PEEL TEST FOR THE EVALUATION OF ENVIRONMENTAL EFFECTS ON FIBER-POLYMER INTERFACE

by

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A thesis submitted in conformity with the requirements for the Degree of Master of Applied Science, Department of Chemical Engineering and Applied Chemistry, in the University of Toronto

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Traditional methods for measuring the adhesion between fiber and polymers, using single fibers, have problems due to the unknown frictional effects, Poisson's shrinkages or expansions, and uncertainties about failure process. Also environmental studies using these techniques are hindered by large environmental exposure time and results are accompanied by a large coefficient of variation. All this made it difficult to quantitatively judge the results obtained from these techniques. The peel test was developed to avoid these problems. In this test, single fibers of carbon, glass and Kevlar were been embedded in the epoxy to depth of about half their diameter in an epoxy resin and then peeled off. The work of fracture $G_I$ can be estimated from the peel force by simple formula, so long as the fibers are fully elastic during peel process. This was true with glass, which had $G_I = 140 \text{ Jm}^{-2}$ and carbon with $G_I = 60 \text{ Jm}^{-2}$. With Kevlar, inelastic effects obscured the results. This technique gave straightforward, rapid and clear results of environmental effects on fiber-polymer interface. The effect of water on the glass-epoxy interface was readily shown, which reduced the fracture toughness to 90% after 40h of $25^\circ\text{C}$ immersion. At elevated temperature the process is much faster and needs a shorter time. Carbon however, required high temperature water at the interface to cause significant losses. Sulphuric and acetic acids at $25^\circ\text{C}$ had about the same effect as water at $90^\circ\text{C}$. Organic fluids such as Kerosene had very little effect. Similar environment effects could also be detected with Kevlar, though further work is required to separate out inelastic contributions.
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1. INTRODUCTION

1.1 Composite Material

A composite is a material made by dispersing particles, of one or more materials, in another material which forms a continuous network around them. The properties of the composite are different from its components. [1]. The components in a composite remain bonded together but they retain their identities and properties. The arrangement of components may be random e.g. stone in concrete, or in an organized pattern such as cellulose fibers in wood.

Natural occurring composites such as feather and wood have been known for thousands of years but man-made composites have only been available for about 7,000 years. Mud with straw brick is an example of a composite material our ancestors used to build their houses. In the Middle East in 5,000 B.C. people used reeds to reinforce pitch for composite boats. Over 3,000 years ago in Thebes and India wood laminated with shellac was produced [2]. Composite materials have played an ever increasing role in this developing world. In this century the development in fibers and polymer brought forward a new class of materials with enormous structural capabilities. This new class of material is called fiber reinforced polymers composite.

1.2 Fiber Reinforced Polymers Composite

Fiber reinforced polymer composite materials consist of three distinct components (1) fibers of high strength and modulus as principal load-carrying members, (2) a matrix, in which fibers are embedded or bonded to keep them in the desired location and protect them from environmental damage [3], and (3) interfaces which provide adhesion between fiber and matrix and act as load transfer medium between them. In this form, both fibers and matrix retain their physical and chemical identities, but, as a whole, produce a combination of properties that cannot be achieved with either of the components acting alone.
Fiber reinforced polymer composite materials are of two types, thermoset plastic composite materials and thermoplastic composite materials. The difference between them is in the behavior of the matrix during processing. The thermoplastic composite materials use thermoplastic polymer as matrix, which can be melted down by elevating the temperature and reshaping many times. This property is due to long linear molecular structures without any cross linkages between them. The large molecular weight produces a very viscous melt of the thermoplastic, which causes difficulty in impregnation and processing. On the other hand, thermoset plastic composite materials utilize the thermoset polymer as matrix, which undergoes a "cure" process after full impregnation at room temperature. During the curing process the molecular chains get cross linked with each other to produce a rigid three dimensional structure. Once this network is formed the matrix cannot be melted. Due to this three dimensional structure of interlinked molecules of polymer the mechanical properties required, such as strength and stiffness, could be obtained more easily with the thermoset [4]. The thermosetting polymers commonly used for structural purposes are epoxy, polyesters and phenolics. The ease of processing and generating required mechanical properties makes thermoset plastic more popular than thermoplastic. Therefore the amount of thermoset plastic composites produced every year is bigger than that of the thermoplastic composites.

The development and use of the glass, carbon and aramid fibers for reinforcing polymer matrices have given us the ability to produce a large family of materials. Glass fibers provide relatively high specific strength at low cost. Carbon fibers provide high strength and stiffness at a higher cost. Aramid fibers provide excellent impact resistance and good ductility with a high specific strength.

The most common form in which fiber reinforced polymer composite materials are used in structural applications is called a laminate. It is obtained by stacking thin layers of fibers and matrix on each other consecutively and consolidating them into the desired thickness. By changing the sequence and orientation of fibers in each layer a wide range of mechanical properties can be achieved. Rods, beams and other structural components with constant cross-section can be produced from pultrusion. In this method
continuous fibers wetted with resin are pulled through heated die. For manufacturing vessels and other hollow structures a filament winding machine is used. In this process continuous reinforcements impregnated with resin are wound onto a mandrel at specific angles. These and other methods are available to produce components of fiber reinforced polymer composite with various shapes and mechanical properties.

The high specific stiffness, strength, light weight, and tailoring of the properties, gave fiber reinforced polymer composite materials huge market and research attention. Fiber reinforced polymer composite materials were used in many cases as substitutes for traditional metals. Much of the research and development in this field of reinforced composite has been carried out by the aerospace and automotive industries, which can benefit primarily from the lightweight and high modulus of composites [5,6]. Sports and recreational equipment manufacturing also take advantage of the light weight and the high modulus of these materials. Other properties, such as high chemical resistance of composite materials, are utilized in the production of tanks, pressure vessels and piping. The communications industry utilizes the low value of thermal expansion in the production of antennae.

1.3 Epoxy Resin

The ease of processing and good mechanical properties of epoxy resins made them the prime matrix for high performance glass, carbon, and aramid fiber composites. They are formed from the combination of epichlorohydrin with bisphenol A in the presence of sodium hydroxide. The resulting product is a diglycidyl ether of bisphenol A (DGEBA) having a chemical structure see Fig. 1.1 [7].

![Fig. 1.1 Chemical structure of epoxy resin (DGEBA) before curing](image-url)
The epoxy functional groups present in the molecule are highly reactive, so when a hardener such as amine with active hydrogen atoms is added, it copolymerizes to form a three dimensional crosslinked structure as shown in Fig. 1.2 [7].

![Curing process of epoxy resin](image)

The hydroxyl groups provide adhesion to the fiber but, on the other hand, due to polarity, they can form hydrogen bonding and become moisture sensitive. The moisture absorption in cured epoxy resins reduces the glass transition temperature (Tg), which causes a decrease in maximum service temperature. The moisture absorption depends largely on the nature of epoxy resin rather than the different curing agents used for the same epoxy. Comyn et al [8] investigated the uptake of water in DGEBA epoxy resins using various hardeners and found it to be 2-5 % at 25°C. The large value of n makes the molecule more flexible and causes decreases in Tg and modulus of cured epoxy but, on the other hand, it improves the ductility. Epoxies are brittle in nature which causes restriction in their use in several applications.

### 1.4 The Composite Interface

The interface is the most important component of the FRPC materials. It is the binder between fiber and matrix and also acts as a medium through which the stress is transferred from reinforcement to the matrix and vice versa. Increasing the adhesion between the fiber and matrix increases the tensile strength, stiffness, fatigue and environmental resistance of the composite. On the other hand, adhesion at the interface
has the opposite effect on the composite toughness i.e. as the bond strength increases the composite becomes more brittle [9]. The interfacial area (1 in.$^3$ of 50-vol % fiber composite with a fiber diameter of 0.0003 in. contain approximately 6500 in.$^2$ [10] ) is so large in a composite that a small alteration in it will largely affect the properties of the composite. This qualitative and quantitative dependence of composite properties on the interface clearly shows that it is the key element in governing the composite properties. In the literature cited the term interface and interphase are sometimes used interchangeably. However, interface is a hypothetical plane of zero thickness between two dissimilar phases, while interphase is a region of finite thickness existing between fiber and matrix, see Fig. 1.3 [11].

Fig.1.3 Conceptual drawing of interface and interphase in fiber reinforced composite[11].

There are several approaches used to explain the interfacial adhesion phenomena, but still it is not clearly understood. Theories developed for this purpose are [12]:

- Adsorption theory: Is based on chemical bond formation across the interface.
- Hooking theory: States that bond strength depends upon surface roughness and microporosity.
- Electrostatic theory: Is based on a concept that bond strength depends upon existence of an electrical double layer at interface.
- The Diffusion theory: Assumes that adhesion at interface depends upon the extent of diffusion of polymer across the interface.
Rheological theory: States that the strength of joints depends upon the mechanical properties of the material and local stress in the joints.

None of the above theories explains completely all experimental results. Kettle et al. [13] described the adhesion phenomena as a complex interpolation of mechanical, physical and chemical interaction between fiber and matrix as shown in Fig. 1.4 by shaded region.

Fig. 1.4 Schematic representation of interfacial adhesion between fiber/matrix
Adhesion is determined by the relative contribution of each component (as indicated by overlap area) [13]

1.4.1 Glass Reinforced Epoxy
Glass fibers used for reinforcement are coated with a coupling agent to improve the adhesion with a matrix. In the case of glass fibers, an organic silane is used [14]. The simplified structure is shown in Fig. 1.5. The $R'$ may be ethyl or methyl groups and $R$ is a resin compatible with reactive functional groups such as amino or epoxy in the case of epoxy resin. After undergoing hydrolysis and condensation the silanol groups deposit on a glass surface in the form of a three-dimensional network of polysiloxane Fig. 1.5 [15].
The chemical composition of silane is different from those of glass fiber and the epoxy matrix, which form identifiable interphase between the fiber and matrix. Secondary ion mass spectrometry and C\textsuperscript{13} NMR have confirmed the presence of this interphase [16]. Thomason [17] measured this interphase using scanning s.i.m.s and found it to be about 1μm thick. The bonding of silane with glass and resin is shown in Fig.1.6 [18,19].

The adhesive bond between silane and epoxy is formed during the curing process from the combination of chemical bonding and the formation of a semi-interpenetrating network between the polysiloxane and matrix resin. The semi-interpenetrating network is formed when the physisorbed oligomer dissolves into the resin during the curing process.
This absorption creates a molecularly porous structure with exposed functional groups into which the matrix resin can diffuse and copolymerize [20]. The presence of this polysiloxane layer on the glass surface improves its resistance to water.

1.4.2 Carbon Reinforced Epoxy

Carbon fibers are manufactured from polyacrylonitrile (PAN), rayon and pitch. The high strength fibers were initially produced from PAN. The fibers are surface oxidized to promote adhesion to matrix resins and then are coated with an epoxy sizing resin to protect them during handling. The surface of oxidized carbon fibers contains oxygen in the form of carboxylic acid, adsorbed water, phenolic hydroxyl and ketonic groups. The location of these functional groups was investigated by Denison et al [21]. According to his research on HS fibers the functional groups were located within the micropores in the surface. It is assumed that the improvement in adhesion may be increased by the introduction of oxygen and nitrogen containing functionalities which have a known reactivity to epoxy groups. Kettle et al [13] showed that functional groups such as carboxylic acid and amine are more effective than hydroxyl groups to promote adhesion. It was also observed that pores present on the surface of the carbon fiber become wider on oxidation. The adsorption of the epoxy groups into these pores improves interfacial bond strength.[22,23]

1.4.3 Kevlar Reinforced Epoxy

The general structure of Kevlar fiber consists of straight-chain aromatic rings alternating with amide linkages, see Fig.1.7 [24]. This straight-chain polymer structure produces high stiffness in longitudinal direction, but is weak in the transverse direction because the polymer chains are held together by hydrogen bonds and Van der Waals' interaction which are weak in nature. The fibers are dressed with spinning aids but surface treatments to promote adhesion are not so effective, therefore, fiber/matrix adhesion is generally poorer as compared to glass or carbon [25]. The presence of polar groups in the polymer chains makes Kevlar fibers more hydrophilic and they can absorb 6% of moisture. The presence of moisture affects the hydrogen bonding and Van der Waals' interaction between polymer chains and reduces the transverse and compressive
properties of the fiber. This moisture is absorbed by small internal microvoids within each fiber.

\[
\text{Figure 1.7 Structure of Kevlar fiber showing chains are held together by relatively weak}
\]
\[
\text{hydrogen bonds and van der Waal's forces (---)}
\]

The transverse mechanical properties and the compressive properties are most affected by the presence of moisture, while there is no effect on the longitudinal tensile properties. The moisture content can reach up to 4.5% w/w, but the polymer chains themselves are not degraded and all properties regain their previous high values upon drying. The use of Kevlar as tyre core, underwater cable, and in the aerospace industry utilizes its strength and stiffness [26].

1.5 Environment

Composite materials during their service period come across different environmental conditions such as temperature, moisture, solvents, acids etc. These environmental agents adversely affect the performance of composite materials. For example 48% of the boats and swimming pools built with glass composite are affected by blistering due to contact with water [27]. Acidic environment causes brittle fracture of insulators made from glass fiber reinforced polymers used in electrical power industries [28]. Many industrial failures of E-glass fiber composite have been reported due to acidic
stress corrosion [29]. Similarly composite material used in aerospace and other industries fails due to harsh environmental conditions. Moisture is one of the most important factors that must be taken into account because it can always be absorbed from the atmosphere.

Moisture affects all components of a composite, most significantly the matrix and the fiber matrix interface but also the fiber. The diffusion of water in matrix produces plasticization, which causes reduction in the glass transition temperature ($T_g$) of the resin. The plasticization process involves interruption of Van der Waals' bond between polar groups of cured resin. This happens when the water interacts with the polar groups present in the resin through hydrogen bonding. The breaking of secondary bonds creates free volume in the resin where water molecules cluster. The effect tends to be more efficient in resin with more polar groups such as epoxy resin matrices, which contain hydroxyl groups in cured structures. Polymers with ketones and amides are more resistant to hydrolysis as they have fewer polar groups. According to Woo and Piggott's [30] findings on absorption of water on DGEBA epoxy cured with amines, the water molecule is not bonded to the resin at hydrogen bonding sites or polar groups present in epoxy resin but it is present in the form of clusters in resin. Marsh et al [31] studied the absorption of epoxy and epoxy-glass composites at 75°C and found that total absorption of moisture in epoxy is greater than in the composite, but the author comments take into account the fact that composites contain 60% less resin. Therefore uptakes of water in both cases are the same. The average decreases in $T_g$ for each 1% of the moisture absorption are about 20K [32]. The moisture absorption also swells the matrix, which reduces the residual stress in the composite. The residual stress was developed due to shrinkage of the matrix during the curing process. Water absorption also causes reduction in the modulus of the matrix.

The effect of moisture on the fiber/matrix interface was pointed out to be two-fold [33]. The interface of glass fiber reinforced epoxy laminate composite under various conditions was plasticized, swelled and debonded by hot and humid conditions. Immersion of unidirectional laminate of glass/epoxy for 100 days at 45°C produces cracks at glass/epoxy interface in composite. The similar cracks appeared just after 35
days when laminates were immersed at 80°C [34]. This clearly indicates that elevated temperature accelerates the attack of water at the interface. A study performed on glass/epoxy pipe for a fluid circuit application showed that rate of damage depends upon the amount of water absorbed by the material [35]. Long term immersion in water reduces the interface properties of the glass/polyester composite [36,37,38]. No effect was observed when Kevlar-49/epoxy laminates were exposed to ultraviolet light [39]. Moisture absorption of about 1% in Kevlar-49/epoxy laminate causes 5%, 4% and 2% drop in compressive, interlaminar share and flexural strength respectively [40]. The shear strengths of Kevlar/epoxy interfaces were reduced after water immersion [41]. The interfacial properties of carbon/epoxy laminates were also affected by hot and humid conditions [42,43,44]. Seawater also reduces the transverse properties of the glass/graphite/epoxy hybrid composite [45].

A stress corrosion resistance study on chemically resistant resin, general purpose resin and toughened resin showed that chemically resistant resin performed badly as compared to toughened resin. The chemical resistance of the resin was in the order of epoxy-modified polyester > isophthalic > toughened isophthalic [46]. Price and Hull [47] investigated the diffusion-controlled cracking due to 0.65 M HCl at 20°C on different resin composites with the same fiber and found that HCl does affect the crack growth but it is not totally dependent upon the diffusion of HCl into matrix.

In glass fiber composites, glass fiber is found to be most significantly affected by acid corrosion [48,49]. According to these findings when glass reinforced polymer was exposed to an acidic environment the glass fibers in the composite were chemically deteriorated as a consequence of the ion leaching process. In this ion-exchange reaction, non-siliceous ions (Ca, Al, B, Mg etc) in glass are replaced by the hydrogen ions in the acid. As a result, the fiber loses its strength, and the composites fracture under relatively low mechanical stress. These acids may arise directly from acid rain, or from the by-products of electrical discharging of certain polymers [50].
1.6 Interface Strength Measurement

There are several methods which can be used to measure the strength of the bond at the interface. The mechanical test methods are most widely used. Methods which can directly observe interface are the electron microscope (SEM), transmission electron microscopy, X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES). Fourier transform infrared (FTIR) has also been used in characterizing the fiber and matrix surfaces.

The techniques which are presently being widely used to measure interface properties are the fiber microcompression test, the microtension test, the single fiber fragmentation test and the pull-out test Fig. 1.8 [51].

Fig. 1.8 Four techniques which are widely used to measure interface properties [51].
The fragmentation test is easy to perform and therefore widely used for measuring interfacial properties of fibers in various kinds of matrices. In this test a single fiber is embedded in the polymer matrix and a tensile load is applied to the specimen. The tension produced causes the fiber to fracture into smaller lengths. The average length of the broken fibers is measured and the critical length $l_c$ is calculated from it. The fiber strength, $\sigma_f$ of fiber having a length $l_c$ is calculated by taking measurements of a longer length of fiber and then extrapolating for $\sigma_f$. The mean interfacial shear strength can be calculated from equation 1.1.

$$\tau = \frac{\sigma_f d}{2 l_c}$$

where $d$ is the diameter of fiber. The advantages of this method are that, during the test the specimen is in a situation similar to that accruing in a fiber composite [52], also Poisson's shrinkage of matrix and fiber is correctly balanced. The disadvantage is that, Dai and Piggott [53] showed that extrapolation for 0.25 mm length is not realistic and can produce an unreliable fiber strength result. Another disadvantage is that it gives only an average value of the shear strength while the shear stress at the interface is not uniform. A new model has been developed for analysis of the stress state by using the principal of minimum complementary energy [54,55].

The pull out method provides a direct measure of interfacial adhesion. It consists of pulling a single fiber out of the plane from the resin. The load-displacement curve obtained during this pulling provides information about what is actually happening at the interface, Fig.1.9. The maximum load point $F_A$ is taken as the debonding force and is used in different computations. The sudden drop in load after $F_A$ is due to vertical displacement of the fiber after debonding, and the wavy part shows the frictional sliding of the debonded fiber being pulled up from the matrix.
The pull out method provides independent information about the friction that follows debonding and coefficient of friction can be calculated [51]. Its disadvantages are it is difficult to perform and results are affected by the reduced interfacial pressure produced due to Poisson's shrinkage of fiber when high fiber stress is applied.

The microtension method and pullout method follow the same principle, i.e., a single fiber is pulled out from a sample of resin. Also both involve high fiber stress that can cause Poisson's shrinkage away from the polymer matrix, which reduces the pressure across the interface [52].

The microcompression/microindentation method is the only one of the four methods that uses a section of a real composite. A piece of unidirectional composite is cut perpendicular to the fiber direction and polished, then the fiber is pushed down. The advantage of this test method is that it takes into account the effect of the surrounding fibers on the interfacial strength of the fiber that is pushed down. The disadvantage of this method is that applied axial force on the fiber causes a Poisson's expansion that increases the pressure at the interface, which gives higher results. This test method cannot be used with polymer fiber such as Kevlar [56].

The results from these four tests do not agree with each other, even testing the same composite [57]. Beckert [58] investigated the single fiber pullout and found that it does not represent the actual interfacial adhesion and suggests that new experiments
should be designed, which employ an external normal and more homogeneous interface load. It was recently pointed out by Piggott [59] that all interface testing using single fiber methods could be misleading because results are affected by frictional effect of unknown magnitude and high stress concentrations at the entry point and at the embedded end [36]. Furthermore, the tests are centrosymmetric, thus imposing a shear process at the interface. Since polymers fail in tension rather than shear, therefore, unreasonably high values of interface strength are sometime obtained [60,61]. Because of this, Piggott [59] recommended that these tests be phased out. Piggott further recommended that instead of doing single fiber testing, an off axis test should be performed on the unidirectional composite to measure the interfacial strength. In the off-axis test the resin and interface control the failure because fibers are perpendicular to the direction of the load.

A recent study of carbon fiber reinforced PEEK (APC2) using a transverse test showed that the interface is stronger than the polymer, and it retained its strength up to 8000 h in 90° water [62]. Meanwhile, the pull out test gave equivocal results, i.e. 57 ± 29 MPa for the 90°C water immersed samples for 3000 h compared with 85 ± 19 MPa for the non immersed samples [63]. It is difficult to quantitatively analyze these results because of the large standard deviation.

The weakness of the transverse test is that it necessarily involves polymer failure as well as interface failure, since the fibers are not continuously in contact across the specimen. Rather, they are separated by webs of matrix which must also be broken. So, if we wish to investigate the effect of environment on the interface, we need to know its effect on the polymer when fibers are not present. In addition, the fiber causes stress and strain concentrations in the polymer, so non-ductile polymers may be weakened by this.

Therefore, in order to investigate environment effects, and to obtain results which are free of these difficulties, an altogether a different test is required.
1.7 PEEL TEST

A peel test is used to measure adhesive strength of flat tapes. In industry the test is used for pressure sensitive tapes. The test results are analysed in terms of the work or energy of adhesion, when at least one of the adhering members is flexible. The peel test exists in a number of forms such as stripping, "T", floating roller and climbing drum tests [64]. These forms of tests are based on a common theme, shown schematically in Fig.1.10. A peel load is applied at some angle to the adhesive through a flexible adherent and results are recorded in the form of a load-displacement curve. It is usually carried out at angles of 90° or 180° but the analysis can be made for any angle [65]. The results are usually expressed as load divided by the strip width in lb/in or N/mm units. The adhesive failure energy per unit area, \( \Theta \), can be calculated from equation 1.2.

\[
\Theta = \frac{P(1 - \cos \alpha)}{w} \quad (1.2)
\]

where \( P \) is the peel load, \( w \) is the width of the peeling strip and \( \alpha \) is the peel angle.

Karbhari and Engineer [66,67] modified the peel test for investigating the bond strength between concrete and composites. For this purpose a unidirectional carbon-epoxy and glass-epoxy composite strip with length of 12 in. and width 1 in. was bonded with a block of concrete using epoxy resin. A schematic of the peel test setup is shown in Fig.1.11. The debonding force was calculated by taking an average of all the peaks appearing in the load displacement curve, see Fig.1.12.
Using an energy balance criterion the interfacial fracture energy $G$ can be calculated using equation (1.3).

$$G = \frac{P(1+\varepsilon - \cos \alpha)}{w} - Ut$$  \hspace{1cm} (1.3)

where $P$ is the applied peel load, $w$ and $t$ are width and thickness of the composite strip, $U$ is the strain energy in the peel arm, $\varepsilon$ is the corresponding strain in peel arm and $\alpha$ is the peel angle.

When the peel tests were performed at different peel angles it was observed that peel force increased with decrease in peel angle. The findings were in agreement with others who performed peel tests on flat tapes [65]. Karbhari and Engineer [66] reported that by increasing the peel angle from 30° to 60° the total interfacial energy of glass-concrete composite was increased to 14.6%, but in the case of carbon composite it
Fig. 1.11. Schematic of peel test setup used for Composite and Concrete adhesion [67]

Fig. 1.12 Typical peel curve obtained from peeling of composite from surface of concrete [67]
remained constant. Because of high stiffness of carbon fiber composite it is not possible to perform the peel test at peel angle $>60^\circ$. Karbhari et al [68] also used the modified peel test to investigate the environmental effects on adhesion of glass/epoxy and carbon/epoxy composite with concrete. Yukinobu et al [69] investigated mechanical properties of 2 or 4 ply glass, carbon and Kevlar fiber reinforced polymer using the T-peeling test and reported the peeling strength in the order of Kevlar> carbon> glass fiber reinforced polymers. The load displacement curve is similar to the curve obtained from the double beam cantilever test (DCB), see Fig.1.13.

1.7.1 Double Beam Cantilever Test

The double beam cantilever (DCB) test has been used for measuring fracture toughness of unidirectional fiber reinforced polymer matrix composites [70]. In this method a rectangular unidirectional laminated composite specimen, containing a non adhesive crack starter strip, is opened from the ends. The applied force and opening distance is recorded in the form of the load-displacement curve, see Fig.1.13. Modified beam theory is applied to calculate strain energy release using equation 1.4.

$$G_I = \frac{3P\delta}{2ba} \tag{1.4}$$

where $P$ is the applied load, $\delta$ is load point displacement, $b$ is the specimen width and $a$ is the delimitation length.

There are several methods available to analyse the fracture energy such as the area method, compliance method, load method and displacement method. A comparative study of these methods was performed by Hashemi et al [71] using carbon-epoxy and carbon-PEEK composites. The results showed different values of fracture energy for the same fiber composite. Similar differences were observed in reported values for the same fiber-composite [71]. It was also observed that the flexural modulus increased with increasing crack length, which suggests that simple beam theory is not correct.
Keary and Ilcewicz [72] suggested that an end correction (a + ∆) should be made because forces and moments cause the end region of the DBC to deform. Smiley and Pipes [73] used the DCB test to investigate the rate effect of crosshead speed on fracture toughness of graphite/epoxy and graphite/PEEK composite and found a decrease in fracture toughness in both composites by increasing the crosshead speed of load cell.

1.7.2 Elastica Test

Sinclair [74] performed the elastica test to measure the tensile strength of glass fiber. A straight glass fiber of 1 or 2 inches in length was stretched from the ends in the form of a loop whose base was supported, see Fig. 1.14. The tensile stress $\sigma$ was calculated using equation 1.5.

$$\sigma = \frac{16TR_m}{\pi r^3}$$

(1.5)

where $T$ is tension in fiber, $R_m$ is the radius of curvature of fiber and $r$ is the radius of fiber.
None of the above test methods described is the same as the peel test developed in this study. Therefore none of the models can be used directly for the present work.

1.8 Objectives Of This Research

According to the above introduction, there are problems in measuring interfacial properties using the present test methods. Also, in order to investigate environmental effects on interface, and to obtained results which are free of these difficulties a different test altogether is required. Looking at these problems the following objectives were set for the current research.

- To develop a new test method which can measure the tensile strength of fiber-polymer bond without frictional sliding and Poisson's shrinkage of fiber.

- To develop a new test method which is more sensitive toward environmental effects.

- To measure the interface tensile strength of glass-epoxy, carbon-epoxy and Kevlar-epoxy systems and study environmental effects on them using the peel test.
2. EXPERIMENTAL METHOD

2.1 Materials

E-glass fibers (diameter, \(d=22 \, \mu m\)) from Fiberglass Canada, Kevlar 49 fibers (\(d=12 \, \mu m\)) from Du Pont, and carbon AS4 fibers (\(d=8 \, \mu m\)) from Hercules were used. An epoxy resin (EPON 815) from Shell with 12% w/w curing agent TETA (triethylenetetramine) was used as the matrix. Potentially harmful liquids used for environmental studies were distilled water, sulfuric acid and acetic acid from BDH, dichloroethane from Caledon laboratory Ltd., hydraulic oil (Tellus-oil 46) from Shell and kerosene oil (for general purpose use) bought from a hardware store.

2.2 Sample Preparation

Polyethylene capsules, 5mm diameter and 11 mm long Fig 2.1 were inserted in a plastic holder which can hold 40 capsules at a time. The liquid resin and the hardener were mixed thoroughly for five minutes and then put under vacuum for 25 minutes to remove the air bubbles. Then it was carefully put in the capsules. These were filled to the top using a dropper. The capsules were kept for the appropriate time at room temperature so that the resin became gel-like, then a fiber was placed on the surface of the resin so that it was "floating" parallel to the polymer surface with less than one half of its diameter submerged. Then the sample was put in the oven at 60°C for two hours, during which the fiber sank the required amount (i.e. until half the diameter was submerged) and the resin hardened. After being taken from the oven, the samples were left overnight at room temperature. Following this procedure 40 samples were prepared at a time. The embedding time and curing conditions for glass, Kevlar and carbon are shown in Fig. 2.2.
Embedded length of fiber (0.5 - 2 mm)

Total length of fiber (3 cm)

Resin
Polyethylene capsule

5 mm
11 mm

(a)

Embedded fiber
Polyethylene capsule

Sample holder
(5 x 8 = 40 samples)

Holes for capsule

(b)

Fig. 2.1 (a) Peel test sample and (b) sample holder
Fig. 2.2 (a) Embedding and curing process for glass fiber: (b) Kevlar fiber: (c) Carbon fiber
2.3 Selection of Samples using Microscope

The samples were checked in an Olympus Universal Research Microscope, Model VANOX using an M 50 objective (1 small division on eyepiece = 2μm). Those samples, which had about 80 ± 20% of their diameter showing, as seen from above, were used for testing, see Fig. 2.3. Care was taken to test the more uniformly embedded end of the fiber, by marking it after observing it under the microscope.

![Diagram of checking procedure under microscope]

Fig.2.3 Schematic diagram for checking procedure under microscope
2.4 Peel Tests Performed on the Instron

The experimental setup for performing peel tests on the Table Model Instron is shown in Fig.2.4. A polyethylene capsule holding a fiber half embedded in epoxy was screwed in the rotatable fixture. The peel angle, $\theta$, between peel load direction and plane of the epoxy, as shown in Fig.2.5, was adjusted to the required value. The free end of the fiber, which was more uniformly embedded, was then placed against the copper sheet and glued using cyanoacrylate glue. The copper sheet was suspended from a 500g load cell. The test was carried out at a cross head speed of 0.5 mm/min. The results, in the form of a force-displacement curve were recorded on a chart recorder at a chart speed of 20 cm/min.

Glass-epoxy and carbon epoxy samples were subjected to the peel test at 10°, 20°, 40°, 60° and 90° peel angles as described in above paragraph. Peel strengths of carbon-epoxy system at 60° and 90° peel angles were very low and unmeasurable using the Instron, so were measured on the "CHAN1000" automatic balance which is more sensitive.

Glass-epoxy samples were divided into three groups, each containing about 60 samples. The first group was wetted throughout the embedded length of fiber with distilled water for 0.25, 0.5, 1, 2, 4 and 8 hours. This was accomplished by continuously adding 2 or 3 drops of distilled water with the help of a dropper on the surface of epoxy at ambient temperature. The peel tests were performed at 60° peel angle after each wetting time interval. Similarly the second and third groups were wetted with dichloroethane and ethanol with the same procedure and the peel tests were performed at 60° peel angle.
Fig. 2.4 Schematic drawing of set-up used for measuring oblique peel strength of fiber-epoxy system

Fig. 2.5 Schematic presentation of peel angle
2.5 Peel Tests Performed on the CHAN 1000 Automatic Balance

These tests were performed with the setup shown in Fig. 2.6. The rotatable fixture was placed on the platform of the balance, which held the sample, in such a way that the embedded fiber was horizontal. A ground rectangular copper sheet was attached to the suspended hook of the balance, and the position was adjusted so that the lower edge of the copper sheet was 5mm above the resin surface. This was accomplished by placing a 5 mm thick metal piece between the resin and the copper sheet. The lower edge of the sheet was adjusted to be perpendicular to the fiber. The more uniformly embedded free end of the fiber was then placed against the copper sheet and glued using cyanoacrylate glue. Attention was paid to make sure that the peel angle, $\theta$, between fiber peel load and plane of the epoxy was 90° see Fig.2.6. The peel tests were carried out at 1mm/min platform speed with a chart speed of 30 cm/min. The load range for glass and Kevlar was 0-10 mN, and for carbon it was 0-2 mN. The force was recorded on a strip chart recorder and also displayed digitally. After checking under the microscope 52 samples of glass-epoxy, 78 samples of Kevlar-epoxy and 83 samples carbon-epoxy were subjected to peel tests at 90° peel angle following this procedure.

2.6 Environmental Effects

Fifty checked samples were divided into two groups. (The first group containing 10 samples was tested without immersion in distilled water). The second group containing 40 samples (10 samples per immersion time) was immersed in distilled water at room temperature (25°C) in 50ml bottles for 5, 10, 20 and 40 hours respectively. The peel tests were carried out using the CHAN 1000 automatic balance.

In the case of 90° C distilled water immersion, 15 checked samples were immersed for each immersion time of 5, 10, 20 and 40 hours. For this purpose a water bath was set up by using a hot plate to provide the heat source to a beaker of 100ml of
Fig. 2.6 Schematic drawing of set-up used for peel test at 90° peel angle on
CHAN 1000 Automatic Balance
distilled water. A thermocouple was used to keep the temperature at 90 ± 1°C. A cover was put on the beaker to minimize the water loss. Regular checks and the additions of distilled water were carried out. After each immersion time peel tests were performed on immersed samples as described in the above paragraph.

For the carbon fiber samples five bottles of about 50ml with lids were filled with distilled water at 25°C and marked as 5 hours, 10 hours, 20 hours, 50 hours and 100 hours respectively. In each 5, 10 and 20 hours bottles 10 checked samples were immersed and covered with lids. In 50 and 20 hours bottles 15 checked samples were immersed in each bottle and then covered with lids. Using the same procedure immersions in 50% sulfuric acid, 50% acetic acid, kerosene oil and hydraulic oil were carried out. For 90°C distilled water immersion for 5, 10, 20, 50 and 100 hours, 15 checked samples were immersed for each immersion time in a distilled water bath at 90°C. The temperature was controlled by thermocouple within 90 ± 1°C. The water bath was covered to minimize the water loss. Regular checks and additions of distilled water were carried out. After immersion, peel tests were performed at 90° peel angle.

Kevlar-epoxy samples were immersed in distilled water at 25°C, at 90°C, 50% sulfuric acid, 50% acetic acid, kerosene oil and hydraulic oil for 5, 10, 20, 50 and 100 hours as described in above paragraph. The peel tests on samples were carried out at 90° peel angle after each immersion on CHAN 1000 automatic balance.
3 EXPERIMENTAL RESULTS

3.1 Peel Curves

Fig. 3.1 shows three typical forms of peel curve. Fig. 3.1a, represents failure of fiber and debonding did not occur at all. Fig. 3.1b, represents failure of the fiber/matrix interface and debonding occurred successively. Fig. 3.1c, represents failure of the fiber/matrix interface and debonding occurred, but after a few debonds, the fiber broke.

Fig.3.1 Three possible forms of peel curve, (a) Unsuccessful peel curve no debonding occurred, (b) Successful peel curve with continuous debonding, (c) Successful peel curve with fiber failure
The peel curves Fig. 3.1b and Fig. 3.1c have two distinct regions. In the first region of the curve from point A to B, the force exerted upon the fiber increases linearly with displacement. This proceeds until point B where fiber/matrix interface fails and debonding of fiber occurs. The second region from point B to C, corresponds to successive debonding of the fiber from epoxy matrix. The zig-zag shape of the curve in this region represents the re-establishment of the force after failure of the interface in every successive debonding. We assume each peak in this region represents a fresh debonding, therefore an average of all the peaks appearing in a curve is taken, except for the large one caused by fiber failure Fig. 3.1c.

3.2 Preliminary Results

These results were obtained using the Instron. The effect of peel angle, \( \theta \), on the peel strength of glass fiber on epoxy is shown in Fig. 3.2. Each result was the average of ten replicate tests, and each test gave several individual readings, as described in the previous section. It can be seen in Fig. 3.2, that the peel strength decreases monotonically with peel angle. In the case of carbon Fig. 3.3, again the peel strength decreases monotonically with peel angle.

Environmental effects on peel strength of glass-epoxy system were studied preliminarily at 60° peel angle because at 90° peel angle the peel strength was very low and was unmeasurable using the Instron. A decrease in the peel strength with increase in wetting time was observed in the case of distilled water and dichloroethane Fig. 3.4 and Fig. 3.5 respectively. However, there was no significant decrease in peel strength when samples were wetted with ethanol, see Fig. 3.6. Each point plotted in this graph is the result of 5 replicate tests.
Fig. 3.2 Oblique peel strength of glass-epoxy system

Fig. 3.3 Oblique peel strength of carbon-epoxy system

* Represents results from CHAN 1000 automatic balance
Fig. 3.4 Immersion effect of distilled water at 25°C on peel strength of glass-epoxy system at 60° peel angle.

Fig. 3.5 Immersion effect of dichloroethane on peel strength of glass-epoxy system at 60° peel angle.
3.3 Peel Strengths of Fiber-epoxy Systems

All the results presented in this section were obtained from a CHAN 1000 automatic balance. The peel test results of glass-epoxy, Kevlar-epoxy and carbon-epoxy systems at 90° peel angle are shown in Table-3.1. The peel test results show that peel strength of glass-epoxy and Kevlar-epoxy are about the same, while peel strength of carbon-epoxy is about six times less than glass and Kevlar. Table-3.1 shows no linear relationship between peel strength and fiber diameter. To check the consistency of the results of carbon-epoxy system three batches were prepared with the same procedure and results are summarized in Table-3.2. The coefficient of variation of these results is about 29%.
Table 3.1: Peel strength of different fibers on epoxy at 90° peel angle

<table>
<thead>
<tr>
<th>Systems</th>
<th>Diameter of Fiber (µm)</th>
<th>Peel Strength (mN) Average ± Std.Dev.</th>
<th># of results</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass-epoxy</td>
<td>22</td>
<td>6 ± 2</td>
<td>27</td>
</tr>
<tr>
<td>Kevlar-epoxy</td>
<td>12</td>
<td>6 ± 1</td>
<td>55</td>
</tr>
<tr>
<td>Carbon-epoxy</td>
<td>8</td>
<td>1.0 ± 0.3</td>
<td>42</td>
</tr>
</tbody>
</table>

Table 3.2: Peel strength results of three batches of carbon-epoxy at 90° peel angle

<table>
<thead>
<tr>
<th>Batch #</th>
<th># of Results in a Batch</th>
<th>Peel Strength (mN)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Batch # 1</td>
<td>18</td>
<td>0.7 ± 0.3</td>
</tr>
<tr>
<td>Batch # 2</td>
<td>20</td>
<td>1.0 ± 0.4</td>
</tr>
<tr>
<td>Batch # 3</td>
<td>42</td>
<td>1.0 ± 0.3</td>
</tr>
<tr>
<td>All Batches (1+2+3)</td>
<td>Total = 80</td>
<td>1.0 ± 0.3</td>
</tr>
</tbody>
</table>

3.4 Environmental Effects

This study was performed at a 90° peel angle on a CHAN 1000 automatic balance. Fig. 3.7 shows decrease in peel strength when glass-epoxy samples were immersed in distilled water at 25°C. This drop in peel strength was even faster when glass-epoxy samples were immersed in distilled water at 90°C and reached to lowest value just after 20 hours of immersion see Fig. 3.8.

The Kevlar-epoxy samples show no significant decrease in peel strength when immersed in distilled water at 25°C (Fig. 3.9). However, decrease in peel strength was observed in the case of distilled water at 90°C, see Fig. 3.10. A decrease in peel strength was observed when Kevlar-epoxy samples were immersed in 50% sulfuric acid and 50% acetic acid, see Fig. 3.11 and Fig. 3.12. Immersion in kerosene oil and hydraulic oil showed no decrease in peel strength of Kevlar-epoxy samples, see Fig. 3.13 and Fig. 3.14.
There was no significant decrease in peel strength of the carbon-epoxy system when immersed in distilled water at 25°C, see Fig. 3.15. In the case of 90°C distilled water immersion, the peel strength decreased with immersion time. Fig. 3.16. When carbon-epoxy samples were immersed in 50% sulfuric acid and 50% acetic, it showed a decrease in peel strength, see Fig. 3.17 and Fig. 3.18. However, there was no effect on peel strength when carbon-epoxy samples were immersed in kerosene oil and hydraulic oil see, Fig. 3.19 and Fig. 3.20. Five replicates were performed for each reported value in these graphs except those which are given in Table-3.3.

<table>
<thead>
<tr>
<th>Immersion liquids</th>
<th>Immersion time (h)</th>
<th># of sample immersed</th>
<th>Fiber loss after immersion</th>
<th>Fiber break off during handling or unsuccessful peel-off</th>
<th># of replicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kevlar-epoxy Sulfuric acid</td>
<td>20</td>
<td>10</td>
<td>6</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>15</td>
<td>8</td>
<td>5</td>
<td>2</td>
</tr>
<tr>
<td>Kevlar-epoxy Acetic acid</td>
<td>50</td>
<td>15</td>
<td>4</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15</td>
<td>10</td>
<td>2</td>
<td>3</td>
</tr>
<tr>
<td>Carbon-epoxy Sulfuric acid</td>
<td>10</td>
<td>10</td>
<td>4</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15</td>
<td>9</td>
<td>4</td>
<td>2</td>
</tr>
<tr>
<td>Carbon-epoxy Acetic acid</td>
<td>50</td>
<td>15</td>
<td>5</td>
<td>7</td>
<td>3</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>15</td>
<td>4</td>
<td>7</td>
<td>4</td>
</tr>
<tr>
<td>Carbon-epoxy Kerosene oil</td>
<td>100</td>
<td>15</td>
<td>7</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Carbon-epoxy Distilled Water at 90°C</td>
<td>50</td>
<td>15</td>
<td>7</td>
<td>5</td>
<td>3</td>
</tr>
</tbody>
</table>
Fig. 3.7 Immersion effect of distilled water at 25°C on peel strength of glass-epoxy system at 90° peel angle

Fig. 3.8 Immersion effect of distilled water at 90°C on peel strength of glass-epoxy system at 90° peel angle
Fig. 3.9 Immersion effect of distilled water at 25°C on peel strength of Kevlar-epoxy system at 90° peel angle.

Fig. 3.10 Immersion effect of distilled water at 90°C on peel strength of Kevlar-epoxy system at 90° peel angle.
Fig. 3.11 Immersion effect of 50% sulfuric acid on peel strength of Kevlar-epoxy system at 90° peel angle

Fig. 3.12 Immersion effect of 50% acetic acid on peel strength of Kevlar-epoxy system at 90° peel angle
Fig. 3.13 Immersion effect of kerosene oil on peel strength of Kevlar-epoxy system at 90° peel angle.

Fig. 3.14 Immersion effect of hydraulic oil on peel strength of Kevlar-epoxy system at 90° peel angle.
Fig. 3.15 Immersion effect of distilled water at 25°C on peel strength of carbon-epoxy system at 90° peel angle.

Fig. 3.16 Immersion effect of distilled water at 90°C on peel strength of carbon-epoxy system at 90° peel angle.
Fig. 3.17. Immersion effect of 50% sulfuric acid on peel strength of carbon-epoxy system at 90° peel angle.

Fig. 3.18. Immersion effect of 50% acetic acid on peel strength of carbon-epoxy system at 90° peel angle.
Fig. 3.19. Immersion effect of kerosene oil on peel strength of carbon-epoxy system at 90° peel angle.

Fig. 3.20. Immersion effect of hydraulic oil on peel strength of carbon-epoxy system at 90° peel angle.
3.5 SEM Results

The pictures obtained from scanning electron microscope showed that glass and carbon fibers come off moderately cleanly. The impressions left by fibers on epoxy showed very little apparent damage to the polymer. The hollow left by partially pulled off glass fiber in Fig. 3.21a is mostly smooth and there is little or no evidence of ductile process in the polymer. Most of the surface of the glass fibers after peel test were clean. Fig. 3.21b shows peeled off glass fiber suspended above its socket. The embedded lower half of the fiber seems to be almost clean. The more magnified view of the lower half portion of fiber, which was embedded in polymer, is shown in Fig. 3.21c. The overall surface of fiber is quite clean, only some adhering polymer which are localized are visible. The glass appears to have an uneven coating of sizing on it.

Partially pulled off Kevlar is shown in Fig. 3.22. The fiber has fibrillated and has lifted some resin off the surface. The depression or holes in the hollow left by the fiber appears to be continuations of similar holes on the undisturbed surface of resin.

Fig. 3.23a shows a pulled off carbon fiber suspended above its socket. The fiber entered the polymer at the right of the picture. The fiber has resin still attached to it, and in Fig. 3.23b, a more magnified view of the socket suggests that material may have been plucked out of the polymer.

Fig. 3.24b shows peeled off glass fiber from peel specimen which had been immersed in distilled water for 20 h at 25°C. It appears that no significant harm was done to the fiber surface and still some localized polymer particles are adhering to the fiber surface. Fig. 3.25c shows peeled off glass fiber from peel specimen, which had been immersed in distilled water for 20 h at 90°C. In this case fiber is clean showing no resin sticking to the fiber surface and harm had been done due to blistering of silane coating.
Fig. 3.21 (a) Partly peeled glass fiber (b) peeled off glass fiber above its socket; (c) glass fiber after peel test.
Fig. 3.22 Partly peeled Kevlar fiber
Fig. 3.23. (A) Carbon fiber above its socket; (b) highly magnified socket showing roughness
4. DISCUSSION

4.1 Reliability of the Data

A large spread in the results of the peel test was always observed irrespective of type of the fiber used and whether the sample were exposed to different environments or not. This large scattering makes the results doubtful. Penn and Lee [76] showed that the scatter in the results is due to inhomogeneity of interface itself and therefore unavoidable. Also small experimental errors would produce large scatter in the result because variables measured are extremely small with units of only mN and μm. Both these factors are inherent in destructive mechanical techniques used to determine adhesive strength at such a small scale. During this work several factors were observed which inhibit the reproducibility of the results such as embedded depth of the fiber on resin, voids present at interface and contamination. The first two factors significantly affect the reproducibility of the results.

To obtain the samples with uniformly embedded depth $h = d/2$ as shown in i.e., Fig.4.1, is very difficult, because this parameter is extremely small i.e for glass fiber $h = 11 \, \mu m$, for Kevlar $= 8 \, \mu m$ and for carbon $= 4 \, \mu m$, therefore it is difficult to control. The variation of $h$ with embedded length of fiber is clearly shown in Fig. 4.2, where the first half of the fiber is embedded $h = d/2$ and the second half of the fiber is embedded $h > d/2$. When $h > d/2$, the peel strength increases because of two reasons. First, the interfacial area of adhesion is increased. Second, the upper curved surface of epoxy as shown in Fig.4.3(a) by shaded portion, provides mechanical blocking to the fiber. Therefore, an extra peel force is required to break this lock and pull the fiber out of matrix, Fig. 4.3(b), clearly shows this blocking effect of resin. As the embedded $h$ increases from $d/2$ the pulling force also increases with it and produces scattering in the results. Although minimizing this variation in results was tried by using the light microscope and selecting only those samples which had about $80 \pm 20\%$ of their diameter, as seen from above, the variation still exist. When $h >> d/2$ the fiber breaks off during peeling, as shown in Fig.4.3(b).
Fig. 4.1 (a), Schematic diagram of fiber embedded in resin $h = d/2$, (b) glass fiber embedded $h \approx d/2$ on epoxy
Fig. 4.2 Variation of $h$ along embedded length of glass fiber on epoxy
Fig. 4.3(a) Schematic representation of mechanical blocking of epoxy when $h > d/2$, (b) glass fiber on epoxy, arrows are pointing towards mechanical blocking of epoxy
When fiber is embedded \( h < d/2 \) the peel strength decreases due to decrease in interfacial area of adhesion. Fig. 4.4, clearly shows that fiber is embedded \( h < d/2 \) on epoxy.

The reproducibility of the results is also affected by the presence of voids between the fiber/matrix interface. These voids usually occur due to the presence of air bubbles on the surface of the epoxy resin, see Fig. 4.5. The presence of voids decreases the interfacial area of adhesion and therefore decreases the peel strength.

4.2 Peel Process

The shape of a force-displacement curve obtained from the successful peel test provides valuable information about the failure process during the peel test. The process has two stages. In the first stage the stress on the fiber is transfer elastically to the matrix through the interface. This elastic behavior of the interface is evident from a straight line from A to B with increasing load and distance, see Fig. 3.1b. In the second stage the sharp force drops after reaching maximum load point indicates the failure of the interface. It could be concluded from this sharp force drop that fracture of the interface is brittle in nature. Also the hollows left by the fibers after peel off are mostly smooth and there is little or no evidence of ductile process in the polymer Fig.4.5 and Fig.4.6. The quick reestablishment and oscillating nature of the force suggest that the fracture or crack produced at fiber/epoxy interface is not longer in length or growing in length. It is proceeding with run-arrest type of fracture. It has been accepted that force on the peak of the peel curve represents the debonding force, therefore an average of all the peaks appearing in a peel curve is taken to represent the debonding force of that system, as shown in Fig. 1.12.
Fig. 4.4 Glass fiber embedded on epoxy $h < d/2$, bright region on fiber showing embedded portion of glass fiber on epoxy.
4.3 Peel Analysis

This test was developed to study the interfacial properties of single fiber and polymer. This method allows us to more accurately quantify and single out the interfacial properties of fibers and, as well, it reveals more rapidly the effect of environment on the fiber/epoxy interface.

Fig. 4.1b, Fig.3.21, Fig.3.22 and Fig.3.23 show that glass, carbon and Kevlar fibers have been successfully embedded on the surface of epoxy in such a way that they can be peeled off. These figures show that the glass fiber came off relatively clean, Kevlar fibrillated, and carbon pulled off the polymer from the surface and, as well, might have torn off some polymer from the socket. These results suggest that during the peel off process glass and carbon fibers behaved elastically.

Elastic behavior of glass and carbon fiber was also shown by a study [76] in which these fibers were pulled off obliquely to the point of break from the polymer surface. This study utilized the elastica test [74] to deduce the following relationship:

$$\varepsilon_{\text{flex}} = 2\phi \sqrt{\varepsilon_f}$$

(4.1)

where $\varepsilon_{\text{flex}}$ is the fiber strain, $\phi$ is oblique pulled angle and $\varepsilon_f$ is the applied fiber strain. Numerical results showed that the error was less than 36% at $\phi = 90^\circ$, and much less at lower angles.

Furthermore very small forces were applied in the peel test which ensured elastic behavior and avoided flexural failure of fibers. Fig. 4.6 shows that in the peel test a maximum force of 100 mN and 30 mN were applied to glass and carbon respectively. The resulting fiber strains ($\varepsilon_f$) were 0.37 % and 0.26% respectively, which give $\varepsilon_{\text{flex}}$ values of about 1.5 and 4.1 Gpa, neglecting any reduction due to the gripping action of the polymer. It was noted that respective values of stress were higher 3.3 GPa and 6.8 GPa at 90° peel angle. Even under these high flexural stress inelastic failure is not
expected, since a study [76] showed that glass and carbon fibers required very high local strains for flexural failure.

Fig. 4.6 Debonding force for glass and carbon vs. peel angle.

As the test was used to investigate the effect of various environments in which peel force was further reduced, therefore, inelastic effects are probably unimportant in these cases. The work of fracture of the interface can directly deduce from the total work of debonding.

Consider the 90° peel case as shown in Fig. 4.7. Let $F_1$ and $F_2$ to be consecutive peel forces required to debond the fiber from polymer. As we assumed that the fibers are behaving elastically, the curve assumed by the fiber after each consecutive peeling should be the same, for $F_1 = F_2$. Also the vertical distance, $\Delta y$, moved by the fiber is equal to the length that has debonded, $\Delta L$. Thus the work done $U$, in debonding fiber from polymer is given by

$$ U = \int F dy \quad (4.2) $$

Which is given approximately by
\[ U_1 \equiv \frac{1}{2} F_1 \Delta y_1 \]  \hspace{1cm} (4.3)

See Fig. 4.7 and, assuming that on debonding the forces droops to zero, although the load cell does not respond fast enough to record this

\[ U_2 \equiv \frac{1}{2} F_2 \Delta y_2 \]  \hspace{1cm} (4.4)

So that, in general

\[ U_k \equiv \frac{1}{2} F_k \Delta y_k \]  \hspace{1cm} (4.5)

The work of fracture, \( G_1 \) is therefore

\[ G_1 = \frac{F \Delta y}{2d \Delta L} = \frac{F}{2d} \]  \hspace{1cm} (4.6)

So for a total of \( n \) debonds, we can estimate the mean work of fracture

\[ G_1 = \frac{1}{2nd} \sum_{i=1}^{n} F_i \]  \hspace{1cm} (4.7)

\[ \bar{G}_1 = \frac{\bar{F}}{2d} \]  \hspace{1cm} (4.8)

For the oblique case with peel angle \( \phi \), Fig. 4.8, consider a total debonded length of \( L \), and a debond of \( \Delta L \). By inspection

\[ L + y = L - \Delta L + \Delta L \cos \phi + y + \Delta y \]  \hspace{1cm} (4.9)

So that

\[ \Delta y = \Delta L (1 - \cos \phi) \]  \hspace{1cm} (4.10)
Using the same development as in equation (4.2) to (4.8)

\[ \mathcal{G}_1 = \frac{F}{2d} (1 - \cos \phi) \]

\[ \Delta y = \Delta L : \text{Self similar} \]

Fig.4.7 (a) 90° peel over length $\Delta L$ and (b) stylized force-distance plot over length $\Delta L$
Ay = ΔL (1 - cosφ) : Self similar

Fig.4.8 Peel at angle φ over length ΔL

so that F vs 1/(1 - cosφ) should be constant if G_i is independent of φ.  The dashed curves in Fig.4.6 are drawn based on the value of G_i estimated at 90°.  As can be seen, the fit is moderately good up to about 20°, but then equation (4.11) predicts values which are too great.  This is probably because we have ignored the fiber tensile strain, which at φ = 10° is quite significant i.e. 0.37% for glass and 0.26% for carbon.  This extra strain could well
assist the debonding process. It is therefore recommended that the peel tests be carried out at angles of 30° or more.

As shown in Fig. 3.22, the Kevlar fiber fibrillated during the peeling process. This is usually observed with Kevlar fibers during fracture [77]. Due to fibrillation Kevlar absorbed energy inelastically, therefore, it cannot be peeled at 90° to yield a work of fracture. Table 4.1 gives the work of fracture estimated from 90°. The value for Kevlar is anomalously large due to fibrillation.

Table 4.1 Peel Strengths and Interfacial Fracture Toughness

<table>
<thead>
<tr>
<th>Fiber</th>
<th>Diameter (μm)</th>
<th>Peel Strength (mN)</th>
<th>Work of Fracture (Jm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass</td>
<td>22</td>
<td>6 ± 2</td>
<td>140 ± 50</td>
</tr>
<tr>
<td>Carbon</td>
<td>8</td>
<td>1 ± 0.3</td>
<td>60 ± 20</td>
</tr>
<tr>
<td>Kevlar</td>
<td>12</td>
<td>6 ± 1</td>
<td>250 ± 40*</td>
</tr>
</tbody>
</table>

* Includes work of fibrillation

It is interesting to note that the glass fiber bond appears to be tougher than the carbon fiber bond. This could perhaps be because the silane coating imparts more toughness than the epoxy sizing used for carbon. The low values for glass and carbon are consistent with opening mode fracture toughness for laminate [78]. Even when bare fibers are produced in these tests, the interface can contribute significantly to the total work of fracture.

4.4 ENVIRONMENTAL EFFECTS

Environmental effects degrade the interfacial properties of the composites. Elevated temperature and moisture are the major factors affecting the interfacial adhesion of the fiber/polymer interface. The peel test gave straightforward, rapidly revealed environmental effects on fiber-polymer interface. The peel test results showed that glass-
epoxy interface is very susceptible to weakening by water, Fig.3.7. Fig.3.8 clearly indicates that elevated temperature accelerated the attack of water at the interface. Fig.3.24 show wrinkles and some blisters on the surface of glass fiber accrued at 90°C immersion for 20h in distilled water. This may be due to accelerated hydration and elevated temperature may cause differential expansion between silane coating and fiber material. The removal of silane coating by pyrolysis have been reported [79].

60° peel also revealed the environmental effects clearly and rapidly at glass-epoxy interface, see Fig.3.4, Fig.3.5 and 3.6. Among water, dichloroethane and ethanol the attack of dichlorethane at interface is much faster as compare to the others. It appears that polarity of the liquids may be promoting some chemical effects in weakening of the interface.

With carbon, the effect of 90° water appears to be quite large, Fig.4.14, while 25°C water has little effect. This may be because of accelerated hydration of the epoxy at the interface at 90°C. Sulphuric and acetic acids at 25°C have about the same effect on carbon, Fig.3.17 and 3.18. The acids must be producing some chemical effect at or near the interface. The interface of carbon-epoxy appears to be very resistant to organics, with kerosene having a barely perceptible effect and hydraulic oil having no effect at all Fig. 3.19 and Fig. 3.20.

In the case of Kevlar, the environmental effects are partially masked by fibrillation of the fiber. Further work is needed to separate the fibrillation and interface effects. However, we note losses in water, particularly marked at 90°C, Fig. 3.10. Sulfuric and acetic acids at 25°C cause large losses, Fig.3.11 and Fig.3.12 but organic fluids have little effect, Fig.3.13 and Fig.3.14.

A comparison of the immersion effect of water at 25°C and 90°C on fracture toughness of glass and carbon -epoxy interface is shown in Fig.4.9. It appears that the glass-epoxy interface was much affected by water, whose fracture toughness was reduced to about
90% just after 40h of immersion, while no significant effect was observed in the case of carbon after 100h of immersion.

Fig. 4.9 Effect of 25°C water immersion on fracture toughness of fiber-epoxy interface

Fig. 4.10 shows that 90°C immersion in water significantly weakened the fracture toughness of carbon to 75% and glass almost lost 95% of its interfacial strength just after 20h.

Fig. 4.10 Effect of 90°C water immersion on fracture toughness of fiber-epoxy interface
5. CONCLUSION

1. The results of the peel test are very promising. Although difficult to do, it has been successfully implemented. The test can be a practical method for estimating the work of fracture of a fiber-polymer interface. So long as the fiber is fully elastic during the peel, the work of fracture is simply the mean peel force divided by twice the fiber diameter.

2. With a 60°C cured epoxy, carbon had lower work of fracture, 60 Jm⁻², than glass with 140 Jm⁻². Peel angles of 30° or more are recommended. Kevlar gave anomalous results because fiber absorbed energy inelastically due to fibrillation.

3. The technique is sensitive towards environmental effects on fiber/polymer interface. It readily and clearly shows the effect of water on glass-epoxy interface. The work of fracture of glass-epoxy interface was reduced by 90 % just after 40 h of immersion at 25°C and even faster in case of 90°C immersion. Elevated temperature also damages the coating of glass fiber. For both carbon and Kevlar, higher temperatures are needed for significant effects.

4. Sulphuric and acetic acid at 25°C are about as weakening as 90°C water. While organics such as kerosene have very little effect on interfacial adhesion.

5. Further work is required to ensure that the peel interface is of the same nature as that occurring in a commercial fiber composite, also work is further needed to separate out the inelastic effects in case of Kevlar fiber.
6. REFERENCES


70 *ASTM Standards*, D 5528-94a.


7. LIST OF NOMENCLATURE

\( \tau \) mean interfacial shear strength (Nm\(^2\))

\( \sigma_f \) tensile strength of fiber (Nm\(^2\))

\( l_c \) critical length of the fiber fragment in fragmentation test (mm)

\( \theta \) adhesive failure energy per unit area (Jm\(^2\))

\( P \) peel load (N)

\( w \) width of the composite strip in peel test (mm)

\( \phi \) peel angle (°)

\( G \) interfacial fracture energy (Jm\(^2\))

\( \varepsilon \) strain in peel arm

\( E \) longitudinal modulus of composite strip (Nm\(^2\))

\( \delta \) load point displacement in double cantilever beam test (mm)

\( b \) specimen width in double cantilever beam test (mm)

\( a \) delimitation length in double cantilever beam test (mm)

\( \sigma \) tensile stress in elastica test

\( T \) tension in fiber in elastica test (N)

\( R_m \) radius of curvature of fiber in elastica test (mm)

\( r \) radius of fiber (mm)

\( d \) diameter of fiber (mm)

\( \varepsilon_{\text{flex}} \) flexural fiber strain at the surface

\( \varepsilon_f \) applied fiber strain

\( F_1,F_2 \) consecutive peel force in peel test (N)

\( L \) total bonded length of fiber in peel test (mm)

\( \Delta L \) debonded length of fiber (mm)

\( y \) total free length of fiber (mm)

\( \Delta y \) vertical distanced moved by the fiber (mm)

\( U \) work done (Nm)

\( G_f \) work of fracture (Nm)
8. APPENDIX

Table-8.1 Oblique peel strength of glass-epoxy and carbon-epoxy system

<table>
<thead>
<tr>
<th>Peel Angle (θ)</th>
<th>Peel Strength (mN)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10°</td>
</tr>
<tr>
<td>Glass-epoxy</td>
<td>98.4 ± 12.4</td>
</tr>
<tr>
<td>Carbon-epoxy</td>
<td>30.6 ± 8.3</td>
</tr>
</tbody>
</table>

Table-8.2 Immersion effect of solvents on peel strength of glass-epoxy at 60° peel angle

<table>
<thead>
<tr>
<th>Immersion Time (h)</th>
<th>Peel Strength (mN) After Immersion in Ethanol</th>
<th>Peel Strength (mN) After Immersion in Distilled Water</th>
<th>Peel Strength (mN) After Immersion in Dichloroethane</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0.0</td>
<td>0.25</td>
<td>0.5</td>
</tr>
<tr>
<td></td>
<td>20.6 ± 6</td>
<td>19.2 ± 4</td>
<td>17.5 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>16.6 ± 5</td>
<td>14.8 ± 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.4 ± 4</td>
<td>8.0 ± 3</td>
</tr>
<tr>
<td></td>
<td>18.8 ± 5</td>
<td>18.0 ± 4</td>
<td>15.4 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>12.3 ± 4</td>
<td>11.8 ± 4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>7.0 ± 2</td>
<td>5.0 ± 1</td>
</tr>
<tr>
<td></td>
<td>17.4 ± 6</td>
<td>12.6 ± 3</td>
<td>8.4 ± 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5.2 ± 2</td>
<td>4.0 ± 1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table-8.3 Hydrothermal effect on peel strength of glass-epoxy at 90° peel Angle

<table>
<thead>
<tr>
<th>Immersion Time (h)</th>
<th>0</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peel Strength (mN) After Distilled Water immersion at 25°C</td>
<td>6.2 ± 1.8</td>
<td>4.7 ± 1.3</td>
<td>3.6 ± 0.8</td>
<td>1.8 ± 0.6</td>
<td>0.4 ± 0.1</td>
</tr>
<tr>
<td>Peel Strength (mN) After Distilled Water immersion at 90°C</td>
<td>6.2 ± 1.8</td>
<td>3.1 ± 0.7</td>
<td>1.2 ± 0.4</td>
<td>0.3 ± 0.07</td>
<td>-</td>
</tr>
</tbody>
</table>
### Table-8.4 Immersion effect of potentially harmful liquids on peel strength at 90° peel angle

<table>
<thead>
<tr>
<th>Systems</th>
<th>Immersion Liquids</th>
<th>Immersion Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0</td>
</tr>
<tr>
<td>Peel Strength of Kevlar-epoxy (mN)</td>
<td>D. Water at 25°C</td>
<td>5.8 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>D. Water at 90°C</td>
<td>5.8 ± 1.3</td>
</tr>
<tr>
<td></td>
<td>50% Sulfuric acid</td>
<td>5.9 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>50% Acetic acid</td>
<td>5.9 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>Kerosene oil</td>
<td>5.9 ± 1.0</td>
</tr>
<tr>
<td></td>
<td>Hydraulic oil</td>
<td>6.1 ± 1.4</td>
</tr>
<tr>
<td>Peel Strength of Carbon-epoxy (mN)</td>
<td>D. Water at 25°C</td>
<td>1.04 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>D. Water at 90°C</td>
<td>1.04 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>50% Sulfuric acid</td>
<td>1.04 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>50% Acetic acid</td>
<td>1.04 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>Kerosene oil</td>
<td>1.04 ± 0.29</td>
</tr>
<tr>
<td></td>
<td>Hydraulic oil</td>
<td>1.04 ± 0.29</td>
</tr>
</tbody>
</table>
Fig. 8.1 Immersion effect of water on peel strength of carbon-epoxy interphase:
(a) at 25°C and (b) at 90°C

To observe significance level of the observed correlation coefficient, Student's $t$ is used

$$ t = \frac{r\sqrt{N-2}}{\sqrt{1-r^2}} \quad (8.1) $$
where $N-2$ is the degree of freedom and $r$ is correlation coefficient, therefore, for Fig. 8.1a
$N = 28$, $r = 0.2589$ and Student's $t = 3.01$ which is slightly $< 1\%$ it means that it is possibly significant. Similarly for Fig. 8.1a $N = 29$, $r = 0.6387$ and Student's $t = 6.9$
which gives value of $0.1\%$ level which is highly significant.

By comparing the slopes of linear regression lines in Fig.8 it is clear that the decrease in peel strength is accelerated at $90^\circ$C.