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The Performance and Environmental Durability of Pultruded Glass Fibre Composite Rebars

by

J. Zhang

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submitted in partial fulfilment of the requirement for the award of the degree of
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Supervisor:    Dr M.O.W. Richardson
Director of Research: Professor D.J. Hourston
Institute of Polymer Technology and Materials Engineering

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Dedicated to my family
Abstract

The work reported is a study of the performance of pultruded unidirectional glass fibre composite rebars, in order to understand and quantify the environmental degradation of the materials in water and alkali solution with, and without, stress. The rebars have been proposed as possible candidates for replacing reinforcing steel in concrete structures.

Firstly, the interfacial strength, mechanical properties and dynamic mechanical properties of the rebar composites were investigated using ILSS and a three point bending test, in conjunction with SEM and dynamic mechanical thermal analysis (DMTA). It was concluded that the surface treatments on glass fibres played a major role in the ILSS of the composites. Likewise, the flexural properties and failure behaviour of the rebars were also affected and all were related to the ILSS values. With increasing ILSS, the flexural strength and modulus increased and the failure features varied from compressive, to mixed compressive-tensile, to tensile. This was because higher interphase strengths delayed the occurrence of fibre microbuckling and increased the instability of glass fibres in the matrix. It was found that the glass transition temperature (T_g), as measured by DMTA, can be used to assess interfacial strength. A strong interphase resulted in a relatively higher T_g (and vice versa). This appears to have been caused by the more efficient transfer of the “restraining effect of glass fibres” on polymer chain mobility.

Secondly, unstressed rebars were exposed to water and alkali solution at 40, 60 and 80°C, respectively for up to one year, and subsequently examined for property deterioration. The flexural strength of water-exposed rebars dropped sharply up to a water uptake of 0.5 wt.% then levelled off at approximate 50% of the ultimate bending strength (UBS) of unexposed samples. The flexural modulus, however, remained stable at about 95% of its original value. Water attack on glass fibres was found to be a predominant feature of the degradation mechanism of rebar strength since the failure mode of the exposed composite was transformed from a mixed compressive-tensile type (of the unexposed) to a tensile type. Increasing the conditioning temperature induced additional damage to the interphase, which was confirmed by a dramatic change in the dynamic mechanical behaviour of the composite when immersed in water at 80°C. This
was because, at high temperature, the water absorption dynamics of the rebars severely deviated from Fickian behaviour and consequently more water was thermally trapped in the interphase region and in defects. The rate and magnitude of flexural property degradation in alkali solution was similar to that in water, except that at 80°C, the modulus was considerably reduced. This was caused by the corrosion of defect inclusions introduced during rebar manufacturing process. The results suggest that the hydroxyl ions in the alkali solution do not diffuse into the polymer matrix. Addition of alkali into water did not lead to a significant difference in water absorption dynamics and DMTA behaviour of pure Atlac 580 vinylester resin.

Thirdly, fractured glass rebars, subjected to stress and water or alkali solution at 40°C, were studied. It was observed that low stresses resulted in relatively planar cracks normal to the applied tensile stress but did not pose significant damage to the interphase. The opposite was true for rebars under high-levels of stress. Alkali solutions accelerated the occurrence of stress corrosion in terms of failure times. It was found that crosslinked vinylester resin exhibited a diphasic structure as detected by modulated temperature differential scanning calorimetry (MDSC). Based on these results, it is proposed that microcracks form in the polymer matrix of the composite (under low stresses) due to the different responses of the two phases to the stress field at crack tips. Microcracking then allows transport of aqueous media into the composite by a percolation process.

**Key words:** pultruded glass composites, composite interphase, interphase degradation, environmental durability, stress corrosion, micro-phase separation, dynamic mechanical thermal analysis (DMTA), modulated temperature differential scanning calorimetry (MDSC), interlaminar shear strength (ILSS).
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PART I

INTRODUCTION

AND

LITERATURE REVIEW
Chapter 1 Introduction

Composite material is a combination of two or more materials, which generally constitutes a reinforcing phase and matrix phase. The specific characteristics and properties of composites are superior, and possibly unique in some respects, compared to the properties of individual components. Fibre reinforced plastic (FRP) is a particular type of composite which consists of fibre reinforcements, such as glass, carbon or aramide, combined with polymer matrix resins. The matrix resins can be classified as thermosets like polyester, epoxy or vinyl ester resin, and thermoplastics, for example polyethylene, polypropylene or polyamides. The reinforcement normally with high modulus and strength is a main load-carrying element, with the matrix of low modulus transferring the load via shear stresses, and also binding and thus protecting the reinforcement. The third phase in composite is an interphase/interface between the fibre and the matrix, whose properties are different from the other two. Although the properties of a composite rely on the properties of fibres, the matrices and the quality of the material, perhaps the interphase plays a most important part in influencing the overall performance of a composite.

Composite materials are therefore heterogeneous and highly anisotropic, resulting in the design of composite structures being very flexible when compared with traditional isotropic materials, e.g. metals. Unidirectional composites in which the fibres are aligned in one direction can produce the most efficient structures along principal stresses. In addition, a variety of choices of different fibres and matrices enable the composite properties to be tailor-made to meet requirements for specific applications. Some of the other advantages include high strength/stiffness to weight ratio, chemical resistance, fatigue life, fire retardance and wear. Composite materials are therefore finding increasing applications in a variety of industries, for example aircraft and space, automobile, ship building and sports. As materials technology makes further advances, the potential markets for composite systems are expanding to include more secondary and primary structural applications. A pultrusion technique is an automated process of
manufacturing FRP composite into continuous, constant cross-section profiles. This process provides the possibility of producing exceptionally strong composites with low cost and enhanced productivity.

One possible application of pultruded glass fibre reinforced plastics (GRP) is to replace steel reinforcement in concrete structures, which is a subject of this research. In addition to the above-mentioned advantages of the materials coupled with reduced cost of pultrusion manufacturing technique and glass fibres, the main attraction of this proposal is in an attempt to mitigate the corrosion of steel in concrete.

Generally, steel reinforcements remain in a passive state inside good quality concrete and will not corrode. However, the steel will lose its passivity either by carbonation, a constant diffusion of carbon dioxide from the atmosphere into the concrete, or the ingress of chlorides that may come from the contamination of fresh concrete, or may penetrate the hardened concrete from the environment [1]. The two main sources are salt water in marine locations and de-icing salts used on highway structures. Corrosion then takes place by dissolving away the steel in the form of ferrous hydroxides. This is a complex electrochemical process with a flow of current from the cathodic region through steel to the anodic region, and back through the concrete. A supply of oxygen and water, passing through the concrete will provide a condition to sustain the reaction. Rust from corroded steel occupies a larger volume than that of the parent metal. This results in an internal expansive stress that is large enough to cause the concrete to crack initially, and eventually spall off or ultimately fail. This risk is notoriously severe for marine and coastal structures with high levels of chloride present in the environment, a ready supply of oxygen and water, and for bridges on motorways where the use of de-icing salts has led to large amounts of contamination.

At present, the conventional measures and techniques in controlling the concrete deterioration are [1]:

- reducing the permeability of concrete by the incorporation of admixtures or application of coatings;
- introducing cathodic protection of reinforcements;
• using coated steel rebars, by means of either fusion-bonded epoxy coating, or galvanising;
• using stainless steel

As the principle behind these solutions, with the exception of the latter, is to isolate corrosive agents from contacting the steel, the effectiveness of the protective measures may vary considerably in the long run. Practical experience has showed that these measures do have varying degrees of both technical and economical limitations. Whilst the stainless steel is obviously much more costly than normal steel, all the remaining methods also place a substantial demand on additional costs, both in terms of construction time and maintenance throughout the service life of the structure. In addition, the use of surface coatings and cathodic protection demands careful installation procedures as well as regular replacement. Epoxy-coated rebars also require extra skill and care, and have not performed as effectively as expected to prevent the occurrence of corrosion. Undoubtedly, a completely different approach would be to substitute steel with a material that is highly corrosion resistant, or immune to the corrosive agents.

GRP composites appear to exhibit excellent resistance to the aggressive environments that normally cause corrosion of typical concrete reinforcement. However, designers in the engineering community are still not sufficiently confident to employ these materials in primary and secondary load-bearing structures. This is mainly because of the unknown long term durability of the glass composites when they are directly exposed to cementitious environments with or without in-service loads, as glass fibres are prone to corrosion in aqueous alkali media. Secondly, as pultrusion could hold the key, in terms of mass marketing of composite structural profiles, the mechanical properties of pultruded GRP composites must also be known before the materials are fully accepted in construction industry. The present project concentrates on study of unidirectionally pultruded glass model rebars with geometry of a square cross-section (8 x 8 mm), which were specially developed and kindly provided by Fibreforce Ltd. (UK).
Objectives:

The first objective of this work was to optimise pultruded unidirectional rebar systems made from glass fibres, with three different types of sizing, and two types of resin. The focus was on how the composite interphase affects the interlaminar shear strength (ILSS), flexural properties and failure characteristics of the rebars. The novelty lies in correlating the interfacial strength with the dynamic mechanical properties of the composites.

The second objective was to study the degradation processes and mechanisms of the rebars immersed in water and simulated concrete pore fluid. The water absorption behaviour and dynamic mechanical properties of conditioned pure resin and its based composite rebar have been performed. By comparing the rate and magnitude of the degradation in flexural properties, an attempt was made to elucidate if addition of alkali into water would pose additional damage to glass fibre composites.

The third objective was to develop a loading method to prestress the strong rebar composites, and subsequently examine the durability of the material under combined stresses and the corrosive environments. This part of work centred on the transport processes of aqueous media into the given polymer composite under low-level stresses.

This thesis consists of four main parts. Part I is a review of current knowledge on properties of glass fibre reinforced plastics (GRP) composites and interphase, experimental techniques and environmental effects on the composite components and mechanical properties. Part II (Chapters 3 to 5) covers experimental procedures and techniques employed for this investigation. Part III reports and discusses the results obtained which are included in Chapters 6 to 8. Chapter 6 describes a systematic investigation into physical, mechanical and dynamic mechanical properties, together with ILSS and failure behaviour of a series of rebars. Durability of a rebar immersed in water and alkali solution without stresses is detailed in Chapter 7, whilst Chapter 8 outlines the stress corrosion behaviour of the material in these two media. Finally, conclusions and recommendations for further work form Part IV (Chapter 9).
Chapter 2 Literature Review

2.1 The Application

2.1.1 Pultrusion manufacturing processes

Pultrusion is an automated process for manufacturing FRP composites into continuous, constant cross-section profile [2]. The history of the process can be dated back to 1951 when the initial patent in the United States was issued [2]. Now it has become a well-established manufacturing technique, which makes it possible to produce fibre composites with exceptionally strong longitudinal mechanical properties and high productivity. The materials used in the pultrusion process generally comprise of fibre reinforcements, matrix resins and additives; the choice of which and their respective properties can therefore provide a broad spectrum of composite properties.

The reinforcements, their positions and volume proportions are the main determinant of the physical and mechanical properties of the pultrusion products, such as tensile and flexural strength. The matrix resins control properties like moisture and chemical resistance, as well as thermal and electrical properties.

The most widely used reinforcements are glass fibres, particularly E-glass, whilst higher performance fibres such as carbon and aramid fibres, or their hybrids in combination with glass fibres, are also utilised to achieve higher strength and modulus of the pultruded composites [2-4]. A variety of forms can be taken in the reinforcement materials [3]. Direct rovings consisting of continuous filaments is the most commonly used form, which allows maximum packing of the fibre in a given volume to yield high mechanical properties in the longitudinal direction of the profile. Another is in the form of continuous filament mat, which consists of long continuous fibres randomly distributed in all directions and bonded with a resin binder. This type of reinforcement imparts the transverse properties to pultruded structural shapes. Stitched rovings and woven reinforcements are also employed, but are less popular. E-glass bulky rovings, which have been provided with extra bulk by a texturising process, are believed to
enhance interlaminar shear strength. Additionally, a surfacing veil of C-glass or thermoplastic polyester is applied on the surface of the composite to give an improved surface finish and possible chemical resistance [2].

The majority of pultrusion products are currently made from thermosetting resins [2]. Unsaturated polyesters are the most common types of resins used in this process. Vinyl esters usually have better corrosion and temperature resistance; therefore they are generally used in applications where the corrosion is of the most concern. Epoxy resins are employed when higher mechanical performance and high electrical and temperature resistance are required. Thermoplastic resins are also being increasingly developed and used in the pultrusion because they are tougher than their thermoset counterparts, and allow easier post-forming and welding [4,5]. Whilst the strength of the composite is provided by the reinforcements, it is the matrix resin that determines the other properties such as corrosion resistance, electrical properties and high-temperature performance; therefore, selection of the resins must also be performed with care.

![Fig. 2.1 The pultrusion manufacturing processes [1]](image)

Additives are included in the resin formulation to provide specific features to the finished products. They are composed of catalyst systems and internal release agents to improve processability, and flame-retardants, low-profile additives and mineral fillers to reduce cost and improve weatherability [4].

The pultrusion process for manufacturing FRP into composite rebars is shown in Fig.2.1. Several spools of fibres in the form of strands are first fed. In some cases, the removal of
any moisture condensation from fibres is carried out beforehand by passing the strands over a series of heaters. The fibres are then pulled through a guide where the desired shape is formed. The reinforcement next goes through a resin bath for impregnation. On exiting the resin bath, excess resin is removed before the resin impregnated fibres pass onto a pre-former. The composite material then enters a heated steel die where a polymerisation reaction is initiated in the thermosetting resins. Eventually a rebar fully cured and with its final cross-section dimensions, exits the pultrusion die. The completed rebar is pulled through the system by continuous caterpillar belts, and cut off to the desired length with a conventional water spray cooled diamond rimmed saw. The pultrusion technique provides an opportunity for the manufacture of FRP composites to be used in the construction industry.

2.1.2 Glass fibre reinforcing bars

Consideration of glass as reinforcement in concrete structures has been initialised since the 1930s [6]. However, such problems as the bonding of bars to concrete, surface protection and soil anchorage obstructed their further development for some 20 years. During this period the research in this field remained largely dormant [6]. With the increasing use of composite materials in such applications as for aerospace, chemical and shipbuilding industry since the 1970s, substantial advance has been made in composite material technology. As a result, some of the initial shortcomings and limitations have been significantly overcome and the renewed interest has been aroused in the use of these materials in civil engineering since the mid-1980s. Especially, with recent development in fibres, resins and manufacturing processes, the cost of fibre reinforced plastics has been reduced to a point where they can compete with conventional materials such as steel.

The pultrusion process is particularly suitable for manufacturing composite structures with continuous, constant cross-sectional profiles, e.g. reinforcing bars (rebars), due to its fast speed of operation, good quality control and relatively low production cost. The shapes and sizes of the rebars produced resemble those of steel rebars to simplify design tasks. In this study, a square cross-sectional profile in the dimensions of 8 × 8 mm was employed.
A large amount of effort has recently been made to characterise the physical and mechanical properties of the GRP pultruded rebars, and to the structural behaviour of rebar reinforced concrete members. It is demonstrated [1] that the ultimate tensile strength (550-1500 MPa) of GRP rebars is significantly higher than the yield strength (280-420 MPa) of steel rebars. In addition to the high tensile strengths of the rebars, other merits include the light density and magnetic neutrality, corrosion resistance, long-term savings in repair and maintenance cost, and the close match to concrete material in terms of the coefficient of thermal expansion, when compared with the metal counterparts.

However, the elastic modulus of GRP rebars is only approximately 25% of that of steel. This shortcoming can be, however, compensated by some measures. For instance, increasing the cross section depth or the quality of the rebars can control deflection. Low compressive and low shear strengths are the other two concerns.

As far as the structural behaviour of concrete beams reinforced with FRP rebars is concerned, it is indicated that their flexural behaviour performs reasonably well in concrete beams [7-9] in a short term. The formation of deformation and textures on the surface of the bars is an effective way to create a relatively firm mechanical bonding between the bar-to-concrete interface [8-10]. The development of a tubular grouted anchor signifies a breakthrough for the anchorage of a high-performance glass composite tendon. A pilot test on application of FRP bars in prestressed tendons has been in operation [1].
2.2 Unidirectional Glass Fibre Composites

2.2.1 Glass fibres

Glass fibres are currently the most popular reinforcement for composites, largely because of their low cost compared to carbon or Kevlar fibres and because they easily form strong bonds with a variety of resin systems. They are commercially available in many types according to different chemical compositions, which include E-glass (E for electrical), C-glass (C for corrosion), S-glass (high strength and modulus) and AR glass (alkali resistant).

The major constituent of these amorphous glass fibres is silica (SiO₂) which is called network former. The structure of glass can be described as a 3-dimensional covalently bonded network of linked SiO₄ polyhedral, combined with other oxides (network modifiers) which are held by ionic bonding to the oxygen atoms inside the network. These oxides modify the glass network and control the properties. For example, the addition of zirconium oxide into the silicon-oxygen-silicon network is to improve alkali resistance of glass fibres [11]. Fig. 2.2 [12] shows a two-dimensional representation of the linked polyhedron network structure in a simple sodium silicate glass. As a result of the network structure, the properties of glass fibres are isotropic.
2.2.1.1 Surface treatments of glass fibres

In order to achieve and retain strong adhesion between glass fibres and the matrix resins, coupling agents are coated onto the surface of glass fibres. They have dual function, i.e. to react with both the fibres and the matrix thus provide a continuous linkage across the fibre/matrix interface.

Organosilanes and organometallic compounds are known to be effective coupling agents for silicate based reinforcements and coated onto glass fibres. In reality, a so-called "size" which includes a coupling agent and other ingredients is applied to the surface of the fibres immediately after they are drawn. A size is a complex mixture of dilute solution, dispersion and/or emulsion and its composition is complex and normally proprietary to manufacturers. The thickness of the sizings ranges between 0.1 and 0.2 µm making up 1-2 wt.% of a composite [13]. Although the contribution of each component of sizing systems to the interfacial properties is not well understood [14], their general ingredients and functions can be summarised as:

(i) A coupling agent is a main ingredient of a size but only takes about less than 10% the total size formulation [15]. A silane compound, e.g. an organotrialkoxysilane, is typically used to improve glass fibre/matrix adhesion and mechanical properties of a resulted composite.

(ii) A film former such as polyvinyl acetate, epoxy or polyester resins in an emulsion form protects glass filaments from damage during manufacturing and handling, and binds individual filaments together.

(iii) A lubricant like fatty acid esters or certain silicones is to prevent abrasive damage during fabrication into rovings or other forms of fibre products.

(iv) An anti-static agent is to reduce the build up of static charges, which may affect the packing of the fibres. Most materials that function as anti-static agents are ionic in character.

2.2.2 Polymer matrix resins

The second phase of polymer composites is matrix resins. They determine the chemical and thermal resistance of the composites and also affect some mechanical and electric
properties, in addition to their main function as a load-transmitting medium. Thermosetting resin based composites are still dominant in the market though thermoplastics are being increasingly used as matrices. The mechanical properties of thermosetting-based composites depend on the molecular units making up the three-dimensional network and on the length and density of the cross-links.

The cross-linked thermosetting resins are normally regarded as brittle solids. Improving the toughness can be achieved by incorporating elastomeric particles [16] and introducing interpenetrating network (IPN) [17] into the network of the thermosets. However, these methods are generally at the expense of the mechanical properties of the resins.

Shrinkage stresses during cure and thermal stresses due to differences between the thermal expansion coefficient of the matrix and fibre may result in additional stresses in composite materials. These stresses sometimes may be sufficient enough to create microcracking even in absence of external load [12].

2.2.2.1 The morphological structure of cross-linked polymer network

The styrenated unsaturated polyester resins (UP) are some of the most widely used polymer system to manufacture composites. Curing of the resin can be described as a free radical copolymerisation process between unsaturated groups and styrene monomer molecules. Traditionally, the structure of crosslinked unsaturated polyester resins is believed to be homogeneous. However, later work [18-22] suggests that heterogeneous network is developed during the crosslinking reaction stage of the resins. For example, by examination of the hydrolytic degradation of cured UP resins, Funke [18] found that the final conversion was dependent upon the initial radical concentration, which is not in agreement with the development of a homogeneous polymer. The assumption of a uniform crosslinking density cannot explain the disintegration of swollen samples under weak mechanical force [19]. Jones and Jacobs [20] favoured a two-phase structure for isophathalic UP resin to interpret its non-Fickian water absorption behaviour. Thus, it is assumed that this inhomogeneous system consists of highly cross-linked domains embedded in a loosely cross-linked matrix [20, 21].
Experimental evidence [22] showed that micro-gel particles can form at an early stage in the polymerisation of a styrenated UP resin, because of the intramolecular crosslinking amongst pendant polyester C=C bonds. Then inter-particle crosslinks may occur through the C=C double bonds at or near the surface of the micro-gel particles with styrene monomer acting as chain extender. Recently, Ganem et al. [23] revealed, by the kinetic data of copolymerisation, that the structure of a DGEBA (diglycidylether of bisphenol A) vinylester crosslinked with styrene is a two-phase system. However, this phase separation has not been clearly observed even though the development of heterogeneous structures within vinylester and polyester resins has become increasingly accepted [18-22].

More recently, Richardson and Zhang [24] have studied the morphological structure of a fully crosslinked vinylester Atlac 580 resin using modulated differential scanning calorimetry (MDSC). The results show that the network of this vinylester resin exhibits a diphasic structure, characterised by the presence of two glass transition temperatures (T_g). It is believed that the two phases are composed of a polystyrene-rich phase and a vinylester-rich phase, which results from phase segregation during radical copolymerisation. The results also indicates that the phase separation is very limited, with a difference in the T_g's of the two phases being approximately 10 deg. C. The implication for this finding may aid to understand the processes and mechanisms of stress corrosion of glass fibre composites in corrosive environments.

The morphological structures of polymers can be studied with by a number of methods [25]. Amongst these, determining the glass transition temperature, T_g, is the most convenient and unequivocal way to judge the homogeneity of such polymers. For amorphous polymers, T_g can be characterised by differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and dielectric relaxation methods [25]. However, these techniques often suffer some limitations. Sometimes it is very difficult to resolve components that have very similar glass transition temperature [24]. Also, if the phase-separated domain sizes are too small, the sensitivity of the above mentioned techniques will not allow them to be detected. With the recent advent of MDSC [26], these difficulties may be overcome with its improved resolution and sensitivity [24, 27-29].
2.2.2.2 Physical ageing of polymers

Polymers annealed [30, 31] below their \( T_g \)s can facilitate to identify the occurrence of phase separation [24, 32]. The behaviour of glassy polymers during annealing process (often referred as non-equilibrium behaviour, enthalpy or volume relaxation or physical ageing) results from the inherent kinetic nature of glass transition [31]. As a polymer is cooled in a normal process from the melt through the glass transition into the glassy state, there occurs a rapid decrease in molecular mobility, which parallels a sudden increase in viscosity and modulus as the transition temperature is approached. The polymer molecules are not, in fact, able to reach their equilibrium conformation and packing with respect to temperature, and as the temperature is further decreased the molecules are essentially “frozen” into a non-equilibrium state of higher energy and volume relative to the corresponding equilibrium state at the same temperature. Since the polymer molecules are in a non-equilibrium state, there exists a thermodynamic potential or driving force for them to approach equilibria by undergoing further packing and/or conformational rearrangements. Physical ageing also adversely affect the toughness of polymer composites [33, 34]

2.2.3 Glass fibre/matrix interphase

Firstly, it may be necessary to point out that composite ‘interface’ is often used synonymously to composite ‘interphase’, though the two-dimensional interface is literally different from the three-dimensional interphase [35]. However, interfacial region may be more precise than the above terms since it refers to a region in the vicinity of the fibres and the matrix, and more importantly its properties are different from those of the other two distinct phases.

There is no doubt that the interphase between glass fibres and the polymer matrix play an important role in determining the overall performance of glass composites. To enhance the glass fibre/polymer bonding, silane coupling agents are normally applied onto glass fibres as mentioned previously. A brief review of the mechanisms of silane coupling agents is presented here.
2.2.3.1 Chemistry and structure of silane coupling agents

Most glass fibres contain silicon hydroxyl groups (Si-OH) as well as additional metal hydroxyl groups (metal-OH) because of a hydrophilic nature of glass. The reaction of atmospheric water with glass fibre surface gives rise to a well bonded hydroxylated layer. The presence of water also results in a significant reduction in glass surface energy (from 500 mJm\(^{-2}\) to 50-70 mJm\(^{-2}\)) [36].

The general chemical structure of a commercial silane coupling agent can be expressed [15] as: RSiX\(_3\), where R is organofunctional group designed to be compatible with polymers; X designates hydrolysable alkoxy groups which are converted to silanol on hydrolysis and then bonded to glass. Therefore, a silane coupling agent contains one end of the molecule that has a potential to react with the glass Si-OH functional groups, typically a trifunctional silicon with either chlorine or alkoxides, and the other end of the molecule can react chemically with the resin. The effectiveness of the silane as a coupling agent parallels with the reactivity of the organofunctional group with a resin. Normally, a silane is chosen to maximise the reactivity of organofunctional group with a polymer to form a strong bond [37].

Silane coupling agents are often applied from water dispersion [38]. Water reacts with organosilanes through hydrolysis. Condensation reactions between silanols on the organofunctional silane and silanols on glass fibres produce siloxanes, linkages between fibre and polymer. Intermediate silanols first hydrogen bond to the glass surface but ultimately condense to form oxane bonds across the interphase.

The interface can be regarded as two interfaces: the glass/silane interphase and silane/resin interphase. Experimental work [39-41] has shown that chemical reaction occurs to the former. Infrared spectroscopic study [39] indicate that the silanol groups of the coupling agent vinyltriethoxysilane chemically reacted with the surface of small particles of silica. Ishida and Koenig assigned infrared absorption bands at 1170 and 1080 cm\(^{-1}\) to antisymmetric stretching of Si-O-Si bond between the coupling agent and silica. Chemical bonding between the coupling and the matrix resin also seems well established. Such bonding is necessary to obtain a high performance of composites. Looking at the loss of radio-labelled resin from non-labelled coupling agents on E glass
fibres, Johnanson et al [42] presented the evidence that the double bond in the coupling agent reacted with either the styrene or the methyl methacrylate monomer. Bjorksten and Yaeger [43] proposed that a chemical reaction between vinylsilane and polyester resin occurred through the vinyl group.

![Diagram of coupling agent deposited on glass fibres](image)

**Fig. 2.3** Schematic illustration of a coupling agent deposited on glass fibres

However, the structure of absorbed silane coupling agent is not so simple [44-47]. A study by Schrader [44], utilising a radio-labelled tracer technique, suggests that a complicated, three layer structure of a coupling agent coating deposited on glass surface as shown in Fig. 2.3. The first layer consisted of a maximum of 98% of the total of silane that was physically absorbed to the surface of the fibre (as much as 270 monolayer equivalents) and was readily removed by cold water. The second layer was chemisorbed polymer (10 monolayer equivalents) and could be removed by an extraction in boiling water for 3 to 4 hours. The third layer was a monolayer that could not be removed after prolonged exposure to boiling water. It appears that the monolayer is chemically bound to the surface of glass through Si₈-O-Si₆ linkages between the glass and the coupling agent.
2.2.3.2 Interdiffusion and IPN interphase

Currently, there are five theories that explain fibre/matrix adhesion detailed in Reference [48]. The chemical bonding theory is one of the most successful and popular theories to explain glass fibre-polymer bonding mechanisms. However, it cannot alone account for the increase in adhesion experienced between non-reactive matrices like polyolefins and inorganic reinforcements in which chemical bonds have not been formed [49]. This led to a proposal put forward by Plueddemann [49] that the interpenetrating network (IPN) is possibly created in the interphase through the interdiffusion of physisorbed and/or chemisorbed silane with matrix molecules. IPN can be defined as a combination of two or more polymers in a network and at least one of which is crosslinked and/or synthesised in the presence of other.

Since then, a number of investigations have been carried out by different researchers to characterise the existence of such a interdiffusion layer [50-52] and their role in controlling interfacial bonding strength [54,55]. The general picture is that the interaction of a silane coupling agent with a polymer matrix is specific to each system, and therefore the presence or absence of an IPN interphase must be characterised and defined for each system by appropriate techniques. Under certain favourable conditions, an IPN interphase can be formed [53]. In addition, the interpenetration of silane polymer segments into polymer matrix segments may be expected to provide improved bond strength. This is evidenced by the fact that more than a monolayer of silane coupling agent is needed to promote the optimum strength during composite production [49, 54]. This may be due to the necessity for the formation of interfacial chemical bonds and IPN networks in the interphase. The beneficial effect related to bond strength has been documented [55, 56].

2.2.3.3 The role of sizings

As mentioned above, commercial glass fibres contain sizings with complicated ingredients. Their role on composite interphase is also complex, depending on the constituents and processing conditions. Incomplete dissolution of the sizing can give rise to an interphase region [57-59], whose properties depend on those of matrix-size interaction. Some work [60, 61] suggests that a concentration gradient was developed at
an interphase region and therefore producing an interphase with a gradation in mechanical properties.

In contrast to the dissolution of sizing systems away from the fibre surface, Drzal et al. [62] proposed that the dissolution of a resin harder into the sizing may cause the formation of an interphase, which in turn lead to the deficient of harder in the interphase compared in the bulk matrix. The deficiency is believed to be greatest on the fibre surface. Consequently, low cross-linking density and low mechanical properties of the resin in the vicinity of glass fibres result.

2.2.3.4 Characterisation of composite interphase by mechanical and dynamic mechanical methods

Interlaminar shear strength (ILSS) test is one of the widely used methods to determine the interfacial strength of unidirectional composite laminate [63]. However, care must be exercised to use ILSS data to assess the glass fibre/matrix interfacial strength as it depends upon a number of factors. Resin strength and composite void content are the two most important ones [64-70]. Studying filament winding GRP composites, Brelant and Pekter [64] have found an essentially linear relationship between the tensile strength of the matrix resin and the ILSS values of ‘void-free’ unidirectional composites. The derived relationship was given as:

\[
\text{ILSS}_{vf} = 0.92\sigma_m
\]  

Where \( \text{ILSS}_{vf} \) is the interlaminar shear strength of void-free composites and \( \sigma_m \) is the tensile strength of the polymer matrix.

Likewise, a nearly linear relationship between composite void content and ILSS was claimed by a number of research workers [63-66]. Wisnom et al. [69] recently reported the results of a study of ILSS reduction by voids in unidirectional glass/epoxy composites and characterised two types of voids, discrete larger voids and small distributed voids. The larger voids acted as crack initiation sites under a shear stress, whereas the increase in stress due to the reduction in net cross-section was the main factor in shear failure of composites with smaller discrete voids. Based on net cross
section reduction, a theoretical relationship between ILSS and void content ($V_v$) was derived by Gresczuk [70] as follows:

$$\frac{ILSS}{ILSS_v} = 1 - \frac{\pi}{4} \left( \frac{6V_v}{\pi(1 - V_f)} \right)^{2/3} \tag{2.2}$$

This equation assumes that the voids are spherical and arranged in a cubic array.

The other method to characterise the interphase bonding of a composite is dynamic mechanical analysis [71, 72]. The theory behind this method is that energy is dissipated at the fibre/matrix interphase when the composite is subjected to a continuous cyclic loading. Based this idea, this interphase energy dissipation could be separated theoretically from the other dissipative mechanisms within a composite. Subsequently, Zorowski and Murayama [71] developed a method to assess the quality of the interfacial adhesion through energy loss measurements, using the following relationships:

$$\tan \delta_{adh} = \tan \delta_e - \tan \delta_{exp} \tag{2.3}$$

$$\tan \delta_e = \left( \frac{\tan \delta_f E_f V_f + \tan \delta_m E_m V_m}{E_f V_f + E_m V_m} \right) \tag{2.4}$$

where $\tan \delta_{adh}$ is a relative measure of energy dissipated because of poor adhesion, $\tan \delta_{exp}$ is the measured energy loss for a composite, and $\tan \delta_e$ is the calculated energy loss for a composite. $E$ is the modulus of elasticity and $V$ represents volume fraction. Zorowski and Murayama further [71] found a reverse correlation between the adhesion factor, $\tan \delta_{adh}$, and the adhesive strength for nylon 6,6 and poly (ethylene terephthalate) cord reinforced rubbers.

Studying the ILSS and dynamic mechanical properties of longitudinal glass fibre reinforced polyester composites, Chua [73] demonstrated that the quality of the interphase can be characterised by $\tan \delta_{Tg}$, which is in turn affected by the reactivity of organosilanes with the polyester resin. A good interfacial strength (ILSS), as associated
with low energy dissipation, consistently exhibits a low \( \tan \delta_{T_g} \) value. However, no correlation was found between Zorowski and Murayama’s equation as well as the \( T_g \) of the composites.

Eckstein [74] investigated glass braids with polyester resin coatings of varying thickness and different types of silane coupling agent. It was shown that both of these two factors affect the damping, the loss and storage modulus as well as the glass transition temperature. The loss modulus seems to be the most sensitive indicator of an efficient stress transfer between glass fibres and matrix.

Most recently, Keusch and Haessler [75] studied the composite interphases between differently treated glass fibres and epoxy resin using dynamic mechanical analysis. It was found that the flexural modulus of the composites with improved interfacial strength is increased over the wholly investigated temperature range. Decrease of the magnitude of \( \tan \delta_{T_g} \) associates with an improvement of interfacial bonding. They concluded that dynamic mechanical analysis is a good additional possibility to characterise interfacial adhesion.

### 2.2.4 Flexural failure of unidirectional composites

When unidirectional glass composites are subjected to flexural stress in a longitudinal direction, failure can theoretically occur on either a tensile or a compressive side or on both sides. However, a fracture usually initiates on the compression surface because of the lower strength of GRP in compression relative to tension and the stress concentration generated by a loading roller. With the movement of the fracture towards the neutral axis, the compressive stress decreases and interlaminar shear stress increases [76]. Therefore, the compressive failure often stops at a shear crack. The flexural compressive failure involves a formation of kink band and fibre micro-buckling [77]. There are a number of factors, which influence the longitudinal compressive strength of fibre composites [12, 78]. The fibre/matrix interfacial strength and the matrix strength are most important ones amongst them [79-82].
However, cracks perpendicular to the direction of the maximum principal stress can also initialise on the tensile surface. It was identified that the brittle failure of the polymer matrix is responsible for the crack initialisation [79]. With increasing the load level, these cracks will expand and meet with neighbouring fibres. There are two cases for the propagation of the cracks. When the interphase is locally so strong that the matrix crack does not "feel" the existence of the interphase [83], fibre fractures will occur locally at the statistically weak points. Alternatively, the crack will propagate along the fibres when the interphase is weak. Both cases often occur simultaneously. Therefore, flexural tensile failure involves matrix cracks, delamination and fibre fractures.

2.3 Environmental Effects on GRP Composite Components

2.3.1 Environmental effects on glass fibres

As the glass fibres are the reinforcement for many commercial composites, the durability of glass fibres under environmental exposure will govern the retention of many of their fibre-controlled mechanical properties, it is therefore necessary to consider the effect of such conditions on glass fibre alone.

Glass fibres are brittle and their strength is sensitive to imperfections and flaws such as voids, cracks and scratches. Their high "virgin" strength is probably due to axial orientation of these imperfections combined with the thinness of the fibre filaments, which reduces the probability of transverse cracks of critical length. The classical brittle-fracture theory that postulated by Griffith [84] assigns the following approximate expression for the brittle strength:

$$\sigma = \sqrt{\frac{\gamma E}{\pi c}}$$

(2.5)

where $\sigma$ is the fracture strength in the presence of a sharp crack, $\gamma$ is the specific surface energy, $E$ is the Young's modulus, and $2c$ is the length of a crack perpendicular to tensile stress axis.
The strength of glass is also very sensitive to water attack. Differing schools of thought have arisen to explain the phenomenon. They all can be related to the Griffith theory. One school of thought postulates a decrease of the cohesive strength as a result of adsorption of environmental agents. This adsorption causes a reduction in the surface energy for fracture and hence a reduction in strength. The other school attributes the loss of strength to the slow growth of a crack until it reaches the critical size for fracture, but the theoretical strength of the material remains unchanged. Hammond and Ravitz [85] have demonstrated their result in a favourable agreement with the adsorption mechanism. Their work has showed that the strength of quartz decreases in certain vapours and follows the predicted linear relationship with the square root of the surface energy. The theory of Charles [86] approaches the growth of Griffith cracks by an ion change mechanism and subsequent bond cleavage. He also describes in detail the chemical events between water and glass that cause stress induced crack growth as follows:

The first stage of attack is involved with the sodium ions migrating outward in the following chemical reactions:

$$\text{Si - ONa} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{Na}^+ + \text{OH}^- \quad (2.6)$$

During the second stage the $\text{OH}^-$ ions disrupt the strong siloxane bond (the main structural backbone of glass), producing a $\text{Si -O}^-$ molecule:

$$\text{Si - O - Si} + \text{OH}^- \rightarrow \text{Si - OH} + \text{Si - O}^- \quad (2.7)$$

Which in turn decomposes another water molecule (the third stage is a repetition of the first):

$$\text{Si - O}^- + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{OH}^- \quad (2.8)$$

Consequently an alkaline medium is created, the $\text{OH}^-$ concentration being equivalent to that of the released $\text{Na}^+$. This in turn raises the pH level (an autocatalytic process).
Charles [86] suggested that the actual fracture of the glass was not due to the removal of Na\(^+\) ions but to the action of hydroxyl ions. He concluded that the leaching of the alkali ions was the rate controlling step, which limited crack growth until the pH at the crack tip had reached such a level as to produce autocatalytic effect.

Later work was extended to glass fibres [87] where it was demonstrated that the rate determining process was hydroxyl ion build up at structural defects to a critical pH when chemical attack of siloxane linkages occurred autocatalytically. Therefore, this mechanism is more favoured as it has been claimed to be better able to explain that fibre strength is virtually unchanged to the point of failure. Water attack to glass fibres is also evidenced by the roughening of glass fibre surface and a reduction of strength [88].

Glass fibres have known to be prone to alkali attack [11, 89-93]. E-glass reinforced cement showed a rapid deterioration in properties [11, 90] due to attack of the glass fibres by alkali cement matrix. Cockram [92] observed that unsized E-glass fibres, after being immersed in a simulated cement extract solution containing sodium, potassium and calcium hydroxides at pH 13 at 50 °C, quickly lost their strength and, ultimately, reduced their strength to zero after two weeks. It was recognised that the property degradation rate of E-glass fibres was faster in the alkali solution than in water [92] but slower than in acids [94]. The mechanism involved is that hydroxyl ions the alkaline media dissolve the basic silicon-oxygen-silicon structural networks [11, 93]:

\[
\text{Si} - \text{O} - \text{Si} + \text{OH}^- \rightarrow \text{Si} - \text{OH} + \text{SiO}^- \quad \text{(in solution)}
\]  

This dissolution of the siloxane bonds is accompanied by a rapid and severe strength loss. It seems clear that the corrosion mechanism of glass fibres in alkali solution is similar to that in water as stated above. The difference is that the external alkali medium worsens the case.

Acidic solutions are more detrimental to the strength of E-glass fibres than alkali solutions and water. The corrosion involves an ion exchange mechanism [91]:

\[
\text{SiONa} + \text{H}^+ \rightarrow \text{SiOH} + \text{Na}^+
\]  

(2.10)
Metcalfe et al. [91, 95] proposed that the ion exchange of the alkali ions leads to a leached outer sheath around a glass fibre. There is a reduction in the molar volume of the leached layer because the alkali ions are replaced by hydrogen ions of aqueous acids. Consequently, a contraction occurs on the surface of the glass fibre as opposed to its unchanged core. The surface tensile stresses are developed and they are large enough to cause spontaneous cracking of the outer sheath even when there is no external stress applied.

Baker, et al. [96] also observed the spontaneous cracking of E-glass fibres in dilute acid. However, they found that the dominant species removed were calcium and aluminium which they considered was far more serious than the leaching of sodium ions. Glass fibres free from these elements were proved to be more resistant.

It appears that there are differences between Charles' and Metcalfe's theory. Charles believed that the ion exchange took place at the crack tip of pre-existing flaws, therefore leading to crack sharpening and propagation by the action of the hydroxyl ion. Metcalfe states that it is the ion exchange of alkali ions, which migrate to the surface that results to the generation of micro-flaws in the corroded surface.

With the introduction of an applied load, the rate of glass fracture is increased. This phenomenon is called stress corrosion. Its exact nature and mechanisms are still under debate. The following empirical equation is commonly used to study stress corrosion of glass.

\[ V = AK_1^n \]  

(2.11)

where the constant A and exponent n depend on the material and the environment, V is the velocity of the growth of the crack, K_1 is the stress intensity factor. V and K_1 can be experimentally measured.

Metcalfe and Schmitz [91] observed that an incubation period existed in the stress corrosion of E-glass in the presence of water followed by a loss of strength. Their results
suggest that it was necessary for water to adsorb onto the surface of the glass filament and form a film, through which the transport of the material responsible for corrosion occurred [97].

Agarwal and Broutman [98] described the general features of stress corrosion. First, the strength of the fibre is independent of the time after application of a load under an inert atmosphere and/or at low temperature. Second, the strength is independent of exposure to active environments (water) before the application of the load. Third, the strength is dependent on exposure to environments under an applied stress; the residual strength of the fibre after its exposure to corrosive environments and an applied stress is less than that for unexposed fibres, suggesting that the applied stress influenced the corrosion of the glass. Fourth, the residual strength for fibres simultaneously exposed to a corrosive environment and an applied stress decreases with increasing temperature.

Aveston et al. [99] measured the time to rupture under stress for E-glass fibres in comparison with that for a corrosion-resistant glass, Cemfil, after previous exposure to water, under either no load or a static load. Wet E-glass fibres that were under static load prior to testing, exhibited a decrease in strength at a rate faster than fibres that had no prior load, regardless of whether the fibres were uncoated or coated in polyester or epoxy. Because of their corrosion-resistant nature, the Cemfil fibres retained their strength to a greater degree than did the E glass fibres. Roberts found that mineral acids were more aggressive than alkalis to ordinary E-glass fibres [100].

Clearly the failure of glass fibres is largely determined by the environmental exposure conditions like moisture, acids and alkalis, stress and glass compositions. It seems that the surface degradation of the fibres is unavoidable [12]. One possible measure to limit this deterioration may be to protect glass fibres by a strongly bonded polymer coating, or to isolate completely the glass fibres from the corrosive environment. Another way may be to replace the commonly used E-glass with corrosion resistant glass, for example AR glass fibres that has been proved to retain much higher strength than E-glass fibres in alkali medium [11, 101]. The enhancement is mainly attributed to the introduction of zirconia into glass fibres.
2.3.2 Environmental effects on the matrix

As mentioned earlier, the role of the matrix resins in polymeric composite materials is two-fold: protection against environmental attack and a load-transmitting medium. Water penetration will cause reversible and irreversible changes in the resin properties.

2.3.2.1 Reversible damage

The reversible effect, which is physical in nature, manifest itself in the plasticisation of the matrix, and the generation of internal stress due to the accumulation of water molecules within the polymer network. The immediate effect of the sorption of water by resins is the lowering of $T_g$, thus causing them to soften at lower temperatures. The major mechanism for the $T_g$ reduction is considered to be the result of water acting as a lower molecular weight plasticiser, or an internal lubricant decreasing the energy barrier for chain segment movements. Another theory attributes this process to the disruption of Van der Waals’ bonding or hydrogen bonding [102], which makes chain segment rotation possible [103].

However, upon drying out, the properties of the resins can be restored. Wimolkkiatisak and Bell [104] demonstrated that the tensile strength of an epoxy resin previously exposed to water at either 50 °C or 100 °C, reduced from 70 MPa to 58 MPa and 62 MPa respectively. Once the wet samples had been dehydrated, their original tensile strength was recovered, or was even higher, which it is suggested, possibly resulted from further crosslinking during thermal treatment.

2.3.2.2 Irreversible damage

This damage includes hydrolysis of chemical bonds, and leaching of water soluble specimens, and microcracking of the matrix. Chemical interaction obviously depends on its chemical composition. Epoxy resins are generally hydrolysis stable and their durability depends mainly on physical processes [105]. Contrarily, polyesters are hydrolysis prone resins due to the ester groups, which are highly susceptible to saponification [106] as follows:
Johnson [107] found that the relative rate of degradation of properties in polyester resins was ortho phthalic ester > iso phthalic ester > vinyl ester > bisphenol-A ester. Presumably this trend resulted from the relative rates of hydrolysis of the polyesters. Looking at the influence of the chemistry of polyester resins on the retention of their mechanical properties by exposing polyester-glass fibre composites to water at 25 °C and 90 °C, Apicella et al. [108] concluded that the relative hydrolytic damage decreased as a result of isophthalic resins > bisphenol-B > bisphenol-A > vinyl ester. This suggested that the susceptibility to hydrolytic attack increased with an increase in the number of ester groups in the polymer repeat unit. They did not, however, perform chemical analysis to confirm if hydrolysis did indeed occur.

Hojo and Tsuda [109] reported that corrosive environments, particularly alkali solutions increase the rate of the hydrolysis. They measured the variation of ester and carboxylate peaks at the specimen surface of vinyl ester resin castings after immersion in water, 10 wt. % HCl and 10 wt. % NaOH, using infrared spectroscopic analysis. Their results indicated that hydrolysis occurred more appreciably in NaOH and moderately in HCl compared with that in water. In a line with their infrared analysis, the retention of tensile strength after immersion obeyed the same trend. This could indicate that the saponification of the ester linkage is accelerated by the high concentration of OH⁻ ions in alkali solutions and significantly causes degradation by destroying the resin backbone.

Another form of irreversible damage is microcracking of the matrix. Water generally causes failure in polymers by inducing crazing or cracking via a mechanism which comprises three regimes. The first two contributions come from the chemical degradation and plasticisation discussed above. The third derives from the generation of internal stresses that, when a combination of these three factors occurs in a particular region, will produce localised failure at stresses much lower than those observed in the absence of the penetrant. Walter and Ashbee [110] observed that swelling caused debonding of the E glass fibres if the generated swelling stress was too great. Possibly the swelling resulted in stresses that were greater than the effective interfacial strength: thus failure at the interface occurred.
2.3.2.3 Effect of external stresses on diffusion in matrix

The effect of external loading on moisture penetration into composite materials is a relevant issue when they are used in applications of load bearing structures. First of all, it is necessary to look at the diffusion dependence of the unreinforced matrix on stress. The main penetration mechanism of diffusion may be considered mechanistically as transport of water molecules through holes in the polymer structure. The ease of transport mobility depends on the size of these holes, which in turn depends on the free volume of the polymer, the latter being the difference between the specific volume of the polymer and the actual volume of its molecules.

Based on Fahmy and Hurt's mode [111], which quantifies the change of the free volume as a function of stress, and the Doolittle equation [112], Marom [103] derived the functional relationship between the diffusion coefficient and stress as follows:

\[
D_{\sigma} \approx D_0 \exp \left[ \frac{(6 \text{ to } 10)\sigma}{G} \right]
\]  
(2.13)

where \(D_{\sigma}\) and \(D_0\) are the diffusion coefficient of polymer in the stressed and unstressed states respectively, \(\sigma\) is the stress which is positive under tension, and negative under compression, and \(G\) is the shear modulus. For moderate stresses, this equation approximates to

\[
D_{\sigma} \approx D_0 \left( 1 + \frac{(6 \text{ to } 10)\sigma}{G} \right)
\]  
(2.14)

The influence of environmental exposure can cause changes in the resin through a diffusion of water into the sample, leading to physical ageing, swelling stress, hydrolysis and microcracking. The chemical composition and high pH aqueous solutions appear to influence polymer susceptibility to hydrolysis. External stresses affect diffusion coefficient by changing its free volume. The equilibrium content of water will determine the degree to which swelling stress, hydrolysis and microcracking occur.
2.3.3 Environmental effects on the interphase

The boundary between matrix and reinforcement can be defined as an interface region that transfers stress from the matrix to the reinforcement. Good adhesion in that interface is essential for a polymer composite to have properties that are advantageous. In order for the composite to maintain its properties on exposure to a given environment, the interface must provide adequate chemically and physically stable bonds between the fibre and the polymer matrix. Numerous direct and indirect evidence [88] suggests that the weakest part of a composite is the interface, and the properties of a composite, particularly mechanical properties, are often limited by failure at the interface. To enhance the bonding in the interface, a silane coupling agent is usually applied on glass fibres as described earlier.

It is generally recognised [88] that the glass-matrix interface is particularly weak in the presence of water. The interaction between the glass-coupling agent and water is believed to be a controlling factor in determining the environmental resistance of composites, as the coupling agent-matrix interface is considered to be chemically stable to hydrolytic attack.

Water can be held at the glass/resin interface. It is proposed that water reaches a bonded interface by diffusion both through the matrix and along the interfacial layer. In addition, water transport by capillary flow along flaws such as cracks, pores and small channels present in the material may also occur. Such imperfections are particularly detrimental to maintaining the integrity of a composite system, possibly due to only a physical bond formed between the fibre and resin being readily replaced by a quick penetration of water through this process [103].

The penetrated water is proposed to cause a hydrolysis reaction of the siloxanes at the glass/resin interface. This process occurs relatively easily, possibly because the activation energy of hydrolysis of siloxane was reportedly as low as 22.8 kcal/mol. when reacted with a KOH solution; and 23.6 kcal/mol. when reacted with water [39].
It is clear from the above that the hydrolysis of the interface can not be completely prevented. The fact is that a coupling agent treated composite can still retain good strength in the presence of water. However, in the absence of the silane coupling agent the glass-resin interface deteriorates rapidly in the presence of water, which can attack the fibre by the hydration processes described in Section 2.3.1. A question arises: what makes such an interface water-resistant? This is not fully understood. Bascom [113] stated that silane finishes did not significantly improve resin wettability neither did they impart an unusually hydrophobic character to the fibre. However, they act against molecular water penetration by diffusion along the glass resin interface. The work by Laird and Nelson [114] also revealed that coupling agents are mainly effective for bond permanence and not for mechanical strength or wetting.

Plueddemann [115] suggests that the reformable nature of silanol is understood as a dynamic equilibrium of the coupling agent competing with small penetrating water molecules. In the presence of water, the covalent M-O bond hydrolyses as shown in Fig 2.4. (a). Since this process is reversible the covalent bond can reform when the water diffuses away. Thus, in the presence of a simple shear stress parallel to the interface (Fig 2.4 (b)), the surface can slide past each other without permanent bond failure. Experimental evidence for this reversible bond has been demonstrated by the reversibility of the mechanical strength of fibre composite after being boiled and followed by evacuation at elevated temperature [116]. The other evidence is reversibility in the intensity of the SiOSi symmetric stretching line at 788 cm\(^{-1}\) for the bonded coupling agent by utilising laser Raman spectroscopy [117].
Molecular water can produce a reversible reduction in properties, but condensed water at the fibre/matrix interphase can generate permanent damage by dissolving away any soluble species in the glass fibres and matrix resins. This may allow water to wick along the fibre/matrix interface due to capillary flow of water. It was identified [118] that the main water soluble impurity is unreacted glycol for polyester resins. Leaching out of the ions from glass fibres is also responsible for the damage to the GRP interphase [119].

Pressure pockets generated at the fibre matrix interface during immersion can cause further disruption of the glass/resin bond [120]. Walter and Ashbee [110] attribute the
formation of internal blisters to an osmotic process involving pockets of water containing dissolved soluble materials from the glass fibres and/or the matrix. The water collects at voids, with the resin acting as a semi-permeable membrane through which the water continues to diffuse until the osmotic pressure generated is sufficient to cause rupture.

The penetrated water weakens the interface and ultimately causes the debonding at the interface. The single-fibre fragmentation test is one of the good techniques for determining the interfacial strength between a fibre and resin. For a system exhibiting plastic deformation of the resin and elastic deformation of the fibre, the effective interfacial shear strength $\tau$ can be related to the strength of the fibre, $\sigma_f$, and the average critical length/diameter ratio of the fibre fragment, $L_c/D$:

$$L_c/D = \sigma_f/2\tau$$

Schutte et al. [121] studied durability of E glass fibres and of interfaces in an epoxy matrix on exposure to both 65 and 75 °C distilled water, using the single fibre fragmentation test. They found evidence that both the strength of the fibre and the interfacial strength degraded on exposure to water as the content of water increased in the sample. Because the $L_c$ increased as a function of time of exposure, it appeared that the relative rate of degradation of the interface was greater than that of the strength of the fibre.

The morphology of the interphase influences its durability. Schrader and Block [45] observed that the presence or absence of the physisorbed phase did not have significant influence on the wet strength of the joint under a load of 50 lb. However, if there was an excessive amount of the physisorbed phase, this presence accelerated the rate of loss of bond strength. They concluded that the larger the proportions of chemisorbed and a monolayer component relative to the physisorbed phase, the greater was the life of the joint.
2.4 Environmental Effects on the Properties of Composites

2.4.1 Water Absorption

In order to account for water or moisture effects on composite materials, knowledge of the diffusion characteristics must be understood.

2.4.1.1 Water diffusion in polymers

Diffusion is the process by which matter is transported from one part of the system to another as a result of random molecular motion. The diffusion behaviour of water in glassy polymers can be classified into the following three categories according to the relative rates of mobility of the penetrant and of polymer segments [103]:

(i) Fickian diffusion, in which the rate of polymer chain mobility is much greater than the rate of water diffusion. Sorption equilibrium is quickly established since the passage of water molecules is not hindered. There is no dependence on swelling kinetics.

(ii) "Super case II" is the opposite of the Fickian diffusion, with the chain mobility being the rate controlling step, and the sorption process strongly depends upon the swelling kinetics of the polymer.

(iii) Non-Fickian or anomalous diffusion is a process when the penetrant mobility and polymer segment relaxation are comparable. Non-Fickian behaviour disappears as the test or environmental temperature approaches the glass transition temperature.

The differences of these three cases can be reflected in their sorption-time relationship:

\[
\frac{M_t}{M_\infty} = kt^n
\]  

(2.16)

where \( M_t \) is the relative weight gain at time \( t \), \( M_\infty \) is the equilibrium weight gain and \( k \) and \( n \) are constants [122]. For case 1 \( n=0.5 \), whilst for case 2 \( n\geq1 \) and \( 0.5<n<1 \).
For a Fickian uptake by a specimen with an infinitely large area exposed on both sides to the same environment, mass uptake is related to time by the following equation (when $t < t_i$):

$$
\frac{M_t}{M_\infty} = \frac{4}{b} \left( \frac{Dt}{\pi} \right)^{\frac{1}{2}}
$$

(2.17)

where $M_t$ and $M_\infty$ have the same meaning as Equation (2.16), $b$ is the thickness of the specimen, $D$ is the one-dimensional diffusion coefficient, and $t$ is the time.

Relative moisture weight gain $M_t$ is given by the equation:

$$
M_t = \frac{\text{Weight of wet material} - \text{Weight of dry material}}{\text{Weight of dry material}} \times 100
$$

(2.18)

![Diagram of moisture content as a function of square-root of time](image)

Fig. 2.5 Illustration of moisture content as a function of square-root of time (for $t < t_i$, $k$ is constant)

Fig. 2.5 shows a typical Fickian absorption behaviour of a polymer. One of the features of Fickian diffusion is that the temperature dependence of $D$ can be expressed by Arrhenius relation [123]:

$$
D = D_0 \exp \left( -\frac{E_a}{RT} \right)
$$

(2.19)
where $D_0$ is the constant, $E_a$ is the activation energy of the diffusion process, $R$ is the gas constant, and $T$ is the absolute temperature.

$D$ is also affected by stress. Marom et al [124] established a theoretical model of describing diffusion of water in composites under stress. Further details about diffusion of polymers are given in references [103, 123].

2.4.1.2 Mechanisms of water penetration in composites

a) Diffusion in composites

The diffusion of water into polymer composites can be assumed to be Fickian and to be governed by a diffusion coefficient [125], although Langmuir two-phase model is also used [123]. The diffusivity of a composite depends upon those of the matrix, $D_m$, and of the fibres, $D_f$, and on the volume fraction of the fibres $V_f$. For polymer based fibre reinforced composites two diffusivities are defined, one parallel (longitudinal) and another perpendicular (transverse) to the fibre direction, denoted $D_{11}$ and $D_{22}$, respectively.

For a unidirectional GRP composite, the longitudinal diffusivity can be obtained by a rule of mixtures [125]:

$$D_{11} = (1 - V_f)D_m$$

(2.20)

The transverse diffusivity can be expressed as:

$$D_{22} = \left(1 - 2\frac{V_f}{\pi}\right)D_m$$

(2.21)

It is assumed in Equations 2.20 and 2.21 that the moisture diffusion of fibres, e.g. glass fibres is very small compared with that of the matrix, and can be neglected.
For a unidirectionally reinforced composite plate whose sides are aligned with the x, y, and z axes of a co-ordinate system, and whose fibres form the angles α, β and γ with respect to the three axes, as shown in Fig. 2.6. The axial diffusivities are expressed by a transformation of the directional diffusivities, $D_{11}$ and $D_{22}$, as follows:

\[
\begin{align*}
D_x &= D_{11} \cos^2 \alpha + D_{22} \sin^2 \alpha \\
D_y &= D_{11} \cos^2 \beta + D_{22} \sin^2 \beta \\
D_z &= D_{11} \cos^2 \gamma + D_{22} \sin^2 \gamma 
\end{align*}
\] (2.22)

The total moisture diffusion into the specimen shown in Fig. 2.6 results from diffusion into the six sides, and it therefore depends on the directional diffusivities and relative dimensions of the plate (the interactions are neglected). By analogy with eqn. (2.17), we obtain:

\[
\frac{M_t}{M_\infty} = 4 \frac{t}{b} \sqrt{\frac{l}{\pi}} \left( \sqrt{D_x} + \frac{b}{l} \sqrt{D_y} + \frac{b}{w} \sqrt{D_z} \right) 
\] (2.23)

which, in terms of a total diffusion coefficient for the composite, $D_c$, may be re-written as:

\[
\frac{M_t}{M_\infty} = 4 \frac{tD_c}{b} \sqrt{\frac{l}{\pi}} 
\] (2.24)

where

\[
D_c = \left( \sqrt{D_x} + \frac{b}{l} \sqrt{D_y} + \frac{b}{w} \sqrt{D_z} \right) 
\] (2.25)

Equation 2.25 which expresses the total diffusion coefficient may also be useful for determining the edge effect in diffusion experiment carried out with a thin plate of homogeneous material. Here the diffusion is isotropic with $D_x = D_y = D_z$, resulting in
where $D_x$ is the isotropic diffusion coefficient of the homogeneous material.

A good account of the mathematics of moisture absorption is given by Springer [125].

\[ D_x = D \left(1 + \frac{b}{l} + \frac{b}{w}\right) \]  \hspace{1cm} (2.26)

Fig. 2.6 A unidirectionally reinforced composite plate whose sides are aligned with the $x$, $y$, and $z$ axes of a co-ordinate system and its fibres forming the angles $\alpha$, $\beta$ and $\gamma$ with respect to the three axes.

As far as maximum moisture is concerned, it has been approximated using a rule of mixture [126]:

\[ M_\infty = M_\infty^m V_m + M_\infty^f V_f \]  \hspace{1cm} (2.27)

When the density is included and the fibres are considered to be impermeable, Equation 2.27 can be refined as:

\[ M_\infty = M_\infty^m V_m \]  \hspace{1cm} (2.28)

where $M_\infty$ is the maximum moisture content, $V_m$ is the volume fraction of the matrix.
Although Fickian behaviour is observed in composites exposed to water at low temperature [126-130], non-Fickian behaviour often occurs. The following describes the factors which influence the water transport in composites.

**b) Other factors affecting water transport**

In practice, moisture gain in composite materials is not always controlled by the diffusion mechanism. Capillary flow and transport by microcracks may lead to a non-Fickian behaviour of water uptake [102]. Each of these two mechanisms becomes active only after the occurrence of specific damage to the composites. The capillary mechanism involves flow of water molecule along the fibre-matrix interface followed by diffusion from the interface into the bulk resin. It is not active unless debonding between the fibres and the matrix has occurred, often as a result of water attack at the interface. Transport of water by microcracks involves both flow and storage of water in microcracks or other forms of micro-damages, which result from environment effects or from service conditions. Therefore the water absorption behaviour of composites also reflects the change in their internal quality and must be inseparable from other performance aspects concerning durability. Thomason [131] pointed out the importance of the void contents of GRP composites in determining the maximum water uptake.

Application of external stress to composites increases the free volume of the polymer matrix as described. This obviously induces the increase in the water absorption. More importantly, if the stress causes the damage of the interphase additional water is absorbed in the damaged area [132].

Introducing salts into water has been reported to decrease the maximum water content and diffusivities of glass/epoxy particulate composites [133] due to the reduction of water activity by the presence of dissolved ions. The same phenomenon was observed in carbon reinforced epoxies [132] and vinyl ester resins [130].

Cyclic exposure of composites to an environment is to simulate a real situation where composites are used. However, this conditioning method often results in the extra increase in the maximum water absorption content and diffusion coefficient because of
the damage caused by early cycles [134]. In summary, any process that causes the changes in the structure of components of composites may give rise to deviation from Fickian absorption [127-130].

2.4.2 Glass transition temperature of composites

In broad terms, glass transition temperature, \( T_g \), of a polymer may be loosely defined as the temperature above which it is relatively soft and below which it is relatively hard, more precisely it is the temperature above which co-ordinated segmental motion of polymer chains can take place. It is well established that water cause the lowering of glass transition temperature of many polymers. As already mentioned, this is mainly attributed to two main mechanisms [102,103]: internal plasticisation and hydrogen bonding disruption. Water acts as a low molecular weight plasticiser and hence an internal lubricant, decreasing the energy required for polymer chain rotation. Alternatively, water molecules disrupt the hydrogen bonds between polymer chain segments, allowing a greater degree of movement.

Water effect can also be explained by the free volume theory [135]. It is estimated [135] that the free volume of polymers takes about 2.5 % of their total volume at and below their \( T_g \)'s. Varying the free volume of a polymer at a given temperature will alter the \( T_g \) [30, 31]. Absorption of water by polymers is believed to increase the free volume thus decreasing the \( T_g \). The extent to which \( T_g \) is depressed depends upon the amount of water absorbed, which has been modelled by the Kelly-Beuche equation [136]:

\[
T_g = \frac{\alpha_p V_p T_{gp} + \alpha_d (1-V_p) T_{gd}}{\alpha_p V + \alpha_d (1-V)}
\]  

(2.29)

where \( \alpha \) is the thermal coefficient of volume expansion, \( V_p \) is the volume fraction of polymer, the suffix p and d represents polymer and diluent (water), respectively. A value for the \( T_g \) for water has to be used and this is usually taken as about 273 K. This equation assumes that a polymer swells to accommodate the absorbed water molecules. If this were not the case, then the water molecules would occupy the polymer's free volume leading to an increase in the \( T_g \), which is obviously opposite to actual observations.
Chapter 2 Literature Review

The effect of water on the glass transition temperature of a polymer composite is similar to that of its matrix. However, the situation may be more complicated by the existence of the interphase in composites and seems to be not fully understood. The measurement of $T_g$ can be carried out by a number of techniques [25].

2.4.3 Environmental effect on GRP mechanical properties

The deterioration of the mechanical properties after a particular exposure cycle is referred to as hygrothermal ageing, implying the combined action of water and heat. Certain combinations of temperature and moisture (and stress) can produce irreversible damage, which degrades the composite properties, especially matrix and interface dominated properties such as shear strength or compressive strength. For instance, 15% to 60% loss of interlaminar shear strength can be expected at temperature and moisture contents expected in service [137].

In compression, the fibres rely on the matrix to provide the support necessary to prevent fibre buckling; under hot and wet conditions the resin softens and the compression strength is reduced. In flexure, failure can in general be either on the tensile surface or on the compression surface. Since the compressive strength is reduced under hygrothermal conditions, the flexural strength shows a similar trend [140] and exhibits compression surface failures.

Chamis et al. [139] have found that the effect of moisture and temperature on resin properties and resin dominated composite properties can be approximated into a simple algebraic expression:

$$\frac{\text{Wet resin mechanical property at test temperature}}{\text{Dry resin mechanical property at room temperature}} \approx \left[ \frac{T_s - T}{T_s - T_0} \right]^{1/2}$$

where $T_s$ is the $T_g$ of the wet resin, $T$ is the test temperature and $T_0$ is 273 K. Their experimental work on 0° laminates showed good agreement between experimental and predicted results (i.e., within 10%).
Gopalan et al. [140] studied the ultimate tensile strength (UTS) and Young's modulus of E glass-epoxy plastics after immersion in water at 70 °C for 20 days. Their results demonstrated a reduction in the UTS of 33.3, 8.0, 13.7, and 20.4% for resin, unidirectional, bi-directional, and chopped strand mat (CSM), respectively. Likewise, for these samples, the Young's modulus decreased 45.2, 5.0, 14.6, and 24.0%. Apparently, the orientation of the fibres in these composites reflects the degree to which the interface and matrix influence the measured properties compared to those that are dominated by the fibre. Analyses of samples by SEM revealed loss of adhesion at the fibre/matrix interface and evidence of leaching of the resin. For unidirectional tensile testing at 0° orientation, the fibres dominate the property, possibly, the fibre also degrades in water; however, the larger drop in properties for samples that are biaxial and random, as in the CSM, illustrates how the interfacial properties dominate the strength.

Stretching the immersed composite prior to immersion in water could also affect the retention of strength of the composite [141]. Stretching the immersed glass composite up to 25% of its ultimate strain resulted in an increase in the tensile strength, (apparently the dominant effect was plasticising of the resin). Strains greater than 25% but less than 40% of the ultimate strain resulted in a decrease in the tensile strength, (possibly both interfacial and fibre degradation occurred under these conditions). At 40% of its ultimate strain, the sample failed during environmental exposure, presumably from the accumulation of damage from both loading and immersion. These results illustrate how the stress influences the degree of damage in the sample after exposure to water. Compared to the strength of unidirectional composites, the modulus is less sensitive to hygrothermal effects [142].

As far as the water effects on the fibre dominated properties are concerned, an empirical relationship, (up to 35000 hours), was found between strength reduction and the amount of absorbed water [88]:

\[ \sigma_u = \alpha + \beta \log W \]  

(2.31)
where $\sigma_u$ is the ultimate tensile strength, $W$ is the amount of absorbed water, and $\alpha$ and $\beta$ are empirical constants, respectively.

Recently, Buck, et al. [143] studied the durability of E-glass/vinyl ester composites subjected to water conditioning and sustained loading. Their results indicated that moisture at elevated temperatures reduces the ultimate tensile strength of the GRP composites. A sustained load accelerates the property degradation, especially at higher temperatures.

The mechanical properties of glass fibre reinforced polymer laminates aged in sea water were also investigated [144]. Gellert and Turley [144] found that flexural strength fell by 15-21% for the water saturated polyester and vinyl ester GRPs, and by 25% for the phenolic GRP, after immersion in sea water at 30 °C for 800 days. Loading at 20% of ultimate strain while under immersion exacerbated only the phenolic laminate degradation (36%). Interlaminar shear strengths decreased by 12-21% for the materials at close to saturation.

2.4.4 Environmental stress corrosion of GRP

Under the combined influence of a stress and a corrosive environment, glass fibre reinforced plastics (GRP) may fail at much lower stresses than in the absence of the environment. This phenomenon has been called environmental stress corrosion (SC) or environmental strain corrosion when constant strain applied [96]. And it has been recognised as an important consideration in the application of composite material to load bearing structures.

2.4.4.1 The mechanisms of stress corrosion in acids

In the last two and half decades, stress corrosion of GRPs in inorganic acids has been rigorously researched [145-157] and the mechanisms are relatively clear. The general SC failure of unidirectional GRPs is characterised by a macroscopically flat fracture. Fibre failure is almost featureless. Fibre pull-out is restricted to very short lengths in contrast to
fracture surfaces in air, which show extensive fibre pull-out. And the final failure is mainly in the crack plane itself.

Roberts [145] suggested that the failure of stressed GRPs in acid environments occurs in two processes. Firstly, pure mechanical stress causes the fibre/matrix debonding followed by resin cracking. This leaves some fibre surfaces exposed and enhances the rate at which acid can penetrate into a laminate. The time required for this process increases as the total strain decreases. Following resin cracking, fracture of exposed glass fibres occurs by hydrogen ion attack, resulting in environmental stress crack propagation. Jones et al. [146] concluded that the stress corrosion resistance of GRP at low strains may be controlled by the rate of degradation of the fibre/matrix interface.

Fig. 2.7 Model of stress corrosion cracking processes in aligned GRP tested in corrosive environment [147]: (a) nucleation of first crack, (b) growth of flat crack by fibre fracture at tip of main crack, (c) development of small amount of fibre pull-out, (d) eventual debonding along the interface.

Hogg and Hull [147] proposed a model (see Fig. 2.7) to explain the SC cracking processes of unidirectional laminates. A matrix crack allows the acid access to a fibre, causing the fibre to crack. The fracture of the fibre and adjacent matrix allow the crack to progress to the next fibre. The applied stress to promote this failure mechanism is too low to lead to failure of the interphase; thus the crack spreads approximately on a single
plane. As the crack extends, the amount of load bearing material decreases and so the stress increases. The failure morphology therefore becomes progressively rougher, with the degree of interface failure increasing, until failure no longer require chemical assistance and overload failure results.

![Diagram of fracture processes occurring in aligned GRP tested in air](image)

Fig. 2.8 Model of fracture processes occurring in aligned GRP tested in air [147]:

(a) fibre fracture and pull-out, (b) delamination

When unidirectional GRP composites are tested under axial tensile loads in air, their failure is characterised by typical “brush-like” fracture surfaces (see Fig. 2.8), with delamination, fibre fracture and a massive amount of fibre pull-outs. Pull-outs arise on GRP fracture surfaces when fibres break at points away from the main fracture. This is due to a random distribution of imperfections along a glass fibre and a finite stress distribution at the tip of a fracture crack. Additionally, local fibre/matrix debonding at the crack tip also contributes to the pull-out. However, this occurrence is greatly suppressed during stress corrosion because the reduction in strength of the fibres by an acid out-performs the random flaw distribution. Thus, all fibres tend to fail in the same plane.

### 2.4.4.2 Applied stress and crack velocity and failure time

With increasing applied stress or stress intensity $K_1$, the environment has less effect on the fracture morphology [148]. This is because the amount of fibre pullouts and the probability of the interface debonding increase with increasing $K_1$, leading to a more brush-like failure [148, 149].
Chapter 2 Literature Review

The stress intensity $K_1$ at the tip of the stress corrosion crack is defined as [148]:

$$K_1 = Y\sigma \sqrt{a}$$  \hspace{1cm} (2.32)

$\sigma$ is the applied stress, $Y$ is a geometrical constant and $a$ is the crack size. This equation assumes that the composite is isotropic and homogeneous.

$K_1$ can be correlated with a crack velocity, $\frac{\partial a}{\partial t}$, by a power law [148, 150]:

$$\frac{\partial a}{\partial t} = AK_1^n$$  \hspace{1cm} (2.33)

where $A$ and $n$ are material constants. These values were determined by Aveston and Sillwood [148] to be $9.6 \times 10^{-11}$ (A) and $-3$ (n) for E-glass fibre reinforced polyester in 1 N sulphuric acid.

The other method to relate applied stress to crack velocity is presented by [151]:

$$100 \frac{\sigma_t}{\sigma_0} = A - B \log t_f$$  \hspace{1cm} (2.34)

where $A$ and $B$ are constants, $\sigma_0$ is a stress below which an instant failure is caused, $\sigma_t$ is the applied stress and $t_f$ is the time to failure. Although this relationship is often used to predict long term properties of composites; however, Phillips’ work showed that this relationship is not always correct as it assumes a unique failure mechanism at all temperatures and under all stress levels [151].

Collins [152] observed that a minimum strain of approximately 0.3 % exists for strain corrosion to occur in GRP laminates. It is likely that at strains above 0.3 %, higher probability of micro-matrix cracking and fibre/matrix debonding may enhance the transport of an environment into composites.
Chapter 2 Literature Review

Other factors such as fibre types, acid concentration, temperature, resin toughness and etc. also affect stress corrosion behaviour of GRPs. Details can be found in References [145-157].

2.4.4.3 Stress corrosion of GRP in alkali

Likewise, stress corrosion occurs in alkali environments but with lesser severity than in acidic environments. However, less work has been done and the mechanisms have not been clearly delineated. Roberts stated [145] that the stress-rupture behaviour in alkali environments approaches the behaviour in air in the short term and the behaviour in acids in the long term. This may be explained on a similar model to the behaviour in acids with a slower rate of alkaline attack on glass requiring higher stresses to induce short term failure. Whilst the mechanism still applies, alkaline hydrolysis of the resins may also contribute to failure.

Work by Sheards and Jones [94] suggested that the hydrolysis of the resin which causes significant weakening, and the attack of fibre/matrix interface by hydroxyl ions are the main contributing factors. In another study, Baker et al. [96] also concluded that the ultimate failure of the stressed pipe rings in 1.3 M alkali solutions appears to be due to a gradual loss of strength and stiffness resulting from degradation of the matrix and the interface. This observation may imply that the retention in the matrix and interface controlled property can indicate the rate and magnitude at which the degradation of the GRP occurs under the combined action of stress and alkali environments. It would be expected that mechanisms leading to exposure of laminate glass fibres and transport or diffusion of the environment to the glass fibre surface would be rate determining.

The occurrence of the ESC in GRP composite is dependent on the type and concentration of corrosive agents, temperature and the level of stresses. It must be stressed that the concentrations of alkali solutions employed in the above studies were much higher than those of actual cementitious environments. Therefore, the stress corrosion in those concentrated alkali solutions may be not representative of real degradation processes of GRP rebars in concrete.
2.4.5 Previous work on the durability of rebars

It is essential for the composite elements to be used in prestressed or pretensioned concrete to retain sufficient strength capacity, during the normal life of the concrete structure, for instance 50-100 years, in any of the environments encountered in practice. In the case of direct embedment in a cementitious matrix, the composite rebars will result in the first instance in alkaline exposure (pH-13), as well as later on, possibly, in carbonated concrete (pH < 10) [1]. The main argument for using non-steel tensile elements, is that steel corrodes in carbonated concrete [1]. The corrosion of steel is seriously enhanced if chlorides are present (e.g. in coast areas, de-icing salts, etc.). Whereas it is generally believed that polymer composites reinforced with glass, aramid and carbon fibres behave satisfactorily in carbonated concrete [1]. However, these composites would deteriorate to a varying degree in alkali environments, as addressed earlier. Durability of the composite rebars in concrete alkali environments would therefore define their practical applicability in concrete. However, less work has been done on the environmental resistance of composite rebars in cementitious media. Literature search indicates that the amount of papers addressing the durability of the rebars, particularly glass rebars are limited.

Pultruded aramid composites exhibit excellent resistance to alkaline solutions. Based on collected data at high temperatures within 90 days, Nanni [158] extrapolated the expected strength retention ratio of aramid tendons to 57 years with 98.2 % at 20 °C using a linear regression technique in a logarithmic scale. Faoro [159] also reported that there was no sign of any reduction in strength for the aramid-reinforced tendons in prestressed concrete elements after three years.

In contrast, the strength of pultruded glass rebars is seriously influenced in alkali media [160-164]. Work by Zayed [160] showed that immersion of E-glass reinforced isophthalic polyester rebars in a saturated calcium hydroxide solution results in high levels of water gain and loss of tensile strength. The non-Fickian behaviour was attributed to localised regions of fibre-matrix debonding. He reasoned that a reduction in strength for exposed samples is possibly due to glass fibre-matrix interface deterioration on exposure to the alkali solution.
A study conducted by Sen et al. [161] indicated that the S-2 glass/epoxy pretensioned concrete beams exposed to wet/dry cycles in 15% salt solution lost their effectiveness within 3-9 months. The subsequent analysis of the results suggests that the most likely cause of the failure was transport of hydroxyl ions from the concrete pore solution through the epoxy resin. They ruled out the possibility of the occurrence of stress corrosion because of the low stress levels (38-23% ultimate strength) and relatively short times (3-9 months) involved.

Porter et al. [162] conducted an accelerated ageing test of GRP pultruded glass rebars in a highly alkali solution (pH 12.5-13.5) at 60 °C. The rebars were made with E glass, and three resins, i.e. isophthalic polyester, another isophthalic polyester and vinylester. After ageing in the alkali solution for 81 days which they claimed equivalent to 50 years of real time, they found that the ultimate tensile strength for all the GRP rebar specimens was significantly reduced by 47 to 65%. However, exposure to the ageing solution had no apparent influence on the modulus of elasticity. No degradation mechanisms were provided; nevertheless they highlighted the importance of a selection of a proper resin to the success of GRP rebars applied in alkali solutions. They stated that the resin must not only protect the fibres, but also have a significant strain elongation without microcracking.

Hou and Martine [163] investigated the alkali resistance of pultruded rebars made with twenty combinations of E-glass fibres treated with different sizes, and polyesters and vinylesters. The rebars were immersed in an alkali solution containing 0.2% Ca(OH)$_2$, 1.4% NaOH and 1.0% KOH for 90 days. The comparison was made for the sample rebars before and after exposure. They concluded that both resin system and sizing chemistry influenced the alkali resistance. The rebars made from vinylester resins retained much higher flexural strength and ILSS than those made from polyester types after exposure. Significant difference has been observed in the strength retention for sample rebars treated with different glass fibre surface finishes, though their initial properties were fairly close in a given resin system. However, they did not give specific information about size chemistries or offer degradation mechanisms. They also compared the unstressed samples and stressed samples, which were subjected to a 0.56%
constant strain in four point flexural fixtures in the same solution. The stressed rebars showed a small decrease in strength retention in comparison with immersed rebars.

Tannous and Saadatmanesh [164] tested the moisture absorption of E-glass/polyester and vinylester rebars in a variety of solutions including 1.044 mole/l NaOH, saturated Ca(OH)$_2$ and various de-icing salts. They tried to relate the degradation in tensile properties to the penetration of the environments. Based on the experimental results, they believed that Cl$^-$ ions in salts and OH$^-$ ions in alkali solutions are the damaging elements to the rebars but did not give detailed evidence.

Clearly, the property degradation of composite rebars in aqueous environments occurred to differing degrees as composite laminates did. The most concern is GRP rebars in alkali media. However, the mechanisms and processes involved in the degradation need to be further understood. Difficulties arise with regarding to addressing this problem. One is that rebars made with different combinations of resins, fibres, coupling agents and other additives were used for investigation. Degradation mechanisms for one rebar system may not apply to other systems. The second difficulty is that the difference of environments and accelerated testing procedures employed by different research workers makes it very difficult to correlate the massive amount of experimental results. Thus, a more detailed study is needed.

2.4.6 Standards and evaluation methods

Ideally, composite materials that are intended for long term uses should be tested in real time and with realistic in-service environments. This is often not viable and necessary because the time involved would significantly delay product development. Thus, accelerated testing is required. The properties of composites in real conditions are then predicted on the basis of the results from accelerated tests and with some appropriate methods and models. It is also necessary to deliberately magnify the environmental effects in laboratory tests, in order to facilitate studying the degradation mechanisms and processes of the materials which is in turn very important for the life time prediction. This is because the changes in some of the properties in normal conditions may not be
readily observed due to the limitations of sensitivity and resolution of available detection techniques.

Temperature and stress can speed up the property degradation. ASTM C 518-74 has been used for a long time to assess the environment durability of GRP composites. However, it focuses on the chemical resistance of the thermosetting resin in GRPs with a glass volume fraction of only 12.5 %, rather than the resistance of a composite as a whole. In addition, the simple immersion test without load may not representative of the actual situation where the composites are employed in loading structures. Therefore, to best simulate the conditions that composite material as a primary or secondary load-carrying element possibly encounters; a load has to be added to composite specimens. However, no standardisation organisations have specified such a testing method. ASTM 3262-73 has been introduced to study stress corrosion of GRPs under external stress since the 1970’s but it is only used for pipe sections. Thus, the environment conditioning methods used highly depend upon individual programmes and features of individual composite structures.

For immersion testing, the results are usually expressed in the terms of the residual value of a particular mechanical property as a function of some parameters related to the exposure conditions, or the material constituent types. [102]. For stress corrosion testing, failure time and cracking velocity are the two quantities usually employed to assess glass fibre composites.

The end users of composites always try to avoid stress corrosion occurring by either reducing the severity of environments or stresses. They are actually interested more in survival than in failure. Thus, the progressive failure of GRP composites is normally studied in the first instance. The properties likely to be sensitive to aggressive environments are shear strength, tensile/flexural/compressive strength and stiffness, and toughness [102]. Shear strength is directly related to the matrix and fibre/matrix interface strength that plays a deciding role in maintaining the integrity and appreciably influencing other properties of composites.
Glass fibres are susceptible to deterioration in alkali media and therefore the change of fibre dominated tensile strength can be used to assess the durability. Flexure test is generally a fair substitute for tensile test [165]; though measured strength values in flexural test tends to be greater. Szymanski et al. [166] state that retention of flexural properties appears to give the most reliable and valuable information. In addition, flexural strength is sensitive to the surface changes of samples. The disadvantage of the flexure test is that the stress distribution is not even along a test specimen.

It must be stressed that apart from these conventional evaluation methods, any changes in other properties that are related to the environmental effects should also be considered. It is essential to record the mode of failure and any changes in this due to exposure since the failure mechanisms may change [142].

The complexity of composites and exposure condition combinations makes it very difficult to develop a general theory by which their property deterioration may be predicted. Literature review indicates such a theory is not currently available. However, a recent study [159] showed that the Arrhenius relationship could be used to predict the durability of the rebars in an alkali environment. The argument is that the degradation of some fibres in alkali environments is in principle governed by the attack from OH⁻ ions arising from the hydration process and reaching the fibres. The Arrhenius approach accelerates this process by increasing the temperature (increasing the movement of the ions), and provided no other disturbing processes occur (in the range of 0-100 °C), it is a valid investigation. The results then can be worked out mathematically by estimating the activation energy, which in this case indicates the temperature dependence of the processes of diffusion and attack on the fibres by OH⁻ ions.

This approach must be, however, used carefully. If a single mechanism dominates the durability of a composite for its lifetime, then the prediction should be simple and easy. However, if the degradation mechanism changes from one to the other or the others at certain stages, then predictions based on one mechanism will be inaccurate. Before any prediction model is to be established, extensive practical work should be done to study the fundamental mechanisms responsible for loss in the properties of composites.
PART II

METHODOLOGY
Chapter 3 Unexposed Rebar Testing Programme

3.1 Raw Materials and Rebars

3.1.1 Glass fibres

Two commercial E-glass and one AR glass fibres (Vetrotex International) were used for composite pultrusion in a form of continuous rovings. According to materials’ supplier, different types of sizes or coatings were applied to these glass fibre surfaces (see Table 3.1). The main chemical compositions of E-glass and AR glass are listed in Appendix 3.1 [167]. Clearly, such elements as Al, Ca and B in E-glass are replaced with zirconia and sodium in AR glass. The element of zirconia is believed to contribute to the alkali resistance.

<table>
<thead>
<tr>
<th>Codes</th>
<th>Types</th>
<th>Silane Types</th>
<th>Tex</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>E-glass</td>
<td>Polyester-compatible</td>
<td>4800</td>
</tr>
<tr>
<td>B</td>
<td>E-glass</td>
<td>Polyester-compatible</td>
<td>4800</td>
</tr>
<tr>
<td>C</td>
<td>AR glass</td>
<td>Cement-compatible</td>
<td>2560</td>
</tr>
</tbody>
</table>

3.1.1.1 Thermogravimetric analysis of glass fibres

To measure the sizing contents and possibly differentiate them present on the glass fibres for processing the composite rebars, thermogravimetric analysis on these fibres were carried out with a Hi-Res. Modulated TGA 2950 thermogravimetric analyser (TA Instruments). Before the analysis was performed, the sample glass fibres were conditioned in a desiccator at room temperature for one week. The weight of the samples used was about 30 mg. The samples were burned off in an air medium at a flow rate of 40 ml/min. The scanning temperature range between room temperature and 700 °C was realised at a heat rate of 20 °C/min.
Chapter 3 Unexposed Rebar Testing Programme

3.1.2 Resins

Two resin systems, Atlac 580 and Daron XP45 (DSM Resins), were used in composite rebar pultrusion.

3.1.2.1 Atlac 580

Atlac 580 is a high-grade bisphenol-A based vinylester urethane resin, which combines good chemical resistance and an outstanding combination of heat resistance and flexibility. It is particularly resistant to alkaline media and hot water [168]. The urethane modification is said to improve glass adhesion and wettability, the latter of which is required for fast production in the pultrusion process. Because it contains unsaturated vinylester groups at the end, and unsaturated double bonds in the middle of the molecule, A580 can be polymerised with vinyl monomers such as styrene in the same way as polyesters. Crosslinking or curing of the Atlac 580 occurs via free radical polymerisation. The initial formation of free radicals occurs through peroxides and cobalt accelerators. The properties of Atlac 580 resin casting [168] are listed in Appendix 3.2.

The chemical structure of Atlac 580 as shown in Fig. 3.1 combines five entities, which contribute to an outstanding combination of properties:

1. Fumarate reactive groups providing the extra crosslinking necessary to improve heat and solvent resistance.
2. Bisphenol-A groups giving the steric hinderance and chemical stability needed to resist hydrolysis in aqueous environments.
3. Urethane groups adding the polarity necessary for good wet out and adhesion to glass. The urethane components also contribute to toughness and flexibility.
4. Methyl groups providing extra steric hinderance to protect against hydrolytic attack.
5. Terminal methacrylate reactive groups giving the low exotherm cure and rapid build-up of molecular weight during cure.

A resin formulation for Atlac 580 based rebar fabrication is listed in Table 3.2.
Table 3. 2 Atlac 580 resin formulation for rebar fabrication

<table>
<thead>
<tr>
<th>Main Components</th>
<th>Parts by Weight</th>
<th>Suppliers</th>
<th>Functions of Components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlac 580</td>
<td>100</td>
<td>DSM Resins</td>
<td>Vinyl ester oligomer in styrene monomer</td>
</tr>
<tr>
<td>Perkadoc 16</td>
<td>1</td>
<td>Akzo Chemicals</td>
<td>Low activity catalyst</td>
</tr>
<tr>
<td>Trigonox C</td>
<td>1</td>
<td>Akzo Chemicals</td>
<td>Catalyst</td>
</tr>
</tbody>
</table>

3.1.2.2 Daron XP45

Daron XP45 is a newly developed (1990) poly(ester-urethane) hybrid resin system combining the best of both chemical backbones [169]. The two distinctive components of the Daron XP45 are (a) the polyester polyol dissolved in styrene and (b) the isocyanate, as shown schematically in Fig. 3.2.

The Daron XP45 resin system consists of two steps of the curing reaction. One step is the chain extension reaction where the polyester polyol reacts with the isocyanate to form urethane linkages. This reaction proceeds at high speed since mainly primary hydroxyl groups are involved. The other step is the radical polymerisation and crosslinking of the double bonds of the polyester polyol with styrene. Usually these reactions proceed simultaneously. An accelerator system can be formulated to control both the chain extension reaction and the subsequent crosslinking reaction. The latter reaction is initialised with a perester peroxide.
The Daron XP45 resin exhibits high processing speed, good mechanical properties, high temperature performance and hydrolysis resistance. These properties may provide pultruded rebars with favourable performance required for reinforcing concrete. Typical properties of unreinforced Daron XP45 casting is shown in Appendix 3.2. A Daron XP45 resin formulation for rebar fabrication is shown in Table 3.3.

\[
\text{HO} - \xrightarrow{\text{O\text{- styrene}}} \text{OH} = \text{polyester polyol in styrene}
\]

\[
\text{U} = \text{OCN-R-NCO} = \text{polyisocyanate}
\]

**Step 1: Chain extension**

\[
\text{HO} - \xrightarrow{\text{OH}} \text{OH} + \text{U} + \text{HO} - \xrightarrow{\text{OH}} \text{OH} + \text{U} + \text{HO} -
\]

**Step 2: Cross linking**

\[
\text{HO} - \xrightarrow{\text{O\text{- U\text{- O}}}} \text{O\text{- U\text{- O}} - \xrightarrow{\text{O\text{- U\text{- O}}}} \text{O\text{- U\text{- O}} -
\]

Fig. 3.2 Chemistry of Daron XP45 resin

<table>
<thead>
<tr>
<th>Main components</th>
<th>Parts by weight</th>
<th>Suppliers</th>
<th>Function of components</th>
</tr>
</thead>
<tbody>
<tr>
<td>Daron XP45-A-2</td>
<td>100</td>
<td>DSM Resins</td>
<td>Polyester polyol in styrene monomer</td>
</tr>
<tr>
<td>Daron XP-B-1</td>
<td>38</td>
<td>DSM Resins</td>
<td>Isocyanate</td>
</tr>
<tr>
<td>Perkadox 16</td>
<td>1</td>
<td>Akzo Chemicals</td>
<td>Low activity catalyst</td>
</tr>
<tr>
<td>Trigonox C</td>
<td>1</td>
<td>Akzo Chemicals</td>
<td>Catalyst</td>
</tr>
</tbody>
</table>

3.1.3 The rebars

The sample rebars were specially pultruded and supplied by Fibreglass Ltd. using different combinations of the glass fibres and resins described above. All the rebars but BAP and ARA systems were made of unidirectional E-glass fibres. BAP was fabricated
with about 30 wt.% of textured glass rovings and 70 wt.% of E-glass fibres (type A). This was attempted to improve interlaminar shear strength by creating waviness of glass fibres inside the bars. ARA was made of AR glass fibres. In all cases, the rebars had a square cross section profile with a nominal dimension of 8 mm wide and 8 mm thick. Surfacing veil (fine organic fibres) that is believed to provide an additional protective barrier to alkali ingress was incorporated onto the outer surface in the pultrusion process. At the same time, rough surface finishes were produced by peel-ply, which was removed after the curing of the resin. This action was used for improving the rebar-to-concrete adhesion by increasing the contact area and mechanical interlocking.

The rebars were made of different combinations of resins and fibres. The details of various rebars are listed in Table 3.4. Atlac 580 based rebars were produced in two series at the different processing conditions, whilst Daron XP45 based rebars were produced at one condition. However, the specific processing conditions were not known due to commercial sensitivity.

Table 3.4 Details of rebars constituents

<table>
<thead>
<tr>
<th>Rebar names</th>
<th>Fibres</th>
<th>Resin Types</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP1</td>
<td>E-glass (A)</td>
<td>Atlac 580</td>
<td>Series I</td>
</tr>
<tr>
<td>AP1</td>
<td>E-glass (A)</td>
<td>Atlac 580</td>
<td>Series II</td>
</tr>
<tr>
<td>AP2</td>
<td>E-glass (B)</td>
<td>Atlac 580</td>
<td>Series II</td>
</tr>
<tr>
<td>ARA</td>
<td>AR glass (C)</td>
<td>Atlac 580</td>
<td>Series II</td>
</tr>
<tr>
<td>BAP</td>
<td>E-glass (A) + textured glass rovings</td>
<td>Atlac 580</td>
<td>Series II</td>
</tr>
<tr>
<td>DP1</td>
<td>E-glass (A)</td>
<td>Daron XP45</td>
<td>Series II</td>
</tr>
<tr>
<td>DP2</td>
<td>E-glass (B)</td>
<td>Daron XP45</td>
<td>Series II</td>
</tr>
</tbody>
</table>

3.2 Sample Preparations

3.2.1 Preparation of rebars
Chapter 3 Unexposed Rebar Testing Programme

The rebars supplied in one metre length were cut into desired lengths in a longitudinal direction using a diamond saw. Specimen lengths were fixed at 55 mm long for ILSS tests and at 180 mm long for three-point bending tests.

Small specimens were also prepared for ILSS testing and dynamic mechanical thermal analysis (DMTA) using a water-cooled diamond saw (Struers Labton). A purpose-built clamping jig was designed to fix sample rebars on the platform of the diamond saw, which enabled thin samples to be obtained appropriate for the desired tests.

Firstly, sample rebars were cut into a section of 60 mm long, a suitable size for the jig on the diamond saw. The outside layers of the cut section were removed on 320 grit wet grinding paper. The ground section was cut into two thin specimens in a longitudinal direction. The thin specimens were approximately 2.5 mm thick and 7.5 mm thick. They were then ground manually to produce smooth surface finishes and parallel surfaces using water, and 320, 400, 600 and 800 grit SiC paper consecutively. Light microscopy revealed that damage induced by cutting to the surface was removed with the SiC paper grounding. This eliminates the possible interference of the cutting on the properties of the composites. To reduce the scatter of data amongst specimens, the dimensions of the finally ground specimens were strictly controlled. For ILSS testing, the thickness, width and length of specimens were 2 ± 0.06, 7 ± 0.1 and 14 mm. For DMTA study, they were 1.7 ± 0.02, 7 ± 0.06 and 25 mm.

3.2.2 Preparation of resin castings

To study the dynamic mechanical thermal behaviour of the pure crosslinked resins, thin (3 mm) resin casting plates with the identical resin formulation of the rebars as described in Section 3.1 were prepared. A mould was constructed with two 5 mm thick square glass sheets and a 3 mm-thick U-shaped rubber strip. Each glass sheet measured 250 mm long and 250 mm wide. The rubber strip fitting the size of the glass sheets was sandwiched between the two sheets to form a mould cavity. Three sides of the mould were closed and one side was left open which was for feeding liquid resin. The sheets were hold together by clamps. The commercial silicone grease had been applied to the
surfaces of the glass sheets before they were assembled. The thickness of the resulting mould cavity was equivalent to the thickness of the rubber sheet, which was 3 mm.

(a) Procedures of making Atlac 580 resin castings

The mould was then preheated at 60 °C in an air circulating oven. About 120 g Atlac 580 resin in a glass beaker was weighed and then warmed at 60 °C in a water bath. It was mixed with 1% Perkadox 16 and then 1% Trigonox C catalysts. The mixture in the beaker was thoroughly mixed with a glass rod for about 5 minutes, in a 60°C water bath to dissolve the catalysts in the resin. The prepared solution was placed into a desiccator that was connected to a vacuum pump, and subjected to degassing under vacuum before use. The weight of the mixture was checked on a balance before and after degassing to ensure that styrene monomer was not lost.

The degassed resin was gently fed into the cavity of the preheated mould through the open side. The mould filled with resin was placed upright in the oven to allow the resin to gel and then cure at 60 °C for about 3 hours. This slows the rate of crosslinking reaction during the cure and helps prevent cracking. Afterwards, the oven was switched off and the resin in the mould was allowed to cool down to room temperature. An air-free and transparent cast resin plate was obtained. This plate was cut into small specimens with a diamond saw. Edges of the cut specimens were then ground on 800 grit SiC grounding paper. The final dimensions of specimens for DMTA analysis were 25 mm long, 7 ± 0.06 mm wide and 3 ± 0.06 mm.

(b) Procedures of making Daron XP45 resin castings

The procedure for preparation of Daron XP45 resin casting plate is similar to that of Atlac 580 except for the curing temperature and water bath temperature. In the present case, 50 °C was used to preheat and cure the resin because Daron XP45 has a less viscosity and a higher reaction rate compared to Atlac 580.

Daron XP45-A-2 was blended with 38 p.b.w. Daron XP40-B-1 in a glass beaker. 1 wt.% perkadox 16 and 1 wt.% Trigonox C were then added into the blend. The mixture was
warmed in a water bath at 50 °C and thoroughly mixed at the same time. Vacuum was applied to remove trapped air in the mixture. The degassed solution was carefully poured into a preheated mould. After it cured in the oven at 50 °C for 2 hours and cooled down to room temperature, a casting plate obtained was cut into specimens which were ground to desired dimensions.

3.2.3 Postcuring conditions

Atlac 580 based rebars and its pure resin casting specimens had been postcured in an air circulating oven at 100 °C for two hours and 150 °C for one hour before they were subjected to testing. Postcuring was also conducted on Daron XP45 resin casting and its based rebars. In this case, the specimens were heated gradually from room temperature to 200 °C in 1.5 hours, and the temperature was maintained for one hour according to recommendations from the resin’s supplier [169].

The “as-received” rebars were postcured in the same conditions as their respective resins. The postcured Atlac 580 resin and its based rebar composites were fully cured as there was no exothermal peak on differential scanning calorimetry (DSC) curves. However, DSC examination revealed that both the postcured Daron XP45 resin and its based rebars did not completely cured as a small exothermal peak still existed.

3.3 Rebar Characterisation Methods

3.3.1 Density, fibre and void content testing

3.3.1.1 Densities of the rebar composites

In order to measure the fibre volume fraction in composites, their densities must be known. A water displacement technique was used to determine the densities of the rebars according to ASTM D792 [170]. Specimens weighing about 3 g were cut from sample rebars using a diamond saw. The outer layer rough surface of these specimens which contain organic fibres was removed on 400 grit silicon carbide paper to make sure that the surface of the specimens is smooth, and reduce the possibility of air bubbles being attached onto the rough surfaces in density measurement. This procedure not only
enabled the accurate content of the fibres (load-carrying element) inside the rebars to be measured, but also facilitated the void content of rebars to be precisely assessed. After being cleaned in acetone, all the samples were dried in an oven at 80 °C for 5 days and then conditioned overnight in a desiccator prior to weighing the samples in air.

Testing was carried out at room temperature (ca. 20 °C) on an analytical balance with an accuracy of 0.1 mg. A beaker containing 200 ml deionised water was utilised in connection with a 0.1 mm-diameter nylon wire. Three measurements were made for each type of the rebars. The density of each specimen can be calculated from the following formula:

\[
p_c = \frac{a}{a + w - b} \rho_w
\]

(3.1)

where

- \( p_c \): measured composite rebar density,
- \( \rho_w \): water density at 20 °C (0.9982 g cm\(^{-3}\)),
- \( a \): weight of specimen in air,
- \( b \): weight of specimen completely immersed and of the wire partially immersed in water,
- \( w \): weight of partially immersed wire.

### 3.3.1.2 Fibre volume fractions

A burn-off test method was used to measure the glass fibre weight fraction of the rebars. The operation was conducted in a muffle furnace at 600 °C for 4 hours in accordance to the standard test method ASTM D2584 [171]. The specimens previously used for the density tests were reused. The glass fibre weight fraction can be obtained by:

\[
w_f = \frac{W_f}{W} \times 100\%
\]

(3.2)

Where \( w_f \): weight fraction of glass fibre
Chapter 3 Unexposed Rebar Testing Programme

\( W_f \): glass fibre weight from burn-off test
\( W \): rebar specimen weight.

Similarly, the matrix resin weight fraction of the respective rebars samples can be obtained at the same time.

After the densities and glass fibre weight fractions of the sample rebars being obtained, the glass fibre volume fraction can be calculated from the following equation:

\[ V_f = \frac{W_f \rho_f}{\rho_c} \times 100\% \]  

(3.3)

3.3.1.3 Void contents

Given the densities and glass fibre content of the sample composites, the void contents can be determined according to ASTM D 2734 [172].

\[ v_v = 100 - \rho_c \left( \frac{w_r}{\rho_f} + \frac{w_f}{\rho_f} \right) \]  

(3.4)

Where \( v_v \): void content, vol. %,
\( \rho_c \): the measured density of the composite samples,
\( w_f \): the glass weight fraction of the composite samples, wt. %,
\( w_r \): the matrix resin weight fraction of the composite samples, wt. %,
\( \rho_f \): the density of glass fibres,
\( \rho_r \): the density of matrix resins.

The densities of E-glass and AR glass are 2.560 [173] and 2.680 [174] g cm\(^{-3}\), respectively. And the densities of Atlac and Daron XP45 are 1.110 [168] and 1.188 g cm\(^{-3}\) (measured), respectively.
3.3.2 Mechanical property testing

3.3.2.1 Flexural testing

Flexural properties of the composite rebars were examined using a 3-point bending test. CRAG 200 [175] was used with a span to depth ratio of 20 as suggested in the specification for glass fibre composites. Longitudinal test specimens of 180 mm in length were cut from composite sample rebars. Support rollers of 10 mm diameter and a loading roller of 25 mm diameter were employed. A crosshead speed of 10 mm/min. was employed, which caused failure within 30-180 seconds.

In a test, a specimen was simply supported on the two support rollers and loaded by a central loading roller through a crosshead until it failed (see Fig. 3.3). A plot of load against deflection was recorded automatically by a computer programme. A slope of the initial linear part of each plot was derived for computing the flexural modulus of elasticity, on the assumption that the crosshead travelling distance is equal to the deflection of the specimen. The maximum load and deflection can be obtained from the plot. Flexural strength is the theoretical value of stress on the surface of the specimen at failure. By assuming a straight line stress-strain relationship to failure, it can be calculated from the maximum bending moment given by the formula:

\[
\sigma_{3f} = \frac{3FL}{2bd^2}
\]  

(3.5)
where $F$ is the maximum load recorded, $L$ is the span, $b$ and $d$ are the thickness and depth of a specimen, respectively.

And the flexural modulus of elasticity can be obtained from the equation:

$$E = \frac{L^3}{4bd^3} \cdot \frac{Y}{X}$$  \hspace{1cm} (3.6)

where the $\frac{Y}{X}$ is the slope of the initial linear part of a load-deflection plot.

### 3.3.2.2 Interlaminar shear testing

Interlaminar shear strength test, also known as short beam shear test, is essentially a three point bending test with a short span-to-depth ratio (see Fig. 3.3). This is by one of the most popular method to generate composite shear strength directly related to the interfacial strength.

The interfacial strength depends largely on the ability of the material adjacent to the fibre surface to support loads. In unidirectional continuous fibre reinforced composites, both the interphase and the thin zones of pure matrix between the fibres are potential sites of failure. Therefore, any external force that sets up shear stresses along these sites can initiate interlaminar failures.

Principally, any factors that affect the interfacial strength of a composite may be reflected in the change of ILSS. Accordingly, this was deemed to be a suitable method to determine the effect of fibre surface treatments on the interfacial strength of composites, and environmental effect on the composite properties.

In reference to CRAG 100 [176], ILSS test was carried out for all composite rebars on a Lloyd test machine (L2000R). At least five specimens were tested in a longitudinal direction at a loading rate of 5 mm/min. Test conditions were given below:
A plot of load against deflection for a specimen was recorded with a computer programme. The maximum failure load and corresponding deflection can be obtained from this plot. The apparent interlaminar shear strength, $\tau$, was calculated using the equation,

$$\tau = \frac{3F}{4bd}$$

(3.7)

where $F$ is the maximum load at fracture recorded, $b$ and $d$ are the width and the thickness of a specimen, respectively.

All the tested specimens were examined to ensure that failure had occurred by interlaminar shear. The failure types and surface fracture morphologies of failed specimens were also documented.

3.3.2.3 Interlaminar shear testing for cut specimens

To validate and complement ILSS test results of thick rebars, small specimens cut from rebars were also tested according to BS 2782 Method 341 A [177]. Again five specimens were used for each test. The width and thickness of a specimen were controlled to be approximately 7 mm and 2 mm, respectively. In this case, different test conditions were employed as listed below:

<table>
<thead>
<tr>
<th>Specimen length</th>
<th>14 mm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Support span</td>
<td>10 mm</td>
</tr>
<tr>
<td>Nominal span/depth ratio</td>
<td>5</td>
</tr>
</tbody>
</table>
3.3.3 Dynamic mechanical thermal analysis

When a purely elastic material is deformed, it stores all of the strain energy, whilst a purely viscous material dissipates all of the deformation energy as heat. A viscoelastic material, lying between an elastic and a viscous material, will dissipate a part of the deformation energy [178].

DMTA provides a method to record a viscoelastic response of a material. It has long been used to study the structure-property relationship in polymers and polymer reinforced composites. Basically, a sinusoidal deformation is imposed on a sample of appropriate geometry in a DMTA test. The properties of the sample are determined as a function of temperature, frequency or time, or both. For each cycle, some of the strain energy is stored elastically; some is dissipated in a viscous manner (internal friction), usually as heat [179].

The fundamental properties recorded are the two components of dynamic modulus (E*), and the mechanical loss tangent or damping factor (tanδ). The dynamic modulus equation is written as:

\[ E^* = E' + iE'' \]  

(3.8)

Where

E* is known as the complex dynamic modulus;
E' is the in-phase component termed as the real, elastic or storage part of complex modulus;
E'' is the out-of-phase component termed as the imaginary or loss part of complex modulus.
Tan delta represents the ratio of the loss modulus to the storage modulus (\( \tan \delta = \frac{E''}{E'} \)), corresponding to the ratio of lost energy dissipated as heat to energy stored under small strain oscillations. It can give an indication of the damping capacity of a material and provides information about the structure.

DMTA can be used to determine a glass transition temperature (\( T_g \)) of polymeric materials. At \( T_g \), tan\( \delta \) or loss modulus values go through a maximum whilst storage modulus \( E' \) undergoes a rapid decrease.

DMTA has also been used to evaluate the degree of interfacial adhesion and bond conditions of composite materials. When a composite is subjected to a continuous cyclic loading, deformation energy is expected to be dissipated mostly in the matrix and possibly in the interphase through dynamic interface frictions and/or interfacial molecular relaxation. These energy losses manifest themselves as an increase in the viscous response of the material. The amount of energy dissipated in the interphase depends on the degree of adhesion. A stronger bond is expected to result in less energy loss, which corresponds to a lower damping factor and vice versa [180]. This method therefore provides a possibility to investigate a composite interphase.

In this study, a DMTA apparatus (Rheometric Scientific, model MR II) was used to perform all the tests in a single bending mode at a strain setting of 64 \( \mu \)m (x 4). Unless otherwise specified, the DMTA was operated at a fixed frequency of 1 Hz and a fixed ramp of 3 \( ^\circ \)C/min. The scanning temperature from 30 \( ^\circ \)C up to 280 \( ^\circ \)C was realised. The rectangular shape specimens were employed for composites in longitudinal direction. The nominal dimension of composite specimens was 25 mm long, 7 mm wide and 1.7 mm thick. The resin casting samples were also tested. The nominal dimensions of the rectangular specimens were 25 long, 10 mm wide and 3 mm thick.

### 3.3.4 Rebar failure morphology

Micro-damage to the fibres, matrix and the interphase due to interlaminar shear and flexural stresses applied to the rebars was examined in electron scanning microscopy (Cambridge Stereoscan 360). Prior to examination, small specimens were coated in a
very thin layer of gold in order to conduct the electrons away and prevent the area under examination from overheating. Delaminations in ILSS test and failure modes in flexural test were also studied by light microscopy (Zeiss Stereo microscope). Sometimes, grounding and polishing were applied on the specimens to improve visibility of the damaged areas.
Chapter 4 Unstressed Rebar Testing Programme

4.1 Environment Conditioning

4.1.1 Environment set-up

Three stainless steel water baths, measuring 600 mm long, 330 mm wide and 280 mm high, were set up to run environment conditioning tests. Temperature of the water baths was controlled to 40, 60 and 80°C, respectively, with a Techne TE-85 Thermoregulator (±0.5°C). Inside of each of the water baths, a polypropylene plastic inner container was fixed to contain alkali solution. The inner containers measured 320 mm long, 260 mm wide and 270 mm high. Cling film and lid were placed on the containers to prevent excessive evaporation. Water and solution levels were checked and topped up on a daily basis. A continuous water compensation system was constructed for 80°C water bath as water evaporated too fast in this case. The solution was replaced after about every 90 days; and therefore assuming that the concentration of the solution remained unchanged during environmental conditioning.

4.1.2 Formulation of alkali solution

Alkali solution used in this study was a mixture of potassium hydroxide, sodium hydroxide and calcium hydroxide, which were dissolved in deionised water. The concentration of each component was detailed in Table 4.1. The formulation simulated main components of concrete pore fluid [181, 182].

<table>
<thead>
<tr>
<th>Chemicals</th>
<th>Assay</th>
<th>Concentration (wt.%</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>KOH (LR)</td>
<td>&gt;85 %</td>
<td>1.4</td>
<td>Supplied by:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Fisher Scientific</td>
</tr>
<tr>
<td>NaOH (LR)</td>
<td>&gt;97%</td>
<td>1.0</td>
<td></td>
</tr>
<tr>
<td>Ca(OH)₂ (LR)</td>
<td>&gt;95%</td>
<td>0.1</td>
<td></td>
</tr>
</tbody>
</table>
4.1.3 Environment exposure

Atlac 580 resin and AP1 rebar samples were immersed simultaneously in tap water and alkali solution at 40, 60 and 80 °C, respectively, after they were prepared. Conditioning was running continuously for 360 days. Subsequent examination and characterisation of exposed samples was carried out as described as follows.

4.2 Water Absorption Measurement

4.2.1 Measuring water absorption of resin

Atlac 580 resin casting plates were prepared as described in Chapter 3. They were cut into specimens of 50 mm long, 50 mm wide and 3 mm thick for water uptake measurements. The specimens were smoothed on edges with 1000 grit SiC grinding paper and cleaned with water before they were postcured, (see postcuring conditions in Chapter 3). Postcured specimens were placed in an air-circulating oven for drying at 80 °C for three days. The dried specimens were allowed to cool down to room temperature in a desiccator overnight. They were then weighed in a balance with a precision of 0.1 mg and immediately immersed in water and alkali solution, respectively, at three temperature levels.

The specimens were periodically withdrawn from their test environments. They were rinsed with cold water and dried with soft tissue paper. Weight gains of resin samples were followed with time. Three specimens were employed for all conditioning. To ensure that the surfaces of pure resin samples were fully immersed in the test environments, a thin plastic wire was used to separate the specimens. The final results were taken from the average of three specimens.

Equilibrium water uptake, coefficient of water diffusion of the resin were measured and calculated in different environments. Activation energies of water diffusion were determined for the resin exposed to both water and alkali solution. To facilitate comparing the water absorption behaviour of the pure resin with that of the rebar, water uptake of the resin with geometry of 8 x 8 x100 mm was theoretically calculated in water.
To examine if some of the resin components leached out during conditioning, 36 resin samples were additionally immersed in each condition from the beginning of experiment. After conditioning in each environment for 30, 90 and 360 days, two of these specimens were taken out. They were rinsed with water and subsequently dried in a vacuum oven at 80 °C for 10 days. During the drying, the weights of the specimens were frequently checked until there was no further change in weight. The weight losses of exposed resin samples were recorded.

4.2.2 Measuring water absorption of rebars

100 mm long sections were cut off from the supplied one metre long rebars for water uptake measurement. Both ends of the cut specimens were firstly cleaned with acetone after cutting, then sealed with a cold-setting epoxy resin to prevent the transport of water along the interphase being otherwise freely accessible, which could result in "wicking". The sealing epoxy resin on the ends was allowed to gel and set at room temperature for about four hours. The whole specimens were then postcured at 100 °C for 2 hours and at 150 °C for one hour. They were dried in an air circulating oven at 80 °C for three days, before they were allowed to cool in a desiccator naturally to room temperature overnight.

After their initial weights were recorded on a balance (0.1 mg), five specimens were immersed each in water and alkali solution at 40, 60 and 80 °C, respectively. The specimens were regularly removed to examine weight changes. Water uptake measurements in alkali solution were terminated after about ten day exposure due to excessive weight loss. At the end of a one year immersion in water, three of five conditioned specimens were withdrawn from water and subjected to vacuum oven drying at 80 °C for one month. The weight losses of the exposed composites in water were documented.

To work out the contribution of water uptake due to the interphase and composite voids, the water absorption behaviour of the rebar (16.2 wt.% matrix) was normalised to that of 100 wt.% matrix. The normalised water uptake was compared with the modelled data from pure resin with the same dimensions as rebar (100 × 8 × 8 mm). The difference was attributed to the absorption by the interphase and voids. With this method, it is assumed that glass fibres did not absorb water.
4.3 Determination of Glass Transition Temperature

4.3.1 Determination of $T_g$ of resin

To study if extended exposure would affect glass transition of pure Atlac 580 resin, 40 specimens were prepared with desired dimensions (see Chapter 3). Twenty of these specimens were immersed in water and alkali solution, at 80 °C. $T_g$ of the resin was followed with increasing water uptake and time for up to one year. Parameters to determine of $T_g$ of the exposed resin samples by DMTA were established in Chapter 3.

To further look into the effect of water content on a reduction in $T_g$, two resin specimens were immersed in water at 40 and 60 °C, respectively for 180 days. Subsequent tests on changes of $T_g$ by DMTA were carried out.

Two resin samples were withdrawn after they were exposed to water and alkali solution at 80 °C for 200 days. They were then redried in a vacuum oven at 80 °C and subjected to DMTA analysis. Their dynamic mechanical properties were compared with those of the unexposed.

4.3.2 Determination of $T_g$ of composite

To investigate effect of environment conditioning on glass fibre/matrix interphase, dynamic mechanical properties of the composite were characterised by DMTA after the rebar samples were exposed to the given environments for one year. Focus was on the changes in glass transition temperature of the main matrix $\alpha$-transition since the interphase strength was directly related to the $T_g$ of composites as addressed in Chapter 6. Care was excised on preparation of DMTA specimens from the conditioned rebar samples (see Chapter 3).

4.4. Testing Flexural Properties of Exposed Rebars

190 mm long sections were cut off from one-metre long supplied rebars for testing degradation of flexural properties of rebars in water and simulated concrete pore solution. Procedures for preparation of these specimens were the same as those described in Section 4.2.2. In total, 200 specimens were prepared and immersed in six
environmental conditions. Five specimens were taken out from each environment after exposure for 10, 30, 90, 180, 250 and 360 days, respectively. These specimens were sealed in plastic bags to avoid water evaporation. They were then subjected to three-point bend testing in the same day. The flexural strength, strain and modulus of exposed rebar samples to both water and alkali solution were tested with the same method described in Chapter 3.

4.5 Post Examination of Exposed Rebars

Physical appearance of rebars after being exposed to water and alkali solution was examined under a ZEISS light microscope. Flexural failure modes of exposed rebars, along with alkali effect to composite defects were also documented. In addition, SEM (Cambridge Stereoscan 360 Instrument) was employed to investigate if conditioning lead to damage to glass fibres, matrix and the fibre/matrix interphase.
Chapter 5 Stressed Rebar Testing Programme

5.1 Materials and Testing Equipment

5.1.1 Rebar sample preparation

The stress corrosion behaviour of a composite rebar was investigated under constant loads and in water or a simulated alkali pore solution. The testing was only carried out on API rebar samples due to limited availability of stressing jigs and the other types of rebar. All the rebar specimens for the stress corrosion tests were postcured. Details of the rebar and postcuring conditions are in Chapter 4. Some of the rebar specimens were lightly polished (on the side under tension in a four point bending test), using 400 grit SiC grinding paper to remove the outer protective layer of the rebar. This enabled some of the glass fibres to be directly exposed to the environments. Tests showed that the effect of this treatment to be negligible to the strength of the rebar.

API rebar samples were cut into specimens 240 mm long using a diamond saw. The ends of the specimens were sealed with epoxy resin to avoid any possible wicking action occurring along the fibres as above.

5.1.2 Resin preparation

Atlac 580 resin, for a morphological structure study, was catalysed using 1.5 phr (per hundred resin) methyl ethyl ketone peroxide (concentration: 50 wt. %), and accelerated using 0.5 phr cobalt octoate (6 wt. %) and 0.9 phr N, N-dimethyl aniline. After the air trapped in the resin was removed by the application of a vacuum, the liquid resin was cast into a glass mould, consisting of two glass sheets separated by a thin rubber strip arranged along the edges. A transparent cast resin sheet was obtained after curing at room temperature (ca. 20 °C) overnight.

The sample sheet was cut into small specimens suitable for DMTA thermal scans using a diamond saw. Postcuring was then carried out in an air-circulating oven at 100 °C for 3
hours and 150 °C for 1 hour. Layers of aluminium foil were used to wrap around the specimens during post-curing to minimise possible oxidation. A DSC thermal scan over the temperature range of -30 to 170 °C indicated that the resin had completely cured.

### 5.1.3 Four point bending test

The four point bending (4-pt) test method was selected as a stressing method during stress corrosion testing, because theoretically it can not only produce a uniform stress distribution over the inner loading area but also reduce stress concentration on the loading points. In order to pre-set the amount of stress on the rebar specimens in the stress corrosion tests, the flexural behaviour under a static four point bending test must be known. Therefore the 4-pt test was conducted on API rebar specimens using a Lloyd testing machine. Fig. 5.1 shows a schematic diagram of 4-pt test conditions. The test parameters were:

- **Test speed:** 10 mm/min.
- **Inner span:** 70 mm
- **Outer span:** 210 mm
- **Load cell:** 10 kN.
- **Load roller diameter:** 25 mm
- **Support roller diameter:** 10 mm

The strength, modulus and maximum surface strain can be obtained for each specimen.

![Schematic diagram of four point bending test](image_url)

**Fig. 5.1 Schematic diagram of four point bending test**
The flexural strength can be represented as [183]:

$$\sigma_{4pt} = \frac{3FL}{4bd^2}$$ (5.1)

where $F$ is the maximum failure load recorded, $L$ is the support span, $b$ and $d$ are the breadth and depth of a specimen, respectively.

If the resultant deflection is in excess of 10 % of the support span, the maximum stress has to be corrected with the following formula [183]:

$$\sigma_{4pt} = \frac{3FL}{4bd^2} \left[ 1 - \frac{0.91(D + \delta)d}{L^2} \right]$$ (5.2)

where $D$ is the deflection at loading points of a specimen, and $\delta$ is the central deflection of the specimen from its unstrained position.

The modulus may be given by [183]:

$$E_{4pt} = \frac{5FL^3}{27bd^3D}$$ 5.3

The maximum surface strain may be estimated by [183]:

$$\varepsilon = \frac{27dD}{5L^2}$$ (5.4)
5.1.4 Stressing jigs

A large amount of time was spent on design and modification of stress jigs. Firstly, the jig must be effective and strong enough to allow the strong unidirectional rebar samples to be pre-stressed to a considerable level. Secondly, the jig must also be compact enough to allow a number of samples on these jigs to be placed in the limited space available in the water baths. A purpose built loading jig is shown in Fig. 5.2. The jig consists basically of a steel base, load and support rollers, two threaded rods and a pair of springs. The outer dimensions of the jig are 260 mm in length, 150 mm in width and 210 mm in height. The desired load can be applied by compressing the springs by tightening the nuts on the threaded rods, then transferring it to the specimens through the loading rollers. The load and support spans in the jigs are the same as those set in the four point bending test. The loading and supporting roller diameters are 25 and 10 mm, respectively. Eighteen jigs were constructed for this project.

<table>
<thead>
<tr>
<th>Spring Types</th>
<th>Constant (Nmm⁻¹)</th>
<th>Maximum Load (N)</th>
<th>Length (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Large spring</td>
<td>70</td>
<td>2668</td>
<td>101</td>
</tr>
<tr>
<td>Small spring</td>
<td>25.2</td>
<td>631</td>
<td>76</td>
</tr>
</tbody>
</table>

Fig. 5.2 A composite rebar on a prestressing jig for stress corrosion test
Two types of springs were used to construct the jigs (see Table 5.1). The large springs were used for applying high level loads (above 40 % UBS) whereas small springs for low level loads (below 30 % UBS). All the springs were calibrated in a Lloyd testing machine before they were used. The jigs were made of a grade of mild steel that is sufficiently inert to alkali solution. Some of the jigs were nickel plated to reduce rusting of steel in water. It was assumed that the amount of load applied to a rebar specimen is constant as long as the deformation of the spring remains unchanged. The pre-load can be calculated by multiplying the spring’s constant with the deformation of two springs.

Preliminary tests showed that stressed samples often prematurely failed at loading points in the environments because the damage caused by stress concentration introduced the solution or water into this contacted area. To eliminate this effect, 1.5-mm thick rubber sheets were placed onto the specimens at the loading points before stressing, which was proved to be successful.

5.1.5 Environment maintaining system

An environment maintaining system for stress corrosion tests is similar to that for the immersion test in Chapter 4 but its size is much larger to accommodate a number of pre-stressing jigs. As shown in Fig. 5.3, the system consists of a water bath, inner containers containing water or the alkali solution, and a Techne TE-85 Thermoregulator. Both the water bath and inner containers were made from polypropylene. The dimensions of the
bath were 130 cm (long), 78 cm (wide) and 64 mm (high). Each inner container accommodated three jigs. The constant temperature of the water bath was controlled at 40 °C by the thermoregulator to a precision of ± 0.5 °C. In total, two water baths and six inner containers were used.

The formulation and concentration of the alkali solution simulating concrete fluid were the same as those in the immersion tests (see Chapter 4).

5.1.6 Thermal analysis techniques

A temperature modulated DSC (MDSC) 2910 (TA Instruments) was used to run the samples from -30°C to 170 °C at a heating rate of 3 °C min⁻¹ under a N₂ atmosphere. The oscillation amplitude and period were 1 °C and 60 s, respectively. DSC heat flow signals were directly obtained from MDSC by averaging the modulated heat flow signals. A Polymer Laboratories MK II DMTA instrument was also used to run the samples from 30 °C to 200 °C at a heating rate of 3 °C min⁻¹ at 1 Hz frequency and x 4 strain level.

5.2 Conditioning and Testing

5.2.1 Stress corrosion testing

A rebar specimen was firstly loaded on a jig to different levels of stress. The range of the stress applied was between 20 % and 70 % of the ultimate 4-pt bending strength (UBS) of the rebar in air. The loaded specimen together with the jig was placed into water or the solution that was maintained at 40 °C in the inner container.

The load was expected to drop during the test as the rebar cracked and the compliance increased. As a result, the deformation of the springs decreased. To maintain constant load, the deformation of the springs had to be frequently monitored and compensated. The frequency of measurement was about 5-15 minutes for high level loads. This was reduced to hours or days for low level loads. The methods would unavoidably introduce an error on accuracy of the amount of load applied. However, this error could be neglected because the quantity of the decrease in the deformation between two measurements was much smaller than the total amount.
Chapter 5 Stressed Rebar Testing Programme

The deformation of the springs was measured with a linear calliper with a precision of 0.02 mm. At the same time, the deflection in the rebar specimens at the loading points was also monitored.

5.2.2 Resin thermal treatment

Postcured resin samples weighing about 10 mg (cut from the post-cured sheets), were placed into DSC aluminium crucibles. They were equilibrated at 170 °C for 10 min. in a DSC cell to eliminate previous thermal history, and subsequently quenched in liquid nitrogen for 10 min. They were then removed and allowed to reach room temperature prior to testing.

Some of these samples were isothermally annealed at 85 °C under a N₂ atmosphere in the DSC cell for 16, 24 and 50 hours, respectively. Samples for DMTA analysis with nominal dimensions of 25 mm x 10 mm x 2 mm were subjected to the same annealing conditions, but using a DMTA furnace.

5.3 Fracture Failure Examination

Macro-scale fractures of the composite rebars were examined under a ZEISS Stereo microscope. The examination was performed on fracture surfaces of the rebars, and transverse crack propagation revealed by polishing cross sections of the specimens. Likewise, SEM micrographs of stress corrosion damage were also taken with a Cambridge Stereoscan 360 instrument. Stress corrosion cracks on the surfaces of the specimens, crack growth, interphase and crack front were all analysed.
PART III

RESULTS AND DISCUSSION
Chapter 6
Characterisation of Pultruded Rebar Composites

6.1 Introduction

This chapter describes a systematic investigation into the influence of the differing glass fibre surface treatments on the mechanical properties of pultruded rebars. Firstly, glass fibre content and quality of the rebar composites were determined. Secondly, identification of the glass fibre surface treatments was then carried out by TGA. Thirdly, the interlaminar shear strength (ILSS) of the rebars, coupled with the fractured surface morphologies was characterised. Focus was on the effect of different fibre/matrix combinations on the shear properties of the rebars. The flexural modulus, strength and strain of the rebars were determined. The effect of the fibre/matrix adhesion on these properties was addressed by correlating the flexural test results with the ILSS data. The flexural failure modes and processes for each rebar were examined to understand the mechanisms by which the fibre/matrix interfacial strength affects the flexural properties. Finally, dynamic mechanical thermal analysis (DMTA) was conducted to characterise the fibre/matrix interactions in the interphase of the composites at a molecular level.

6.2 Glass Fibre Content and Quality Measurement of Composites

It is well known that the fibre content and quality of composites play an important role in determining the performance of composites; thus it is always important to characterise the composites with respect to these two aspects before any other tests start. Table 6.1 presents the testing results of the composites densities and their component weight fractions. The calculated fibre volume fractions and void contents of the different rebar systems are listed in Table 6.2. The densities of Atlac 580 resin, E-glass and AR glass fibres were quoted from relevant references (see Table 6.3), whereas the density of Daron XP45 resin matrix was measured using the standard test method [170] because there was no existing data available in literature.
### Table 6.1 The densities and component weight fractions of rebar samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\rho_c$ (g cm$^{-3}$)</th>
<th>$w_f$ (%)</th>
<th>$w_r$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series I rebars</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP11</td>
<td>2.0669 ± 0.0021</td>
<td>85.04 ± 0.04</td>
<td>14.96 ± 0.04</td>
</tr>
<tr>
<td>AP12</td>
<td>2.0961 ± 0.0017</td>
<td>85.31 ± 0.06</td>
<td>14.69 ± 0.06</td>
</tr>
<tr>
<td>AP13</td>
<td>2.1228 ± 0.0025</td>
<td>85.37 ± 0.10</td>
<td>14.63 ± 0.10</td>
</tr>
<tr>
<td>AP14</td>
<td>2.1371 ± 0.0031</td>
<td>85.76 ± 0.07</td>
<td>14.24 ± 0.07</td>
</tr>
<tr>
<td>AP15</td>
<td>2.1542 ± 0.0015</td>
<td>86.65 ± 0.09</td>
<td>13.45 ± 0.09</td>
</tr>
<tr>
<td>AP16</td>
<td>2.1689 ± 0.0015</td>
<td>87.30 ± 0.05</td>
<td>12.70 ± 0.05</td>
</tr>
<tr>
<td><strong>Series II rebars</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP1</td>
<td>2.1016 ± 0.0015</td>
<td>83.80 ± 0.08</td>
<td>16.20 ± 0.08</td>
</tr>
<tr>
<td>AP2</td>
<td>2.1919 ± 0.0034</td>
<td>87.71 ± 0.09</td>
<td>12.30 ± 0.09</td>
</tr>
<tr>
<td>ARA</td>
<td>2.2226 ± 0.0018</td>
<td>86.10 ± 0.07</td>
<td>13.91 ± 0.07</td>
</tr>
<tr>
<td>BAP</td>
<td>2.1472 ± 0.0017</td>
<td>86.04 ± 0.06</td>
<td>13.96 ± 0.06</td>
</tr>
<tr>
<td>DP1</td>
<td>2.1113 ± 0.0018</td>
<td>81.71 ± 0.06</td>
<td>18.29 ± 0.06</td>
</tr>
<tr>
<td>DP2</td>
<td>2.2076 ± 0.0039</td>
<td>86.65 ± 0.10</td>
<td>13.35 ± 0.10</td>
</tr>
</tbody>
</table>

### Table 6.2 Calculated volume fractions of glass fibres, matrix resins and voids in rebar samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$v_f$ (%)</th>
<th>$v_r$ (%)</th>
<th>$v_v$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series I rebars</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP11</td>
<td>68.66 ± 0.08</td>
<td>27.86 ± 0.21</td>
<td>3.48 ± 0.26</td>
</tr>
<tr>
<td>AP12</td>
<td>69.85 ± 0.13</td>
<td>27.74 ± 0.14</td>
<td>2.41 ± 0.12</td>
</tr>
<tr>
<td>AP13</td>
<td>70.79 ± 0.06</td>
<td>27.98 ± 0.10</td>
<td>1.23 ± 0.09</td>
</tr>
<tr>
<td>AP14</td>
<td>71.59 ± 0.10</td>
<td>27.42 ± 0.15</td>
<td>0.99 ± 0.17</td>
</tr>
<tr>
<td>AP15</td>
<td>72.91 ± 0.09</td>
<td>26.10 ± 0.20</td>
<td>0.99 ± 0.18</td>
</tr>
<tr>
<td>AP16</td>
<td>73.97 ± 0.10</td>
<td>24.82 ± 0.12</td>
<td>1.21 ± 0.10</td>
</tr>
<tr>
<td><strong>Series II rebars</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP1</td>
<td>68.79 ± 0.11</td>
<td>30.81 ± 0.24</td>
<td>0.54 ± 0.08</td>
</tr>
<tr>
<td>AP2</td>
<td>75.09 ± 0.12</td>
<td>24.28 ± 0.20</td>
<td>0.63 ± 0.11</td>
</tr>
<tr>
<td>ARA</td>
<td>71.40 ± 0.05</td>
<td>27.94 ± 0.16</td>
<td>0.66 ± 0.15</td>
</tr>
<tr>
<td>BAP</td>
<td>72.16 ± 0.09</td>
<td>27.01 ± 0.10</td>
<td>0.83 ± 0.12</td>
</tr>
<tr>
<td>DP1</td>
<td>67.39 ± 0.10</td>
<td>32.50 ± 0.10</td>
<td>0.13 ± 0.03</td>
</tr>
<tr>
<td>DP2</td>
<td>74.72 ± 0.14</td>
<td>24.80 ± 0.13</td>
<td>0.47 ± 0.15</td>
</tr>
</tbody>
</table>

It can be seen that in Table 6.2 the void contents of series I composite rebars made of Atlac 580 resin and E-glass fibres (Type A) are consistently higher than those of series II rebars made of different resin-glass fibre combinations. This difference between the two series samples was caused by the different rebar pultrusion processing parameters. Series II rebars were manufactured under improved conditions based on the ones used in...
manufacturing series I rebar samples; however, due to the commercial sensitivity the details cannot be quoted.

Fig. 6.1 Typical void distribution in the rebar composites ($V_v=0.5\%$, E-glass)

Indeed, the processing conditions clearly affect the quality of the rebar samples if one compares series I rebars to rebar API of series II samples, which were made of exactly the same resin formulation and glass fibres (Type A) but under the different conditions. The void volume fraction was reduced from the level varying approximately from between 1% and 3.5 vol.% to about 0.5 vol.%.

Incidentally, series I samples were originally prepared for studying the fibre volume fraction effect on the mechanical properties of the rebars, and series II sample for optimising the fibre-resin combinations. Unexpectedly, series I samples produced a varying degree of void content whereas series II samples maintained relatively low and stable levels with an average of about 0.5 vol.%. 

Fig. 6.1 highlights the typical void distribution in the composite rebars. The voids appear to occur around the glass fibre surfaces and are distributed fairly evenly. There were no large imperfections or holes inside the matrix caused by volatiles [64-67]. Thus it is most likely that voids were caused by incomplete displacement of air trapped in the fibre rovings during the rebar pultrusion process, which is very common during practical
composite production processes. The effect of voids on the mechanical properties of the composites will be discussed in Section 6.4.

Table 6.3 Densities of composite rebars constituents

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g cm⁻³)</td>
<td>1.1100</td>
<td>1.1881</td>
<td>2.5600</td>
<td>2.6800</td>
</tr>
</tbody>
</table>

* Measured value

Fig. 6.2 Typical glass fibre distribution \((V_f=71\%)\), showing closely packed fibres and localised resin-rich areas (AR glass)

Fig. 6.2 demonstrates that the glass fibres are closely packed and their distribution is fairly homogeneous in spite of some localised resin-rich regions.

6.3 Identification of Glass Fibre Surface Treatments

Thermogravimetric analysis (TGA) measures mass flow into a sample (weight gain) or out of a sample (weight loss). In many cases, TGA can provide a quantitative measure of the percentage of fillers in thermosetting materials. In this study, quantification of the amount of coating on the glass fibre was determined. Also differences in the thermal stability of the coatings on the glass fibres were used to assess differences in their
chemical structure or compositions. Fig. 6.3 presents a comparison of the sizing contents on the glass fibres and shows that they are dramatically different. The levelling-off of the curves at around 500 °C in Fig. 6.3 represents the completion of oxidation of coating materials. During testing, it was assumed that all the components present on the glass fibres were consumed at 700 °C and the glass fibres themselves were inert. Thus, the weight loss truly reflected the sizing contents (Table 6.4).

---

**Fig. 6.3 Weight loss of glass fibre sizings vs. temperature in TGA**

**Fig. 6.4 Derivative weight of glass fibre sizings vs. temperature**
Table 6.4 Glass fibres used for composite preparation

<table>
<thead>
<tr>
<th>Codes</th>
<th>Types</th>
<th>Tex</th>
<th>Silane types</th>
<th>Sizing contents (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>E-glass</td>
<td>4800</td>
<td>Polyester-compatible</td>
<td>0.62</td>
</tr>
<tr>
<td>B</td>
<td>E-glass</td>
<td>4800</td>
<td>Polyester-compatible</td>
<td>1.01</td>
</tr>
<tr>
<td>C</td>
<td>AR glass</td>
<td>2560</td>
<td>Cement-compatible</td>
<td>1.53</td>
</tr>
</tbody>
</table>

Fig. 6.4 compares the derivatives of weight loss of the coating materials against temperature. It is shown that there are different numbers of peaks on the curves in this figure, which probably represents the number of different compositions existing in the coatings on the glass fibres. The positions of these peaks are also different, as associated with the different thermal stabilities of the different chemical compositions. This suggests that the chemical structures and therefore compositions of these coatings are different. Although a glass fibre sizing consists mainly of a silane coupling agent, a film former and other auxiliary agents, glass fibre manufacturers have their own proprietary formulations and are reluctant to disclose their sizing ingredients. With TGA, however, it was possible to distinguish the contents of the coatings on the glass fibres and the differences in their compositions.

6.4 Interlaminar Shear Strength of Rebars

A summary of the interlaminar shear test results for all the rebars is given in Table 6.5. Table 6.6 tabulates the ILSS test results of small specimens cut from some of the rebars. A discussion on each of these results is given below.

6.4.1 Failure modes

Shear failure was observed for all the series II rebars in the short beam shear test; and therefore all the ILSS test results in Table 6.5 are valid according to the CRAG standard [176]. However, Fig. 6.5 shows that there was a difference in the shear failure modes between these rebars. Series II rebars also exhibited quite different load-displacement responses as depicted in Fig. 6.6.
Chapter 6 Characterisation of Pultruded Rebar Composites

![Images of AP1, AP2, ARA, BAP, DP1 showing single and multiple cracks](image)

For the tests described in Table 6.1, a single crack formed in specimens for load levels $1.5p$, $2p$, and $2.5p$. On the other hand, in the strain tests for single specimens, multiple cracks formed in specimens for load levels $0.5p$ and $p$. A crack can be formed from the strain test for the bilayer. It is also known that the load level $p$ gives the maximum strain deformation. It also affects the load level. In the initial section, the load is constant. We discover a single crack.
For those rebars of API, BAP and DPI that have relatively higher ILSS values, a single crack predominately occurred at or near the mid-plane of these sample rebars as shown in Figs. 6.5 (a), (d) and (e), respectively. Fig. 6.6 demonstrated that these rebar specimens failed suddenly with a large drop in load. This is an indication of a brittle-type failure. Acoustic emission accompanied the fracture and an audible sound could be distinctly heard.

On the other hand, for those rebars of AP2, ARA and DP2 with relatively lower ILSS values, multiple cracks occurred across the depth of these samples as shown in Figs. 6.5 (b), (c) and (f), respectively. Therefore, the possibility of premature delamination is increased in these cases. A muffled audible sound also accompanied the progression of the failure. Failure of these rebars was marked by a smaller drop in load, compared to that in those of the comparatively stronger rebars (API, DP1 and BAP). The rest of the deformation took place at a relatively constant load, at which the increased number of delaminations across the thickness occurred. The general picture for series II rebars is that the lower the ILSS, the more cracks developed in them.

In the initial test of series I rebars, a single crack at or near the mid-plane, occurred in all the cases.
It must be pointed that whitening on the loading point of the rebar specimens occurred during ILSS testing prior to interlaminar shear failure. Fig. 6.7 shows a representative picture of the central part of the tested rebars under a low magnification light microscopy. Actually, this whitening process was caused by a ‘vertical’ compressive stress on the top of rebar specimens under a loading roller. In view of this, a question was raised as to how this compressive stress affects the ILSS data of the rebars, which will be discussed in the following Section.
6.4.2 Validity of rebar ILSS data

Bearing in mind the above question, it was thought that the whitening might be eliminated if thin specimens were used. Therefore, it was decided to carry out interlaminar shear test on thin specimens cut from the rebars, using BS standard 2782 [177]. The central deflection rate of the thin specimens was similar to that of the rebars.

Table 6.5 Interlaminar shear test results of the rebars

<table>
<thead>
<tr>
<th>Rebar Types</th>
<th>Max. Load, (N)</th>
<th>Def. At Max. Load, (mm)</th>
<th>Sample Width, (mm)</th>
<th>Sample Thickness, (mm)</th>
<th>ILSS (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Series I rebars</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP11</td>
<td>3336 ± 171</td>
<td>2.33 ± 0.19</td>
<td>8.00</td>
<td>8.00</td>
<td>39.1 ± 2.0</td>
</tr>
<tr>
<td>AP12</td>
<td>3526 ± 179</td>
<td>2.27 ± 0.19</td>
<td>8.00</td>
<td>8.00</td>
<td>41.3 ± 2.1</td>
</tr>
<tr>
<td>AP13</td>
<td>3887 ± 222</td>
<td>2.25 ± 0.09</td>
<td>8.00</td>
<td>8.10</td>
<td>45.0 ± 2.6</td>
</tr>
<tr>
<td>AP14</td>
<td>4185 ± 105</td>
<td>2.35 ± 0.14</td>
<td>8.00</td>
<td>8.20</td>
<td>47.8 ± 1.2</td>
</tr>
<tr>
<td>AP15</td>
<td>4354 ± 106</td>
<td>2.07 ± 0.21</td>
<td>8.00</td>
<td>8.30</td>
<td>49.2 ± 1.2</td>
</tr>
<tr>
<td>AP16</td>
<td>4447 ± 145</td>
<td>2.27 ± 0.32</td>
<td>8.10</td>
<td>8.40</td>
<td>49.0 ± 1.6</td>
</tr>
<tr>
<td><strong>Series II rebars</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AP1</td>
<td>4631 ± 247</td>
<td>2.34 ± 0.32</td>
<td>7.90</td>
<td>7.90</td>
<td>55.7 ± 2.9</td>
</tr>
<tr>
<td>AP2</td>
<td>4078 ± 206</td>
<td>2.01 ± 0.08</td>
<td>8.10</td>
<td>8.10</td>
<td>46.6 ± 2.3</td>
</tr>
<tr>
<td>ARA</td>
<td>2148 ± 118</td>
<td>1.46 ± 0.06</td>
<td>7.90</td>
<td>7.90</td>
<td>25.8 ± 1.4</td>
</tr>
<tr>
<td>BAP</td>
<td>4664 ± 226</td>
<td>2.01 ± 0.07</td>
<td>8.10</td>
<td>8.10</td>
<td>53.3 ± 2.5</td>
</tr>
<tr>
<td>DP1</td>
<td>5676 ± 271</td>
<td>2.61 ± 0.22</td>
<td>8.00</td>
<td>7.92</td>
<td>67.2 ± 3.3</td>
</tr>
<tr>
<td>DP2</td>
<td>3931 ± 119</td>
<td>2.24 ± 0.20</td>
<td>8.05</td>
<td>8.01</td>
<td>45.7 ± 1.5</td>
</tr>
</tbody>
</table>

Table 6.6 Interlaminar shear test results of small specimens cut from rebar samples

<table>
<thead>
<tr>
<th>Rebar Types</th>
<th>Width, (mm)</th>
<th>Thickness, (mm)</th>
<th>Max. Load, (N)</th>
<th>Def. at Max. Load, (mm)</th>
<th>ILSS, (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP1 (non-pc)</td>
<td>7.06</td>
<td>2.02</td>
<td>1248 ± 64</td>
<td>0.47 ± 0.05</td>
<td>65.5 ± 1.6</td>
</tr>
<tr>
<td>AP1</td>
<td>6.96</td>
<td>1.98</td>
<td>1217 ± 30</td>
<td>0.50 ± 0.02</td>
<td>66.1 ± 2.1</td>
</tr>
<tr>
<td>DP1 (non-pc)</td>
<td>7.12</td>
<td>1.99</td>
<td>1428 ± 70</td>
<td>0.59 ± 0.05</td>
<td>75.7 ± 2.1</td>
</tr>
<tr>
<td>DP1</td>
<td>7.06</td>
<td>2.02</td>
<td>1574 ± 21</td>
<td>0.56 ± 0.02</td>
<td>82.8 ± 2.3</td>
</tr>
<tr>
<td>AP2</td>
<td>6.99</td>
<td>2.03</td>
<td>972 ± 51</td>
<td>0.45 ± 0.02</td>
<td>51.6 ± 2.3</td>
</tr>
<tr>
<td>ARA</td>
<td>6.99</td>
<td>2.02</td>
<td>567 ± 39</td>
<td>0.29 ± 0.04</td>
<td>30.3 ± 2.0</td>
</tr>
<tr>
<td>AP16</td>
<td>6.95</td>
<td>2.00</td>
<td>1069 ± 20</td>
<td>0.45 ± 0.02</td>
<td>57.7 ± 1.2</td>
</tr>
</tbody>
</table>

* Non-pc: non-postcured.
Chapter 6 Characterisation of Pultruded Rebar Composites

Cutting specimens from the rebars by a diamond saw may induce damage on the surface of the cut specimen [184]. To remove the possible effect of the damage on ILSS, post-grinding on a series of grades of grinding SiC paper was conducted on the surface of cut thin specimens before they were used for ILSS tests. Figs. 6.8 (a) and (b) compare the surface morphologies of the cut and post-ground specimens. Fig 6.8 (b) demonstrated that the induced damage was superficial and no cracks and internal damage were found. Thus, it was believed that the use of the thin cut specimens after grinding posed no effect on ILSS. All the cut thin specimens were ground manually before ILSS tests started.

Fig. 6.8 Surface morphology of the cut specimens before grinding (a) and after grinding (b), (All magnifications: 100 x).
It was found that central whitening area was also present on the thin tested specimens. A similar phenomenon was also found in the past [185]. A possible solution to mitigate the stress concentration is to use a compliant sleeve around the loading roller, but this will alter the stress states applied to the composites.

By comparing the ILSS results of Tables 6.5 with Table 6.6, it is noticed that the ILSS values obtained from the thin specimens are approximately 10-18% higher than those obtained from the rebars. This suggests that the normal compressive stress reduces the true interlaminar shear strength of composites and small size specimens can reduce this effect. The change in the size of the test specimens, however, did not alter the order of the strength of the rebars. Therefore, the ILSS data from the rebars are still valid for comparison purposes, which is very important in this study.

As mentioned above, the reason for the reduction in the apparent ILSS is caused by the compressive damage on the top central area. The stress distribution across the thickness of a specimen may be no longer parabolic (predicted by simple beam theory), with the maximum stress $\tau = 3P/4bt$ in the mid-plane. As a matter of fact, the compressive damage reduces the effective thickness of the rebars. This caused the shifting of the mid-plane downwards as clearly seen in Fig. 6.7 (a). However, when calculating the ILSS of the rebars, the original dimensions of the specimens were used; obviously thereby causing the errors. It is possible to conclude from this analysis that the ILSS can be corrected by using the effective thickness of specimens.

### 6.4.3 Effect of fibre surface treatments on ILSS

The interlaminar shear test is one of the most popular methods to generate a composite shear strength, that is directly related to the interfacial strength. However, it must be pointed out [63] that this composite shear strength also depends on the fibre/matrix stiffness ratio (controlling the stress concentration around the fibre), on the matrix shear strength (an upper boundary for the ILSS), on the composite quality (e.g. void content, fibre distribution), and on the fibre compressive strength (controlling premature failure in the compressive part of the beam). Hence, ILSS data should be interpreted carefully and be used only for comparative studies.
However, a comparison can be made if some of the above mentioned influencing factors remain unchanged. Measurements of ILSS for all the series II composite rebars were made to determine the effect of the interaction between the different coupling agents and the resins on the fibre-matrix bonding. It can be seen from Fig. 6.9 that series II composites differ significantly in their ILSS values. This discrepancy may be attributed to the different fibre surface treatments causing the varied levels of interaction between the matrices and the coupling agents, assuming that the siloxane bond between the glass fibres and the coupling agents is strong enough [40,41,47].

The lowest ILSS of ARA among series II rebars was expected as the cement-compatible sizing applied on the AR glass fibres was not compatible with Atlac 580 resin. Consequently, an intimate interphase was not developed. This was confirmed by the post SEM examination of the ILSS fracture surface as shown later in Fig. 6.12 (e).

Both rebar API and AP2 were prepared with E-glass fibres and with the same resin formulation under identical processing conditions, in addition to possessing similarly low level of void contents. However, API (55.7 MPa) exhibited an about 20 % higher interlaminar shear strength than AP2 (46.6 MPa). Thus the only sensible explanation for this difference is that the coupling agents and/or the sizing formulations applied onto
these E-glass fibres (fibre types A and B) may interact with the same liquid Atlac 580 resin in different ways during the rebar pultrusion process. TGA testing confirmed that the chemical compositions of one glass fibre coating was different from those of the other as indicated in Fig. 6.4 in spite of these surface treatments being claimed by the manufacturers to be polyester compatible. The ILSS results suggest that a stronger interphase in composite AP 1 was formed in comparison with AP 2.

Fig. 6.10 Cross-section view of BAP rebar, the central white star-shaped area mainly consists of straight fibres, whilst the relatively dark area around edge mainly consists of textured fibres, (magnification: 6.5 ×)

Table 6.5 also shows that there is no statistically significant difference between AP 1 and BAP in terms of ILSS value. BAP was made of a combination of about 70 % glass fibre A and 30 % textured E-glass fibres. It was intended that the textured fibres could produce waviness inside the composite to improve ILSS. This intention appears not to have been achieved. A possible reason is the fact that the textured fibres were distributed randomly (see Fig. 6.10) around the edge of the rebar rather than the mid-plane where the interlaminar shear stress is theoretically at a maximum.

In the case of Daron XP45 based rebars DP 1 and DP 2, the same trend was observed with fibre A reinforced rebar DP 1 (67.2 MPa) being about 45 % stronger than fibre B reinforced rebar DP 2 (45.7 MPa) in ILSS. Again this large variation can only be attributed to the different interactions between the coupling agents on glass fibre A and B, and Daron XP45 liquid resin, thereby resulting in the interphases of these composites with different strength.
It is also interesting to note from Table 6.5 that the resin types (Atlac 580 and Daron XP45) also affected the ILSS of rebars reinforced with the same glass fibre A, by comparison of AP1 with DP1. This may be accounted for by the difference in the chemistry of the two resins which interacted with a silane coupling agent to form interphases with different strength. Alternatively, the matrix shear strength of the two resins which controls the upper boundary of composite ILSS may contribute to the difference in their ILSS levels. Unfortunately this data was not available from the resin supplier. In contrast, glass fibre B reinforced rebars AP2 and DP2 showed little difference and low absolute ILSS values in ILSS.

In summary, surface treatment on glass fibre B has a tendency to develop a strong interphase region with the resins studied.

6.4.4 Postcure effect on ILSS

Examination of postcure effect on ILSS was only made on two types of rebar (AP1 and DP1) using thin specimens. It can be seen from Table 6.6 that postcure only has a slight effect on the ILSS of AP1, implying that the "as-received" AP1 composite crosslinking was nearly complete. The other three Atlac 580 based rebars may have the same crosslinking degree as AP1, since they were processed under the same conditions and using the same resin formulation. In contrast, the ILSS of DP1 was increased by about 10% by postcuring. A similar thing probably happened to the other Daron XP45 based rebar DP2. This highlights the importance of postcure on the mechanical properties of rebar composites.

6.4.5 Void effect on ILSS

The detrimental effect of voids on the ILSS of composites has long been documented [65]. The primary reason of the effect is attributed to a rise in stress concentration at the sites of voids, causing the premature shear failure of composites [65]. This effect was also identified in series I composite rebars, which were made using the same glass fibres (type A) and the same resin formulations (Atlac 580), and documented in Fig. 6.11. A good linear relationship between the ILSS and the void contents of the rebars was found.
The same phenomenon had been observed early by other research workers even for different fibre-matrix systems [12].

The level of voids in composites may be associated with fibres, the properties of resins, the compatibility of the fibres and resins and composite production conditions and techniques [66]. In pultrusion, it has been recognised that the pressure was directly related to the void contents of the processed composites [67]. The viscosity of resins, the die temperature and its distribution, the pultrusion speed and other processing parameters may also be equally important in influencing the void content. This may be the reason why the rebar manufacturer was not willing to disclose these parameters. By comparing AP 1 to all the rebars in series I that were pultruded with the same glass fibres and the same resin but under the different conditions, the effect of processing conditions on the void levels and in turn on ILSS can clearly seen in Tables 6.2 and 6.5.

Fig. 6.11 may also suggest that there is no direct relationship between the ILSS values and the fibre contents of the composites investigated. It is void content that directly affects the ILSS.

![Fig. 6.11 The effect of void content on the ILSS of the rebars (series I samples)]
6.4.6 Shear fractured surface morphologies

The shear fracture surfaces for all series II sample rebars were examined under SEM, which showed large regions of uniform failure features. Although all the ILS specimens failed in shear, representative photomicrographs were taken to document the differences in the fracture surfaces. To facilitate the discussion and eliminate the possible interference of matrix toughness on the shear fracture morphology, the five types of rebars are divided into two groups. Group One consists of Daron XP45 based rebars, i.e. DP1 and DP2 whereas Group Two consists of Atlac 580 resin based AP1, AP2 and ARA. BAP is omitted because information on the textured fibre coating is unknown.

Figs. 6.12 (a) and (b) show that there are significant differences in the fracture surface morphologies between DP1 and DP2. DP1 with very high shear strength has rougher fracture surfaces and more tortuous failure paths than DP2 with low shear strength. These tortuous failure paths result from the coalescence of tensile microcracks in the matrix, which occur at an orientation of about 45° towards or away from the direction of macroscopic crack propagation [78]. Larger and highly denser hackles were developed in the matrix between the glass fibres in DP1. These hackles are the results of the failure path varying from predominately fibre/matrix interfacial failure to a combination of cohesive matrix failure and fibre/matrix interfacial failure [78]. Larger and denser hackles are evidence of higher levels of fibre/matrix adhesion, suggesting that a stronger interphase has formed. In contrast, hackles are hardly seen in Fig. 6.12 (b) though some amount of the matrix still adheres to the glass fibres. This indicates that a relatively weak interphase was formed in DP2.

Amongst the rebars based on Atlac 580, AP1 has largest hackles as shown in Fig. 6.12 (c). This figure may also exhibit the hackle formation process by brittle cracking of the matrix normal to the direction of the maximum principal tensile stress. The occurrence of cracks that have deeply extended into the matrix, suggests that a strong interphase has developed.
Chapter 6 Characterisation of Pultruded Rebar Composites
Fig. 6.12 (c) clearly shows that failure occurs at the fibre-matrix interface. The shear failure initiates from the tips of hackles. In comparison, smaller hackles are observed on the fracture surface of AP2 in Fig. 6.12 (d). Although a significant amount of the matrix remained on the fracture surface of AP2, it seems that the matrix cracks did not develop well into larger versions due to relatively weak fibre/matrix adhesion.

In summary, Section 6.4 discusses the fibre/matrix interaction and composite properties.
Fig. 6.12 (e) clearly shows that failure occurs at the fibre/matrix interface in the shear specimens of ARA. The fibre surfaces have almost no matrix adhering to them. The shear failure propagates predominately along the fibre/matrix interface, as this is the route of lowest fracture energy due to low fibre/adhesion. Therefore, it can be concluded that the cement-compatible sizing applied on AR glass fibres is not compatible with Atlac 580 resin.

In summary, these results are qualitatively in an agreement with the ILSS results in Section 6.4.3. The differences in the shear fracture surfaces are due to the variations in the fibre/matrix adhesion or ILSS, which in turn are dependent on the fibre surface treatments and the interactions between the fibres and liquid matrix resins during the composite processing stage.

6.5 Flexural Properties of Rebars

Unidirectional composite rebars are proposed to replace steel as reinforcements in structural concrete. Obviously the load bearing property in the fibre direction must be known. Tensile strength is a direct measurement of this load bearing property. However, initial tests showed that it was very difficult to determine the tensile strength of the rebars. This was because the very high longitudinal tensile strength and relatively low transverse compressive strength caused 'squashing' and premature failure at the gripping ends of the rebars. In an attempt to avoid the 'squashing' problem, long machined steel sleeves were bonded and fitted onto the ends of the rebar samples using a specialised strong adhesive, the tests, however, ended up with the slipping of the samples from the gripping sleeves. The failures were identified either in the adhesive or in the thin outer layer of the rebars, which was obviously weak. Although much time and effort was spent to overcome the above problems, the tensile test was not successful. Therefore, the results are not considered here.

It was then decided to use a three-point flexural test to characterise the load carrying properties of the rebars in a longitudinal direction. In contrast to the tensile test, flexural testing can eliminate the specimen-gripping problem and is easily carried out. To a certain extent, the flexural strength can aid the estimation of tensile strength though the
measured value of the flexural strength tends to be higher than that of the tensile strength. This Section documents the measured flexural properties of Series II rebars, which are given in Table 6.7. The full discussion is given below.

### 6.5.1 The load-deflection response

![Typical load-deflection response of the rebars in flexure test.](image)

Fig. 6.13 Typical load-deflection response of the rebars in flexure test.

Typical load-deflection curves at the central loading point for all the Series II rebar specimens are shown in Fig. 6.13. It is noted from the graph that all the composite rebars tested behaved linearly until failure at the maximum load condition and the lines of these curves are very smooth. This linearity in slopes and the smoothness in curves may imply that there is no obvious internal damage in the rebar samples during stressing until failure at the maximum load. This allows the maximum stress at failure of the composite rebars to be calculated by simple elastic beam theory according to Equation 6.4.

Fig. 6.13 also shows that there were two different failure processes in the flexure test. The load dropped off in a gradual, non-catastrophic manner after the maximum failure deflection for DPI rebar specimens. Alternatively, all the other rebars failed in a
catastrophic way with an abrupt drop in load; but these catastrophic failures did not cause specimen separation. This difference may be associated with the different failure mechanisms of these composites and these will be discussed in Section 6.5.4. Overall, the load-deflection curves revealed that the macroscopic response of the rebars to flexural stresses was elastic.

Table 6.7 Average flexural properties of the rebars

<table>
<thead>
<tr>
<th>Rebar Types</th>
<th>Sample Width, (mm)</th>
<th>Sample depth, (mm)</th>
<th>Max. Load, (N)</th>
<th>Def. at Max. Load, (mm)</th>
<th>Max. Strain (%)</th>
<th>Flexural Modulus, (GPa)</th>
<th>Flexural Strength, (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AP1</td>
<td>7.88</td>
<td>7.82</td>
<td>2173 ± 139</td>
<td>14.90 ± 0.80</td>
<td>2.74 ± 0.15</td>
<td>41.10 ± 1.29</td>
<td>1083 ± 61</td>
</tr>
<tr>
<td>AP2</td>
<td>8.10</td>
<td>8.10</td>
<td>2044 ± 116</td>
<td>11.68 ± 0.83</td>
<td>2.21 ± 0.16</td>
<td>43.64 ± 0.85</td>
<td>923 ± 50</td>
</tr>
<tr>
<td>ARA</td>
<td>7.90</td>
<td>7.90</td>
<td>1172 ± 119</td>
<td>8.79 ± 0.63</td>
<td>1.63 ± 0.12</td>
<td>37.46 ± 0.56</td>
<td>570 ± 56</td>
</tr>
<tr>
<td>BAP</td>
<td>8.10</td>
<td>8.10</td>
<td>2208 ± 55</td>
<td>13.44 ± 0.61</td>
<td>2.55 ± 0.12</td>
<td>43.49 ± 0.45</td>
<td>997 ± 32</td>
</tr>
<tr>
<td>DP1</td>
<td>7.94</td>
<td>7.84</td>
<td>2431 ± 113</td>
<td>16.01 ± 0.81</td>
<td>2.94 ± 0.15</td>
<td>41.13 ± 1.09</td>
<td>1195 ± 52</td>
</tr>
<tr>
<td>DP2</td>
<td>8.06</td>
<td>8.03</td>
<td>2043 ± 102</td>
<td>12.25 ± 0.62</td>
<td>2.31 ± 0.12</td>
<td>42.93 ± 1.03</td>
<td>944 ± 53</td>
</tr>
</tbody>
</table>

Average results obtained from five test specimens.

6.5.2 Flexural modulus

The flexural modulus was calculated using Eqn. 6.1:

$$E_b = \frac{L^3m}{4bd^3}$$  \hspace{1cm} (6.1)

Where \(L\) is the span, \(m\) is the slope of the load-deflection curve, and \(b\) and \(d\) are the specimen width and thickness, respectively.

The results are listed in Table 6.7. The load-deflection curves in Fig. 6.13 indicate that the moduli for all the rebars are very uniform in the whole loading ranges. However, from close examination of the flexural modulus results for all the rebars in Table 6.7, it is found that the absolute values of the flexural modulus are consistently lower than the values of the tensile modulus predicted by the rule of mixtures. Probably, this discrepancy was caused mainly by a small span-to-thickness ratio of 20, as recommended by CRAG [175], which induced shear deformation added to the total deflection of the longitudinal unidirectional composites [186]. Consequently, the
apparent flexural modulus calculated by Equation 6.1 was underestimated as the load-deflection slope was apparently reduced by the shear deformation.

Normally a large span-to-thickness ratio is used when measuring the flexural modulus of composites [186], as the apparent flexural modulus asymptotically approaches the tensile modulus with increasing aspect ratio. However, if the span to thickness is too large the specimen may be pushed through the testing jig rather than fail in flexure. Considering that both the flexural modulus and strength were required from one test in this study, a choice of 20 as a span to thickness ratio was made to ensure flexural failure and to reduce the possibility of unduly large deflection and non-linear effects [185]. In this case, the flexural modulus obtained was corrected using Equation 6.2 [186]:

\[
E_b = \frac{PL^3}{4bd^3D} (1 + S)
\]

(6.2)

Where S is a correction factor for shear deformation given by Equation 6.3 [183]:

\[
S = \frac{3d^2 E_b}{2L^2 G_{xz}}
\]

(6.3)

Where \(G_{xz}\) is the shear modulus of the composite in a longitudinal plane through the thickness.

Table 6.8 Flexural modulus and strength of the rebars

<table>
<thead>
<tr>
<th>Rebars</th>
<th>AP1</th>
<th>AP2</th>
<th>ARA</th>
<th>BAP</th>
<th>DP1</th>
<th>DP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calculated Modulus (GPa)</td>
<td>48.15</td>
<td>52.56</td>
<td>51.41</td>
<td>-</td>
<td>47.17</td>
<td>52.30</td>
</tr>
<tr>
<td>Measured Modulus (GPa)</td>
<td>41.10</td>
<td>43.64</td>
<td>37.46</td>
<td>43.49</td>
<td>41.13</td>
<td>42.93</td>
</tr>
<tr>
<td>Corrected Modulus (GPa)</td>
<td>44.78</td>
<td>47.83</td>
<td>40.88</td>
<td>47.67</td>
<td>44.91</td>
<td>46.96</td>
</tr>
<tr>
<td>Measured Strength (MPa)</td>
<td>1083</td>
<td>923</td>
<td>570</td>
<td>997</td>
<td>1195</td>
<td>944</td>
</tr>
<tr>
<td>Corrected Strength (MPa)</td>
<td>1120</td>
<td>939</td>
<td>574</td>
<td>1022</td>
<td>1243</td>
<td>963</td>
</tr>
</tbody>
</table>

The shear deformation was accounted for in Equation 6.3 by assuming \(E_b/G_{xz} = 25\) [186], which resulted in an average 6% correction to the measured flexural modulus for all the
Chapter 6 Characterisation of Pultruded Rebar Composites

rebars but ARA. Table 6.8 compares the theoretically calculated (i.e. the Rule of Mixtures), experimentally determined and corrected flexural modulus of all the rebars.

It should be noted that the fibre volume fractions of different rebar systems are not identical (Table 6.2). It is well known [12] that both the tensile and the compressive strength of composites increase with increase in the fibre volume fraction. For a convenient comparison, it was assumed here that both the flexural modulus and strength increase linearly with fibre volume fraction. Therefore, the corrected flexural modulus for all the rebars except ARA (AR-glass reinforced) shown in Table 6.8 was linearly scaled to an average fibre volume fraction of $V_f = 71.6\%$. The glass content of ARA rebar ($V_f = 71.4\%$) is in fact identical to that average value; therefore the modulus remains unscaled.

![Graph showing the comparison of longitudinal flexural moduli of the rebar composites](image)

*Fig. 6.14 Comparison of the longitudinal flexural moduli of the rebar composites; the modulus values were scaled to the average fibre volume fraction of about 71.6\%.*

The scaled modulus results are shown in Fig. 6.14. It appears that there is no statistical change in the flexural modulus amongst all the rebar samples except ARA. However, the large difference in the modulus between the ARA rebar and the other five types of rebar could not reconciled by the small variation in the Young's modulus between AR glass...
fibres (72 GPa) [8] and E-glass fibres (70 GPa) [173]. This implies that the flexural modulus may be affected by the fibre-matrix adhesion since the ILSS of ARA is the poorest amongst the rebars studied.

To clarify this point, the flexural modulus values of the rebars were correlated with the ILSS data that represents the fibre-matrix adhesion level (Fig. 6.15). In this figure, the longitudinal flexural modulus data of all the rebars in Fig. 6.14 was normalised to that of rebar AP1, and the ILSS data of all the rebars in Fig. 6.9 was also normalised to that of AP1. This non-dimensionalised format clearly shows the dependence of the flexural modulus on the fibre adhesion of the rebar composite systems. The flexural modulus continuously increases with the increase in the fibre/matrix adhesion. The underlying reason for this was due to the fact that flexural failure of composites was often caused by the local instability and micro-buckling of fibres [12]. The strong fibre/matrix interphase strength can provide additional flexural rigidity for the composites. The opposite is true for composites having poor interphase strength. However, the sensitivity of the tensile modulus to the change in the fibre/matrix interphase strength was insignificant [187]. This is because there were no fibre micro-bulking problems with the tensile test.
6.5.3 Flexural strength and strain

The strength of rebars listed in Table 6.6 were calculated from the first term of Equation (6.4). However, ASTM D790 method [183] for the three-point flexure test recommends use of the full terms of this equation for the calculation of flexural strength when large span/thickness ration are used.

\[
\sigma = \frac{3F_{\text{max}}}{2wt^2} \left[ 1 + 6 \left( \frac{D}{S} \right)^2 - 4 \left( \frac{t}{S} \right) \left( \frac{D}{S} \right) \right]
\]  

(6.4)

where \(F_{\text{max}}\) is the maximum failure load, and \(D\) is the mid-point deflection.

![Graph showing comparison of maximum flexural strains](image)

Fig. 6.16 Comparison of the maximum flexural strains of the rebars

Equation (6.4) provides an approximate correction for the end forces that are developed in beams where the thickness/depth ratio is large and where relatively large deflections exist. Normally when the ratio of a deflection to span exceeds 10% the correction is used. It can be seen from Table 6.7 that only rebar DP1 is in excess of that level. However, for accuracy of comparison, the average longitudinal flexural strength for all the rebars were corrected and the corrected values are given in Table 6.8.
Table 6.7 also lists the average values of maximum longitudinal flexural strain calculated from the cross-head displacement using Equation (6.5).

\[ \varepsilon = \frac{6Dt}{S^2} \]  

(6.5)

The deflection was assumed to be the same as crosshead displacement in the calculation, i.e., the machine compliance was not taken into account. The maximum failure strains of all the rebars are compared in Fig. 6.16.

![Comparison of longitudinal flexural strengths of rebar composites](image)

**Fig. 6.17** Comparison of the longitudinal flexural strengths of the rebar composites, the strength values were scaled to the average fibre volume fraction of about 71.6%.

It should be noted that the fibre volume fractions of different rebar systems are not identical (Table 6.2). Thus, for a better comparison, the flexural strengths for all the rebars, except ARA (AR-glass reinforced), are linearly scaled to an average fibre volume fraction of \( V_f = 71.6\% \). The glass content of ARA rebar \( (V_f = 71.4\%) \) is coincidentally identical to that average value. The scaled results of the longitudinal flexural strengths are compared in Fig. 6.17 for all the rebars. Figures 6.14 and 6.15 show the same trend, because the moduli of the rebars are very close and the stress-strain relationships follow linear behaviour as indicated in Fig. 6.13.
Fig. 6.17 shows that the longitudinal flexural strengths of the rebars are very sensitive to glass surface treatments. For example, rebars AP1, BAP and DP1 made with surface treatment A are generally stronger than rebars AP2 and DP2 made with surface treatment B, and rebar ARA made with surface treatment C which is the poorest in strength amongst the three main types. The large difference in the flexural strength between ARA rebar and the rest of the other five cannot be attributed to the types of glass fibres (E-glass and Cem-fil AR glass), because there is barely any difference in strength between the two types of glass rovings (1700 MPa) [173, 174]. This sensitivity may have resulted from variations in fibre/matrix adhesion between the rebars.

By comparing the maximum flexural strengths of the rebars made with the same E-glass type A, but with the two different matrices, it appears that DP1 (Daron XP45 based) shows greater improved strength than its counterpart AP1 (Atlac 580 based). The same thing was also observed with DP2 and AP2, which were reinforced with the same E-glass fibre type B, but based on these two different matrices, respectively. This matrix effect is in contradiction to a general view that the longitudinal flexural strength of a continuous unidirectional fibre composite is fibre controlled. Actually, this contradiction is caused by the difference in the fibre/matrix adhesion or the interactions between the specific matrix and silane coupling agents (A or B) which existed in these rebar composites as addressed in Section 6.4.3.

This observation suggests that there might be a relationship between the maximum flexural strengths and the shear strengths of the rebar composites. Again, the average scaled flexural strength values and the unscaled maximum strain values of the rebars are plotted in Fig. 6.15 in a non-dimensional format. All the flexural property values of the composite rebars are normalised to the corresponding value of rebar AP1, and the ILSS values are normalised to the corresponding value of rebar AP1. The results in Fig. 6.15 clearly display that flexural strengths and maximum strains continuously increase with increase in interlaminar shear strengths of the composites. This consistent dependence is much stronger than that of the flexural modulus. The reason for this may be attributed to the fact that the high interphase strength can prevent or suppress the compressive failure of the composite rebars caused by delamination and fibre micro-buckling. The prevention or delay of the delamination and fibre micro-bulking occurrence allows the
composites to fracture during large deflection, and allows the fibres to develop high
tensile strength to a maximum or large extent.

6.5.4 Flexural failure modes and characteristics

The mechanisms by which the fibre/matrix adhesion influences the flexural properties of
the rebar composites can be understood by studying the effect of ILSS on their flexural
failure modes and processes. In order to carry out this examination, tests were run so that
the rebar specimens were unloaded as soon as the deflection at maximum load was
reached. This allows the fracture processes at maximum load to be precisely
documented. The computer controlled universal testing machine permitted the
implementation of this instantaneous unloading of the specimens. The central part of the
specimens were sectioned at the mid-point of the specimen width, and then briefly
ground onto a 800 grit wet SiC paper to enhance the clarity of the damaged areas. The
failure areas were firstly examined under a low magnification light microscope, and then
examined under SEM.

6.5.4.1 Flexural failure modes

The rebar failure modes in the flexural test indeed affected their flexural strength and
strains, and this is supported by the following observations. Figs. 6.18 to 6.23 show that
there are three distinct flexural failure modes present in the rebars studied, i.e. tensile,
mixed tensile and compressive, and compressive. By cross-examination of Fig. 6.14 and
Figs. 6.18-23, it is found that DP1 with the highest flexural strength failed in the tensile
side of the specimens (Fig. 6.18). AP1 and BAP specimens having the higher flexural
strengths fractured in both tensile and compressive sides (Figs. 6.19 and 6.20). For DP2,
AP2 exhibiting the intermediate, and ARA exhibiting the lowest flexural strength,
failures initiated on the compressive side as shown in Figs. 6.21-23, respectively. The
reason can be attributed to the following. In a 3-point bending test, a composite specimen
is actually subjected to tensile stresses on one side, and to compressive stresses on the
other side. The failure modes and therefore the strengths will depend upon which side
fails first. Normally, the compressive strength of a composite, (rather than a
homogeneous material), is lower than its tensile strength [12]. Thus, if a composite fails
in compression, the apparent flexural strength is lower than if it fails in tension.
However, flexural tensile failures do occur in composites when they have high compressive strengths that have resulted from good fibre/matrix adhesion and high modulus of the matrix [12].

Fig. 6.18 (a) Side view of the central part of DP1 specimen in flexure test, (b) Enlarged view of the tensile fracture region.
Fig. 6.19 Side view of the central part of AP1 specimens in flexure test, showing the mixed mode failure, (b) enlarged view of tensile fracture region, (c) enlarged view of the compressive fracture region
Fig. 6.20 (a) Typical side view of the central part of BAP specimen in flexure test, showing the mixed mode failure, (b) enlarged view of the compressive fracture region
Fig. 6.21 (a) Typical side view of the central part of DP2 specimen in flexure test, showing the compressive failure mode, (b) enlarged view of the compressive region

Fig. 6.22 (a) Typical side view of the central part of AP1 specimen in flexure test, showing the compressive failure mode, (b) enlarged view of the compressive region
Further examination of Fig. 6.6, Fig. 6.14 and Figs. 6.18-23 revealed that the flexural strengths of the rebars increased with increasing ILSS, corresponding to the flexural failure modes transforming from the compressive to the mixed and finally to the tensile. This can be explained by the fact that the compressive strength of composites is affected by the fibre/matrix adhesion and its shear strength \[81,188\]. In the current study, the highest ILSS of DP1 prevented the compressive failure occurrence and allows the fibre controlled tensile strength to be explored. As a result, DP1 specimens exhibited the highest flexural tensile strength amongst the rebars studied. In contrast, the generally lower ILS strengths of AP2, DP2 and ARA led to premature compressive failures in these rebar specimens and therefore lower flexural compressive strengths resulted. In the
case of AP1 and BAP, the compressive failure occurrence was effectively delayed with their higher levels of ILSS, and therefore their flexural strengths were in between the above two cases.

The flexural strains of the rebars follow the same trend as that of the flexural strengths, because the fibre/adhesion interphase bonding had less effect on the flexural moduli than on the flexural strengths. Therefore, the higher strength permits the composites to undergo larger deflections, and vice versa.

It should be emphasised that the compressive strength of a composite is also dependent upon matrix properties, (strength or modulus), in addition to the interphase strength. Apparently, it is better to make comparisons between compressive strengths of composites based on the same matrix. However, it is reasonable to believe that the interlaminar shear strength is a predominate factor in the current case, as there are only marginal differences in the tensile strength and modulus between Atlac 580 and Daron XP45 (see Table 6.9). Thus, the above argument still holds for all the rebars based on both of the two different matrices.

Table 6.9 Comparison of the tensile property of Atlac 580 [168] and Daron XP45 [169].

<table>
<thead>
<tr>
<th></th>
<th>Atlac 580</th>
<th>Daron XP45</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile Strength (MPa)</td>
<td>83</td>
<td>70</td>
</tr>
<tr>
<td>Tensile Modulus (GPa)</td>
<td>3.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Tensile Elongation at break (%)</td>
<td>4.2</td>
<td>2.5</td>
</tr>
</tbody>
</table>

6.5.4.2 Flexural failure characteristics

The general failure modes in the flexural test were examined, which largely depend upon the strength of the fibre/matrix bond and determine the flexural properties. It is also important to understand the failure processes and the specific features of each failure mode on a micro-scale. This is particularly true for rebars that failed in a generally compressive mode. It was expected that there would be a difference between these composites as their ILSS and flexural properties were different.
Fig. 6.18 (a) shows that extensive delamination splitting in a longitudinal direction occurred on the tensile side of DP1 specimens. Close examination of that area under SEM in Fig. 6.18 (b) demonstrates that there exists matrix debris, fibre/matrix debonding and fibre breakages in that region. It is believed that tensile failure was initialised by matrix cracking, because the maximum flexural failure strain of the DP1 specimens exceeded the critical tensile failure strain of the matrix resin Daron XP45 (2.5 %). It was also indicated by the appearance of matrix debris. The matrix tensile failure induced the fibre/matrix debonding, then the debonded fibres broke from the weak sites on their surfaces. As a result, a transverse crack towards the neutral plane was formed. Fig. 6.18 (a) indicates that longitudinal splitting progressed faster than the transverse crack movement within DP1 specimens, suggesting that interphase debonding always occurred ahead of the fibre fractures. This is because the tip of the formed transverse crack was blunted by splitting at the fibre-matrix interphase [189]. This lead to a considerable decrease in the high tensile stress level ahead of the crack. Consequently, the primary load bearing elements (fibres) in this composite can sustain high levels of load before their final fracture. This failure process allows the longitudinal strength of DP1 rebars to be fully developed.

After the maximum load to failure of DP1 specimens, with the crosshead moving downwards, the matrix strain on the new fractured surface reached a maximum again. Longitudinal splitting took place continuously and transverse cracks extended upwards from the bottom of the specimens. However, the load gradually dropped off as the effective thickness was reduced. That is the reason why DP1 failed in a non-catastrophic way in Fig. 6.13. The progressive propagation of the delamination and fibre fractures can be clearly seen and heard during the post failure phase. The same thing did not occur to the other five types of rebars, in which the maximum load to failure dropped dramatically. This indicates that the flexural failure mechanisms are distinctively different those of the others.

As far as API is concerned, both the compressive and tensile damage zones can be clearly seen in Fig. 6.19 (a). However, the fact that the compressive crack is considerably larger than the tensile one indicates that the failure started from the compressed side. With the movement of the compressive crack towards the neutral plane, increased tensile
strain in the opposite side initiated fast failure. Fig. 6.19 (b) highlights that fibre pull-out, fibre fractures and delamination occurred in the localised area of the tensioned side. On the compression side, multiple fibre breaks and localised rotation of broken fibres (or featured as columns) [78] were observed in Fig. 6.19 (c). This type of failure is actually triggered by fibre buckling which was also found in the compressive failure of E-glass fibre bundles embedded in Epon 815 epoxy matrix [12]. The failure pattern as shown in Fig. 6.19 (c) suggests that the micro-buckling of the fibres may stem from a single fibre and then quickly extend to neighbouring fibres. The thin crack lines starting from the compressed area and extending towards the ends of the AP1 specimens, was caused by the compressed and fractured surfaces being pushed against each other.

Fig. 6.20 (a) shows that the mixed mode fracture behaviour of BAP is similar to that of AP1. However, a seeming difference is that a kink band has developed as seen in Fig. 6.20 (b). The formation of such a band is actually a result of the fibre micro-buckling. Thus, there is no fundamental difference between AP1 and BAP in terms of failure characteristics. The orientation of the kink band at about 45° to the fibre direction suggests that the compressive failure took place on the maximum shear stress plane. The compressive failure of AP1 and BAP can be mainly characterised by fibre micro-buckling whereas the tensile failure features fibre pull-out, interfacial failure and fibre fracture.

Figs. 6.21 (a) and (b) show that intensive delaminations, another typical compressive failure feature [78], occurred to DP2 whereas both delaminations and multiple transverse cracks took place on the compressed side of AP2 as observed in Figs. 6.22 (a) and (b). Therefore, the major compressive failure of DP2 and AP2 can be described as delamination.

In the case of ARA, the compressive failure was dominated by severe interfacial breakdown. This is indicated by multiple delamination lines in Fig. 6.23 (a), and by no trace of matrix adhering to the glass fibres. The irregular pattern of fibre damage or fibre crushing, is believed to be post-damage after the fibre/matrix interface separation.
Table 6.10 Correlation between the fibre silane coupling agent types, matrix types, ILSS, flexural properties and flexural failure modes and characteristics

<table>
<thead>
<tr>
<th>Coupling agent types</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass fibres</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Atlac 580 rebars</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Daron XP45 rebars</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ILSS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural modulus</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural strain</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural strength</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Coupling agent types</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass fibres</td>
<td>E-glass</td>
<td>E-glass</td>
<td>AR glass</td>
</tr>
<tr>
<td>Atlac 580 rebars</td>
<td>AP1, BAP*</td>
<td>AP2</td>
<td>ARA</td>
</tr>
<tr>
<td>Daron XP45 rebars</td>
<td>DP1</td>
<td>DP2</td>
<td></td>
</tr>
<tr>
<td>ILSS</td>
<td>highest</td>
<td>higher</td>
<td>intermediate</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural strain</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Flexural strength</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Reinforced with Type A glass and textured glass fibres.

The effect of ILSS on the flexural compressive failure characteristics and properties can be understood as follows: the lowest ILSS associated with ARA severely reduces the effectiveness of the "matrix supporting" function as a foundation. At a very low load level, the fibres are separated by lateral stresses due to poor fibre/matrix adhesion. Further increased load forces, the bare fibres to be crushed, resulting in a very low flexural strength. In composites like DP2 and AP2 with low ILSS, the separation of glass fibres from their matrices is delayed by improved fibre/matrix adhesion, but delamination still occurs at certain higher levels of load. Once delamination takes place, the whole composite system loses its stability under the compressive stress. For the composites having higher ILSS (AP1 and BAP), interfacial failure and delamination are effectively contained by their higher fibre/matrix adhesion. However, the much improved interfacial strength cannot mitigate interfacial failure occurring in localised areas, so that localised micro-buckling may commence and quickly propagate to the adjacent fibres. Consequently, the ultimate failure of the whole composite system results.
Likewise, the increase in ILSS will decrease the severity of the instability of the fibres surrounded by the matrix, and in such cases the rigidity of the composites may be increased. The effect of glass fibre sizing types on ILSS is correlated with the effect of ILSS on flexural properties and failure modes and characteristics in Table 6.10.

It can be concluded that differences in ILSS contribute to variations in the flexural failure modes, which, in turn, are responsible for changes in flexural failure modes and strengths. The flexural strengths and strains of the rebars increased when the failure modes changed from compressive, to the mixed and to tensile. The high flexural properties of DPI are due to fracture characteristics of the rebar occurring in tension. Failure is believed to initiate from the ultimate matrix failure and is followed by interfacial delamination and fibre fracture. The strong sensitivity of strength and maximum strain to ILSS for rebars failing in compressive mode, is attributed to the ability of the fibre/matrix interface to delay localised micro-buckling, delamination and interfacial breakdown. Similarly, the increase in flexural modulus with increasing ILSS is because of the ability of the strong fibre/matrix interface to decrease the severity of the fibre instability.

6.6 Dynamic Mechanical Thermal Analysis of Composite Interphase

6.6.1 Influence of interphase on glass transition temperature

In Section 6.4.4, it was demonstrated that the fibre/matrix adhesion levels or the ILSS values of the rebar composites were significantly affected by the choice of fibre sizings or silane coupling agents. It was established that this was attributable to differences in the interphases formed during the composite fabrication process. In Section 6.5, it was found that this difference considerably influenced the flexural properties and the failure mechanisms of the rebars. It is therefore fundamentally important to further understand and investigate the interphase region in these composites at a molecule level.

In this Section, DMTA testing is reported which was used to explore the possibility of characterising the interphase of the composite using $T_g$. This quantity was judged to be sensitive to contributions from the fibres, the matrix and the interphase [73]. In this study, the flexural storage modulus $E'$, the loss modulus $E''$, damping factor $\tan \delta$ and
glass transition temperature $T_g$ for all the composite samples and the neat virgin resin castings were measured, and are shown in Figs. 6.24 to 30. Here $T_g$ is defined as the temperature at maximum loss modulus. BAP was excluded from this examination because the mixture of the “two-type” glass fibres in BAP would complicate the investigation.

Table 6.11 DMTA properties of the composites and pure resin samples

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ ($^\circ$C)</th>
<th>$\Delta T$ ($^\circ$C)*</th>
<th>$T_{gi}$ ($^\circ$C)</th>
<th>Tan $\delta$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atlac 580 resin</td>
<td>131</td>
<td>-</td>
<td>-</td>
<td>1.10</td>
</tr>
<tr>
<td>AP1</td>
<td>151</td>
<td>20</td>
<td>112</td>
<td>0.13</td>
</tr>
<tr>
<td>AP2</td>
<td>145</td>
<td>14</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>ARA</td>
<td>136</td>
<td>5</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>Daron XP45 resin</td>
<td>224</td>
<td>-</td>
<td>-</td>
<td>0.16</td>
</tr>
<tr>
<td>DP1</td>
<td>237</td>
<td>12</td>
<td>-</td>
<td>0.037</td>
</tr>
<tr>
<td>DP2</td>
<td>230</td>
<td>6</td>
<td>-</td>
<td>0.089</td>
</tr>
</tbody>
</table>

* $\Delta T = T_g$ of the composite $- T_g$ of the corresponding matrix.

Table 6.11 gives the $T_g$s for both the neat resins and their corresponding composites. It can be seen that addition of glass fibres in the composites raised the $\alpha$-transition $T_g$ of their corresponding matrices in all cases. This is a common phenomenon [190] generally attributed to an interaction between the matrix and fibre surfaces that restricts the mobility of the matrix molecules, thus increasing the matrix $T_g$. It is known that the process that influences the glass transition is co-operative [191]. This means that the change in $T_g$ is reflected in the restrictive effect not only on those polymer molecules that have come in direct contact with the glass surfaces, but also on the molecules remote from such surfaces. If this were not the case, it would be impossible to detect any changes in glass transition temperatures of composites.
Chapter 6 Characterisation of Pultruded Rebar Composites

Fig. 6.24 DMTA thermograph of Atlac 580 pure resin

Fig. 6.25 DMTA thermograph of AP1 composite sample

Fig. 6.26 DMTA thermograph of AP2 composite sample

119
Fig. 6.27 DMTA thermograph of ARA composite sample

Fig. 6.28 DMTA thermograph of Daron XP45 pure resin

Fig. 6.29 DMTA thermograph of DP1 composite sample
Fig. 6.30 DMTA thermograph of DP2 composite sample

Whilst this general effect is the same, the extent of the increase in $T_g$ is widely varied (Table 6.11), depending on the individual composites, or the interaction of the matrix resins with different coupling agent systems. To generalise the effect of the composite interphase on the $T_g$ of the matrix, the increment of $T_g$, $\Delta T_g$ is used here, and the $T_g$ of the each matrix is used as a baseline for their corresponding composites. (The difference in $T_g$ between these two matrix resins of Atlac 580 and Daron XP45, depends upon the nature of their component chemical compositions and rigidity, and their crosslinking density). Fig. 6.31 correlates the ILSS strength with $\Delta T_g$ values and shows an approximately linear relationship between ILSS and $\Delta T_g$ within the composites made of the same matrix. One possible explanation is that the strong interphase of composites like API and DPI, facilitates the enhanced stress transfer from the matrix to the fibres, thus leading to the high values of ILSS. It is reasonable to believe that this strong interphase should also facilitate the effective transfer of the restrictive effect of the fibre surfaces back into the matrix molecules, thereby leading to a higher increase in $T_g$. On the contrary, the lower ILSS data of AP2 and DP2 (in comparison to those of AP1 and DP1) is synonymous with their lower $T_g$ increments. As an extreme case of ARA with very low ILSS, the $T_g$ is very close to that of the pure resin Atlac 580. This is apparently poorly interactive with the matrix, thus limits adhesion and also any restrictive effect that would influence $T_g$. The result is in agreement with incompatibility of the coupling agent with the resin, as shown previously by Fig. 6.12 (e).
From a statistical point of view, the strong interphase of a polymer composite with an improved ILSS, means a greater probability that the silane coupling functional groups physically and chemically interact with the active groups of the polymer matrix. This results in a smaller quantity of polymer free ends in the interphase region. The reduction in free ends in turn leads to a decrease in the number of conformations of the polymer molecules [191] and therefore a decrease in $T_g$. By contrast, for a composite with a poor interphase and low ILSS, a smaller number of such interactions would be involved. Consequently, more free ends and more conformations of the polymer molecules may result in a poor interphase region, and therefore a lower $T_g$. The results in Fig. 6.31 indicate that the increment in $T_g$ of the composites, (which is influenced by the magnitude of the interaction between the matrix and fibres), is directly related to the values of composite ILSS; and thus to the fibre/matrix interphase strength. The latter in turn resulted from the differing levels of the interactions between the coupling agents on the glass fibres and the liquid resins during composite processing.

![Graph showing correlation between ILSS and Tg increment.](image)

Fig. 6.31 Correlation of ILSS with the increment in glass transition temperature of the composites ($\Delta = T_g$ of a composite - $T_g$ of the corresponding matrix)
Tan δ may be also linked to the interphase bonding, as it is a parameter used to assess the capacity of a material to dissipate energy [75]. Indeed, in the Atlac 580-based composites, AP1 (with the higher ILSS) tended to dissipate less energy, and correspondingly to possess a lower tan δ value (0.13) (see Table 6.11), because the greater the transfer of stress from fibre to matrix, the lower the energy dissipated. In contrast, AP2 and ARA (with the lower value of ILSS), tended to dissipate more energy, and correspondingly to have a higher tan δ value (0.19) compared to AP1. The same conclusion can be made for the composites based on the Daron XP45 matrix. However, the effect of the interphase condition on tan δ is not as prominent as on Tg. This is indicated by the fact that the tan δ value of AP2 is identical to that of ARA, though their interphase strengths are dramatically different.

However, it should be emphasised that the absolute values of tan δ are not directly comparable between the composites based on these two different matrices. This is because they were generated from the addition of individual tanδ values of both the matrix and the interphase (glass fibres can be considered to be elastic), and a large variation in tan δ between these two respective matrices exists (Table 6.11).

6.6.2 Influence of interphase on loss modulus

A polymer composite interphase can be also assessed by changes of its loss modulus after incorporation of glass fibres. By comparing Fig. 6.25 with Figs. 6.25-27, it was found that large differences in the shapes of loss modulus exist between Atlac 580-based composites. It is interesting to note that there is a shoulder on the E'" curve of AP1 (Fig. 6.25); however, this is not true for the other two (Figs. 6.26-27). This indicates that there must be another transition existing in composite AP1 in addition to the matrix α-transition. In fact, these two transitions simply overlapped because the value of E'" in Fig. 6.25 is the result of the arithmetic addition of the two individual loss moduli produced by two different molecular motions. Thus, the lower transition appeared as a shoulder rather than a peak.

It is impossible that the lower transition resulted from glass fibres [73], as they were essentially elastic within the scanning temperature (up to 250 °C). Neither did it result
from the pure resin as exhibited in Fig. 6.24 because there was no such second transition occurring below the matrix \( \alpha \)-transition. In other words, if this lower transition for AP1 had been generated from the matrix resin, the same thing should have occurred in both AP2 and ARA, because these composites were produced under the same conditions and using the same resin formulations as composite AP1.

Fig. 6.32 DMTA thermograph of AP1 composite sample at 10 Hz and 3 °C/min.

Fig. 6.33 DMTA thermograph of AP1 composite sample at 1 Hz and 1 °C/min
In order to exclude the possibility of the shoulder being induced by an artefact which had been reported earlier in a similar test on dynamic mechanical analysis (DMA) [192], the repeatability of its occurrence was examined at a higher frequency of 10 Hz and a lower heating rate of 1 °C min^{-1}. However, the shoulder consistently occurred as shown in Figs. 6.32-33. The only difference observed is the shifting of the main α-transition and the lower transition temperature. This is a general phenomenon that the glass transition temperature measured in DMTA depends upon the thermal scanning conditions. It is therefore concluded that this low temperature shoulder is probably attributed to the interphase which was developed during the composite processing stage. The transition temperature of this interphase, defined as T_{gi}, cannot be accurately determined but can be estimated to be 112 °C at the turning point of the shoulder as shown in Fig. 6.34 at a 1 Hz frequency and 3 °C min^{-1}.

Thomason [59] found a similar behaviour in a glass/epoxy composite. He attributed the second low temperature transition to fibre coating. Alternatively, the other possibility is that copolymerisation and interpenetrating network (IPN) may be developed in the interphase by interaction of the organofunctional group in a silane with a liquid resin [49]. This theory has successfully explained why silane coupling agents can improve the mechanical properties of glass fibre reinforced thermoplastics composites [49]. However, as suggested in theory [49], the conditions for the development of IPN interphase in thermosetting composites are very restricted. Experimentally, Gentle et. al. [53] have
found that the inter-diffusion of coupling agents with polymers is maximised only when the solubility parameters of polymer and coupling agent are matched.

In the case of the AP2 system, no clearly defined second transition occurred (Fig. 6.26), but the broadness of its loss modulus curve, suggests that there are more than one transitions occurring, each with slightly different T_g. This may be due to the formation of a degraded interphase where variable degrees of copolymer are formed in the interphase region. However, it could also be that two transitions occur which overlap thus masking the presence of an IPN.

However, it is impossible to conclude which mechanism is dominant in these two systems. This is partly because it is very difficult to experimentally obtain specific information about the composition of the interphase, and partly because access to complicated ingredients of the glass fibre sizings was prohibited by commercial sensitivity. Although there are differences in the E'' curves between API and AP2, one thing is in common that the loss modulus curve was broadened and the interphase was an inter-diffused region. The variation in the composition of interphase between AP1 and AP2 accounts for the difference in the shapes of E'' curve and therefore the ILSS values.

With regarding to the ARA system, a very narrow E'' curve (Fig. 6.27) indicates that such an interphase, as existing in the AP1 and AP2, does not occur. It is likely that there is a discrete interphase because of the incompatibility between the resin and the fibre coating.

Careful examination of Figs. 6.29 and 30 further confirms that the stronger interphase DP1 in comparison with the DP2 system leads to a broader E'' curve resulting from an inter-diffused region.
Chapter 7 Immersion Degradation of Rebars

7.1 Introduction

Water can diffuse into polymer composites, which leads to the deterioration of their properties. It is very important to know the rate, magnitude and mechanisms of the water effect on the composite rebar. In addition, it is also pertinent to understand if introduction of hydroxyl ions into water can possibly speed up the degradation of the composite. This Chapter centres on experiments:

(1) to measure the water absorption behaviour of the pure Atlac 580 resin and the rebar in water and simulated alkali solution at three temperature levels;
(2) to monitor the environmental effect on the dynamic mechanical properties of the resin and composite;
(3) to quantify the environmental effect of the flexural properties of the rebar.

7.2 Water Absorption Characteristics of resin

7.2.1 Equilibrium water content

In a parallel with API rebar conditioning, the neat resin plates of Atlac 580 resin were immersed in water and alkali solution at 40, 60 and 80 °C, respectively. The water uptake of the resin is expressed in terms of weight gain against square root of time as shown in Figs. 7.1 and 7.2. The data of the plots were based on the average results from three specimens. The equilibrium water uptake content of the resin in each condition can be directly read from these figures and is included in Table 7.1.

Figs. 7.1 and 7.2 shows that the water uptake of the resin specimens quickly reached equilibrium and then levelled off to a plateau in various environments, which is Fickian behaviour [127]. Increasing environment temperature increased diffusion rate however; it is noted that the $M_w$ of Atlac 580 in both water (Fig. 7.1) and alkali solution (Fig. 7.2)
depended upon temperature. This dependency is registered in Table 7.1 as an increment increase in equilibrium water content of about 0.1 wt. % per 20 °C. A similar behaviour was also found in Derakane 441-400 vinyl ester resin immersed in water [193]. A possible reason is that clustering of water molecules occurred and increased with increasing temperature.

Table 7.1 Summary results of the water absorption behaviour of Atlac 580 resin in water and alkali solution

<table>
<thead>
<tr>
<th>Media</th>
<th>Temp. (°C)</th>
<th>M_o (%)</th>
<th>$D_e \times 10^{-6}$ (mm$^2$s$^{-1}$)</th>
<th>$E_a$ (kJ mol.$^{-1}$)</th>
<th>$D_0$ (mm$^2$s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>40</td>
<td>0.728</td>
<td>2.81</td>
<td>36.41</td>
<td>3.27</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.822</td>
<td>6.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.964</td>
<td>13.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Alkali</td>
<td>40</td>
<td>0.721</td>
<td>2.75</td>
<td>33.52</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.806</td>
<td>6.37</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>80</td>
<td>0.912</td>
<td>11.7</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 7.1 Water uptake vs. time for Atlac 580 resin immersed in water at 40, 60 and 80 °C, lines are fitted to Fickian model
Fig. 7.2 Water uptake vs. time for Atlac 580 resin immersed in alkali solutions at 40, 60 and 80 °C, lines are fitted to Fickian model

It is also noted from Table 7.1 that alkali solution reduced the water Mo values of the resin at all temperature temperatures, though not significantly. This is probably accounted for by the presence of ions in alkali solution that reduced the activity of water [133].

It must be pointed out that conditioning may result in weight loss due to leaching out low molecule weight substances from resin samples [103]. To confirm if this occurred in the present study, the weight loss of the redried resin samples was examined as listed in Table 7.2.

Table 7.2 Weight loss of Atlac 580 resin samples during conditioning

<table>
<thead>
<tr>
<th>Time (days)</th>
<th>Weight loss in water (wt. %)</th>
<th>Weight loss in alkali solution (wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40 °C</td>
<td>60 °C</td>
</tr>
<tr>
<td>30</td>
<td>0.030</td>
<td>0.035</td>
</tr>
<tr>
<td>90</td>
<td>0.028</td>
<td>0.032</td>
</tr>
<tr>
<td>360</td>
<td>0.032</td>
<td>0.031</td>
</tr>
</tbody>
</table>

It is observed from Table 7.2 that the weight loss of the resin was generally not significant and stabilised after about 30 days' immersion in the most conditions.
However, for the specimens immersed in the solution at 80 °C for one year, the loss doubled the average value. In addition, the weight loss also appeared to be independent of the environment and time and may be mainly caused by erosion of some loose materials on the specimen surfaces. The good chemical resistance of Atlac 580 resin structure along with the fully crosslinked network reduced the tendency to leach out some components.

7.2.2 Diffusion coefficient

Diffusion coefficient is another variable to characterise the moisture absorption behaviour of a material. It describes the absorption rate at which the moisture uptake approaches the asymptotic maximum; however, it is not an independent quantity describing the rate of transport of moisture through the material as indicated in Eqn. 7.1. In order to obtain the diffusion coefficient of the resin in various environments, the gradient of the initial linear part of each curve in Figs. 7.1 and 7.2 was calculated by using a least square fit as shown in Figs. 7.3 and 7.4. Given the equilibrium water uptake data and the gradient values, the apparent diffusion coefficient can be computed using Eqn. 7.1.

Fig. 7.3 Slope calculation of the initial linear portion of weight gain vs. square root of time for Atlac580 resin in water at 40, 60 and 80 °C, respectively
Fig. 7.4 Slope calculation of the initial linear portion of weight gain vs. square root of time for Atlac580 resin in alkali solution at 40, 60 and 80 °C, respectively.

Fig. 7.5 Temperature dependency of water diffusivity for Atlac 580 resin in water and alkali solution.

\[ D = \left( \frac{K_h}{4M_\infty} \right)^2 \pi \]  (7.1)

Where

- \( M_\infty \) = equilibrium water content,
- \( h \) = the thickness of the resin plates (3 mm),
K = the slope,

D is then corrected for edge effects through Eqn. (7.2) as suggested by Shen and Spinger [125].

\[
D_x = D \left(1 + \frac{h}{l} + \frac{h}{n}\right)^{-2}
\]  

(7.2)

D_x is the corrected one dimensional diffusion coefficient; h, l and n are the thickness, width and length of a sample, respectively. The values of D_x for the resin in the two media are included in Table 7.1.

As expected, the diffusion coefficient of the resin samples was dependent on the conditioning temperature, i.e. the D_x value increased with increasing temperature. It can also be found from Table 7.1 that the D_x value in the solution is consistently less than that in water at each temperature level. And the discrepancy tends to increase with increasing temperature. As stated previously, this was caused by the reduced activity of water in the solution due to existence of such ions as Na^+, K^+, Ca^{2+} and OH^-. However, the influence of the ions on the diffusivity was not considerable in terms of absolute value.

The temperature dependence of the water diffusivity for the resin can be calculated by using an Arrhenius relationship (Eqn. 7.3).

\[
D_x = D_0 \exp \left(-\frac{E_a}{RT}\right)
\]  

(7.3)

Where D_0 is the pre-exponential term, E_a the Arrhenius activation energy, R the gas constant, and T the absolute temperature.

Fig. 7.5 compares the Arrhenius plots for Atlac 580 resin in water and the solution. These plots indicate that the relationship between water diffusivity and temperature in both cases did not deviate from linearity, suggesting a single mechanism for water
diffusion over the given range of temperatures. As shown in Table 7.1, the absolute value of activation energy for the resin in alkali solution is lower that that in water if water uptake by a polymer is treated as an exothermic process as suggested by El-Sa'ad et al [194]. The result further confirmed the hindrance of ions in the water diffusion process.

7.2.3 Modelling the water absorption of the resin

Water absorption of Atlac 580 resin plates can modelled by using Eqn. (7.4), as the material under went Fickian diffusion.

\[
\frac{M_t}{M_\infty} = 1 - \exp \left\{ -7.3 \left( \frac{D_t t}{h^2} \right)^{0.75} \right\}
\]

Figs. 7.1 and 7.2 show that the modelled behaviours agree fairly well with the experimentally determined ones.

7.3 Water Absorption Characteristics of Rebar

7.3.1 Water uptake of rebar in water

AP1 composite rebar samples were simultaneously immersed in water under the same environmental conditions as the pure resin. The moisture uptake data for AP1 rebars in water were plotted as a function of square root of time and temperature as shown in Figs. 7.6. It is clear that with increasing temperature, the rate of moisture absorption increased and so did the moisture content. However, unlike the pure resin, the moisture absorption behaviour of the rebar was complicated by incorporation of glass fibres, which can be described as a three stage process.

In the first stage, the weight gain versus square root of time within one day was characterised by a quick growth. This is a process in which the absorption is mainly dominated by the concentration gradient of water, and therefore is a diffusion controlled process. Increasing the temperature of a water bath lead to a corresponding increase in the rate of uptake.
In the second stage between about 20 and 400 hours, the rate of uptake was reduced at all temperature levels. The reduction was caused by closely packed glass fibres. Although the amount of water absorbed increased with increasing temperatures, the absolute values were not significantly different at different temperatures. This can be accounted for by the temperature effect on the matrix resin.

In the third stage, beyond about 400 hours, the curves in Fig. 7.6 demonstrate that the uptake for API rebar specimens deviated from classical Fickian behaviour, especially at 80 °C, with continuing weight gain rather than a plateau for the extended immersion time. The deviation may have suggested that an additional water uptake process operated. It is very important to understand this process as it may indicate the different mechanisms for the property degradation of glass composites.

Since a glass composite consists of glass fibres, matrix, the interphase, and flaws like voids, it is logical to think that the latter three are responsible for moisture absorption, if it is assumed that glass fibres do not contribute. This relationship can be expressed as:

\[ M = M_m + M_i + M_v \]  

(7.5)

Where \( M \) is the total mount of water absorbed by the composite, \( M_m, M_i \) and \( M_v \) are the amount of water absorbed by the matrix, the interphase and voids, respectively. Thomason [131] highlights the importance of water absorption contributed by glass composite voids when their contents are more than 1 % in volume. High density and connected voids can accelerate the ingress of water, and increase the final equilibrium level. Closed voids will provide extra sites for storage of water at much higher concentration than in the resin matrix. In addition, if the glass fibres are degraded by water, then additional room will be left for water storage too.
Fig. 7.6 Water absorption of AP1 rebar specimens as a function of time and temperature

Fig. 7.7 Normalised water uptake of the rebars to 100% matrix and modelled absorption behaviour of the pure resin with the same dimensions as the rebar
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Fig. 7.8 Water uptake attributed to voids and interphase.

However, the complication of absorption in glass composites makes it difficult to precisely work out the amount of water in voids and the interphase. To simplify the calculation in the present study, the weight gain of the rebar specimens were normalised to the matrix content as shown in Fig. 7.7. Also, a modelled behaviour of Atlac 580 pure resin with the same dimensions of the rebar is presented in this figure, according to the parameters obtained in Section 7.2. The summation of $M_i$ and $M_v$ was quantified by subtracting the modelled data from the normalised data at each temperature. The neat virgin polymer result is shown in Fig. 7.8.

Fig. 7.8 clearly indicates a relatively steady increment in water absorption in the initial time within the initial 400 hours. For further longer times the increment due to the voids and interphase grows with time. The rate of the growth strongly depends upon temperature, and is particularly serious at 80 °C.

Given the void content of API rebar, 0.54 vol.%, a possible maximum amount of water absorbed by the voids was estimated to be 1.1 wt.%. By reviewing Fig. 7.8, it is found that the incremental uptake did not exceed this maximum even at 80 °C. However, this does not preclude the possibility of water uptake by the interphase since the water distribution inside the rebar specimens is not even. It is rather likely that the two
Chapter 7 Immersion Degradation of Rebars

processes occurred simultaneously, and they were activated progressively inward. This possibility is indicated in Fig. 7.8 that the additional absorption smoothly increased with time in all the cases. At the end of one year conditioning, it did not tend to stop. Particularly at 80 °C, this effect is much faster than that at 40 and 60 °C, and the extra uptake is significantly higher. The result highlights that the degradation mechanisms of glass composites at high temperature may be different from those at low temperature, which poses a problem for composite lifetime prediction at high temperatures.

Table 7.3 Weight loss on re-drying rebar samples after exposure to water for one year

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Weight Loss (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>0.200 ± 0.031</td>
</tr>
<tr>
<td>60</td>
<td>0.119 ± 0.028</td>
</tr>
<tr>
<td>80</td>
<td>0.135 ± 0.043</td>
</tr>
</tbody>
</table>

Table 7.3 shows the percent weight loss of the rebar specimens after being exposed to water for one year. The loss at 80 °C was slightly higher than that at 40 and 60 °C but generally the absolute values are not particularly serious in all cases. For ease of analysis, these losses were not considered when plotting Figs. 7.6 to 7.8.

7.3.2 Water uptake of rebar in alkali solution

Fig. 7.9 shows the weight gain of AP1 rebar specimens in alkali solution at three temperatures. Weight loss was found. This was identified later as organic fibres on the
rebar surface being "etched away" by alkali solution (see Section 7.6). The experiment was terminated after about ten days. However, it is expected that the kinetics of moisture absorption for the rebar in alkali solution should be similar to that in water as there is only marginally difference in water equilibrium content and diffusivity for Atlac 580 immersed in these two media.

7.4 Effect of Conditioning on Glass Transition Temperature of Resin

In order to monitor changes that occur physically and possibly chemically during extended conditioning, the glass transition temperature of the pure resin was studied by using DMTA. Focus was on samples conditioned in water and alkali solution at 80 °C because high temperature can facilitate the possible physical and chemical effects to be easily identified.

Fig. 7.10 shows the variation of the glass transition temperature with time for the resin conditioned in both water and alkali solution (see Appendices 7.1 and 7.2). It was found that the $T_g$ was reduced from about 131 °C to 122 °C. the change was accomplished within approximately the initial 20 days; but afterwards remained stable for up to one year. The magnitude of reduction in $T_g$ due to exposure to water and alkali solution was identical (9°C). The implication of this is that physical degradation caused by water may predominate to Atlac 580 resin immersed in these two media. Although this cannot preclude the possibility of chemical degradation, such as ester bond hydrolysis of the resin during long-time immersion, the effect may be limited, which did not significantly affect the $T_g$.

Fig. 7.11 relates the glass transition temperature with water content. It is clear that the $T_g$ reduction was only associated with the amount of water uptake no matter whether the resin was in water or alkali solution. The relationship can be described as a second order polynomial curve. A good fit to all the data points was found with a factor of 0.94. It is also interesting to note that a change in the slope of the curve, $dT_g/dM$ decreased with increasing $M$, which means that the rate of the drop in $T_g$ slowed down with increasing water absorption. This is perhaps because the water absorbed by the polymer was not all purely in the form of molecules. Some of the absorbed water clustered together which
was not as effective as "molecular water" in plasticising the polymer. Also the probability of clustering escalated as moisture absorption increased. Jacobs and Jones [157-159] came to an identical conclusion by examining the sensitivity of the glass transition temperature of Crystic 272 polyester resin to uptake moisture. They found that clustering occurred above 0.39 wt.% moisture content of that resin. To further confirm this mechanism, the glass transition temperature of the resin was examined after it had been conditioned in water at 40 and 60°C and reached equilibrium at 0.73 wt.% and 0.82 wt.%, respectively. The results (Fig. 7.10 (b)) agreed well with the fitted line.

Figs. 7.12 and 13 compare the dynamic mechanical properties of the resin before and after being exposed to water and alkali solution at 80°C for 360 days, respectively. Clearly, the variation of the properties was very similar for the resin in these two differing environments, again suggesting that alkali solution did not impose significant additional effect to the resin. It may be water that is a primary mechanism for the degradation.

In addition, conditioning caused the increase in the intensity of $E''$, which can be easily understood by the well known plasticising effect as revealed in Figs. 7.12 and 13. Furthermore, the $E'$ values in the glassy and rubbery region were also slightly affected. To explain this, one has to believe that the crosslinking density of the resin was possibly enhanced during the extended high temperature conditioning, though the resin samples had been postcured before environmental exposure and a DSC scan showed no exothermic peak for the postcured sample. It is well known that it is very difficult for styrenated polyester or vinyl ester resins to achieve complete crosslinking. Minor amount of unreacted components may be still buried in polymer networks even after postcuring. Long term and high temperature exposure may facilitate to further chemical reaction in this respect.

The combined effect of the increase in both $E'$ and $E''$ led to a broadening of the damping peak and a decrease in its height as shown in Fig. 7.12 and 13. Shibayama and Suzuki [198] believe that these changes are associated with increased crosslinking density, as is an increase in the modulus of the resin in the rubbery plateau. They
suggested that for lightly crosslinked systems the crosslinking density ($\rho_E$) can be evaluated from the rubbery modulus ($E'$) from the following formula:

$$\rho_E = \frac{kE'}{3RT}$$

(7.6)

where $k$ is the specific volume, $R$ is the gas constant and $T$ is the temperature. However, the applicability of this formula to highly crosslinked systems remains to be questioned, which was supported by the results in Figs. 7.14 and 15. These two figures show that the state of tan $\delta$ curves for two resin specimens, after being exposed to water and alkali solution, respectively at 80 °C for one year, had recovered almost to that of the original specimen.
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Fig. 7.11 Effect of water content on the glass temperature of Atlac 580 resin

Fig. 7.12 Effect of exposure to water on the dynamic mechanical spectra of Atlac 580 resin. (Conditioned at 80 °C for one year)
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Fig. 7.13 Effect of exposure to alkali solution on the dynamic mechanical spectra of Atlac 580 resin. (Conditioned at 80 °C for one year)

Fig. 7.14 Dynamic mechanical properties of Atlac 580 resin before and after exposure to water at 80 °C for 200 days and being redried
Jacobs and Jones [197] consider that the broadening of tan δ peak due to water uptake, is indicative of heterogeneity of the crosslinked polyester structure with differing crosslink densities. This result is coincident with that from Zhang and Richardson [24], who observed that crosslinked Atlac 580 resin network is a two-phase structure.

Figs. 7.14 and 15 show that the $T_g$ and tan δ of the redried resin samples after exposure to water and alkali solution almost superimposed to those of the virgin dry sample. However, the intensity of $E''$ was raised, which may imply a permanent change induced in the structure of the resin.

### 7.5 Effect of Conditioning on Dynamic Mechanical Properties of Rebar

#### 7.5.1 Effect of conditioning in water

Table 7.4 Variations of the glass transition temperature of AP1 composite and its interphase before and after conditioning in water for 360 days

<table>
<thead>
<tr>
<th>°C</th>
<th>Dry AP1</th>
<th>AP1 in water</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>40 °C</td>
</tr>
<tr>
<td>$T_{gi}$</td>
<td>112</td>
<td>109</td>
</tr>
<tr>
<td>$T_g$</td>
<td>150.9</td>
<td>139.6</td>
</tr>
</tbody>
</table>

Fig. 7.15 Dynamic mechanical properties of Atlac 580 resin before and after exposure to alkali solution at 80 °C for 200 days and being redried

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<td>109</td>
</tr>
<tr>
<td>$T_g$</td>
<td>150.9</td>
<td>139.6</td>
</tr>
</tbody>
</table>
Fig. 7.16 (a) Effect of conditioning in water on storage modulus of AP1 rebar composite

Fig. 7.16 (b) Effect of conditioning in water on loss modulus of AP1 composite
Fig. 7.16 (c) Effect of conditioning in water on damping factor of AP1 composite

Fig. 7.17 Time dependence of $T_g$ and $T_g'$ of the composite in 80 °C water
Table 7.4 gives the changes in the glass transition temperature of AP1 composite rebar samples and the interphase, after being conditioned in water at three temperature levels for one year, respectively. Glass transition temperature, $T_g$, was taken from the temperature at maximum of the loss modulus $E''$. Glass transition temperature of the interphase, $T_{gi}$, was estimated from a temperature of the turning point on the shoulder of $E''$ curve as previously mentioned in Chapter 6. The experimental error of $T_g$ measurements is about 1 °C, and the results in Table 7.4 are from two or three specimens.

Figs. 7.16 (a), (b) and (c) show the representative changes of the dynamic mechanical properties of AP1 samples before and after conditioning in water for 360 days at 40 °C, 60 °C and 80 °C, respectively. Some general features observed in these figures and Table 7.4 are listed as follows:

(i) Conditioning seems not affect the storage modulus in the glassy region for all the cases. The change in $E'$ is within the experimental error (Fig. 7.16 (a)).

(ii) The intensity of $E''$ becomes larger and the breadth of the $E''$ curves becomes narrower with increasing environmental temperature (Fig. 7.16 (b)).
The results may suggest that the damage to the interphase increased with increasing temperature. For the samples in 40 and 60 °C water baths, the $T_g$ reduction is equivalent to that of the pure Atlac 580 resin (9 °C, see Fig. 7.10) in water. As mentioned in Section 7.4, this decrease in $T_g$ was mainly attributed to the water plasticising effect. The interphase may be not seriously affected since the state of the interphase directly related to the $T_g$ of the composite as addressed before. Further evidence to support this is a small drop of the $T_g$ in these two cases.

However, the opposite is true for AP1 samples in water at 80 °C. The magnitude of $T_g$ reduction (26 °C) was more than the effect induced monotonically by the water plasticisation mechanism. It is likely that a severe degradation of the interphase additionally contributed to the large decrease in the $T_g$ of the main matrix resin. This was evidenced by the fact that the $T_{gi}$ was suppressed drastically, which was not observed in the case of 40 and 60 °C water baths. As a result of the fibre/matrix interphase degradation, the fibre-matrix interaction was adversely affected, which was also indicated by a large increase in the peak of tan $\delta$ as shown in Fig. 7.16 (c). The result corresponds to increasing the mobility of the matrix molecules and reducing the constraint effect from glass fibre surface. Therefore, it can be concluded that the interphase of AP1 composite conditioned at 80 °C was degraded to a much larger degree than at 40 and 60 °C. This finding coincides with the results of water uptake dynamics of the rebars. Further evidence, as shown in Fig. 7.17, was that the depression of $T_g$ and $T_{gi}$ was time dependent or water content dependent. The fundamental reason is that the degree of the interphase degradation was proportional to the water it absorbed.
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The damage to the interphase also can be spotted from the change in storage modulus in Fig. 7.16 (a). Fig. 7.18 highlights this small step change of $E'$ which was attributed to the interphase. It also further proved that the interphase did exist in AP1 composite.

7.5.2 Effect of conditioning in alkali solution

Table 7.5 Variations of the glass transition temperature of AP1 composite and its interphase before and after conditioning in alkali solution for 360 days

<table>
<thead>
<tr>
<th></th>
<th>Dry AP1</th>
<th>AP1 in alkali solution</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{si}}$</td>
<td>$T_{\text{g}}$</td>
</tr>
<tr>
<td></td>
<td>112</td>
<td>109</td>
</tr>
<tr>
<td></td>
<td>150.9</td>
<td>139.7</td>
</tr>
</tbody>
</table>

Fig. 7.19 (a) Effect of conditioning in alkali solution on $E''$ of AP1 composite
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The temperature dependencies of $E'$ and $t\delta$ of AP1 samples in the alkali solution are given in Table 7.5. Fig. 7.19 illustrates the mechanical properties of the composite. The temperature dependency of the alkali solution was observed to be accelerated by temperature. The $E'$ and $t\delta$ of AP1 composite were measured in the solution at 40, 60, 80, and 120°C. The data show that the $E'$ and $t\delta$ of AP1 composite were increased with an increase in temperature.

**Fig. 7.19 (b)** Effect of conditioning in alkali solution on $E'$ of AP1 composite.

**Fig. 7.19 (c)** Effect of conditioning in alkali solution on $t\delta$ of AP1 composite.
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The temperature dependence of $T_g$ and $T_{gi}$ of AP1 samples in the alkali solution is given in Table 7.5. Figs. 7.19 (a), (b) and (c) present the dynamic mechanical properties of the composite before and after exposure to the solution at the different temperatures.

By comparing the results for the composite samples in water and the alkali solution, it was found that the changes of the dynamic mechanical properties were very similar in these two environments at the respective temperatures. There was no accelerating effect of the alkali on the glass transition temperatures of the rebar and interphase. In fact, the amount of the reduction in $T_g$ and $T_{gi}$ in the alkali medium was slightly less than that in water at 80 °C. This suggests two things. Firstly, the water absorption dynamics of AP1 in the solution may be similar to those in water. Secondly, water may be the direct reason for the deterioration of the rebars. Such ions as $K^+$, $Na^+$, $Ca^{2+}$ and $OH^-$ might not have diffused into the polymer matrix, as otherwise the diffused hydroxyl ions would have accelerated hydrolysis of silane/glass fibre interface.

7.6 Effect of Environmental Exposure on Flexural Properties

7.6.1 Physical appearance of exposed rebars

Fig. 7.20 shows that small cracks were developed on the surface of a rebar sample after being conditioned in 80 °C water for one year. This occurrence was less obvious at lower temperature (40 and 60 °C). Fig. 7.21 shows that these cracks sometimes extended to the inside of the outer surface layer. However, the main body of the rebar appeared intact as indicated in Fig. 7.22. The interphase debonding and cracking of the resin-rich zones, as reported [199] in a glass/epoxy composite immersed in water at 80 °C for 600 hours, was not observed even for the samples conditioned at 80 °C for 360 days (Fig. 7.21).

Immersion of the rebar in alkali solution resulted in severe damage on the surface of samples. Fig. 7.23 demonstrates that some material was removed from the sample surface, and holes and cracks were left. The removed material was identified to be organic fibres in the outer layer as shown in Fig. 7.24. Fig. 7.25 shows the enlarged view of this damaged area. The corrosion of the organic fibre in the outer layer also occurred to sample rebars at lower temperatures (60 and 40 °C), but the time involved was longer.
Leaching out of the corroded organic fibres was probably mainly responsible for the significant weight loss in determining the weight gain of the rebar previously.

Fig. 7.20 Surface appearance of rebar after exposure to water at 80 °C for one year

Fig. 7.21 Development of cracks in the surface layer for sample as shown in Fig. 7.21

Fig. 7.22 Cross view of rebar conditioned in water at 80 °C for one year
Fig. 7.23 Surface appearance of rebar after exposure to alkali solution at 80 °C for one year.

Fig. 7.24 Cross section view of a rebar sample as shown in Fig. 7.23.

Fig. 7.25 Corrosion of organic fibres in the surface layer of rebar conditioned in alkali solution.
Fig. 7.24 also indicates that the alkali solution had directly contacted with the organic fibres that were not resistant to the alkali. It is possible that the contact mainly resulted from the transport of the solution through hygrothermal induced cracking (see Fig. 7.21) in the outer layer. It is less likely that the transport was a result of diffusion through the matrix. Otherwise, the glass fibres would have been severely corroded like the organic fibres (Fig. 7.24). Actually, Fig. 7.24 clearly highlights that few glass fibres next to the corroded organic fibres had shown a sign of corrosion by a reduction in diameter, which was caused by the glass fibres being directly contacting with the alkali. However, no further spreading of this corrosion was found possibly because of the semi-impermeable nature of the polymer matrix [200]. Again, no debonding or matrix cracking in the middle of the composite was observed.

Another effect of conditioning is the browning or darkening of the rebar samples aged both in water and alkali solution. The severity increased with increasing temperature and time. The change of the colouring may represent the ageing of the matrix and/or oversaturation of water in the interphase.

### 7.6.2 Effect of exposure to water on flexural properties

It is natural to link the properties of exposed glass composites to water content, as water is responsible for the possible changes of composite properties. Figs. 7.26 to 7.28 summarise this relationship for the rebar conditioned in water. Detailed results are listed in Appendix 7.3. For ease of comparison, the flexural properties of environmental exposed rebars were normalised to those of unexposed ones. Every data point was an average value obtained from five specimens. For clarity, standard deviation of each data point was not included in Figs. 7.26-28.

Fig. 7.26 shows that the flexural strength of the rebar decreased by over 50 % of its original UBS as the moisture content increased. The decrease was initially fast, but then slowed down. The turning point was approximately at 0.5 wt.% water uptake level. Above this value, the strength degradation appeared to level off. Fig. 7.27 demonstrates that the modulus of AP1 rebar retained above 95 % of its original value. It seems that there was no obvious dependence of the modulus on water moisture level or conditioning
temperature. The strain to failure as shown in Fig. 7.28 follows the same trend as the strength since the modulus did not vary considerably.

Fig. 7.26 Correlation of the flexural strength with water content for AP1 rebar conditioned in water

Fig. 7.27 Correlation of the flexural modulus with water content for AP1 rebar conditioned in water
Fig. 7.28 Correlation of the flexural strain with water content for AP1 rebar conditioned in water

Fig. 7.29 Transition of failure mode: compressive-tensile failure of the unexposed rebar transformed to tensile failure of the exposed
As addressed in the literature review, the dependence of properties of the glass composites on water content, can be generally attributed to four possible reasons:

(i) physical degradation such as swelling;
(ii) degradation of matrix resin due to chemical reaction with water;
(iii) degradation of the fibre/matrix interphase due to hydrolysis of the coupling agent on the surface of glass fibres;
(iv) weakening of the strength of glass fibres due to dissolution of metal ions.

In the present study, however, the fact that no sign of the interphase debonding or matrix cracking was found (Fig. 7.22) suggests that swelling stress was not particularly serious. This was possibly due to limited amount of both water absorption of the matrix, (less than 1 wt.%) and the low matrix content of the rebar composite, (about 20 wt.%). Although the matrix and interphase were degraded; nevertheless the degree of the degradation might be limited to a certain degree (no interphase debonding or matrix cracking). Progressive attack on the glass fibres by water may play a dominant role in determining the strength deterioration of glass rebars.
This was supported by a change in the failure features of the rebar before and after conditioning as shown in Fig. 7.29. As pointed out in Chapter 6, for the unexposed rebar, this consisted of a mixed mode of compressive-tensile failure. The compressive failure was possibly preceded by the tensile mode as indicated by the differing extent of damage to the compressive and tensile sides (Fig. 7.29). However, the mixed mode was transformed into a tensile failure when exposed rebar samples were fractured in three point bending test. This transition started in the rebar samples after being immersed in water at 80 °C for about 90 days, at 60 °C for 180 days, and at 40 °C for 360 days. Clearly, the initiation point of the transition was associated with water uptake, and therefore with the extent of attack on the glass fibres.

The difference in the load-deflection traces of the composite rebars (Fig. 7.30) also shows that the dominant compressive failure gave way to the tensile failure for the subsequently exposed samples. The failure of the dry sample was characterised by an abrupt drop in load, indicating that buckling of the glass fibres had occurred. However, the load was lowered in a gradual manner for wet samples.

![Fig. 7.31 Progressive propagation of transverse crack from tensile side of rebar after exposure to water](image)

The change in the failure mode strongly indicates that the glass fibres degraded faster than the matrix and interphase, because the tensile strength of the rebar is mainly determined by the glass fibres whilst the compressive strength is dependent upon the matrix and interphase strength. The failure mechanism involved the cracking propagation of the tensile side in a transverse direction. Progressive fracture of the glass fibres occurred, which then induced matrix cracking and interfacial debonding (Fig. 7.31).
The drop of the flexural strength resulted from the attack of moisture to the glass fibres. It is well known that glass fibre in water is prone to leach out metal ions like Na\(^+\), K\(^+\), Al\(^{3+}\) and Ca\(^{2+}\) from the glass surface. Ion exchange between these ions and H\(^+\) occurred and resulted in development of shrinkage stresses and cracks at the glass surface. The energy for crack growth was also reduced by water. The total effect in turn led to a premature failure of the immersed rebars when subjected to bending tests. By increasing the amount of water diffusing into the matrix, the chance of the water access to the glass fibres and the occurrence of the ion exchange were enhanced. This explains the initial strong dependence of the strength of the conditioned rebars on the moisture content.

However, when the moisture content was greater than 0.5 wt.\%, which was accomplished by conditioning at 80 °C, the dependence of the strength on moisture was reduced and the degradation appeared to level off at round 50% UBS (Fig. 7.26). This may imply that material degradation is not unlimited. The removal of these metal ions from the glass fibres was in fact restricted by their solubility, which was a constant at a certain temperature because it was not possible that these ions diffused outward into the matrix due to their ionic nature and the non-ionic nature of the polymer matrix. From this point of view, to maintain the ion exchange and strength degradation of the composite, the amount of water surrounding the glass fibres has to increase steadily. However the quantity of absorbed water by the rebar samples in 80 °C did not necessarily completely gain access to the glass fibres. It is likely that most of the water was thermally trapped in composite imperfections. Thus its effect on the strength was not as prominent as diffused water through the matrix. The slowing down in strength reduction may also signify that the weakening of glass fibres approaches saturation because of limited solubilities of the leached ions.

It appeared from Fig. 7.26 that strength was a function of moisture content and not the concentration profile or the way by which the moisture content was achieved. However, it should be emphasised that a high temperature introduced an extra effect that might not occur at a low temperature because it drove more water into the vicinity of the glass fibres by enhanced solubility of the ions. As a consequence, more metal ions were removed and more severe strength degradation resulted. Therefore, the life time of glass
composites at low temperatures predicted on the basis of data collected at high temperatures is questionable.

The flexural modulus of the rebar (Fig. 7.27) was only slightly affected, possibly due to fibre straightening or measurement scattering effects. This is in agreement with the results from other work [142]. The flexural modulus of unidirectional glass fibre composites is mainly attributed to the Young’s modulus of the glass fibres which was not seriously influenced. Thus, the effect of water on the modulus of the rebars can be considered to be negligible. The calculated strain to failure in Fig. 7.28 had the same trend as the strength because the modulus maintained relatively stable during conditioning.

### 7.6.3 Effect of exposure to alkali solution on flexural properties

The effect of exposure to alkali solution on flexural strength, flexural modulus and the strain to failure of the rebars is summarised in Figs. 7.32 to 34. Detailed results are listed in Appendix 7.4. In these figures, the correlation of the normalised flexural properties with water content is made. It is assumed that water absorption behaviour of the rebar specimens in alkali solution is the same as that in water at each temperature level, because it is very difficult to accurately measure the water absorption of the rebars, (due to severe weight loss resulting from corrosion of organic fibres). This assumption is firstly supported by the fact that the equilibrium water content and diffusivity of the pure Atlac 580 were very similar in water and alkali solution, though small differences did exist because of reduced water activity in the alkali solution. Secondly, the dynamic mechanical properties of the conditioned resin and composite samples as addressed previously were principally identical.

Fig. 7.32 shows that flexural strength declines with increasing water content. The final strength of the alkali exposed sample retained about 48 % UBS of the dry sample. This value was only 2 % less than that of water-exposed rebar. By comparing Fig. 7.26 with Fig. 7.32, it was found that the overall trend of the strength degradation AP1 rebar in alkali solution paralleled with that in water, if the standard deviations of the data points were taken into account. The results imply that the hydroxyl ions in the solution did not
diffuse into the polymer matrix or the composite, and the detrimental effect was mainly caused by diffusion of water.

Fig. 7.32 Correlation of the flexural strength with water content for AP1 rebar conditioned in alkali solution.

Fig. 7.33 Correlation of the flexural modulus with water content for AP1 rebar conditioned in alkali solution.
A possible explanation may be attributed to the ionic character of these ions and non-ionic nature of the polymer matrix. Alkalis such as sodium hydroxide, potassium hydroxide and calcium hydroxide exist in aqueous solution as hydrated ions like Na\(^+\), K\(^+\), Ca\(^{2+}\) and OH\(^-\). These ions do not tend to enter a non-ionising medium of a dry polymer structure because their inherited strong affinity to water, which drags themselves away from the uncharged polymer molecules. Even after the polymer matrix absorbs water, it cannot be expected that the absorbed water (of about 1 wt.%) can form a continuous phase in the polymer network, in which the ions can move and dissolve. Water, however, can freely disperse in polymer networks as it predominately exists in the form of molecules and is therefore compatible with (or can move alongside) polymer molecules.

The result obtained is in an agreement with conclusions from the literature [201-203]. In an early attempt to follow the penetration of both water and hydrochloric acid into an E-glass/polyester composite material with a gel coat barrier layer, Regester [201] concluded that the composite was readily permeable to water but there was no detectable penetration of hydrochloric acid through the barrier layer. Similarly, Caddock et al. [202,203] found that the diffusion of hydrochloric acid into polyester resins is negligible.
On the other hand, if hydrated ions in alkali solution had freely diffused and dissolved in polymer networks, it would be expected that the diffused hydroxyl ions would have continuously disrupted the backbone bonds (Si-O-Si) of the glass fibres. With the continuous removal of Si-O\(^-\) into solution, as occurs in E-glass fibres directly exposed to an aqueous alkali medium [92], the glass fibres would have been etched away and finally separated from the matrix. Consequently, the deterioration of the rebars would have taken place at a much faster rate and more severely in alkali solution than in water. This is obviously contradicted by experimental observations indicated in Fig. 7.24. Thus, it is concluded that the occurrence of diffusion (or dissolution) of hydroxyl ions is not possible in the polymer matrix. Accordingly, extra damage caused by hydroxyl ions does not occur in the rebars.

Fig. 7.35 Progressive propagation of transverse crack from tensile side of rebar after exposure to alkali solution

Fig. 7.36 Defect inclusion is clearly seen in rebar after being conditioned in alkali solution at 80 °C for one year
Similar to composite samples in water, failure modes change from “mixed” to “tensile” in rebars subsequent to alkali solution as shown in Fig. 7.35. It was also found that conditioning at 80 °C magnified the defect inclusions in rebars but it seemed not affect the flexural strength significantly.

The change in flexural modulus of rebars immersed in alkali solution can be divided into two cases (Fig. 7.33). When conditioned at low temperatures (40 and 60 °C), the modulus reduction level was identical to that in water (5%), again implying the detrimental effect of water. However, for rebar samples exposed to 80 °C alkali solution, the magnitude of the reduction was greatly increased (up to 25 % loss), thereby suggesting an additional effect of the solution on the modulus. This was caused by the solution gradually attacking defects in the rebar (Fig. 7.36). The defects were identified as surfacing organic fibres that had been accidentally included during the manufacture of the composite. When a conditioned sample was separated and examined along the defect line, it was found that the organic fibres were completely corroded after being immersed at 80 °C for one year (Fig. 7.37). Consequently, when exposed samples were tested, cracks were created along the defect and the rigidity of the rebar was reduced.

However, for the samples conditioned at lower temperatures, the corrosion of the defect inclusion was found not to be significant. This highlights firstly, the importance of the
quality of composites, and secondly the variation in environmental effect at differing temperatures.

The strain to failure is related to strength and modulus. At lower water contents, no significant difference in influence was found between water and alkali solution (Figs. 7.28 and 7.34). At higher water contents, (achieved by conditioning the rebar samples at 80°C for longer times), the strain to failure was less affected in the solution because of a greater reduction in modulus and the same magnitude of decrease in strength.
Chapter 8 Stress Corrosion of Rebars

8.1 Introduction

The behaviour of glass fibre composite materials under the combined effect of a stress and corrosive environments is equally important, particularly for their applications in primary load-bearing structures. Therefore, the stress corrosion (SC) of rebars in a simulated alkali pore solution was investigated. Time dependent failure of the material in water was also examined for comparison purposes. In addition, the morphological structure of the matrix resin network was studied, in an attempt to elucidate the transport processes of aqueous media in the composite. The objectives of this part of work were:

(1) to characterise the failure processes and morphology of the composite rebar under stress corrosion conditions;

(2) to quantify the rate of the stress corrosion in terms of the time to failure;

(3) to compare the difference of the stress corrosion behaviour for the rebar in water and a simulated alkali pore solution;

(4) to identify the process by which a corrosive environment gains access to the glass fibres in the composite during stress corrosion.

8.2 Four Point Bending Test

Four point bending test results for unexposed AP1 rebar samples are listed in Table 8.1. It can be seen that the values of the average strength and modulus obtained from the 4-pt test are very close to those from three-point bending test (Chapter 6). The average maximum surface strain at failure is estimated at about 2.7% according to Equation 5.4. Fig. 8.1 indicates that the relationship between the load and deflection of the rebar specimens is almost linear up to ultimate failure. This characteristic facilitates estimation of the initial strain level for SC test specimens at a given load. The stiffness is very consistent and the scatter of strength data is about 8 %. As desired and exactly designed for the stress corrosion test, the failure initiated on the tensile side of the rebar specimen
and within the inner span region. As shown in Fig. 8.2, the typical tensile failure was characterised by fibre fracture, massive longitudinal splitting, and delamination.

Table 8.1 Four point bending test results for AP1 rebar specimens

<table>
<thead>
<tr>
<th></th>
<th>Max. load (N)</th>
<th>Def. at Max. load (mm)</th>
<th>Modulus (GPa)</th>
<th>Strength (MPa)</th>
<th>Specimen width (mm)</th>
<th>Specimen thickness (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spec. 1</td>
<td>2996</td>
<td>27.32</td>
<td>43.45</td>
<td>1170</td>
<td>8.40</td>
<td>8.00</td>
</tr>
<tr>
<td>Spec. 2</td>
<td>2502</td>
<td>24.79</td>
<td>42.81</td>
<td>977.3</td>
<td>8.40</td>
<td>8.00</td>
</tr>
<tr>
<td>Spec. 3</td>
<td>2841</td>
<td>25.89</td>
<td>43.81</td>
<td>1123</td>
<td>8.30</td>
<td>8.00</td>
</tr>
<tr>
<td>Spec. 4</td>
<td>2951</td>
<td>27.75</td>
<td>43.58</td>
<td>1167</td>
<td>8.30</td>
<td>8.00</td>
</tr>
<tr>
<td>Mean, (S.D)</td>
<td>2823</td>
<td>26.44, (1.36)</td>
<td>43.41, (0.43)</td>
<td>1109, (90.5)</td>
<td>8.35, (0.06)</td>
<td>8.00, (0.00)</td>
</tr>
</tbody>
</table>

Fig. 8.1 Load vs. deflection curves for four point bend testing on AP1 rebars in air
8.3. Fractographic Features of Stress Corrosion Cracking

8.3.1. Fracture in alkali solution

Rebar fracture, under the combined action of stress and alkali solution, is different from that in air. In the former, cracks normal to the fibres initiated on the surface and propagated down the inside of the rebar along the depth direction as shown in Figs. 8.3 and 8.4 for a 30 % UBS stressed rebar. The section view of the SC crack in Fig. 8.4 also reveals that localised delamination sometimes occurred due to the localised fibre/matrix debonding, and “crosslinked” with the normal crack. The most characteristic feature of stress corrosion fracture is the relative planar cracking normal to the tensile stress, as opposed to the longitudinal splitting and “brushy” morphology for the rebar tested in air. A large longitudinal crack in Fig. 8.4 resulted from an overload failure.

The SC failure morphology for rebars is directly associated with the level of load applied. When an initial load was greater than 60 % UBS, the planar crack became less obvious possibly because it did not have time to develop extensively before the thickness of the rebar was reduced by an amount which meant that the unbroken part failed by overload. Fig. 8.5 compares the fracture surfaces of the rebar tested in air, in the alkali solution at 60 % and 30 % UBS, respectively. Planar cracking has been earlier reported for stress or strain corrosion of polyester/E-glass composites in aqueous acid media [145-...
Hogg and Hull [147, 149] have given a detailed description of the stress corrosion processes of glass composites.

Fig. 8.3 Stress corrosion crack on the surface of a rebar normal to the tensile stress in the alkali solution at 40 °C.

Fig. 8.4 Cross section view of a stress corrosion crack, showing a normal crack and localised delamination. A large longitudinal crack resulted from overload failure.

Fig. 8.5 Comparison of the failure morphologies for rebars: (A) in four point bend testing in air; (B) and (C) in stress corrosion testing under 60 % and 30 % UBS stress, respectively, in alkali solutions at 40 °C.
Fig. 8.6 shows typical deflection versus time traces for a constantly stressed rebar specimen in alkali solution. This curve reflects the whole failure process of rebar specimens held on the stressing jig in the solution. Initially, the deflection increased approximately linearly with time, which may be attributed to initiation of microcracks on the surface. This was followed by a second linear increase, which corresponded to the smooth growth of normal cracks. Then there was a sudden jump in deflection within a short period of time, which may be due to a localised delamination (Fig. 8.4). After this, the stress on the remaining part of the rebar was redistributed, and new cracks formed and propagated continuously but at an accelerated rate. This is represented by the third part of the curve. When the deflection reached to a certain extent, the remaining unbroken part of the rebar no longer had the ability to carry the given load. The final failure was caused by over load and crack propagation was disrupted. The final part of the curve reflects this dramatic and almost instantaneous increase in deflection.

![Deflection vs. time curve for a surface ground rebar under a 30% UBS stress in alkali solution at 40 °C](image)

**Fig. 8.6** Deflection vs. time curve for a surface ground rebar under a 30% UBS stress in alkali solution at 40 °C.
As illustrated in Fig. 8.4, overload failure is characterised by a large and long delamination and is different from SC failure characterised by a normal crack, and localised and suppressed delamination. This is because the stress is large enough to fracture the fibre/matrix interphase when the moment of overload has been reached. The SC crack length produced at the final failure of specimens depends upon the amount of a pre-load. The larger the amount of a pre-load, the shorter the crack. This is because the overload failure came earlier at a high pre-stress level than at a low level. The crack length ranges around 2-3 mm for rebars under a 30 % UBS stress in an alkali solution at 40 °C.

![Fig. 8.7 (a). The tensile side surface morphology of a 20 % UBS stressed rebar after being exposed to alkali solution for 180 days (the rebar did not completely fail).](image1)

![Fig. 8.7 (b). A cross section view of crack growth in the rebar specimen as shown in Fig. 8.7 (a).](image2)
A 20 % UBS stressed rebar specimen did not completely fail within the exposure period of 180 days, but suffered an approximate 3 mm increase in deflection at loading points. The tensile side surface cracks (Fig. 8.7 (a)) and its section view (Fig. 8.7 (b)) were subjected to examination. Fig. 8.7 (a) shows that some of the SC fractures coalesced either directly or via localised delamination to form a characteristic normal crack. This crack extended about 300-400 µm inside the rebar (Fig. 8.7 (b)).

Fig. 8.8 The interphase close to the stress corrosion crack for a 30 % UBS stressed rebar in alkali solution at 40 °C

Fig. 8.9 The crack tips arrested at the matrix region
Fig. 8.7 (b) also shows that the interphase close to the normal SC crack appears intact. This was true for most cases of low loaded rebars, unless localised delamination was accompanied and “crosslinked” with a normal crack. Fig. 8.8 is a close up view of the interphase region neighbouring the SC crack for a 30% UBS stressed rebar. This is in line with the macro-appearance of the SC crack together with localised delamination. This is because a low level pre-stress cannot lead to interphase fracture. Thus stress corrosion cracking does not result from the fibre/matrix interfacial failure which would allow the passage of alkali medium to the glass fibres. In addition, the transport of the environment along the fibre/matrix interphase also contradicts the phenomenon of planar fracture encountered in the alkali SC, which can only be explained by the attacking species being confined to a small region of the composite specimen at the crack tip. In most cases, localised fibre/matrix interphase damage was induced by stress at the crack tip probably due to the existence of some defects, i.e. voids sporadically distributed in the interphase.

Fig. 8.9 shows that crack tips were arrested in the matrix region, suggesting that matrix failure of the rebar under low load is a process rather than an instantaneous event. It is obvious that matrix failure process plays an important role in influencing the way that the environment accesses glass fibres, and eventually controls the crack growth rate. The failure of the matrix is in turn dictated by its structure and properties.
The stress corrosion behaviour of the ungrounded rebar compares with that of ground one. It was thought that direct exposure of glass fibre might accelerate the stress corrosion process. However, this was not the case, (detailed results in Section 8.4.2). SEM examination in Fig. 8.10 indicates that randomly distributed organic fibres in the outer layer of the rebars were debonded from the matrix under the combination of stress and corrosive environment. It is highly likely that the solution transported through the debonded sites along the organic fibres by “wicking” and in direct contact with the glass fibres. Therefore, the fractured appearance of the ungrounded specimens, as shown in Fig. 8.11, is identical to that for the ground ones. The length in the crack for both cases is similar. The outside layer of the rebars under tensile stresses is not effective in protecting the glass fibres from the contacting corrosive environment.
8.3.2. Fracture in water

The stress corrosion behaviour of “surface ground” rebar specimens in water was also examined. The surface fracture for specimens stressed above 40% UBS, as shown in Fig. 8.12, is characterised by localised and irregular fibre fractures, and longitudinal splitting. The same clear, normal crack, as that in the alkali solution, was not observed. This indicates that water has less effect than alkali solutions on stress corrosion.

Fig. 8.13 (a). Tensile-side surface morphology of stress corrosion in a ground rebar stressed at 20 % UBS in water at 40 °C for 180 days

Fig. 8.13 (b) The cross section view of the stress corrosion crack growth of the rebar specimen shown in Fig. 8.13 (a).
For specimens prestressed below 40 % UBS, complete failure was not found within 180 days exposure. 20% UBS loaded rebars in water showed only a minor further deflection (about 1 mm) in that period. Post-SEM examination of the tensile side surface showed the formation of fibre fractures, as illustrated in Fig.8.13 (a), indicating that stress corrosion did occur to directly exposed glass fibres. However, as demonstrated in Fig. 8.13 (b), this occurrence was very limited to a depth of about three fibre diameters. It can be concluded that the alkali environment accelerated SC crack propagation, if one compares Fig. 8.13 with Fig. 8.7.

8.3.3. Post failure

Fig. 8.14 shows post SC attack on the glass fibre ends of a fractured rebar specimen in alkali solution. It can be seen that the glass fibres had been etched away. This extensive post-failure damage hinders detailed fractographic observations of fibre ends because the SC growth rate is slow resulting in a long exposure time of the fibre ends.

Fig. 8.14 Post stress corrosion failure morphology of the fractured glass fibre ends in alkali solution
8.4 Failure Time of Stress Corrosion

8.4.1. Definition of time to failure

With the initiation and propagation of transverse SC cracks along the depth of a rebar, the load carrying ability of the rebar was reduced as a result of the reduction in the effective thickness of the loaded specimen. Consequently, the deflection progressively increased due to maintaining the pre-set load at a constant level. When this load level exceeded the load carrying ability of the unbroken part of the rebar, ultimate failure occurred due to overload. The time to failure, \( t_f \) is defined as the time duration starting from the beginning of a test to the occurrence of overload failure.

There is no definitive method to define the failure time of composite stress or strain corrosion [152]. \( t_f \) is normally determined according to the stressing configuration and specimen geometry. For the stress corrosion of a pipe section in acids, ASTM 3262-73 defines failure time in terms of a given escape of liquid from the specimen. Sometimes, \( t_f \) is determined as the time to complete fracture of a test piece when a constant tensile load is applied to a composite specimen in a liquid environment [151]. In the present case, \( t_f \) is defined as the time between the end of cracking caused by stress corrosion, and the start of the failure caused by overload. The SC failure is a slow process and characterised by planar cracks and delamination. The overload failure is almost instantaneous and characterised by extensive delamination, as shown in Fig. 8.4

8.4.2. Stress versus failure time

Normally the method of presenting results of SC tests is to plot applied stress (\( \sigma_t \)) on a linear scale with \( t_f \) on a logarithmic scale. The functional relationship between the two can be written in the form [151]:

\[
100 \frac{\sigma_t}{\sigma_0} = A - B \log t_f
\]

where \( A \) and \( B \) are constants, \( \sigma_0 \) is a stress below which an instant failure is caused. Here \( \sigma_0 \) refers to the 4-pt strength of the rebar tested in air.
This model was actually derived from the work of Zhurkov [151]. It was believed that the fracture of a material is a thermally activated process based on the breaking of chemical bonds. Applying a tensile stress was considered to reduce the activation energy for bond rupture by an amount proportional to its magnitude. The following equation governs the time to failure:

\[ t_f = \tau_0 \exp \left( \frac{U_0 - \gamma \sigma_t}{KT} \right) \]  

(8.2)

where

- \( \tau_0 = \) the period of atomic vibrations \((\approx 10^{-13}\text{s})\),
- \( U_0 = \) the thermal activation energy for bond rupture,
- \( \sigma_t = \) applied tensile stress,
- \( \gamma = \) the stress/activity energy coefficient (a constant for a material),
- \( K = \) Boltsman’s Constant,
- \( T = \) the absolute temperature.

Equation 8.2 assumed that the same failure mechanism operates at all stress levels. Although the question of the appropriateness for this assumption remains to be answered, this model has been widely used and quoted.

For simplicity in the current study, the stress vs. the failure time was plotted in line with Equation 8.2. The constant B or the slope was derived by a linear regression technique and used to assess the stress corrosion resistance of the rebar in the various environments. This method is believed to be more statistically meaningful and quantitative than using a single point value because of the wide scatter of \( t_f \) data.

Figs. 8.15-17 present the raw data for SC tests in two environments. As expected, the results for the time to failure are widely spread. However, the trend is very clear in every case and was “fitted” as a linear stress versus log \( t_f \) relationship.

The line of best fit is:
Chapter 8 Stress Corrosion of Rebars

\[
100 \frac{\sigma_t}{\sigma_0} = 62.34 - 15.76 \log t_f \tag{8.3}
\]

for the surface ground rebar in the alkali medium; and

\[
100 \frac{\sigma_t}{\sigma_0} = 62.21 - 12.06 \log t_f \tag{8.4}
\]

for the surface ground rebar in water; and

\[
100 \frac{\sigma_t}{\sigma_0} = 61.27 - 15.24 \log t_f \tag{8.5}
\]

for the ungrounded rebar in alkali medium.

In all the cases, the standard deviation SD_{y/x} for the best fitted lines ranges between 2.7 and 4.1, and the correction factor is below -0.95.

![Graph](image)

Fig. 8.15 Stress vs. the time to failure for surface ground rebars in alkali solution at 40 °C
Fig. 8.16 Stress vs. the time to failure for surface ground rebars in water at 40 °C

Fig. 8.17 Stress vs. the time to failure for surface ungrounded rebars in alkali solution at 40 °C
By comparing the slopes of Figs. 8.15 and 8.16. It is clear that the SC cracking rate is much higher in the alkali solution than in water. This is in line with the conclusion obtained from microscopic observation of the crack growth rates (Figs. 8.7 and 8.13). The reason for this will be discussed in the next Section.

In contrast, the line slope and therefore the SC cracking rate for the surface ground specimens (Fig. 8.15), are very similar to those for the ungrounded ones (Fig. 8.17) in the solution, indicating the loss of the protective function of the outer layer. This agrees well with the SEM observation, which indicates the separation of organic fibres from the matrix (Fig. 8.10), thereby leading to a flow path for the movement of corrosive medium directly into the composite.

### 8.4.3 Error analysis

It was observed during experimentation that once the rebar deflected to a certain extent, failure was almost instant as shown explicitly in Fig. 8.6. The accuracy of the measured $t_f$ is dependent upon the frequency of checking and adjusting the deformation of the stressing springs to maintain the constant load. In fact, the pre-set load levels fluctuated at small amplitudes as readjustment of the springs' deformation always lagged behind the relaxation of their deformation due to the progress of the SC cracks and delamination. Therefore, the measured $t_f$ is somewhat longer than the actual value. However, the amount of the load fluctuation or relaxation is much smaller than the pre-load levels. On the other hand, $t_f$ for composite SC tests is widely scattered as demonstrated in this work and work done by the other [151]. Thus, the error of $t_f$ measurement induced by the method in this investigation can be neglected.

### 8.5 Assessment of Testing Method and Results

It is well known that difficulties exist in designing effective and meaningful testing methods for composite materials, particularly under the combined action of a stress and environment. Methods used have had largely to depend on specimen geometry and the actual loading conditions to which a specimen is subjected in service. In the past, 3- and 4-point bending stress [145,146], tensile stress [150,151] and ASTM 3262-73 [147, 156]
methods have been employed to study GRP stress corrosion cracking. In the present investigation, the 4-point bending method was chosen to stress the rebar samples. This loading configuration was considered to simulate "real" conditions which the rebars might be expected to experience. In addition, the uniform stress region created within the central part of the specimens, (with this loading method), makes the measured $t_f$ data more statistically meaningful. The $t_f$ data shown in Figs. 8.15-17 indicates that a relatively good degree of reproducibility can be obtained. Moreover, the mode of loading is compact and easy to set up, thereby overcoming some difficulties encountered with tensile tests (Chapter 6). Finally, it can also facilitate the observation the SC fracture process as indicated in Section 8.2. However, this method did suffer some limitations as also mentioned earlier. The pre-set load is not strictly constant and the recording of $t_f$ and the deflection is not automatic. These need to be improved and upgraded in future work.

In order to obtain SC data within a reasonable time, and considering that the stress corrosion process is slower in the alkali solution than in acidic conditions [145], the environment was maintained at 40 °C to speed up the process. This temperature is believed not to cause a significant relaxation of the matrix induced by its viscoelastic behaviour because the temperature is far away from the onset point (about 100 °C) of the glass transition region. Therefore, the deflection recorded in Fig.8.6 can be purely attributed to stress corrosion.

The formulation of the alkali solution used simulates the pore solution of Portland concrete [181, 182]. Thus, the data obtained represent the SC rate and magnitude of the SC in a "real" environment, and provide guidance for practical applications and further development for this kind of material.

8.6 Environment Transport Process Through Matrix

From the above Sections, it can be concluded that the stress corrosion process is faster in alkali medium than in water. This is logical since the concentrated OH$^-$ ions in the alkali solution speed up the stress corrosion of glass fibres [92], though the mechanisms are not very clear. The main cause of SC failure may be the weakening of the load carrying capacity of glass fibres by chemical corrosion [91]. The prerequisite for reaching the
above conclusion is that the alkali medium has to gain access to the surface of the glass fibres. The dilemma remains, however, in how to explain the glass fibre, (surrounded by the matrix), made contact with the solution to which the fibres had been unexposed directly. There are three possible processes by which this may occur:

(1) the alkali medium gains access to the glass fibres by diffusion through the matrix. The matrix is homogeneous and remains intact;

(2) the matrix cracks immediately after the crack front has passed through a glass fibre;

(3) micro-cracks or flaws in the matrix may exist, which allow passage of the corrosive medium to the fibre by a percolation process without need to diffuse. These micro-cracks are induced and promoted by the heterogeneous or two phase structure of the matrix

The results in Chapter 6 suggest that it is not possible for the alkali solution to diffuse through the matrix, because the magnitudes of degradation in the flexural properties of the rebars in water and in the solution are very similar. By using radioactive tracer methods to measure chloride ion mobility, Caddock et al. [202, 203] concluded that hydrochloric acid does not diffuse or dissolve in unstressed polyester resin. They assume that the need to overcome electrostatic attraction forces will preclude the possibility of solvated protons into polymer. This may imply that the same thing occurs in alkali solution.

The second possibility may be also excluded because it contradicts the experimental observation shown in Fig. 8.9. Otherwise, the crack front would not have stopped at the matrix.

It is highly likely that the third mechanism operates. This mechanism was suggested by Jones [157], and has been used successfully to explain the experimental results of Caddock et al. [202, 203]. By using moisture diffusion data [20] and scanning acoustic microscopy [157], Jones also found a two phase structure of a polyester resin. To
investigate the possibility of this mechanism in the current study, the structure of the vinylester resin was studied and this is presented in the next Section.

8.7 Micro-Heterogeneity of Vinyl Ester Resin structure

The most convenient and unequivocal way to judge the homogeneity of a polymer is to determine whether there are two or more glass transitions present. The following describes the results using three thermal analysis techniques.

8.7.1 DSC and MDSC characterisation

Fig. 8.18 shows the heat flow curves of samples from a conventional DSC. They are equivalent to the total heat flow signals from MDSC. Curve (a) was obtained from the quenched sample whilst Curves (b), (c) and (d) were from the samples which had been annealed at 85 °C for the various times shown in the figure. From this figure, it seems that only “one step” changes are observed, which indicate a single glass transition. The (b), (c) and (d) endotherms are typical of the normal non-equilibrium behaviour of glassy polymer [31]. They are caused by relaxation of excess enthalpy during the annealing process. The postcuring regime used made it certain that the samples had been fully cured before further investigation started, as indicated in Fig. 8.18 Curve (a) where no exothermic peak occurred. This eliminated the possibility of any further polymerisation in the later annealing and thermal scanning processes.

Studying the miscibility of polystyrene (PS)/styrene-co-methyl methacrylate (S-MMA) copolymer blend by DSC, Feijoo et al. [32] comment that it is very useful to ascertain, by physical ageing or annealing, if the polymers are miscible or immiscible. They observed two glass transitions for physically aged PS/S-MMA blends, which were marked by the presence of two “step changes” on heat flow curves. However, this method did not appear to work successfully in the current investigation. Even worse, the $T_g$s were obscured by the endotherms, making it difficult to determine the glass transition temperature accurately. This was because DSC measures the sum of all thermal events in a sample.

However, MDSC, by its definition [26],
\[
\frac{dQ}{dt} = C_p \frac{dT}{dt} + f(t, T)
\]  

(8.6)

where \(Q\) is the total heat evolved, \(C_p\) is the thermodynamic heat capacity, \(T\) the absolute temperature, \(t\) the time, and \(f(t, T)\) the kinetic response of any physical and/or chemical transformation, can separate the thermodynamic events and kinetic responses. Fig. 8.19 shows that the \(T_g\)'s for annealed samples can be clearly derived from the heat capacity versus temperature signal from MDSC without any interference from different thermal histories of the samples. There was still only one \(T_g\) observable for both quenched and annealed samples.

![DSC heat flow curves for samples quenched and annealed for different times](image)

Fig. 8.18 DSC heat flow curves for samples quenched and annealed for different times

As a point of fact, the glass transition is thermodynamically not a true transition but a spectrum that reflects the segmental motions of different chain length [27]. \(T_g\) represents the temperature at which segmental motions with an average length begin, which corresponds to the inflection point of the heat capacity versus temperature graph of the polymer. Alternatively, this inflection point can be measured by the differential of heat...
capacity with respect to temperature, $dC_p/dT$ (see Fig. 8.20). A glass transition temperature at half vitrification measured by the $dC_p/dT$ maximum is only governed by the time scale of modulation in MDSC [204]. Thus, glass transition temperature of a polymer can be expressed with the temperature where the $dC_p/dT$ reaches a maximum. Hourston et al. [27-29] have successfully used this technique to study polymer glass transitions, physical ageing and morphology of interpenetrating polymer networks.

![Heat capacity curves](image)

**Fig. 8.19** MDSC heat capacity versus temperature curves for samples quenched and annealed for different times.

**Fig. 8.21** shows $dC_p/dT$ vs. temperature data for the same samples as those presented in Figs. 8.18 and 8.19. It is very evident now that there are two peaks in Figs. 8.21 (b), (c) and (d), which represent two glass transitions. The results strongly suggest that two phases exist in these networks. However, the glass transition temperatures of these phases are so close that they nearly completely overlap. This is the reason why the separated phases of the vinylester cannot be sensed by conventional DSC even for annealed samples (Fig. 8.18), whilst the same phenomenon can be easily observed for aged PS/S-MMA blends [32] using the same method. Conversely, this minor change
cannot be discerned from the \( C_p \) signals (Fig. 8.19). It is the \( dC_p/dT \) signal that is capable of clearly disentangling these overlapping processes.

Fig. 8. 20 Comparison of heat capacity and the differential of heat capacity vs. temperature for the quenched sample in MDSC

Fig. 8. 21 (a) \( dC_p/dT \) vs. temperature curve for quenched sample.
Fig. 8.21 (b) $\frac{dC_p}{dT}$ vs. temperature curve for sample annealed at 85 °C for 16 hours.

Fig. 8.21 (c) $\frac{dC_p}{dT}$ vs. temperature curve for sample annealed at 85 °C for 24 hours.
The phase segregation may result from the inhomogeneous course of the vinyl divinyl crosslinking copolymerisation such as in styrenated UP and vinylester resins. The primary microgel particles due to intermolecular and intramolecular reactions tend to develop a higher cross-link density than the external regions linking these primary regions [22]. The external regions contain a higher content of styrene based blocks since the methacrylate copolymerisation in a styrene-vinylester mixture stops long before complete consumption at a certain stage whereas styrene continues to react to form large homopolymer sequences [23].

Atlac 580 urethane vinylester may have the same phase segregation mechanism as DEGBA and UP resins since it contains both the fumarate groups which exist in the UPs, and the methacrylate groups which exist in vinylester resins generally. This could mean that a higher crosslink density region was formed in a vinylester rich phase whereas a lower crosslink density was formed in a polystyrene rich phase. It is well known that a glass transition temperature is proportional to a crosslink density. Thus, it is reasonable to assign the lower peak in Figs. 8.21 (b), (c) and (d) to a polystyrene rich phase with a lower \( T_g \), and the higher peak to the vinylester-rich phase with a higher \( T_g \).
Chapter 8 Stress Corrosion of Rebars

It should be noted that the difference between the two Tgs is only about 10 deg. C, which may imply that the extent of the separation is very limited probably because of the restriction of the crosslinked network on the simultaneously occurring phase segregation process. Additionally, the intrinsic $T_g$ value of the pure vinylester network may be close to that of polystyrene. It is difficult to obtain fully cured vinylester homopolymer experimentally and the size of the domains may be very small as is indicated by the transparency of the sheets.

It is worthwhile to point out that in the current investigation the segregation phenomenon is not the result of the isothermal annealing. The annealing process can only result in conformation rearrangement of a polymer, leading to the excess enthalpy and volume relaxation [31]. However, it can be seen that the process can make the overlapping two phase structure more clearly identified, if one compares Fig. 8.21(a) with Figs. 8.21(b), (c) and (d). This is because the relaxation rates of the two phases are different. Generally, the width of a glass transition temperature range will become narrower and the peak of $dC_p/dT$ becomes higher as the isothermal annealing progresses. This is because the increment of heat capacity, $\Delta C_p$, in the transition region remains relatively unchanged [28]. As indicated in Fig.8.21, whilst the height of the $dC_p/dT$ peak increases with increase in the annealing time, the width of the $T_g$ transition decreases from about 30 to 25 °C for the whole network. Individually, the relaxation rate of the polystyrene rich phase is faster than that of the vinylester rich phase. In other words, if the network were a one phase structure, there should only be one peak, even after the isothermal annealing (Fig.8.21).

On the other hand, it appears that there is only one peak present in Fig. 8.21(a) for the quenched sample. However, looking at the asymmetric shape of the curve with the left part being less steep than the right, it may be concluded that a multi-component structure exists and they just simply closely overlap. Experimental evidence indicates that, for pure polymers or miscible polymer systems, the distribution complies with a Gaussian function [29].

The difference in the relaxation rate of the two phases also supports the formation of the two domains with two differing crosslink densities. Because the lower crosslink density...
domains tend to have statistically more molecular segments which can involve conformation rearrangement due to a less restriction from crosslink joints; whilst the case is reverse for the higher cross link domains. Accordingly, the polystyrene rich phase with a lower cross link density will relax faster as opposed to the vinylester rich phase with a higher cross link density, which is showed explicitly in Fig. 8.21.

8.7.2 DMTA characterisation

Fig. 8.22 shows the DMTA response to quenched samples (i.e. open symbols) and the sample annealed for 50 hours (i.e. solid symbols). The behaviour of the samples annealed for less than 50 hours is consistently similar to that of the 50 hour annealed sample. It can be noticed from Fig. 8.22 that the samples after annealing have a higher peak value of tan δ, a slightly higher T_g, and a narrower width of the transition region, compared to the quenched sample. With the exception of these, however, there is no indication of the existence of two T_g's, as observed in MDSC, in either the storage modulus E' or loss tan δ signals. Thus, DMTA may still suffer certain resolution problems, as does conventional DSC but the technique can separate the phases if there is a large difference in T_g's [25, 205].

It was evident that urethane vinylester crosslinked with styrene monomer is a diphasic structure characterised by the presence of the two characteristic glass transitions. One phase is probably polystyrene rich with a lower crosslinking density and the other phase vinylester-rich with a higher crosslinking density. The phase separation is very restricted as indicated by the difference of the glass transition temperatures for these two phases being only approximately 10 deg. C and by the fact that DSC and DMTA cannot detect its existence.
8.8 Matrix Micro-cracking Processes

To explain the transport of the corrosive alkali medium in the rebar to cause stress corrosion failure at low stresses or strains, micro-cracking of the matrix resin at the crack tip was assumed. The formation of micro-cracks can be understood by the different responses of the two phases to the stress field at the crack tip.

For the fully crosslinked and phase separated vinylester resin matrix, it is not unreasonable to assume that the failure strengths of the two phases are similar. However, their moduli may be markedly different because it is well known that the modulus of a polymer is proportional to its crosslinking density. Therefore, there exists a lower modulus and higher failure strain in the polystyrene rich phase with a lower crosslinking density as opposed to a higher modulus and lower failure strain in the vinylester rich phase. According to the “rule of mixtures”, and assuming that the interface between these two phases is perfect, the vinylester rich phase will take a larger proportion of stress under a certain constant stress or strain. Also it will fail first when its failure...
strength is exceeded. The unloaded stress may be partly transferred to the glass fibres via the strong fibre/matrix interphase, and partly to the polystyrene rich phase. The increased stress carried by the polystyrene rich phase does not necessarily cause the immediately complete failure of the bulk resin, as this phase possesses a higher failure strain. Therefore, the matrix as a whole around the crack tip looks intact macroscopically whilst the environment has percolated through the microcracks of the matrix. Jones [157] reported that the size of micro-cracks in a polyester resin was smaller than 50 nm. The fact that the phase segregation in the vinylester is very limited is consistent with the Jones' finding.

As an ultimate result, the occurrence of the matrix micro-cracking permits transport of the alkali solution by a percolation process. Although this model may be far from ideal, it does relate the stress corrosion behaviour of the rebar to the inhomogeneous structure of the matrix resin.
PART IV

CONCLUSIONS

AND

FURTHER WORK
Chapter 9 Conclusions and Recommendations

9.1 Conclusions

9.1.1 Characterisation of pultruded rebar composites

1. The sizing contents of E-glass fibres A (polyester-compatible), E-glass fibres B (polyester-compatible) and AR glass fibres C (cement-compatible) were measured to be 0.62 wt.%, 1.01 wt.% and 1.52 wt.%, respectively. The chemical compositions of the three-type sizings were also varied considerably as determined by TGA.

2. Postcuring raised the ILSS of Daron XP45 based rebar by about 10% whilst it had no effect on Atlac 580 based rebars.

3. Void affected interlaminar shear strength. With void content varying from 0.5 vol.% to 3.5 vol.%, the ILSS changed from 55.7 to 39.1 MPa for Atlac 580/E-glass fibres A rebars.

4. The ILSS values of thick rebars tested according to CRAG standard were 10-18% lower than those of cut thin specimens according to BS standard. The reason is that the thick specimens caused more stress-concentration damage than thin specimens on the central area, next to loading roller of the test jig and therefore the effective thickness and ILSS of the rebars were more reduced. However, this did not change the nature of using the rebars' ILSS data for comparison purposes.

5. The interlaminar shear strength of the rebars greatly depended upon glass fibre surface coatings or sizing formulation. Based on ILSS test results, Daron XP45/fibre A (DP1) and Atlac 580/fibre A (AP1) rebar systems were optimised with shear strength of 67.2 MPa and 55.7 MPa, respectively. Surface coating A tended to form a
stronger interphase with Daron XP45 and Atlac 580 resins than surface treatment B and C.

6. A single shear crack near a mid-plane was observed on strong rebars (DP1, AP1 and BAP) as opposed to multiple cracks on rebars with relatively low ILSS (DP2, AP1 and ARA systems). In line with shear failure mode, large and high density of "hackles" orientated at about 45° towards or away from the direction of macrocrack propagation were produced on the fractured surface of DP1 and AP1 rebar specimens whereas the opposite was true for DP2, AP2. For ARA rebar (AR glass/Atlac580), there was almost no matrix adhering to the fibres, indicating the incompatibility of the silane coupling agent with Atlac 580.

7. As with the ILSS testing, the flexural properties of six types of rebar (DP1, AP1, BAP, DP2, AP2 and ARA) were determined. Large differences in the flexural strengths of the rebars were documented with a span of change between 1195 to 570 MPa. The corresponding calculated maximum strain to failure varied from 2.94% to 1.63%. The measured flexural modulus fluctuated at 42 ± 1 GPa for the most rebars but ARA (37 GPa). The corrected flexural modulus due to shear deformation only deviated an average 6% from the theoretically calculated value calculated according to the "a rule of mixtures". The shear deformation did not lead to significant difference in flexural strength.

8. When normalisation was applied to the flexural strength and ILSS for each of rebars (and assuming that the flexural strength is linearly proportional to fibre content), it was found that the flexural strength was very sensitive to the ILSS and therefore to the various surface treatments on different glass fibres. This same conclusion was drawn with respect to flexural strain. The fundamental reason is that the shear strength affects flexural failure modes which in turn is determined by the ability of the glass fibre to resist the occurrence of microbuckling in composites. DP1 rebar with a higher ILSS failed in tensile mode whilst a mixed compressive-tensile failure was identified in AP1 and BAP rebars with intermediate ILSS values. For AP2, DP2 and ARA rebars possessing lower ILSS, failure initialised on the compressed side.
With increasing ILSS, occurrence of fibre microbuckling was delayed and therefore the strength and strain were enhanced.

9. The dependence of flexural modulus on ILSS was evident in the same way as for strength and strain but to a lesser degree. This was because an increase in ILSS reduced the severity of the fibre instability surrounded by the matrix (and vice versa), and as a result the rigidity of composite was improved.

10. A stronger interphase resulted in a greater increase in the main glass transition temperature of the composites, which can be interpreted by the restrictive effect of glass fibres on the mobility of the matrix polymers. An approximately linear relationship between ILSS and the increment ($\Delta T_g$) of increase in $T_g$ was found within the composites made of the same matrices. The good agreement between $\Delta T_g$ and ILSS indicates that this method can be used to study the strength of the composite interphase. DMTA studies also reveal that strong interphases tend to broaden the loss modulus curve or produce a second low-temperature transition.

9.1.2 Immersion degradation of rebars

11. Water absorption behaviour of the vinyl ester resin immersed in water generally followed classical Fickian theory, and therefore can be predicted. The equilibrium of water uptake increased from 0.73 wt.% to 0.96 wt.% within a 40-80 °C temperature range (ca. 0.1 wt.%/20 °C), which was caused by clustering of water in the polymer. The good fit of the diffusion coefficient to the Arrhenius equation indicated a single absorption mechanism, with an activation energy of 36.4 kJmol$^{-1}$. Addition of alkali into the water caused a marginal reduction in equilibrium water content, diffusion coefficient and activation energy. This was attributed to the decrease of the water activity in the solution.

12. Water uptake of rebars immersed in water deviated from Fickian behaviour. The deviation became severe with increasing temperature, especially at 80 °C. This was attributed to thermally activated water traps at or near the fibre/matrix interphase and
voids during conditioning. Therefore doubt is cast on the validity of accelerated tests at high temperature.

13. The glass transition temperature of the resin was depressed due to a water plasticising effect, and it was only associated with water content absorbed and not with the differing media or temperature. Extended exposure did not result in further depression. The rate of the drop in $T_g$ decreased with increasing water uptake since the probability of clustering of water molecules in the polymer free volume was raised. On redrying the resin conditioned in water and alkali solution at 80 °C for 200 days, the $T_g$ recovered to almost its original value but the loss modulus enhanced, implying that a permanent change had occurred to the resin. In total, the $T_g$ was suppressed by about 9 deg.C.

14. Conditioning in water caused a decrease in $T_g$ and an increase in the loss properties of rebar composites. Increasing the temperature accelerated the degradation of the interphase, thereby reducing the constraining effect of glass fibres on the mobility of the polymer molecules. This was reflected by the fact that the $T_g$ reduction of the composite conditioned at 40 and 60 °C was only 11-13 °C, which is approximately equivalent to the water plasticising effect on the matrix. However, for the composite exposed at 80 °C the $T_g$ was decreased by 26 deg.C, which cannot be accounted for by plasticisation. The other indication is that the glass transition temperature of the interphase ($T_{gi}$) was suppressed by 7 deg.C for the rebar immersed at 80 °C in water, whereas the $T_{gi}$ (3°C) was less affected for the samples in 40 and 60 °C water. The variation of loss properties ($E'$ and tan δ) also suggests that the interphase was aged to differing degrees by different conditioning temperatures. The results agree well with the water absorption behaviour of the composite and highlight the limitation of accelerated test in quantifying the interphase. In addition, it was found that conditioning in alkali solution fundamentally had no extra effect on the dynamic mechanical properties of the composite, implying that ions such as $K^+$, $Na^+$, $Ca^{2+}$ and $OH^-1$ did not diffuse into the polymer matrix.

15. The strength of the glass reinforced rebars showed a strong dependence on water content initially, which was followed by levelling off for water contents greater than
0.5 wt.%. The final reduction in strength was in the order of 50% UBS of the unexposed rebar. The predominant mechanism of degradation was identified as water attack on glass fibres, as evidenced by a change in the failure mode from mixed to tensile. The modulus had little dependence on water content, with a retained level above 95% of the original value.

16. The strength of the rebar in alkali solution was degraded by a similar level to that in water in terms of both magnitude and rate. This suggested that the primary degradation mechanism involved water and that the ions in the alkali solution did not diffuse into the composite. The influence on the modulus was affected by temperature. At 40 and 60 deg.C, the rigidity of the rebars was reduced by about 5%; identical to the value caused by water. However, at 80 deg.C, the modulus was considerably reduced by up to 25%. The reduction was caused by gradual corrosion of the defect inclusions in rebars. The results highlight the importance of composite quality and its effect on the environmental resistance, and the great differences induced by high temperature. The organic fibres around the rebar edge were not resistant to alkali.

9.1.3 Stress corrosion of rebars

17. An effective stressing method has been developed to study the stress corrosion behaviour of strong unidirectional pultruded composite rebars in corrosive environments. With this method, the stress corrosion cracking process can be readily observed and documented. Also a good degree of reproducibility of failure time measurements can be obtained.

18. The stress corrosion fracture morphology and the time to failure were directly associated with the level of loads applied. At low loads, the fracture is characterised by a relatively planar crack normal to the tensile stress, together occasionally with localised delamination, probably due to the existence of some defects randomly distributed in the fibre/matrix interphase. It appears that low level pre-stressing did not result in the damage of the interphase during the progress of the stress corrosion crack. At high loads, however, the planar crack was less prominent because it had
less time to fully develop within a short period of time. The failure time decreased with increase in applied stress.

19. A linear relationship can be obtained between the applied stress on a linear scale and the failure time on a logarithmic scale. The slopes of the fitted lines can be used to quantify the stress corrosion resistance of composites in different environments.

20. The stress corrosion behaviour of rebars was less severe in water than in alkali solutions. This was reflected in terms of both longer failure times for completely broken samples, and shorter crack growth for unbroken samples in water under comparable loads. In addition, planar normal cracks were not observed for rebar specimens stressed above 40% UBS in water. This is probably because OH⁻ ions in the solution accelerated the stress corrosion of glass fibres.

21. No protective role was demonstrated by the outer layer of the rebar to stop or delay stress corrosion. This is due to the fact that the organic fibres randomly distributed on the surface were debonded from the matrix under pre-loads which allowed the corrosive medium to transport through this layer and reach the glass fibres in the composite.

22. It has been found that the crosslinked matrix vinylester resin is a biphasic structure with one phase probably being polystyrene rich, and the other vinylester rich. This is indicated by the presence of the two characteristic glass transition temperatures associated with the system. The glass transition temperatures for these two phases are only approximately 10 deg.C apart. The differential of heat capacity signal enables MDSC to resolve micro-heterogeneity of polymers in contra-distinction to DSC and DMTA, which cannot detect such a minor change.

23. As a result of the two phase structure, it is proposed that micro-cracks are formed in the matrix of the rebar composite under low stresses due to the different responses of these two phases to the stress field at the crack tip. Micro-cracking thus allows transport of aqueous media into the composite by a percolation process.
9.2 Recommendations for Further Work

From this investigation there are some questions which require further clarification. Also many new interesting areas have come to light which could be the subject of further studies.

1. DMTA study showed that variations in the interphases of the composites due to different combinations of glass fibre coatings and matrix resins triggered different changes in the shape of loss modulus curves, especially when comparing AP1, AP2 and ARA systems. However, the morphologies of the interphases were not clear. Clarification of this point would further understand the mechanisms of formation of the composite interphase and is obviously important to aid developing new coupling agents or fibre coatings.

2. Whilst an empirical relationship between the increment (\(\Delta T_g\)) of increase in \(T_g\) with ILSS was found, (for given composite systems made with the same matrix resin formulation), and adequate explanation was given, quantitative assessment of the interphase strength with \(\Delta T_g\) could be the subject of new research.

3. In this research, the glass transition temperature \(T_{gi}\) was only estimated because it was masked by a main matrix \(\alpha\)-transition. Discovering how to deconvolute the \(T_{gi}\) may help to accurately measure the environmental effect on the interphase.

4. It is known that AR-glass fibres were originally developed for reinforcing concrete. The incompatibility of the glass fibre coating with Atlac 580 resin highlighted an immediate need to develop new fibre sizing formulations and to remedy this deficiency. It would be expected that the resulting polymer composite possessing strong interphase could possibly mitigate stress corrosion with inherited alkali resistance of AR-glass fibres.
5. It was very interesting to note that the strength of AP1 rebar remained at approximately 50% UBS for 180 days when conditioned at 80°C in water. The changes occurring on the surface of glass fibres needs to be explored further.

6. Organic fibres on the surface of the rebars were proved to be not resistant to alkali. Thus they need to be replaced or removed.

7. The incorporation of automatic timers onto existing pre-stress jigs (for stress corrosion test) would improve the accuracy and efficiency of measuring failure times.

8. This project employed alkali solutions simulating concrete pore fluid at high temperatures but not real environments. More work needs to be done in correlating the results obtained in this study with the behaviour of rebars in real concrete fluids. It might be possible to produce a model to predict long term properties of the composites.
References


References


18. Funke, W., Kolloid Z. Z. Polymer 197 (1964) 71.


References


References


170. ASTM D792-(91), Standard test methods for density and specific gravity of plastics by displacement.


Appendices

Appendix 3.1 Main chemical compositions of E glass and AR glass [167]

<table>
<thead>
<tr>
<th>Chemical compositions</th>
<th>E-glass (wt.%)</th>
<th>AR glass (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>52-56</td>
<td>71</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>12-16</td>
<td>1</td>
</tr>
<tr>
<td>B₂O₃</td>
<td>8-13</td>
<td>-</td>
</tr>
<tr>
<td>CaO</td>
<td>16-25</td>
<td>-</td>
</tr>
<tr>
<td>MgO</td>
<td>0-6</td>
<td>-</td>
</tr>
<tr>
<td>Li₂O</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0-1</td>
<td>11</td>
</tr>
<tr>
<td>TiO₂</td>
<td>0-0.4</td>
<td>2.2</td>
</tr>
<tr>
<td>ZrO₂</td>
<td>-</td>
<td>16</td>
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Appendix 3.2 Typical properties of Atlac 580 and Daron XP45 resins [168,169]

<table>
<thead>
<tr>
<th>Property</th>
<th>Atlac 580</th>
<th>Daron XP45</th>
<th>Unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tensile strength</td>
<td>83</td>
<td>70</td>
<td>MPa</td>
</tr>
<tr>
<td>Tensile modulus</td>
<td>3.5</td>
<td>3.2</td>
<td>GPa</td>
</tr>
<tr>
<td>Tensile elongation</td>
<td>4.2</td>
<td>2.5</td>
<td>%</td>
</tr>
<tr>
<td>Flexural strength</td>
<td>153</td>
<td>140</td>
<td>MPa</td>
</tr>
<tr>
<td>Flexural modulus</td>
<td>3.6</td>
<td>3.4</td>
<td>GPa</td>
</tr>
<tr>
<td>Elastic shear modulus</td>
<td>1690</td>
<td>-</td>
<td>MPa</td>
</tr>
<tr>
<td>Charpy impact</td>
<td>15</td>
<td>15</td>
<td>KJ/m²</td>
</tr>
<tr>
<td>Barcol hardness</td>
<td>40</td>
<td>45</td>
<td>-</td>
</tr>
<tr>
<td>Density</td>
<td>1.110</td>
<td>-</td>
<td>Kg/m³</td>
</tr>
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</table>

Appendix 7.1 Variation of glass transition temperature with time and water content for Atlac 580 resin conditioned in water

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Water content (wt.%)</th>
<th>T_s (°C)</th>
<th>Conditioning Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>131.0</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>0.377</td>
<td>125.2</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>0.788</td>
<td>123.3</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>0.870</td>
<td>122.1</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.927</td>
<td>122.0</td>
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</tr>
<tr>
<td>216</td>
<td>0.937</td>
<td>121.9</td>
<td></td>
</tr>
<tr>
<td>480</td>
<td>0.957</td>
<td>121.8</td>
<td></td>
</tr>
<tr>
<td>960</td>
<td>0.963</td>
<td>121.7</td>
<td></td>
</tr>
<tr>
<td>4320</td>
<td>1.00</td>
<td>122.3</td>
<td>60</td>
</tr>
<tr>
<td>4800</td>
<td>1.00</td>
<td>121.6</td>
<td></td>
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<tr>
<td>8640</td>
<td>1.00</td>
<td>121.6</td>
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</tr>
<tr>
<td>4320</td>
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<tr>
<td>4320</td>
<td>0.730</td>
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### Appendix 7.2 Variation of glass transition temperature with time and water content for Atlac 580 resin conditioned in alkali solution

<table>
<thead>
<tr>
<th>Time (hours)</th>
<th>Water content (wt.%)</th>
<th>(T_g (°C))</th>
<th>Conditioning Temperature (°C)</th>
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<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>131.0</td>
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<tr>
<td>4</td>
<td>0.337</td>
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</tr>
<tr>
<td>24</td>
<td>0.720</td>
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</tr>
<tr>
<td>48</td>
<td>0.802</td>
<td>121.0</td>
<td></td>
</tr>
<tr>
<td>120</td>
<td>0.857</td>
<td>121.3</td>
<td></td>
</tr>
<tr>
<td>216</td>
<td>0.873</td>
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<td></td>
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<tr>
<td>480</td>
<td>0.900</td>
<td>122.5</td>
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<td>960</td>
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<tr>
<td>4320</td>
<td>0.910</td>
<td>122.3</td>
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<td>8640</td>
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<td>121.9</td>
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### Appendix 7.3 Variation of the flexural properties with time, temperature and water uptake for AP1 rebar conditioned in water.

<table>
<thead>
<tr>
<th>°C</th>
<th>Property</th>
<th>Days of exposure</th>
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<tr>
<td></td>
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<td>10</td>
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<tr>
<td>Dry</td>
<td>strength</td>
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<tr>
<td></td>
<td>modulus</td>
<td>41.10</td>
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<tr>
<td></td>
<td>strain</td>
<td>2.70</td>
</tr>
<tr>
<td></td>
<td>wt.%</td>
<td>0.115</td>
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<tr>
<td>40</td>
<td>strength</td>
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<tr>
<td></td>
<td>modulus</td>
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<tr>
<td></td>
<td>strain</td>
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</tr>
<tr>
<td></td>
<td>wt.%</td>
<td>0.143</td>
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<tr>
<td>60</td>
<td>strength</td>
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<tr>
<td></td>
<td>modulus</td>
<td>40.36</td>
</tr>
<tr>
<td></td>
<td>strain</td>
<td>2.49</td>
</tr>
<tr>
<td></td>
<td>wt.%</td>
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</tr>
<tr>
<td>80</td>
<td>strength</td>
<td>970.4</td>
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<tr>
<td></td>
<td>modulus</td>
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<td></td>
<td>strain</td>
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<tr>
<td></td>
<td>wt.%</td>
<td>0.171</td>
</tr>
</tbody>
</table>
Appendix 7.4 Variation of the flexural properties with time and temperature for AP1 rebar conditioned in alkali solution.

<table>
<thead>
<tr>
<th>°C</th>
<th>Property</th>
<th>10</th>
<th>30</th>
<th>90</th>
<th>180</th>
<th>250</th>
<th>360</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>strength</td>
<td>1093 (69)</td>
<td>1053 (73)</td>
<td>1063 (88)</td>
<td>1078 (66)</td>
<td>1023 (35)</td>
<td>945.5 (17)</td>
</tr>
<tr>
<td></td>
<td>modulus</td>
<td>41.51 (1.00)</td>
<td>42.74 (2.21)</td>
<td>42.17 (1.61)</td>
<td>42.53 (3.01)</td>
<td>40.20 (0.64)</td>
<td>39.91 (1.89)</td>
</tr>
<tr>
<td></td>
<td>strain</td>
<td>2.71 (0.16)</td>
<td>2.61 (0.19)</td>
<td>2.58 (0.23)</td>
<td>2.59 (0.20)</td>
<td>2.63 (0.08)</td>
<td>2.63 (0.28)</td>
</tr>
<tr>
<td>40</td>
<td>strength</td>
<td>1070 (73)</td>
<td>1034 (49)</td>
<td>997.4 (60)</td>
<td>956.3 (56)</td>
<td>915.1 (16)</td>
<td>807.9 (40)</td>
</tr>
<tr>
<td></td>
<td>modulus</td>
<td>41.51 (1.20)</td>
<td>42.09 (1.40)</td>
<td>40.98 (1.65)</td>
<td>42.42 (1.51)</td>
<td>40.81 (1.42)</td>
<td>39.41 (1.75)</td>
</tr>
<tr>
<td></td>
<td>strain</td>
<td>2.63 (0.22)</td>
<td>2.58 (0.32)</td>
<td>2.46 (0.21)</td>
<td>2.45 (0.08)</td>
<td>2.39 (0.11)</td>
<td>2.41 (0.18)</td>
</tr>
<tr>
<td>60</td>
<td>strength</td>
<td>981.2 (68)</td>
<td>983.4 (74)</td>
<td>838.2 (29)</td>
<td>693.1 (58)</td>
<td>622.7 (79)</td>
<td>523.1 (25)</td>
</tr>
<tr>
<td></td>
<td>modulus</td>
<td>39.95 (1.70)</td>
<td>40.28 (0.64)</td>
<td>37.44 (0.55)</td>
<td>35.43 (0.84)</td>
<td>34.07 (0.98)</td>
<td>31.15 (1.26)</td>
</tr>
<tr>
<td></td>
<td>strain</td>
<td>2.64 (0.12)</td>
<td>2.59 (0.18)</td>
<td>2.50 (0.11)</td>
<td>2.25 (0.10)</td>
<td>1.98 (0.09)</td>
<td>2.05 (0.06)</td>
</tr>
</tbody>
</table>

Appendix 8.1 Time to failure of stress corrosion test for ground AP1 rebars in alkali solution at 40 °C.

<table>
<thead>
<tr>
<th>% of UBF</th>
<th>70 %</th>
<th>66 %</th>
<th>60 %</th>
<th>50 %</th>
<th>40 %</th>
<th>30 %</th>
<th>20 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-stress (MPa)</td>
<td>776</td>
<td>732</td>
<td>665</td>
<td>555</td>
<td>444</td>
<td>333</td>
<td>222</td>
</tr>
<tr>
<td>Pre-strain (%)</td>
<td>1.89</td>
<td>1.78</td>
<td>1.62</td>
<td>1.35</td>
<td>1.08</td>
<td>0.81</td>
<td>0.54</td>
</tr>
<tr>
<td>Days</td>
<td>0.13, 0.24, 0.27</td>
<td>1.17</td>
<td>1.58, 1.81, 2.46</td>
<td>8.50, 8.81, 10.00</td>
<td>11.00, 13.10, 22.10</td>
<td>65.51, 66.30, 83.98, 90.71</td>
<td>Did not fail at 180 days</td>
</tr>
<tr>
<td>Log (days)</td>
<td>-0.89, -0.62, -0.57</td>
<td>0.07</td>
<td>0.20, 0.26, 0.39</td>
<td>0.93, 0.94, 1.00</td>
<td>1.04, 1.12, 1.34</td>
<td>1.82, 1.82, 1.92, 1.96</td>
<td>2.26</td>
</tr>
</tbody>
</table>
### Appendix 8.2 Time to failure of stress corrosion test for ground AP1 rebars in water at 40 °C.

<table>
<thead>
<tr>
<th>% of UBF</th>
<th>70 %</th>
<th>60 %</th>
<th>55 %</th>
<th>50 %</th>
<th>40 %</th>
<th>30 %</th>
<th>20 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-stress (MPa)</td>
<td>776</td>
<td>665</td>
<td>610</td>
<td>555</td>
<td>444</td>
<td>333</td>
<td>222</td>
</tr>
<tr>
<td>Pre-strain (%)</td>
<td>1.89</td>
<td>1.78</td>
<td>1.49</td>
<td>1.35</td>
<td>1.08</td>
<td>0.81</td>
<td>0.54</td>
</tr>
<tr>
<td>Days</td>
<td>0.64, 0.75, 1.64, 1.98, 2.46</td>
<td>4.17</td>
<td>13.80, 15.00</td>
<td>35.00, 41.30, 69.50</td>
<td>Did no fail at 180 days</td>
<td>Did not fail at 180 days</td>
<td></td>
</tr>
<tr>
<td>Log (days)</td>
<td>-0.19, -0.12</td>
<td>0.21, 0.30, 0.39</td>
<td>0.62</td>
<td>1.14, 1.18</td>
<td>1.54, 1.62, 1.84</td>
<td>2.26</td>
<td>2.26</td>
</tr>
</tbody>
</table>

### Appendix 8.3 Time to failure of stress corrosion test for unground AP1 rebars in alkali solution at 40 °C.

<table>
<thead>
<tr>
<th>% of UBF</th>
<th>70 %</th>
<th>60 %</th>
<th>50 %</th>
<th>40 %</th>
<th>30 %</th>
<th>20 %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-stress (MPa)</td>
<td>776</td>
<td>665</td>
<td>555</td>
<td>444</td>
<td>333</td>
<td>222</td>
</tr>
<tr>
<td>Pre-strain (%)</td>
<td>1.89</td>
<td>1.78</td>
<td>1.35</td>
<td>1.08</td>
<td>0.81</td>
<td>0.54</td>
</tr>
<tr>
<td>Days</td>
<td>0.21, 0.20</td>
<td>0.98, 1.67, 2.06</td>
<td>6.30, 6.80, 12.00</td>
<td>13.41, 18.95, 24.80, 25.70</td>
<td>76.50</td>
<td>-</td>
</tr>
<tr>
<td>Log (days)</td>
<td>-0.70, -0.68</td>
<td>-0.01, 0.22, 0.31</td>
<td>0.80, 0.83, 1.08</td>
<td>1.23, 1.28, 1.39, 1.41</td>
<td>1.88</td>
<td>-</td>
</tr>
</tbody>
</table>
Publication