of glass fibre-polyamide 6 (GF-PA6) composites measured by the microbond method. Four different coupling agents were applied to heat cleaned commercial E-glass fibres (Owens Corning 111A rovings). Results on the microbond determined average IFSS were presented without discussion of the potential effects of absorbed moisture or the large scatter which is common with this technique and the consequent significance (or lack of thereof) of the differences discussed. Keeping that in mind the authors reported that the interface strength in the GF-PA6 system increased with an increase of the chemical reactivity of the silane. The microbond test results were ranked in the order of chloropropyl > methacrylate ≈ epoxide > diamine silane greater than 111A commercial size. These results were correlated to the interlaminar and thermal properties of woven glass fabric/PA6 composites in a further paper [197]. Woven glass fabric/PA6 composites were fabricated by compression moulding using a film stacking method. The authors stated that the results indicated that the interfacial characteristics obtained using short beam shear testing, DMA and SEM agree well with each other. However, it is notable that there was no apparent correlation with their micromechanical results on IFSS [196]. Once again there was no discussion of the state of these samples with regard to moisture absorption which is well known to result in very large changes in the performance of polyamide based materials. Laura et al. [198] studied the effect of silane based glass fibre sizings on the mechanical properties of injection moulded glass fibre reinforced, rubber-toughened PA6. Five different silanes were used to size heat cleaned E-glass fibres (Owens Corning). Silanes with anhydride, epoxy, or amine functionality, were found to have little effect on the composite mechanical properties when no maleated ethylene-propylene rubber was present in the polyamide matrix. However, when the rubber toughener was present, the composite tensile strength and Izod impact strength were lowest for the aminosilane and highest for the anhydride silane. Cinquin et al. [199] reported on the influence of matrix additives and fibre size formulation on the mechanical and viscoelastic properties of unidirectional GF-PA66. Vetrotex Saint-Gobain provided the E-glass fibres with three different sizings based on APTES and a PU film former. The presence of the APTES in the sizing improved the mechanical

properties of the composite. A higher level of coupling agent resulted in significantly higher composite flexural strength and interlaminar shear strength. The addition of APTES also significantly lowered the magnitude of the DMA $\tan \delta$ damping peak at the matrix T_g but did not influence the low temperature matrix transition peaks associated with the motion of amide group without or with hydrogen bonds.

Thomason and Adzima [4] presented some insights into aspects of the development and application of sizings for polyamide compatible glass fibres from a commercial sizing developer's viewpoint. They reviewed the role of sizings from fibre manufacture through to performance of composite parts. The review was illustrated with practical examples of sizing development and results from more fundamental studies of sizing application and absorption. They investigated E-glass fibres sized with a combination of APTES coupling agent and a commercially available PU dispersion produced at an Owens Corning pilot facility. They used XPS and SP analysis of the fibre surface isoelectric point (IEP) to examine the adsorption of sizing onto the fibre surface over a 24 h period (representative of the normal wet state time of glass fibres in a slow drying process) and correlated these results with measurements of the SFTS. Their results indicated an initial rapid adsorption of the APTES with a continuing slower adsorption, and increasing surface coverage, of the film former during this time. This was accompanied by an increase in average fibre strength caused by a reduction in the number of fibres in the strand exhibiting very low strength values. They also presented an overview of a typical sizing optimization experimental design involved the same two component sizing evaluated by the mechanical performance of injection moulded GF-PA66 composites. The results showed that the tensile and impact strength of such composites were strongly dependent on the amount of aminosilane deposited on the glass fibres. A broad maximum in composite performance was observed at around 0.08% wt. aminosilane on the fibres (equivalent to a silane interphase of approximately 15 monolayers). Thomason [7] expanded on these results in a further paper which showed that the performance of GF-PA66 composites is considerably better when the combined APTES/PU emulsion sizing system is applied than when the glass fibres are only coated with either the silane or the film former alone. He concluded that there exists a significant synergy between the coupling agent and the film formers used in sizing for thermoplastic compatible glass fibres and that this should not be surprising given the chemical nature of these materials, their intimate proximity in the sizing systems, and the temperature history which glass fibre products experience.

Thomason also reported the results of an extensive study of influence of two different sizings on the performance of injection-moulded GF-PA66 composites [200]. The E-glass chopped strand samples (123D-10C and 173X-10C from Owens Corning) used in this study were both coated with sizings that were designed for polyamide reinforcement. 123D was a typical sizing designed to maximize the "dry as moulded" (DaM) performance of glass reinforced polyamides where the main ingredients were aminosilane coupling agent and a commercial PU dispersion. 173X sizing contained some extra components, including the homopolymer of an acrylic acid monomer, which enhance the retention of composite mechanical properties in elevated temperature hydrolytic environments. Samples of both sized glass fibres were compounded and moulded at 4–50% weight fibre with PA66. Results for the composites mechanical properties, DaM and after hydrolysis conditioning, residual fibre length, and interfacial shear strength obtained by a macromechanical analysis method, were reported. Mechanical properties generally improved with increasing glass content for both sizings. The IFSS was found to be in the range of 30–36 MPa for composites in the DaM state. No significant difference in the DaM IFSS was detected between the two sizing systems investigated. Using the results for the interfacial strength and fibre average orientation in the Kelly-Tyson equation resulted in an excellent fit between calculated composite strengths and the experimental data. Conditioning the composites in either boiling water or water/glycol mixtures led to a

dramatic drop in both tensile modulus and tensile strength. After conditioning, the 173X sized glass delivered a significantly higher level of composite tensile elongation at all fibre contents.

It has been recognized for some time that the chemical nature of glass fibre sizing can have a strong influence on the retention of some mechanical properties of certain types of thermoplastic composite exposed to hydrothermal conditioning. Ishak et al. [201] investigated the effect of coating glass with an aminosilane coupling agent on the tensile properties of hygrothermally aged injection moulded short glass fibre reinforced poly(butylene terephthalate) composites. They reported that the presence of the APTES coupling agent improved the retention of tensile properties of these composites, especially under adverse hygrothermal conditions. Thomason has cooperated with a number of co-workers [201–206] in a systematic study, based on two different sizing formulations, of the structure-performance changes in injection moulded GF-PA66 composites undergoing hydrothermal ageing. Composite samples with 30% weight fibre content were produced using two chopped E-glass products (DS1143 and DS1110, 3B Fibreglass) coated with sizings designed for polyamide reinforcement where the main ingredients are aminosilane coupling agent and a commercial PU dispersion. One sizing contained extra components which enhance the retention of composite mechanical properties in hydrothermal environments. Results reveal that hydrothermal ageing results in significant changes in the mechanical performance, weight, and dimensions of these materials. The negative effects of conditioning could be mitigated to some degree by the appropriate choice of the glass fibre sizing; however the magnitude of this positive sizing effect diminished with increasing conditioning time.

Rudzinski et al. performed FTIR and TGA (under nitrogen) measurements on PA compatible sizings both as macroscopic cast films and as sizing (0.5% LOI) on in-house prepared E-glass fibres [207]. The sizings consisted of combinations of APTES with PU, polyacrylate or epoxy film formers and all sizings also contained a nonionic surfactant. They reported that the peak maxima of the degradation of the sizing on the fibres were shifted to lower temperatures by up to 100 °C in comparison to the degradation of the cast films. At a typical processing temperature of GF-PA66 of 300 °C, the mass of the sizing consisting of only PU film former was reduced by 65% and at 400 °C it was completely degraded. The presence of the silane (PU/APTES sizing) reduced the mass loss by about 15%, but the sized fibres still exhibited a 50% loss of sizing material at 300 °C. A further reduction of thermal degradation of the sizing was obtained by the addition of a second film former. The sizing systems containing epoxy or acrylate gave a mass loss of only 35% up to 300 °C. The authors concluded that while the thermal-oxidative ageing of GF-PA66 composites is mostly affected by the ageing of the PA66 matrix, glass fibre reinforcement sized with a suited sizing can result in interphases which improve the thermal stability of the composites.

7. Concluding remarks

The formulation and application of glass fibre size to reinforcement fibres is a critical component in the cost-effective production of glass fibres and their processability into composite materials with optimized short and long term performance. However, due to the nature of the composites supply chain, the generally available understanding of these complex chemical mixtures does not reflect the level of importance that these sizes have in determining the success of any GRP in a specific application. 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 a very small number of researchers in glass fibre manufacturers' laboratories. These very limited numbers of researchers operate in an isolated and restricted environment with little or no open exchange of information. Consequently it appears likely that the nature of all the 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. Because of the lack of any comprehensive or reliable database on the science and technology of glass fibre sizes, any attempt at a classical review is challenging and it is difficult to draw any significant conclusions about the state of play and whether real progress is being made in this important area of composites science. This review shows some academic progress in the applications of nanotechnology to sizings and the interphase and some evidence of a shift in opinion on the relative importance of mechanical bonding and residual stresses on the mechanism of adhesion at the interphase. However, there is little evidence of any uptake of these ideas in commercial glass fibre sizings development. It is the experienced opinion of the author that 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. It seems highly likely that this problem is a serious barrier to the innovation of better GRP materials and is something that urgently needs to be addressed on an industry-wide level.

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