

INTERFACES AND INTERFACIAL EFFECTS IN GLASS REINFORCED THERMOPLASTICS

J.L. Thomason

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

ABSTRACT

Optimization of the fibre-matrix interphase region is critical to achieving the required performance level in thermoplastic matrix composites. Due to its initial location on the fibre surface, the sizing layer is an important component in the formation and properties of the composite interphase. Consequently, any attempt to understand the science of the composite interphase must encompass an understanding of the science of sizing. In this paper the role of sizings from fibre manufacture through to performance of composite parts is reviewed. In particular the role of organosilane coupling agents and how the formation of a polysiloxane interphase is influenced by the surface properties of the fibre is examined. The influence of the sizing film former in terms of its level of interaction with the silane coupling agent is also examined. The importance of residual stresses in thermoplastic composites in the values obtained for the apparent adhesion levels in these systems is highlighted. These residual stresses are shown to play a significant role in determining the level of interfacial strength in thermoplastic composites and in particular in polyolefin matrices. By applying some of the available models for this phenomenon this analysis is extended to explore the effect of the anisotropic fibre microstructure of carbon, aramid and natural fibres on the apparent interfacial strength in thermoplastic composites.

1. INTRODUCTION

There has been a rapid growth in the development and application of fibre-reinforced thermoplastic polymer composites in recent years. Parallel to this growth has been the increasing recognition of the need to better understand and measure the micro-mechanical parameters which control the structure-property relationships in such composites. The properties of thermoplastic composites result from a combination of the fibre and matrix properties and the ability to transfer stresses across the fibre-matrix interface. Variables such as the fibre content, aspect ratio, strength, orientation and the interfacial strength are of prime importance to the final balance of properties exhibited by injection moulded thermoplastic composites. Although the

field of composite materials is highly diverse in terms of the raw materials used as reinforcement, matrix and additives, it is well known that glass fibres represent more than 95% of the fibre reinforcement used today in the global composite materials market. In terms of the critical role of the interface region in these composite materials one must fully understand the role of fibre sizings. Sizing is a surface coating of mainly organic materials applied to nearly all types of man-made fibres during their manufacture. In the case of glass-fibres, sizing is probably the key component influencing the success or failure of most reinforcement products. This is due to the major role played by the sizing in the profitability, processibility, and performance of that product. Due to its physical location on the fibre surface, sizing is also a critical component in the formation and properties of the fibre-matrix interface region or the interphase (Thomason and Adzima 2001; Wu, Dwight and Huff 1997). Therefore, any attempt to understand the science of the composite interphase must encompass an understanding of the science of sizing. In this paper we will review the role of sizings from fibre manufacture through to performance of composite parts. In particular we will examine the role of organosilane coupling agents and how the formation of a silane interphase is influenced by the surface properties of the fibre. We will further examine the role of the sizing film former in terms of its level of interaction with the silane coupling agent.

The ability to transfer stress across the fibre-matrix interphase in thermoplastic composites is often reduced to a discussion of 'adhesion' which is a simple term to describe a combination of complex phenomena on which there is still significant debate as to what it means and how to measure it. Certainly, one of the generally accepted manifestations of 'adhesion' is in the mechanically measured value of interfacial shear strength (IFSS). However, many methods of determining IFSS exist and there is no overall consensus as to which method is 'best'. This situation is further complicated by the fact that sample preparation for many of these techniques is not optimised for use with thermoplastic matrices. Despite the elegance of the many techniques which have been developed for the quantification of composite micro-mechanical parameters, these techniques have found little enthusiastic support in the industrial product development environment. It is unfortunate that many of these techniques are indeed viewed as time consuming, complex, inefficient, labour intensive, and in many cases unproven or inapplicable in 'real' systems. Consequently their application in most industrial product development programmes is rare (Thomason 2002a). This leads to a classic situation where, because these methods have little support in an industrial environment, they rarely get the time and development to show their usefulness. This occurs despite the fact that the underlying science of even the most apparently mundane industrial development often necessitates solutions which require a deep understanding of structure-performance and micro-structural analysis. Most laboratories involved in the development of thermoplastic composites will routinely measure composite mechanical properties such as tensile strength, and determine residual fibre length. A series of papers by Bader and Bowyer (1972; 1973) in the early seventies presented a method for deriving values for the IFSS from a simple combination of the tensile stress-strain curve and the composite fibre length distribution. It is interesting to note that, despite the recent wealth of activity in the development of micro-mechanical test techniques (or perhaps because of it) there has been little follow-up to these papers. In this paper we present results on the IFSS in various thermoplastic composites obtained using an improved version of this method and compare those results with more traditional single fibre pullout data. We discuss these data in terms of the adhesion levels found in typical thermoplastic composites and illustrate the synergistic role of film formers and coupling agents in determining composite performance.

Finally we highlight the role of residual stresses in thermoplastic composites in the values obtained for the apparent IFSS in these systems. Our analysis indicates that residual stress may play a significant role in determining the level of IFSS in thermoplastic composites and in particular in polyolefin matrices. Although glass fibres are accepted as having a generally homogeneous structure many of the other fibres used for polymer composite applications are highly anisotropic in structure. By applying some of the available models for this phenomenon we extend our analysis to examine the role of fibre microstructure, such as found in carbon, aramid or natural fibres, on the apparent interfacial strength in thermoplastic composites.

2. RESULTS AND DISCUSSION

2.1 Introduction to Sizing. Continuous glass fibres were first manufactured in substantial quantities by Owens Corning in the 1930's. Today glass fibres account for 95% of fibre reinforcements used in the composites industry, primarily due to of their highly attractive performance/price ratio. The basic fibre forming process is shown in Figure 1. The molten glass flows to platinum/rhodium alloy bushings and then through individual bushing tips with orifices ranging from 0.75 to 2.0 mm. On exiting the bushing the glass is rapidly quenched and attenuated (to prevent crystallization) into fine fibres with diameters ranging from 3 to 24 μm . As a result of the high lineal speeds of the glass fibres (mechanical winders or choppers pull the fibres at velocities up to 60 m/s), the very high cooling rates and the immediate interaction of the fibres with a coolant water mist, unique compositions and structures are created in the top layer of the fibre surfaces (Thomason and Adzima 2001; Wu, Dwight and Huff 1997; Lowenstein 1993).

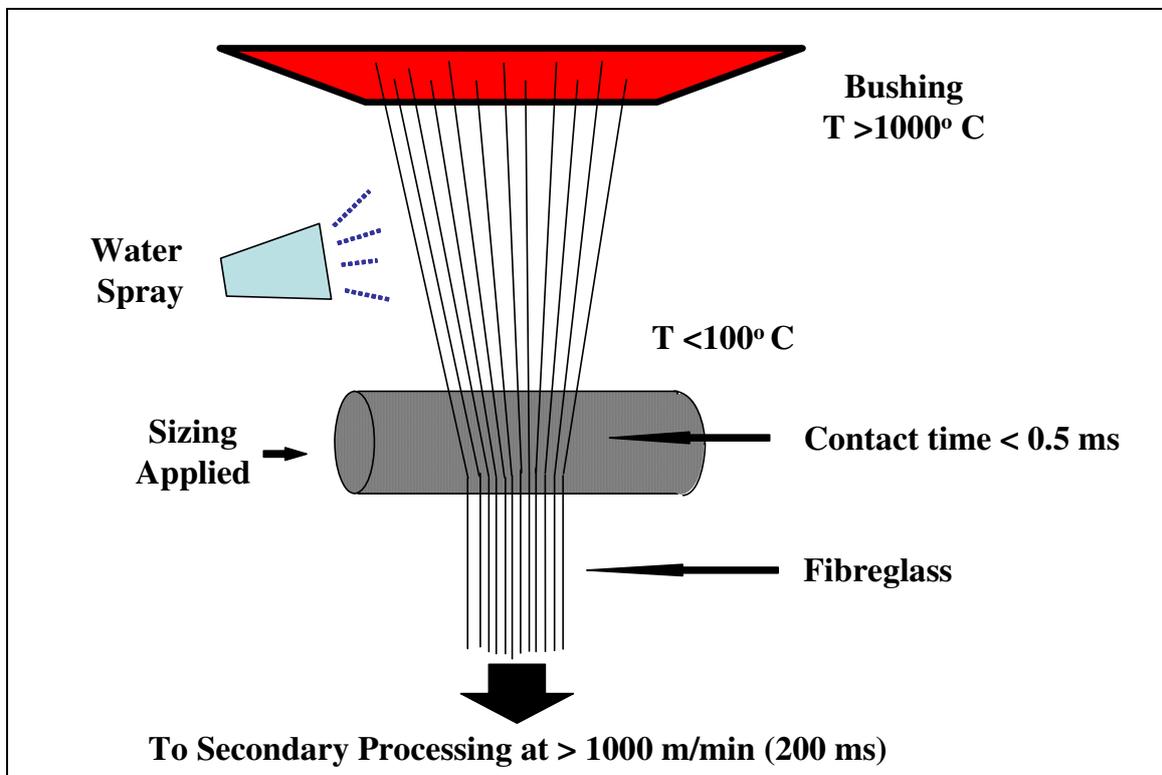


Fig. 1 Schematic of glass fibre forming and sizing operation

Within milliseconds of forming and cooling, this unique glass fibre surface is coated with a sizing - commonly by contacting an applicator roll carrying a layer of the aqueous mixture or emulsion. The sizing pickup occurs over a contact distance of less than 10 mm and therefore occurs in less than 0.5 ms. The fibres are then brought together in a strand and pass on to the secondary processing stage, which will be reached in approximately 0.2 s. In terms of processibility during chopping or winding, the sizing must therefore perform certain functions within a fraction of a second after it has been applied. After drying (2 minutes to 1 day, depending upon the type of product) the sizing must provide a new set of properties to optimize composite processing and performance. All this combines to make sizing formulation and application one of the major technological challenges of glass fibre production, and attaining the optimum composition and coverage one of the major challenges to the subsequent formation of the composite interphase.

Optimizing the sizing layer is a complex art involving a compromise of manufacturing, marketing, technical and economic factors. Such an optimised sizing requires the correct balance of (Thomason 1999; Thomason and Adzima 2001) profitability, processibility and performance. As with all balancing acts these three key properties are closely linked. The importance of sizing to the glass fibre composites industry cannot be understated since practical glass-fibre-reinforced composites cannot be made without it. Furthermore, sizing is one of the most important factors that differentiate one glass reinforcement product from another. To achieve this delicate balance, sizings have been developed which are aqueous chemical systems containing 0.05-10% "solids", the remainder is water. The composition of these "solids" generally consists of a number of multi-purpose components. There will be a film former which, when dried, holds the filaments together in a strand and protects the filaments from damage through fibre-fibre contact and fibre-process contacts. Film formers are chosen to be as closely compatible to the intended polymer matrix as possible and still fulfil 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 polyurethanes for polyamide compatible products; maleic anhydride modified polyolefins (MAPP) for polypropylene reinforcement, and polyurethanes and/or modified epoxies for thermoplastic polyester applications (Lowenstein 1993, Thomason and Adzima 1999; Campbell 1999). Emulsion/dispersion technology allows many of these high molecular weight and water insoluble materials to be applied to glass fibre surfaces. Sizing will nearly always contain an organofunctional silane commonly referred to as a coupling agent. However, these multifunctional molecules perform many roles other than just the simple fibre-matrix link which is implied by this name. Indeed, the non-coupling aspects of silanes are one of the areas where a much more fundamental understanding is needed in order to develop improved sizings and composites. Sizings may also contain cationic or non-ionic lubricants to reduce fibre-fibre abrasion. There may also be a number of other additives, such as anti-static agents, emulsifiers and wetting agents. The amount of sizing on any particular glass reinforcement product is also a carefully controlled parameter which is usually expressed as the "loss on ignition" (LOI), which is the percentage weight loss obtained by burning off the sizing. Finally it is worth mentioning the importance of water in the glass manufacture process. Water is used in large volumes of relatively high purity in a number of roles. It is used to cool the fibres and it acts as a carrier for the sizing. Since small amounts of size are applied to a huge surface area, water is used as a diluent so that the correct amount of sizing is applied. Water wets glass easily and aids the distribution of the sizing on the glass surface. During the fibre forming process water also acts as a lubricant to some degree.

2.2 Silane in Thermoplastic Sizings. 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 interfacial strength and hydrothermal resistance of the composite interface (Pluddemann 1982; Emadipour, Chiang and Koenig 1982). The silane coupling agents have the general structure $[R'-Si(OR)_3]$ where R is methyl or ethyl and R' contains a group which may interact with either or both the film-former and the composite resin. The nature of this interaction is intuitively accepted as being of a chemical nature when the matrix resin is thermosetting and consequently the R' group on the silane has the opportunity to react with the matrix components. It is not quite so clear that chemical reactions play a role when reinforcing high molecular weight thermoplastic polymer matrices. On the other side of the silane molecule, the hydrolysed silanol group may interact and react with the glass surface, primarily through condensation with surface hydroxyl groups.

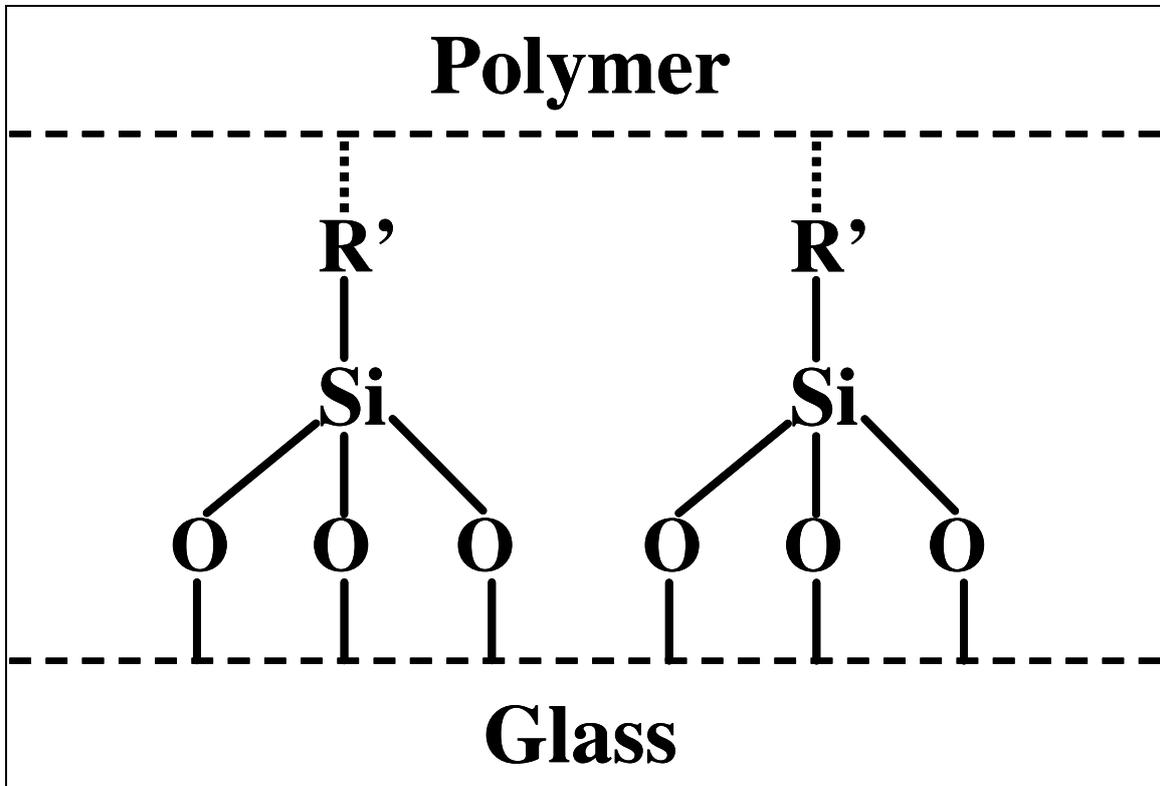


Fig. 2 Simple schematic of silanes at an interface

When the silane is used to treat the glass fibres in an aqueous sizing it is first hydrolysed to a (tri-)ol named silanol. This unstable silanol can be condensed onto the fibre glass by the elimination of a water molecule to produce a siloxane network. Si-OH groups on the glass surface may also participate in the process, with the result that the siloxane network becomes covalently bonded to the fibre glass surface. When glass fibre is then used in the polymer matrix it has to reinforce, the R' reactive groups of the silane may still be available to react with the reactive functions of the polymer which can lead to a strong network bridging the fibre-polymer interface. This situation is often depicted as shown in Figure 2 with three condensed silanol groups reacted with the glass surface and the R' group interacting with the polymer matrix.

Although there are very many different silane molecules available the glass fibre industry has

focused its sizing products mainly on the (Pluddemann 1982; Lowenstein 1993) four shown in Figure 3 where the R' group contains amino, epoxide, carbonyl and carbon - carbon double bonds. Once again 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. However, it is the aminosilane versions which form the largest proportion of silanes employed. When we come to consider sizings for thermoplastic polymer reinforcement it is, once again, less clear that we are dealing primarily with chemical interactions. Furthermore, it is interesting to note that a review of the available literature and patents on sizings indicates that aminosilanes are used almost universally for thermoplastic compatible sizings. Consequently any progress in the interface region in thermoplastic composites will require an improved understanding of the role the ubiquitous aminosilane molecule.

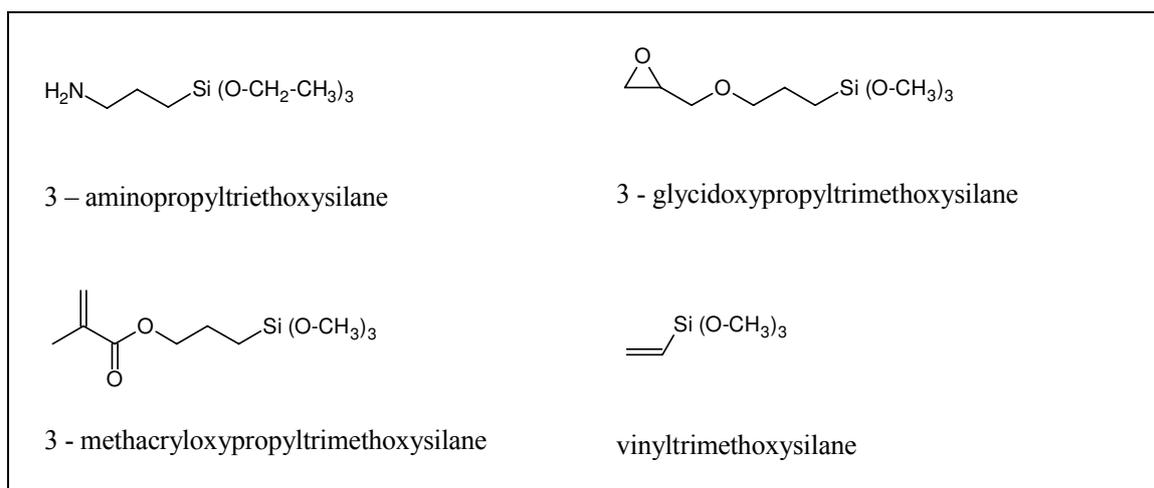


Fig. 3 Typical silanes used in glass fibre sizing

Examination of the simple cartoon in Figure 2 raises some other important points about the strength of the fibre-matrix interface. One could presume that the strength of this interface might be expected to be, in some way, proportional to the bond density across the interface. Consequently we might also expect that the interfacial strength may be proportional to the hydroxyl group density on the glass surface since this will play a role in determining the silane concentration in the first layer(s) of the interphase.

2.3 Quantification of hydroxyl group concentration on glass surface. Surface hydroxyl groups are the primary site on the surface of silica and glass for the adsorption and reaction of water and organic molecules. Zhuravlev (1993) has extensively reviewed work on the adsorption of water and the role of hydroxyl groups on the surface of silica. For a completely hydroxylated surface, the average number of silanol groups was found to be $4.9 \text{ OH}/\text{nm}^2$, which includes the number of free, isolated silanol groups and the vicinal OH groups which are hydrogen bonded (Zhuravlev 1987; 1993). It has also been shown that the bonded hydroxyl groups can be removed from the silica surface by treatment in the temperature range from 200 to 400-500 °C. Thus, the concentration of silanol groups on a silica surface at 400 °C, $2.35 \text{ OH}/\text{nm}^2$, corresponds to the concentration of isolated hydroxyl groups. The concentration of OH groups continues to drop with an increase in temperature from 400 to 1100 °C ($< 0.15 \text{ OH}/\text{nm}^2$) by silanol condensation to form siloxane bonds as the mobility of the network chains increases. In addition, Zhuravlev (1993) has also investigated the rehydroxylation of silica surface. It was found that the complete rehydroxylation of silica surface can be achieved easily for those samples of silica which were subjected to heat treatment at temperature below 400 °C. After the treatment at a higher temperature, only partial rehydroxylation takes place.

Since glass surfaces are also silica rich they have an analogously hydrated structure. Nishioka and Schramke (1983) compared the thermal desorption of water from E-glass fibres with powdered silica and observed more water per unit area adsorbed on E-glass fibres. However, the immediate surface was considered to be a multilayer of hydrogen bonded water molecules. They concluded that three molecular layers of adsorbed water were desorbed between 55°C to 200°C and silanol group condensation occurred at temperatures above 200°C. Sub-surface water desorbed at 300°C and at this temperature, silica skeletal bonds are reported to be hydrolysable, so that the surface composition of the fibres is highly variable. The quantity of water desorbed between 500°C and 800°C was suggested to result from the diffusion of bulk water from the inner structure. Pantano, Fry and Mueller (2003) employed solid state ¹⁹F nuclear magnetic resonance (NMR) to study (3,3,3-trifluoropropyl) dimethylchlorosilane (TFS) labelled silanol groups on glass fibre surfaces and determined the concentration of hydroxyl groups to be 0.50 to 1.44 OH/ nm² depending on the boron content of the glass. Carré, Lacarriere and Birch (2003) have estimated the density of silanol groups at the surface of microscope slide glass as 2.5 silanol groups per square nanometre. They showed how this value could be calculated from the contact angle of water under octane at the point of zero charge (pzc). The interaction between water and the non-charged glass surface at the pzc is non-dispersive and primarily generated by hydrogen bonding. Therefore, from the water contact angle at pzc, the non-dispersive hydrogen bonds energy of interactions expressed per unit of interface area and from the molar energy of hydrogen bonds, the number of hydrogen bonds per unit interface area could be obtained which also corresponds to the density of hydroxyl groups.

Liu, Thomason and Jones (2007) have used the same method to investigate the surface concentration of hydroxyl groups on the surface of an E-glass formulation used for glass fibre production. They studied the contact angle made by water droplets of different pH on the surface of polished E-glass slides under dry octane. Figure 4 show the results for E-glass slides in a fully hydrolysed state and after dehydroxylation for one hour at 600°C under dry nitrogen gas. In both cases a maximum in contact angle is clearly observed at a pH of 3. This value is in good agreement with other published values of the pzc of bare E-glass obtained by Electrokinetic Analysis (Mäder, Jacobasch, Grundke, and Gietzelt 1996; Wu et al. 1997). There is also a clear difference in the level of interaction between the water and the two surfaces as indicated by the large difference in the level of contact angle values with the dehydrolysed glass being much less hydrophilic. Table 1 summarizes these results and gives the values for hydroxyl group concentration. The value of 2.3 OH/ nm² is in good agreement with the value obtained by Carré et al. (2003) and, if we follow the model of silane condensation onto glass shown in Figure 2, translates into a silane surface density of 0.8 molecules/nm².

Table 1 Surface density of hydroxyl groups on E-glass

	Hydrolysed E-glass	Dehydrolysed E-glass
Max Contact Angle	39 ± 3	71 ± 2
pH of pzc	3	3
n _{OH} (nm ⁻²)	2.29 ± 0.04	1.71 ± 0.03

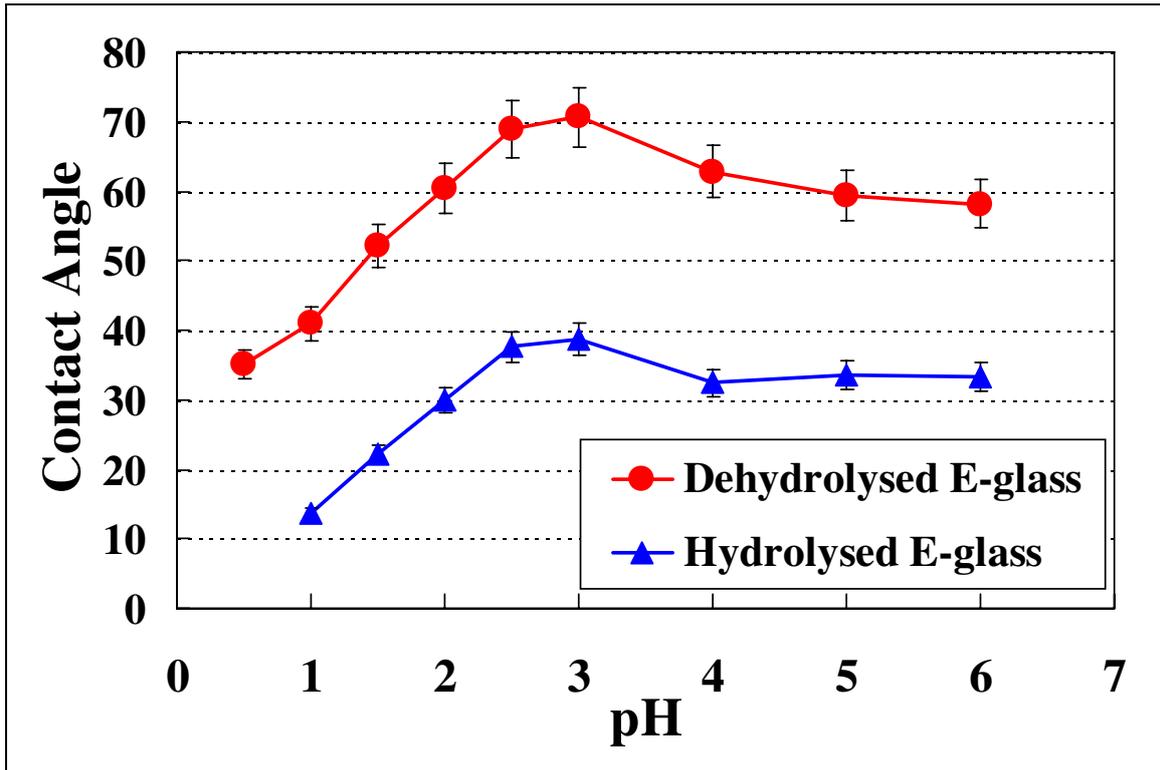


Fig. 4 Contact angle of water on glass under octane

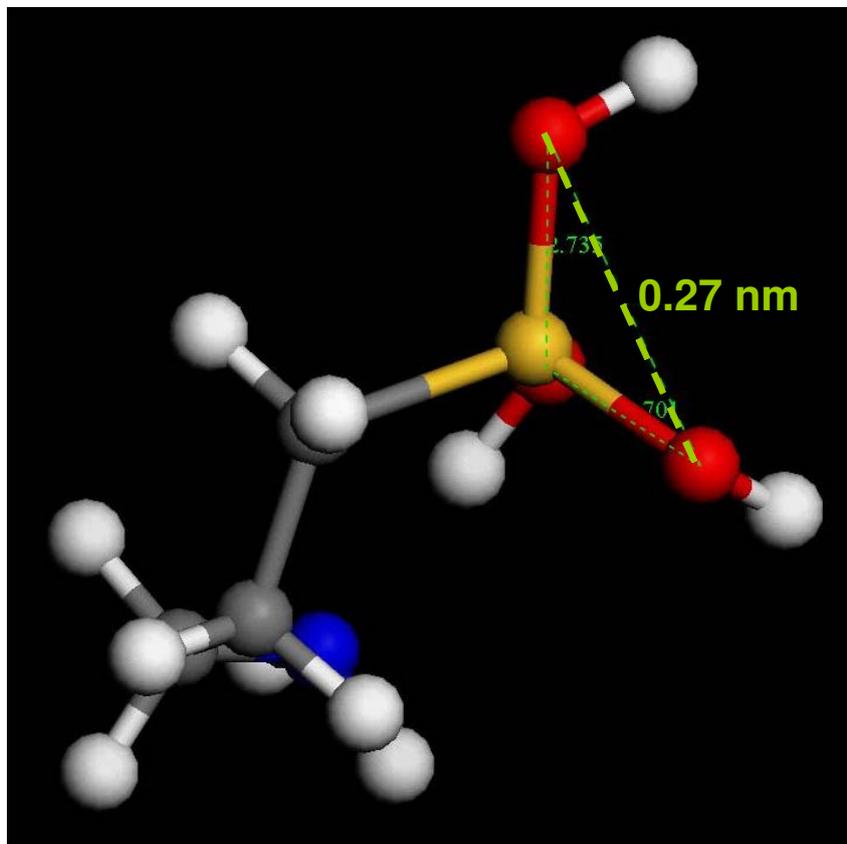


Fig. 5 Model of hydrolysed APS molecule

However, this value of hydroxyl group concentration actually has significant consequences for the veracity of the cartoon of silane-glass interaction shown in Figure 2. A value of 2.3 OH/nm^2 translates into an average hydroxyl group spacing of 0.7 nm for a uniform surface distribution. Figure 5 shows the result of a molecular dynamics simulation of one of the lowest energy states of a hydrolysed aminopropylsilane (APS) molecule. It can be seen that the average spacing of the oxygen atoms of the silanol groups is only 0.27 nm. This implies that it is extremely unlikely that any silane molecule will condense with more than one glass surface silanol. Moreover, it is also unlikely that silane molecules which have condensed with individual surface silanols will be close enough to react with each other. If we assume that each glass surface silanol reacts with an individual aminosilanes molecule then we obtain approximately 0.5 mg/m^2 of APS reacted with the glass surface. Combining typical sizing silane concentrations with typical LOI values for glass reinforcement indicates the presence of between $4\text{-}12 \text{ mg/m}^2$ of aminosilanes on the surface of dry thermoplastic compatible glass reinforcements. In contrast to Figure 2 this implies the presence of a more complex multi-layer interphase on the surface of these glass fibres and subsequently in their composites. If distributed uniformly on the fibre surface this would result in a polysiloxane interphase of up to 10nm on the surface of each fibre. Clearly the presence and properties of such an interphase could have significant influence on the performance of the macroscopic composite and requires further investigation.

2.4 Silane-Film Former Synergies. Following the example of many others in this area we have simplified the above discussion on the formation of a silane interphase by the lack of consideration of the other sizing components. However, in the real world the silane coupling agent forms approximately only 10% of the active material in a sizing formulation. Indeed the bulk of the sizing formulation is usually made up of the film former(s). It is interesting to observe that in the case of thermoplastic compatible sizings there is more intuitive expectation of reaction between any aminosilane coupling agent and the film former than with the polymer matrix of the composite. Consider the chemical nature of the typical film formers, blocked polyurethanes, epoxy resins, maleic anhydride modified polyolefins, which all offer the possibility of chemical reactions with amino groups. Consider also that the film former and the coupling agents are intimately mixed in the sizing and may be heated to temperatures in excess of 200°C during the drying process. It seems quite possible that, in many cases, the silane coupling agent may already be partially or completely reacted with film formers long before the sized glass fibres come in contact with the composite matrix polymers.

The potential synergies between APS coupling agent and thermoplastic film formers are further illustrated in Figures 6-8. Figure 6 shows some single fibre pullout results of Thomason and Schoolenberg (1994) on the influence of sizing on the IFSS of glass fibre with unmodified polypropylene homopolymer. Bare glass fibre gave an IFSS of 3.6 MPa which was increased to 4.5 MPa by the application of APS to the fibre. However when the fully sized fibres were investigated, values of 10.3 and 15.4 MPa were obtained for IFSS. In both these cases the sizing contained both APS coupling agent and a maleic anhydride modified polyolefin film former which may certainly react together. In a similar vein Figure 7 summarizes data from two papers by Thomason (2002b; 2007) on IFSS in glass reinforced polypropylene obtained by the improved Bader and Bowyer method. In this Figure we can see how the presence of MAPP in either the sizing or added to the PP homopolymer matrix affects the apparent IFSS in glass PP composites. Once again the system without any MAPP exhibits a very low IFSS in the region of 2 MPa. Addition of MAPP to either the sizing or the composite matrix raises the level of IFSS to approximately 8 MPa and when MAPP is present in both sizing and matrix an IFSS of 16 MPa

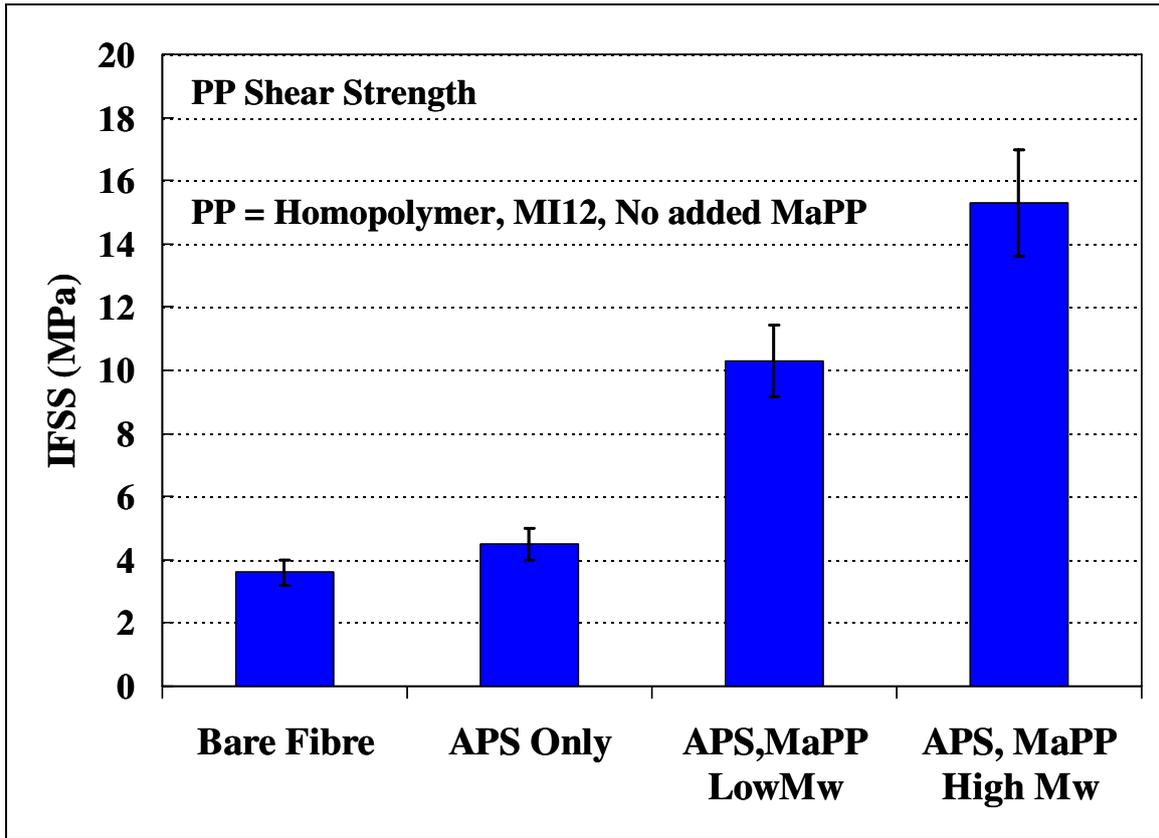


Fig. 6 IFSS in single glass fibre polypropylene samples

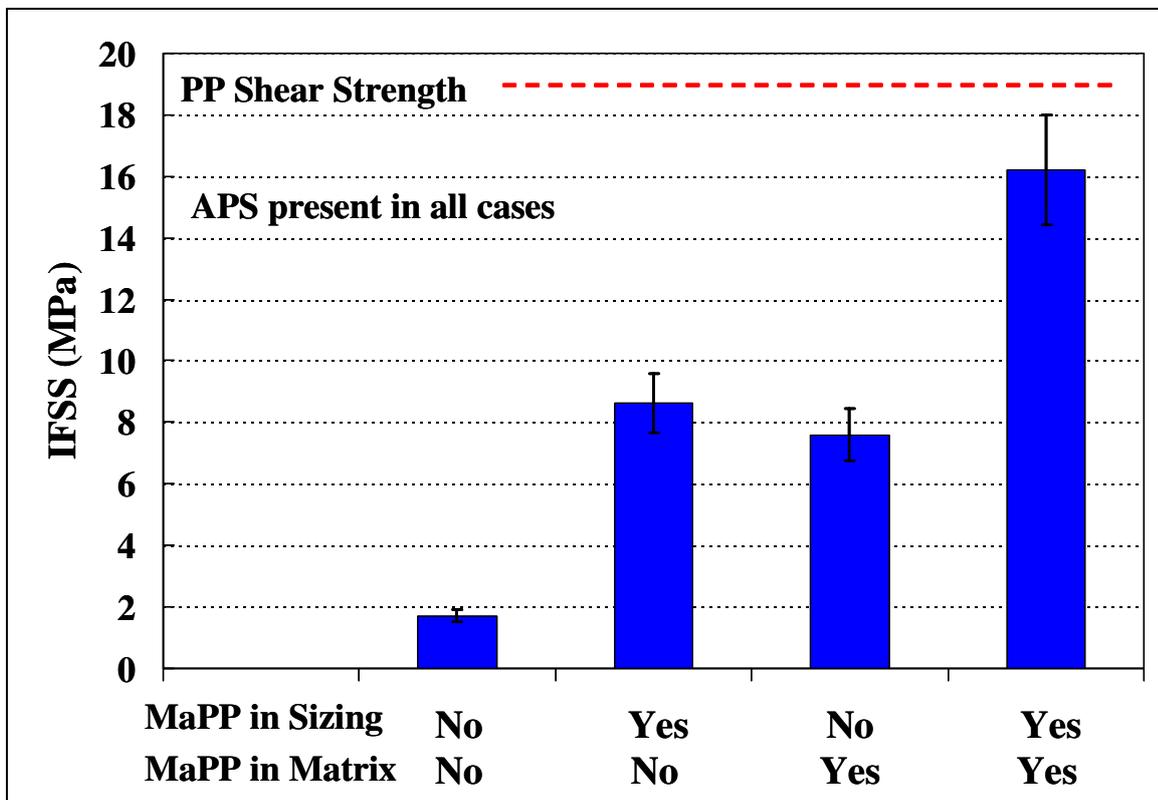


Fig. 7 IFSS in glass fibre polypropylene composites

is observed. It should be noted that this is close to the upper limit of measurable IFSS defined by the shear strength of polypropylene. Figure 8 shows data of Thomason and Adzima (2001) on the effects of sizing on the mechanical performance of injection moulded glass fibre reinforced Polyamide 6,6. They presented data on a simple sizing system containing only APS coupling agent and a PU emulsion. It can be seen that the performance of the combined sizing system is considerably better than when the glass fibres are only coated with either the silane or the film former alone. It seems quite likely from these results that there exists a significant synergy between the coupling agent and the film formers used in sizing for thermoplastic compatible glass fibres. As discussed above this is perhaps not so surprising given the chemical nature of these materials, their intimate proximity in the sizing systems, and the temperature history which glass fibre products experience. However, it does indicate once more that the simple model of fibre-matrix interface shown in Figure 2 is not particularly useful in understanding the performance of real thermoplastic composite systems. In this context it is interesting to note the comment of Thomason and Schoolenberg (1994) on their results of IFSS between PP and bare glass or silane only coated glass where no MAPP was present in the system. They observed that the levels of apparent IFSS observed in these cases could be explained by the residual stresses and resulting fibre-matrix friction in this system.

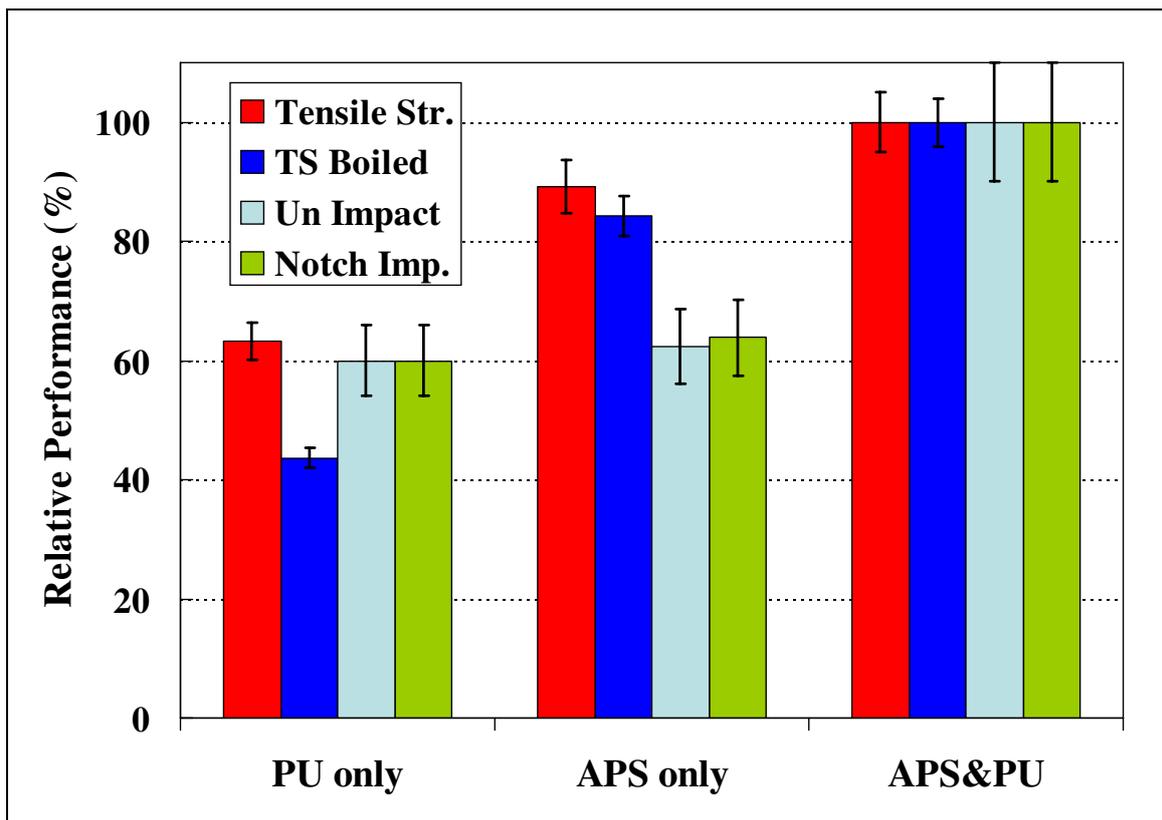


Fig. 8 APS-PU synergy in glass fibre polyamide composites

2.5 IFSS and Residual Stresses in Thermoplastic Composites. Thomason (2002a) has recently published data comparing the apparent IFSS in injection moulded glass fibre reinforced composites based on four different thermoplastic matrices. The polymer matrix materials studied were Polyamide 6,6 (PA66), Polybutyleneterephthalate (PBT), Polypropylene homopolymer (PPh) and Polypropylene containing 2% of maleated-PP coupling agent (PPm). These were compounded with 4 mm chopped strands containing 14 mm diameter E-glass fibres coated with the appropriate sizings for polymer matrix compatibility whose formulations followed the descriptions given in previous sections of this paper. The mechanical performance ranking of these composites (PA66 > PBT > PPm > PPh) was as expected and it was noted that the strength of the GF-PP mouldings were significantly increased by the addition of the MAPP polymer coupling agent. Figure 9 shows their results for the apparent IFSS in these systems based on Thomason's modified version of the Bader and Bowyer method of analysis of the composites tensile stress-strain performance. The values for IFSS are ranked in the order that one might expect from the fibre-matrix combinations and in all cases are realistically below the upper limit of apparent IFSS set by the shear strength of the polymer.

A number of authors have commented on the role of shrinkage stresses contributing to the stress transfer capability at the interface (Di Landro and Pegoraro 1996; Wagner and Nairn 1997; Nairn 1985; Piggott 1980). Most composite materials are shaped at elevated temperature and then cooled. Since in most cases the thermal expansion coefficients of thermoplastic polymers are much greater than reinforcement fibres this cooling process results in compressive radial stress σ_r at the interface. Assuming that the coefficient of 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 interface these frictional stresses can make up a large fraction of the apparent IFSS. An exact calculation of the frictional fraction of the IFSS requires detailed knowledge of the interfacial friction and the temperature dependence of the stiffness and thermal expansion coefficient of the composite constituents which was beyond the scope of this study. However, they did estimate the magnitude of σ_r in their glass reinforced thermoplastics using a number of different models and fixed room temperature values of the required input parameters (Nairn 1985; Piggott 1980; Thomason and Vlug 1996). The relevant model input values are shown in Table 2. The results from all three models followed the same general trends, differing only in the absolute level of radial stress predicted. In Figure 9 we compare the results from Nairn's model for radial shrinkage stress with the measured IFSS values. It can be seen that results follow a similar trend. By an appropriate choice of coefficient of friction it is possible to obtain a good fit of any of the three models with the experimental data. Figure 9 also shows an example of the predictions of Nairn's model combined with $\beta = 0.67$ to give an estimate of the frictional component of the IFSS. It can be seen that there is excellent agreement with the experimental data. The excellent agreement in the observed trends does imply that shrinkage stress and interfacial friction may play an important role in the IFSS of these materials. Thomason (2001a; 2001b; 2002b; 2006; 2007) has expanded on this original work in a series of papers examining the apparent IFSS in various thermoplastic matrix composites varying the matrix type, the fibre content, the fibre length and the level of MAPP present in the GF-PP system. In all these cases the data for the apparent IFSS in these systems can be well fitted by the residual stress model of Nairn when an appropriate value for the static coefficient of friction is selected.

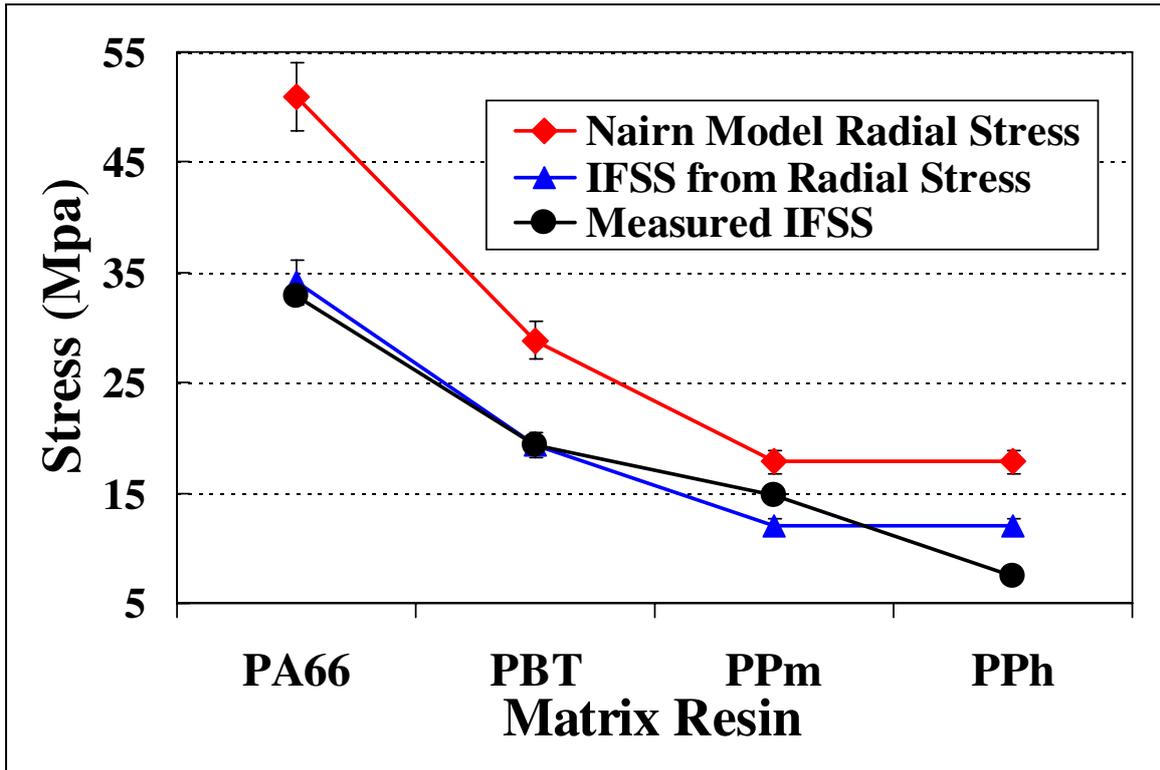


Fig. 9 IFSS in glass fibre thermoplastic composites

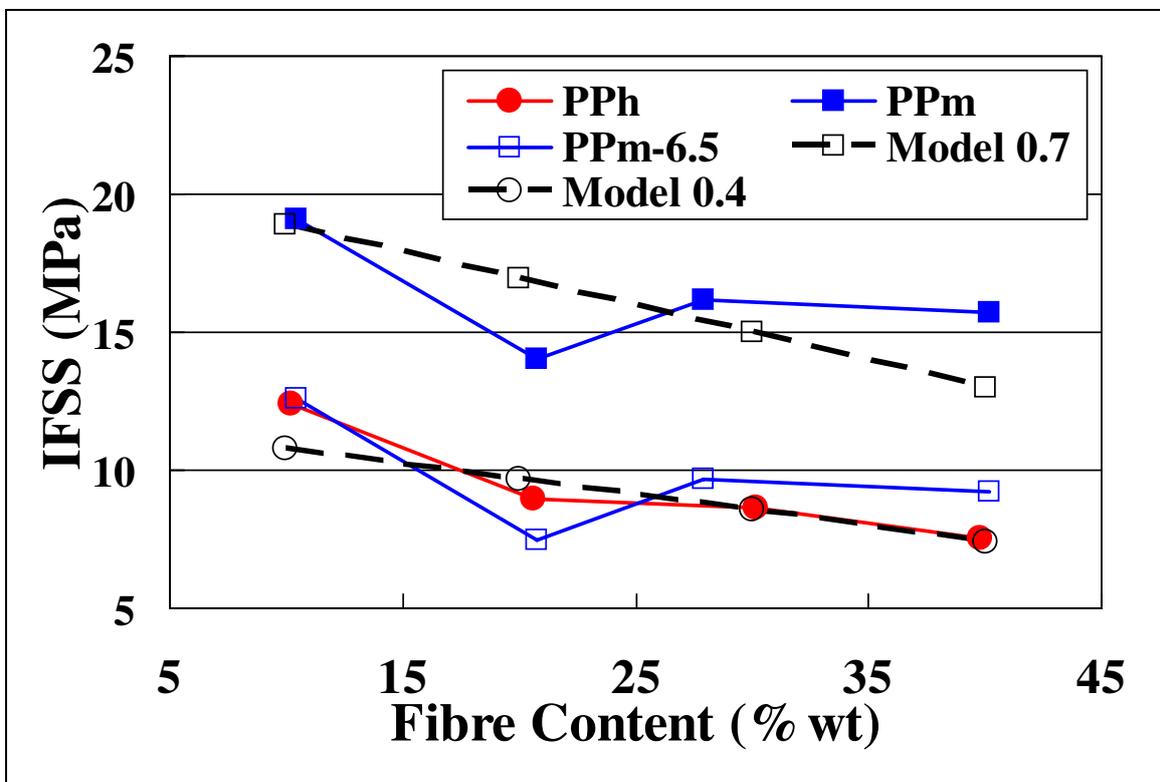


Fig. 10 MAPP effect on IFSS in glass fibre polypropylene composites

Figure 10 presents data from one of these papers showing the effect on apparent IFSS of adding MAPP to the matrix of GF-PP system at different glass fibre contents. The IFSS appears to be decreasing with increasing glass content and the trend appears to be approximately the same for both the PPh and the PPM series. The influence of the MAPP polymer coupling agent can be seen as giving an increase in the apparent IFSS of approximately 6.5 MPa. In this case the sizing system on the glass fibre also contained a maleic anhydride modified polyolefin (Campbell 1999). We have again estimated the magnitude and fibre content dependence of σ_r in glass reinforced PP using Nairns model and fixed room temperature values of the required input parameters. The results are shown in Figure 10 and it can clearly be seen that the values obtained for the apparent IFSS follow a similar trend to the model calculations of the radial compressive stresses at the interface due to fibre-matrix shrinkage mismatch. By an appropriate choice of coefficient of friction it is possible to obtain a good fit with the experimental data. Figure 10 shows an example of the predictions of the model combined with values of β of 0.4 and 0.7 to give an estimate of the frictional component of the interfacial shear stress. It can be seen that we get excellent agreement with the experimental data is obtained. At this point it is stressed that there should not be any strong relevance attached to the absolute value of β since the theoretical analysis requires a much greater level of detail (i.e. temperature dependence of many parameters) before it can be considered realistic. However the excellent agreement in terms of the observed trends does imply that shrinkage stress and interfacial friction may play an important role in the IFSS of these materials. Furthermore the reduction in IFSS with increasing fibre content is a factor which, in combination with the fibre length reduction, may explain the reduction of reinforcement effectiveness at high fibre loading (Thomason 2005; 2007).

The above results indicate that the apparent IFSS in glass reinforced PP can be matched by the calculated frictional contribution from the radial thermal stresses when an appropriate value (0.4-0.7) for the coefficient of static friction is selected. Although these might appear to be relatively large values, it should be noted that this refers to a coefficient of static friction which can be significantly higher than the more common dynamic value. Schoolenberg and Elmendorp (1995) have shown that the apparent IFSS in single fibre pullout testing of glass fibre and polypropylene can be explained fully by residual interfacial compressive stresses and a coefficient of static friction of 0.65. Although it is unlikely that the frictional contribution actually contributes 100% of the IFSS in all fibre-matrix combinations the fact that the trends can be explained by only residual frictional stresses is a strong indication that they do contribute significantly. In this context the result shown in Figure 10 merits further discussions. It is well known that the addition of the MAPP “coupling agents” can result in improved mechanical performance in glass fibre reinforced PP (Thomason 2007). This improvement in performance is often attributed to the possible formation of chemical bonds across the fibre-matrix interface between the polymeric coupling agent and the silane coupling agents in the fibre sizing which are assumed to be chemically reacted to the fibre surface. The increase of 6.5 MPa seen in Figure 10 could be taken as supporting evidence for this hypothesis. However, in this case the glass fibres used in these experiments were coated with a sizing which already contained maleated polymers which, as discussed above, had already had sufficient opportunity to react with the silane coupling agent in the sizing. This casts some doubt on the hypothesis that additional MAPP in the PP matrix would have the opportunity to form further covalent bonds across the interface region. One alternative explanation which could be pursued is that the wetting of the fibres by the PP matrix has been significantly improved at the molecular level and that this results in an increase in the coefficient of static friction and consequently the frictional component of the apparent IFSS. Clearly this is a hypothesis which merits further investigation.

2.6 Influence of fibre structure on interface strength. It would appear from the foregoing results and discussion that we can make a case for residual thermal stresses contributing a significant

amount to the apparent IFSS in thermoplastic composites. Moreover, the relative proportion of this contribution is higher in polyolefin basin composites where the levels of other fibre-matrix physical and chemical interaction are low. The magnitude of these residual stresses can be adequately estimated using models such as that of Nairn (1985). The main missing requirement in converting these residual stresses into IFSS is an accurate estimation of the coefficient of static friction for any particular system. A better understating of the role of wetting and interfacial interaction on this coefficient of friction is also required. It may be that many of the chemical modifications applied to thermoplastic composites which are assumed to improve adhesion through increased chemical bonding across the interface may actually be changing the level of matrix-fibre wetting and consequently the static coefficient of friction. Notwithstanding these points it is interesting to compare the relative levels of residual compressive stress in polypropylene composites where different reinforcements are used. Unlike glass, many of the other typical reinforcement fibres available are anisotropic in their mechanical and thermal properties and this may have significant influence on the residual stress state in any composite.

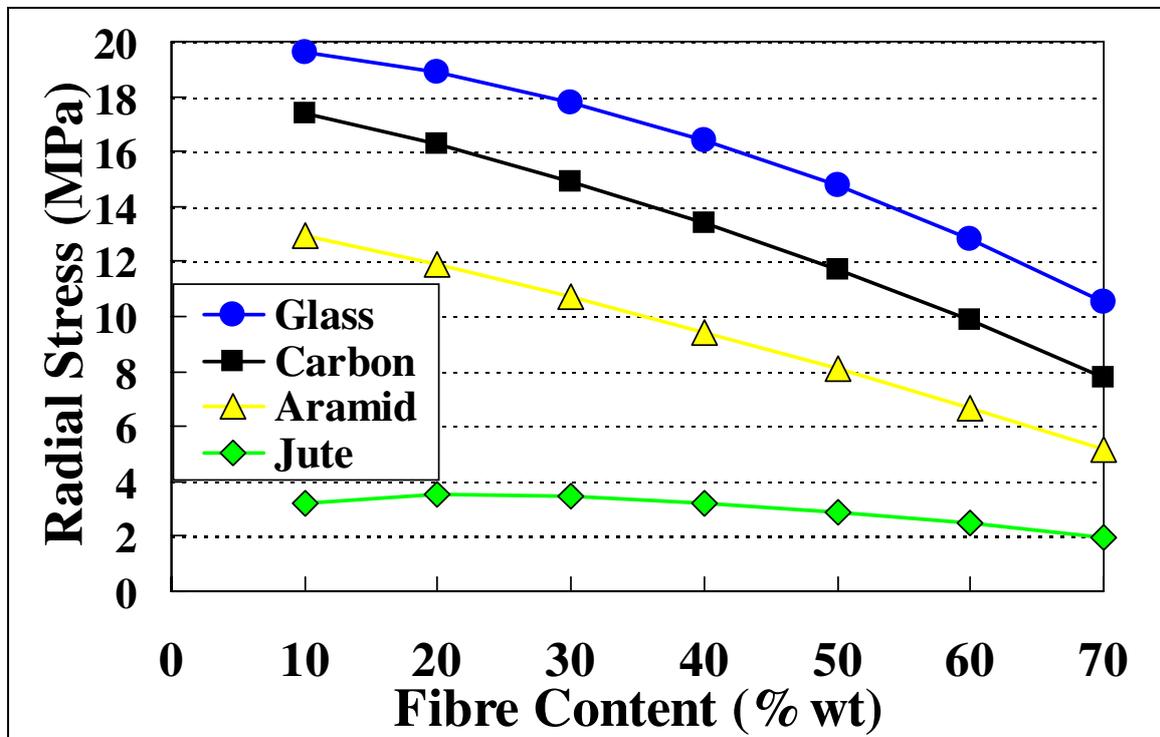


Fig. 11. Residual radial compressive stress at the interface in polypropylene composites.

To illustrate this point Figure 11 shows results of calculations of the residual radial compressive stress present at the fibre-matrix interface in polypropylene containing glass, carbon, aramid and natural (jute) reinforcing fibres. The relevant input parameters for the calculation are given in Table 2 (Nairn 1985; Wagner and Nairn 1997; Thomason 2002a; Cichocki and Thomason 2002). As indicated above it can be seen from Table 2 that carbon, aramid and jute are highly anisotropic in comparison with glass. These fibres all have small but negative LCTE's in the fibre direction and much larger positive LCTE's (approaching polymer matrix values) in the transverse direction. The effect of this anisotropy is clearly illustrated in Figure 11. All these systems exhibit compressive residual stress at the interface at room temperature and all show a mild dependence on the fibre content as previously discussed. However, the magnitude of these residual stresses is strongly dependent on the fibre properties. Glass fibres exhibit the highest

levels of residual stress with carbon fibres lower but at a similar level. Aramid fibres show significantly lower levels and the natural fibres have a very low level of residual radial compressive stress at all fibre contents. These results are well in line with the generally accepted view on interfacial adhesion in thermoplastic composites that glass and carbon are often well bonded, aramid fibres present some challenges to obtained good adhesion, and that there are serious problems with IFSS levels in natural fibre composites. Although the explanations and remedies for these issues are often sought in the chemistry of the system, these results suggest that, for improved reinforcement of polyolefins, we also need to better understand the role of fibre structure, the levels of residual stress, and the interfacial friction, on the apparent interfacial strength in thermoplastic composites.

Table 2. Input parameters for residual thermal stress calculations

	Glass	Carbon	Aramid	Jute	PP	PBT	PA66
Longitudinal Modulus (GPa)	72	220	130	39.4	1.5	2.8	1.5
Transverse Modulus (GPa)	72	14	10	5.5	1.5	2.8	1.5
Longitudinal Poisson Ratio	0.22	0.08	0.3	0.11	0.35	0.35	0.35
Transverse Poisson Ratio	0.22	0.01	0.1	0.01	0.35	0.35	0.35
Longitudinal LCTE ($\mu\text{m}/\text{m}\cdot^{\circ}\text{C}$)	5	-0.36	-3.6	-0.6	120	90	110
Transverse LCTE ($\mu\text{m}/\text{m}\cdot^{\circ}\text{C}$)	5	18	50	77.2	120	90	110
Temperature Range ($^{\circ}\text{C}$)					100	160	220

3. CONCLUSIONS

The optimization of the fibre-matrix interphase region is critical to the end-use performance of glass-fibre reinforced thermoplastic matrix composites. An essential requirement to improving that optimization process is acquiring a better understanding of the function of the various components of the fibre sizing in the formation of the interphase. In particular for thermoplastic composites an improved model for the role of aminosilanes in these systems is required. A combination of results from glass surface hydroxyl group concentration and molecular modelling of silane molecule dimensions indicates that the majority of silane molecules which react with the glass surface can only do so through formation of a single Si-O-Si bond. Furthermore, it appears that the majority of silane molecules in the first layer(s) of the interphase are not directly bonded with the glass surface. The likely interactions between the silane coupling agent and the typical film formers are shown to be important in the performance of the interphase and in determining composite performance. It is shown that for most glass fibre reinforced thermoplastics it is unlikely that the coupling agent interacts directly with the polymer matrix. More probable is the formation of a copolymerised aminosilane-film former interphase on the glass surface during the fibre manufacturing process with subsequent more complex interactions within the composite. It is clear that in many cases there is a need for an improved model of the interphase in the determination of the fibre-matrix adhesion performance in thermoplastic composites. It is suggested that an important component of this model should be a consideration of the role of residual radial compressive thermal stresses at the interface. In this context a much better understanding of the quantification of, and the factors that affect, the coefficient of static friction is needed in thermoplastic composites. The use of the thermal stress model also indicates the importance of fibre microstructure in determining the level of residual

stress contribution to the apparent interfacial strength and appears to be a possible explanation for the poor levels of adhesion exhibited by many natural fibre thermoplastic composites.

ACKNOWLEDGEMENTS

The authors wish to thank Dr X. Liu of the University of Sheffield for her assistance with the contact angle data and Dr N.T. Huff of Owens Corning for providing the molecular modelling Figure.

REFERENCES

- Bader, M.G., and Bowyer, W.H. (1973). An improved method of production of high strength fibre reinforced thermoplastics. *Composites* 4, 150-6
- Bowyer, W.H., and Bader, M.G. (1972). On the reinforcement of thermoplastics by perfectly aligned discontinuous fibres. *J. Mater. Sci.* 7, 1315-1321.
- Campbell, L.E. (1999). *Handbook of Polypropylene and Polypropylene Composites*. (Marcel Dekker, New York)
- Carré, A., Lacarriere, V., and Birch, W. (2003). Molecular interactions between DNA and an aminated glass substrate. *Journal of Colloid and Interface Science* 260, 49-55.
- Cichocki, F.R., and Thomason, J.L. (2002). Thermoelastic anisotropy of a natural fiber. *Compos.Sci.Technol.* 62, 669-678.
- Di Landro, L. and Pegoraro, M. (1996) Evaluation of residual stresses and adhesion in polymer composites. *Composites Part A* 27, 847-853.
- Emadipour, H., Chiang, P. and Koenig J.L. (1982). Interfacial strength studies of fibre-reinforced composites. *Res.Mech.* 5, 165-176.
- Loewenstein, K.L. (1993). *Glass science and technology 6, The manufacturing technology of continuous glass fibres*. (Elsevier, Amsterdam)
- Liu, X., Thomason, J.L., and Jones, F.R. (2007) The concentration of hydroxyl groups on glass surfaces and their effect on the structure of silane deposits. Manuscript in preparation
- Mäder, E., Jacobasch, H.J., Grundke, K. and Gietzelt, T. (1996) Influence of an optimized interphase on the properties of polypropylene/glass fibre composites, *Composites Part A* 27, 907-912.
- Nairn, J.A. (1985). Thermoelastic analysis of residual stresses in unidirectional, high-performance composites. *Polym. Compos.* 6, 123-30.
- Nishioka, G.M. and Schramke, J.A. (1983). Desorption of water from glass fibres, in *Molecular Characterisation of Composite Interfaces*. (Plenum, New York).
- Pantano, C.G., Fry, R.A., and Mueller, K.T. (2003). Effect of boron oxide on surface hydroxyl coverage of aluminoborosilicate glass fibres: a ¹⁹F solid state NMR study. *Phys. Chem. Glasses* 44, 64-68.
- Piggott, M.R. (1980). *Load-bearing fibre composites* (Pergamon Press, Oxford) p. 203-209.
- Pluddemann, E.P. (1982) *Silane Coupling Agents* (Plenum Press, New York)
- Schoolenberg, G.E. and Elmendorp, J.J. (1995). Some wetting and adhesion phenomena in polypropylene composites, Chapter 3.6 in *Polypropylene: Structure, blends and composites*. (Chapmann and Hall, London).
- Thomason, J.L. (1999). The influence of fibre properties of the performance of glass-fibre-reinforced polyamide 6,6. *Compos.Sci.Technol.* 59, 2315-28.
- Thomason, J.L., (2001a). Micromechanical Parameters from Macromechanical Measurements on Glass Reinforced Polyamide 6,6. *Compos.Sci.Technol.* 61, 2007-16.
- Thomason, J.L., (2001b). Micromechanical Parameters from Macromechanical Measurements on Glass Reinforced Polybutyleneterephthalate. *Composites Part A* 33, 331-39

- Thomason, J.L., (2002a). Interfacial Strength in Thermoplastic Composites – At Last an Industry Friendly Measurement Method ? *Composites Part A* 33, 1283-8.
- Thomason, J.L., (2002b). Micromechanical Parameters from Macromechanical Measurements on Glass Reinforced Polypropylene. *Compos.Sci.Technol.* 62, 1455-68.
- Thomason, J.L., (2005). The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene: 6) The properties of injection moulded long fibre PP at high fibre content. *Composites Part A* 36, 995-1003.
- Thomason, J.L. (2006) Structure-property relationships in glass reinforced polyamide: 1) The effects of fibre content. *Polymer Composites* 27, 552-562.
- Thomason, J.L., (2007). The influence of fibre length and concentration on the properties of glass fibre reinforced polypropylene: 7) Interface strength and fibre strain in injection moulded long fibre PP at high fibre content. *Composites Part A* 38, 210-216.
- Thomason, J.L. and Adzima, L.J. (2001). Sizing up the interface: an insider's guide to the science of science. *Composites Part A* 32, 313-321.
- Thomason, J.L., and Schoolenberg, G.E. (1994). An investigation of glass fibre/polypropylene interface strength and its effect on composite properties. *Composites* 25, 197-203
- Wagner, H.D., and Nairn, J.A. (1997) Residual thermal stresses in three concentric transversely isotropic cylinders: application to thermoplastic-matrix composites containing a transcrystalline interphase. *Compos.Sci.Tech.* 57, 1289-1302.
- Wu, H. F., Dwight, D. W. and Huff, N.T. (1997), Effects of silane coupling agents on the interphase and performance of glass-fiber-reinforced polymer composites, *Compos.Sci.Tech.* 57, 975 - 983.
- Zhuravlev, L.T. (1993). Surface characterization of amorphous silica : a review of work from the former USSR. *Colloids Surf. A Physicochem. Eng. Asp.* 74, 71-90.
- Zhuravlev, L.T. (1987). Concentration of Hydroxyl Groups on the Surface of Amorphous Silicas. *Langmuir* 3, 316-318.