

Environmental damage and degradation of FRP composites: A review report

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Abstract

FRP composites are prime choice materials in various civil engineering structures and high performance aerospace components. They exhibit superior mechanical properties than their metallic counterparts. However, they are susceptible to environmental damages and degradations. In order to utilize the full potential of FRP composite materials their physical, chemical and mechanical behavior in different environmental conditions should be well established. Present review is an attempt at highlighting different damage/degradations that may be caused to the FRP composite on its exposure to various environmental conditions.

Introduction

The literature related to fibre – reinforced plastics (FRP) is quite extensive. In the last two decades, there had been an unprecedented world – wide growth of research activities in the area of FRP. This has led to publications of a large number of research papers, and scientific and technical reports / books on several aspects of FRP composites. The work involved includes detailed experimentations on fibres, resin systems, composite materials and their development and manufacturing, NDT and quality control, fibre – resin load transfer and interface problems, physical, mechanical and electrical properties, failure and fracture, micro and macro – mechanics, structural response, environmental effects, etc. FRP composites essentially consist of two or more physically distinct different materials that interact in a complex manner, especially when subjected to temperature and moisture environments [1-6]. There are several factors that may contribute towards these complex interactions which decide the end use of the material, having an important say on its behavior in the specific environment it is exposed to.

In the present review, attention has been primarily focused only on those such as chemical and physical characteristics of fibres and resins, fibre–resin interface behavior, failure mechanism, hygrothermal diffusion, thermo-mechanical behavior and other factors that constitute important parameters which influence the end use of the composite material.

Carbon Fibres

Carbon fibres represent a third generation group of fibres. Their manufacturing technology is based on the high temperature pyrolysis of organic compounds, primarily fibrous polymer materials. This process of pyrolysis of the organic compounds is conducted in an inert atmosphere. At present, an overwhelming number of different carbon fibres are being produced varying in their structural form, properties, production technologies and sources of initial raw materials. The classification of carbon fibre is based on the final heat-treatment temperature (HTT) employed during production of these fibres [7]. As the pyrolysis temperature increases, the products obtained become more and more enriched with carbon. Accordingly, carbon fibres may be subdivided into three groups.

- i) Partially carbonized fibres (HTT 500° C, carbon content upto 90 wt. %).
- ii) Carbonized fibres (HTT 500-1500° C, carbon content over 99 wt. %).
- iii) Graphitized fibres (HTT 2000-3000° C, carbon content over 99 wt. %).

The first group of materials, to be more accurate, belongs to the class of pyropolymers. At present polyacrylonitrile (PAN) is the main raw materials for producing high strength and high modulus carbon fibres. The final heat-treatment temperature for these carbon fibres are in excess of 1000° C, and the carbon content amounts to 95-98 wt. %. PAN-based fibres contain a lot of bound nitrogen (upto 6 wt. %). To improve upon some of their characteristics (e.g. sorption capacity, electrical conductivity, fire resistance, strength, etc.) other elements (phosphorus, transition metals, sulfur, boron, etc.) should be introduced into the carbon fibres [8-10].

The process of producing PAN-based carbon fibres includes two principle stages; viz stabilization and carbonization. Stabilization is conducted by heating in oxidative media at temperature upto 350° C. At this stage the formation of the chain ring structures takes place. During stabilization PAN combines with about 8 – 16% oxygen. Oxygen becomes bound to the polymer in many forms. The PAN stabilization process also includes cyclization and dehydration reactions. Carbonization of the stabilized fibres results in gradual cross-linking of the chains, aromatization and finally results in formation of graphite- like structural elements [7].

The modulus of the carbon fibre is determined by the orientation of the graphite crystallites within the carbon fibrils, wherein the strength is a function of the interfibrillar bonding [11]. The high activity of element-carbon fibres with their active groups and fibre elements upon

interaction with the polymer binder make it possible to increase the fibre-to-matrix adhesion. This also intensifies reactions that occur on the surface layer and in some cases, brings about the grafting of the binder to the fibre surface [7]. Carbon fibres containing amino groups display high activity upon interaction with the epoxy resin. The desire to improve the economics of bio refineries for fuel production, and to provide lighter, low-cost materials for automobiles to reduce fuel consumption, have led to an increased interest in low-cost carbon fiber manufacture from lignin [12]. U.S. Department of Energy (DOE) has drawn significant attention to reduce carbon fiber manufacturing costs by lowering processing costs through advanced oxidation techniques. From the textile grade PAN precursors, and from the synthesis of new melt-spinnable PAN precursors carbon fibres with strengths of 2.52 GPa and 1.03 GPa, respectively have been produced [13-14]. The lignin carbon fibers were projected to cost much less than any other known process of carbon fiber production [15-16].

Glass Fibres

Glass fibre materials possess quite a few useful properties such as fibre and corrosion resistance, high strength, comparatively low density, excellent optical and electrical properties, good thermal and sound insulation characteristics. Glass fibres of substantially different properties are possible by selecting their specific properties and production methods [17]. Two main forms of glass fibres are known: Continuous glass-fibres and staple-glass-fibres. The continuous fibre produced by drawing from the glass melt is characterized by indefinite large length, straight-linerity and parallel arrangement of filaments in fibre tows; whereas staple fibres produced by disintegration of glass melt steam by means of air, steam or gas flow are characterized by small length, twist and random disposition.

Continuous glass fibres are mostly used for the manufacture of textile materials and products in various branches of technology. Staple glass fibres are fabricated into bulk fibre, mats and fabrics with the use of organic binders. These materials from staple glass fibres are used for thermal, sound and electrical insulation; for anticorrosive protection, and filtration of chemically aggressive high temperature mediums.

In recent times, glass reinforced plastics are widely used for the production of corrosion resistant pipelines, storage containers and apparatus in the chemical, oil and gas industries. These

materials are also used in ship-building, rail, road transport, as well as other engineering applications. Glass is assumed to possess a micro-heterogeneous structure where heterogeneous molecules do not penetrate mutually where as homogeneous molecules interact mutually forming independent structural micro-groups. Observations indicate that micro heterogeneous structure of the glass melt is clearly seen in the glass fibres [18]. The great importance for the quality of resultant glass for glass drawing are homogenization and degassing of glass melt, utilization of thin crushed complex raw materials, high temperature glass melting (1600° C and greater), complete mixing of glass mass, and use of glass-resistant refractories, etc.

The strength of the fibre is influenced by thermal history of glass, method and condition of its formation and most importantly, by the physic-chemical interaction of the environment and the fibre surface defects [8]. The chemical composition of glass determines basic physico-chemical properties of bulk glass and glass fibre (chemical resistance, thermal resistance, electrical and optical properties). However, mechanical properties of glass fibres are an exception to the above. It is found that absorption of moisture or aqueous solutions of surface active substances on the fibre surface facilitates formation of micro cracks and promotes reduction of the strength of the fibre by 15-30% independent of the chemical composition of glass [18]. The adhesive phenomena of polymers to glass fibres play an important role in the production processes of FRP composites. These are explained by both intermolecular attraction and intramolecular cohesion forces. It has been pointed out that the adhesion depends on the chemical nature of the polymer and the substrate [19].

Epoxy Resins

Epoxy resins are characterized by a three-membered ring known as the epoxy, epoxide and oxirane or ethoxyline group. Commercially epoxy resins contain aliphatic, cycloaliphatic or aromatic backbones. The capability of the epoxy ring to react with a variety of substrates imparts versatility to the resins [20]. High chemical and corrosion resistance, good mechanical and thermal properties, outstanding adhesion to various substrates, low shrinkage upon cure, flexibility, and ability to be processed under a variety of conditions are characteristics of epoxy resins. The most used epoxy resin is obtained by reacting Bisphenol A, HO-R-OH with epichlorohydrin. Two common industrial processes are used for producing higher molecular weight uncorcrosslinked epoxy resins; the taffy process and the advancement process [21]. In the

taffy process, bisphenol A is reacted at 90 – 95° C with a controlled excess of epichlorohydrin to give macromolecules with glycidyle ether groups on both ends, in presence of NaOH and an inert solvent. A common side reaction may take place between the secondary hydroxyle and the glycidyle ether groups, leading to branching.

In the advancement process, bisphenol A is reacted with a prepolymer, usually the diglycidyle ether of bisphenol A (DGEBA) along with some higher oligomers in the presence of suitable catalysts. The reaction occurs in the homogeneous phase. Epoxies are one of the best adhesive for bonding a wide range of adherends, in both specific and mechanical adhesion. They adhere well to most metals, plastics, wood, glass, concrete, ceramics etc. [22]. This is mainly due to their wetting and penetrating ability, their low viscosity, and the presence of highly polar groups in the molecules. Wetting allows the adhesive, in a low-viscosity liquid form, to come into intimate contact with the adherent, which allows the adhesive forces to become active (Van der waals force of interaction between absorbent and absorbate). The fact that the epoxy molecule also contains a variety of functional groups, both polar and non-polar, is advantageous because this provides good affinity between dissimilar substrates. In general, epoxies wet almost any adherent that can be wetted with other type of adhesives, if the surface tension is low or has been sufficiently lowered by surface-preparation techniques.

Epoxy resin adhesives are capable of bounding a variety of materials with bonds that retain their strength from -50° C to 300° C [20]. The internal strength (cohesive strength) of epoxies to resist cohesive failure is generally good, although this may be affected somewhat by the choice of fillers, modifiers, and bond-line thicknesses [22]. Moisture can penetrate into most epoxies and may create interfacial problems at the adherent surface. However moisture does not seriously degrade the cohesive properties of epoxy. Epoxies have outstanding resistance to solvents, weak acids and alkali compounds. In the area of chemical resistance, although epoxies are considered good, certain generalization must be avoided, since the nature and the type of chemicals, their concentration and temperature, joint design, properties of adherents, and environment are all interrelated factors which must be considered as a whole. In some specific applications epoxies are modified with incorporating soft, small second-phase particles, eg. addition of small rubber/thermoplastic leads to the improvement of fracture toughness of epoxies [23]. Simard et al. [24] have been shown that that the incorporation of reduced SWCNT (r-SWCNT) into brittle epoxy matrices can increase the fracture toughness

by 40% at loadings as low as 0.2 wt % with an overall toughening rate value, dK_{IC}/dwt_f , of $200 \text{ MPa m}^{0.5}$ without any significant effect on elastic or storage moduli. The incorporation of fillers in a polymeric matrix is a cost-effective and faster way of achieving a desired set of properties [25-26]. From these aspects, a growing effort has emerged on the research and development of thermosetting polymer materials from renewable resources with similar properties to conventional epoxy [27]. Epoxidation of various vegetable oils leads to epoxidized vegetable oils (EVOs) with remarkable properties from both technical and economic points of view. Different epoxidized vegetable oils (primarily epoxidized linseed oil-ELO and epoxidized soybean oil-ESBO due to their low cost) have been successfully used as thermosetting epoxy resins as coatings and polymer matrices for a wide variety of reinforcements [28-29].

Hygrothermal Characteristics and Causes

Hygrothermal diffusion in polymeric materials usually takes place in presences of moisture and thermal gradients. The diffusion and/or solubility characteristics of H_2O and other molecular species in polymer materials have been discussed in numerous papers [30-32]. These investigations have highlighted the limited understanding of the actual solution and transport processes in resins and resin-glass composited, particularly the role of chain chemistry and sinks, i.e., chain sites or cavities, in affecting the sorption-desorption process. The molecules dissolve in the surface of a polymer, equilibrating with the atmosphere establish a chemical potential, and diffuse down the gradient. Thus, two fundamental properties are of interest, which lead to an understanding of the phenomena [32].

Transport phenomena in polymers are generally explained by a number of free volume-based theories [33]. The free volume is defined here as the difference between the measured volume of a polymer and the occupied volume, which is the volume occupied by the actual mass of a molecule plus the volume it occupies because of thermally dependent vibration. The free volume is a result of “holes” and “voids” caused by packing irregularity [34].

Water penetration in composite materials of different interfacial strengths is studied as the result of two parallel processes, i.e., diffusion through the polymer matrix and through a network of micro-channels formed along the imperfectly bonded polymer-fiber interface [35]. The mechanical behavior in shear of the glass fibre/epoxy specimens, conditioned at different relative

humidities 0, 60, and 96% RH at 60° C, tested in uniaxial tension at constant imposed displacement rates has shown that the influence of the moisture concentration for the specimens oriented at 45° is very important at 96% RH [36].

The basic similarity between the thermal and moisture diffusion was earlier recognized by Fick [37] following the work of Fourier [38]. Fick's law is generally applicable to rubbery polymers but often fails to describe the diffusion process in glassy polymers [4]. The transition from a glassy to rubbery state occurs at glass transition temperature (T_g). Vrentas and Duda [39] used a new version of the free volume theory of diffusion to describe polymer – solvent diffusion both above and below T_g . Their analysis, which is based in a modification of Fujita's theory [40], corresponds with their conclusion that the diffusion transport could be described by the equation of the classical theory with a concentration independent diffusion coefficient, D . The influence of the thermal/moisture environment upon the behavior of polymeric composites can be divided into three basic problem areas. First, the physics of moisture diffusion in an anisotropic, heterogeneous medium is not well understood. Second, the absorption of moisture has been shown to reduce the T_g of the polymeric matrix. Finally, moisture absorption of the matrix results in swelling of the composite. Since swelling of the composite lamina is restrained in the fibre direction, significant residual stresses are induced in the multidirectional laminate by moisture absorption. In addition, the non-uniform moisture distribution resulting from changes in relative humidity ϕ (RH) of the environment may also produce large residual stresses within the laminate [1].

Moisture absorption in polymer composites is influenced by internal (fibre fraction and its orientation) and external (relative humidity and ambient temperature) factors [5]. Investigators [41] reported on the influence of these factors on the moisture absorption in carbon/epoxy composites, where the carbon fibres are impermeable to moisture.

Epoxy resins which are widely used as matrices in carbon fibre, glass fibres and aramid fibre – reinforced composites, absorb water from the atmospheres with surface layer reaching equilibrium with the surrounding environment very quickly followed by diffusion of the water into all of the materials. The water absorbed is not usually in the liquid form but consists of molecules or groups of molecules linked by hydrogen bonds to the polymers. Liquid water can also be absorbed by capillary action along any crack which may be present or along the fibre – matrix interface [42-45]. The equilibrium moisture content of epoxy resins is very much

dependent upon the relative humidity, but only slightly dependent upon the temperature of exposure [46]. Epoxy resins can absorb moisture up to about 3-4% of their original weight [47]. The equilibrium moisture content $[M_m]$ of a polymer composite is related to the relative humidity (ϕ) term,

$$M_m = a (\phi)^b \dots\dots\dots(1)$$

Where a and b are constants which are to be evaluated experimentally [41]. For a material immersed in liquid, M_m is constant.

The following expression is valid for a graphite/epoxy composite exposed to humid air

$$M_m = 0.00014 (\phi)^2 \dots\dots\dots(2)$$

For a glass/epoxy composite [48] the expression can be given as

$$M_m = 0.01 (\phi)^1 \dots\dots\dots(3)$$

The temperature dependence of composite-diffusion co-efficient (D_c) can conveniently be characterized by an Arrhenius relationship. This relationship for glass composites have been reported [32] as,

$$D_c = 0.1 \exp (-4.429 \times 10^3 - RT) \dots\dots\dots(4)$$

The ability to predict the total moisture content and its distribution within a laminate throughout its lifetime of exposure to steady or changeable environments is important for determining safe allowable on structural strengths. This prediction has been made based on Fick's law.

At time t ,

$$\frac{\partial c}{\partial t} = \frac{\partial (D \frac{\partial c}{\partial x})}{\partial x} \dots\dots\dots(5)$$

Where C is the moisture concentration. A more useful form for composites in terms of moisture level M , and considering D is independent of concentration is given by the following expression

$$\frac{\partial M}{\partial t} = D \frac{\partial^2 M}{\partial x^2} \dots\dots\dots(6)$$

A computer programme for modeling moisture diffusion using the finite difference method to solve the Fick's law has been described [49]. The prediction of moisture diffusion using Fickian theory has been found adequate for most practical purposes, provided that the resin exhibits approximate Fickian absorption [50-51]. This modeling provides a powerful analytical tool for

designing accelerated ageing procedures that use either steady or non-steady environmental conditioning.

Anomalous Fickian Behavior

Non-Fickian behavior is a material characteristic. The change of polymer structure and moisture distribution determines the diffusion mode. When the polymer structure changes much faster than the moisture concentration the diffusion follows Fick's law. If relaxation processes inside the material progress at a ratio comparable to the diffusion processes, the diffusion is said to be non-Fickian. The absorbed moisture may change (generally decrease) the T_g thereby affecting the diffusion behavior of the materials [4]. Fick's law is generally applicable to rubbery polymers, but fails to characterize the diffusion process in glassy polymers. The anomalous Fickian behavior is supposed to govern the diffusion behavior under the following conditions: (a) cracks develop in the materials and delamination occurs, (b) moisture diffuses through the fibre/matrix interface, (c) there are voids in the matrix, and (d) the matrix itself exhibits non-Fickian behavior. Pritchard et al.[52] have modified the model proposed by Berens et al.[53] model to analyze the anomalous Fickian behavior of unreinforced polyester resins. They have stated that the observed water absorption is the sum of a Fickian term, M_F and a resin relaxation term, M_R . The M_R term allows for the relaxation of the polymer matrix under the influence of swelling stresses. The true water absorption, M_t is given by:

$$M_t = M_F + M_R$$

Where

$$M_F = M_{F_{max}} \left[1 - \frac{8}{\pi^2} \sum_{j=0}^{\infty} \frac{\delta^2}{2j+1} \exp\left[-\frac{Dt}{h^2} \pi^2 (2j+1)^2\right] \right] \dots\dots\dots(7)$$

and the relaxation term for polyester resin is taken as

$$M_R = M_{R_{max}} [1 - \exp(-Kt^2)] \dots\dots\dots(8)$$

In the above expression, 'D' is the diffusivity, 'h' is the sample thickness and 'K' is the relaxation rate constant.

Experimental determination of $M_{R_{max}}$ for the cast resin is not possible as it may disintegrate before the necessary quantity of water is absorbed. An assumed value may be considered from

that observed for the laminates, taking the volume fraction of resin into account. The activation energy for the relaxation stage is much higher compared to that of Fickian stage. It relates to the creation of additional free volume by viscoelastic effects, hydrolysis or by a combination of the two. Crack formation [54], and fibre/resin debonding may also contribute to it.

There is a maximum safe temperature and, in some case, a maximum safe humidity above which moisture diffusion deviates from that described by Fick. Whitney et al. [55] have shown (for HC 3501 resin system) that at a temperature of 71° C, Fickian diffusion is no longer apparent. For Ciba-Geigy 914 resin system it has been demonstrated [51] that Fickian diffusion is apparent for temperature upto 96% RH. Bao et al. [56] compared and analyzed moisture diffusion behaviors of the bismaleimide resin and various composites at four different temperatures, i.e. 35° C, 50° C, 70°C and 90° C. They reported that temperature affects moisture absorption in several aspects and an increase in temperature accelerates short term diffusion and increases the diffusion coefficient. In some treatments and conditioning temperatures, Langmuir and Fickian models could be statistically equivalent [56]. However, the Langmuir model should be favored when studying adhesive or carbon/epoxy conditioned in anti-icing additive: it is a more accurate model and may capture the moisture uptake. Grace et al. [57] proposed a new method to characterize three-dimensional, anisotropic moisture absorption in polymer matrix composites using experimental gravimetric absorption data. They achieved it by using the three-dimensional hindered diffusion model to recover the moisture absorption properties of composites which may exhibit Fickian or non-Fickian behavior.

Fickian Solution and Causes of Departure

It has been argued that under most conditions the moisture content of composites may be calculated using Fick's law [32]. As an improvement over the one – dimensional theoretical prediction (Fickian solution), some three dimensional analyses [58] and a two phase moisture absorption model [59] have also been reported.

According to one–dimensional diffusion law, average moisture concentration (weight percentage) after time, t, in a specimen of width 2L, is given as [60] presented in equation (9) and (10)

$$M_m = M(\pm L, t) \dots\dots\dots(9)$$

$$M(x, 0) = 0 \dots\dots\dots(10)$$

$$t^* \frac{Dt}{L^2} \text{ (a non - dimensional time)}$$

Where D denotes the co-efficient of diffusion.

For sufficiently short time ($0 < t^* < 0.55$)

Equations (9) and (10) give

$$M(t) = 2M_M (t^*/\pi)^{1/2} \dots\dots\dots(11)$$

Whereas for long time ($1.32 < t^*$) an expression of the form

$$M(t) = M_m \left[1 - \frac{8}{\pi^2} e^{-\frac{\pi^2 t^*}{4}} \right] \dots\dots\dots(12)$$

Is obtained.

Eqns. (11) and (12) together are known to show the following special features:

- a) It is concentration and history independent.
- b) A clearly defined saturation level is attained.
- c) The temperature dependence enters through a non – dimensional time t^*Dt/L^2
- d) When plotted versus $\sqrt{t^*}$, the total moisture weight gain M is given by a straight line upto about 62% of saturation.

But the actual weight gain data, however, do not fully confirm to the classical prediction of Eqns. (11) and (12). The most important departure as reported by Upadhyay et al. [61] are presented below.

- i) Saturation may not be attained. Some materials may either gain weight on a continuous basis, or revive the weight – gaining process after an apparent pause.
- ii) The process may be concentration dependent.
- iii) The process may exhibit history dependence.
- iv) The co-efficient of diffusion may be quite sensitive to temperature.

The probable causes of departure of the experimental data from the classical prediction has been analysed [61]. The classical model assumes the diffusion phase to be a ‘free’ phase. But in case of moisture, the molecules are not free; they are feebly bonded with hydrogen bonds even in the vapour state at room temperature. Therefore, the actual quantity of moisture diffusion into the polymer-matrix should be lower than the classical prediction provided the other factors do not overlap. The classical diffusion model assumes that a material can absorb moisture to its capacity instantaneously and the boundary moisture concentration is established instantaneously. But in

reality some finite time is always required for the establishment of the boundary condition. This implies that the actual time taken for reaching a given concentration level in the material will always exceed the prediction of the classical model.

Swelling of the matrix and the resulting stresses, which are consequences of moisture sorption, increase the co-efficient of moisture diffusion. Thus the process of moisture diffusion is inherently concentration dependent.

In actual practice the co-efficient of diffusion is quite sensitive to environmental temperature. Higher temperatures result in higher kinetic energy and mobility of molecules and pave way to higher co-efficients of moisture diffusion.

The investigators [61] have modified empirically the Fickian solution and given the solution for $M(t)$, the expression for moisture content (% weight) at any time,

$$t \text{ as, } M(t) = M_0 (1 + d/2M_0)^2 \dots\dots\dots(13)$$

Also $M_0(t)$ is given as under:

$$M_0(t) = \frac{2}{\pi} - b - M_m - \frac{D_R \exp \left(\frac{A}{T_R} - \frac{A}{T} \right) \cdot (t - t_s)}{L^2} \dots\dots\dots(14)$$

In which

$M_0(t)$ is moisture content when concentration dependence is neglected.

d is a constant (to be determined empirically)

b is a dimensionless constant ($0 < b < 1$)

t_s is a measure of time required for the establishment at the boundary concentration.

D_R is the co-efficient of diffusion at absolute reference temperature T_R .

A equals to E/k , where E is the activation energy and k is Boltzman constant.

Although the quantitative accuracy of the above suggested modifications have yet to be tested, it seems to satisfy the minimal conditions of variability and is able to explain the departure of the Fickian model with the recorded experimental data.

Hydrothermal Effect on Mechanical Behavior

Glass Transition Temperature

Research is being continued to understand the relationship between structural integrity of FRP composite materials and forces and environment to which they are subjected, in order to explore their full potential. The moisture is absorbed by the polymer matrix causing it to swell, and this can induce internal stresses or relieve residual stresses caused by contraction during curing of polymers. This may result in microvoids or cracks which would weaken the polymer or the polymer/fibre interface bond [62]. It has been reported that the moisture content above 1% shows a linear relationship between amount of water absorbed and overall volume or thickness change [45, 63]. Water also acts as a plasticizing agent and as such will lower the T_g and related properties (e.g. heat distortion temperature) of a resin. It is observed that for each 1% water pick-up there is a drop in T_g of about 20°C [64]. The Bueche – Kelley theory provides the following estimates of T_g [65]

$$T_g = \frac{\beta_r (1 - v_f) T_{gr} + \beta_f v_f T_{gf}}{\beta_r (1 - v_f) + \beta_f v_f} \dots \dots \dots (15)$$

where β_r and β_f and v_r and v_f are the moisture expansion co-efficients and the volume fractions of the resin and the fibre.

Residual Stresses

Composite materials deform when they absorb moisture or when the temperature changes. In the linear theory the resulting non-mechanical strains are simply added to the mechanical strains induced by the stress to obtain the total strain.

To determine the resulting strain Tsai et al. [3] have assumed that the composite is elastic in nature and that the response of the material does not depend on the history of the input but only on the initial and final states. i.e. it is a state function and not a path function. We also conceptionally imagine that temperature is changed first, followed by moisture absorption and finally the application of stress (Fig.1). Let us denote the strains induced by the temperature change and moisture absorption by e^T_i and e^H_i , respectively. The mechanical strain due to σ_i is given by $S_{ij}\sigma_j$. It should be noted that since stress is applied at temperature T and moisture concentration C , $S_{ij}(T, C)$ is the compliance measures under such condition. The final strain (e_i) is the sum of the foregoing three types of strains.

$$e_i = e_i^T + e_i^H + S_{ij} \sigma_j \quad \dots \dots \dots (16)$$

In general, e_i^T and e_i^H are non – linear functions of T and C, respectively. However, the thermal expansion co-efficient α_i and the swelling co-efficient β_i can be used to calculate e_i^T and e_i^H , respectively, that is

$$e_i^T = \alpha_i * (T - T_0) \quad \dots \dots \dots (17)$$

$$e_i^H = \beta_i * C \quad \dots \dots \dots (18)$$

Typical values of thermal expansion co-efficients for a graphite/epoxy (T300/5208) unidirectional composite are 0.02 $\mu\text{m/mK}$ (longitudinal) and 22.05 $\mu\text{m/mK}$ (transverse) [3].

Residual stresses are also induced in polymeric composites during fabrication [2]. This curing or fabrication stress in certain graphite/epoxy laminate may be large enough to cause ply failure in the absence of applied stress or premature failure upon tensile loading [66]. Determination of curing stresses in a composite laminate requires some understanding of the fabrication process involved. This stress is induced by the thermal expansion mismatch during fabrication. As the curing progresses, a change in the internal structure of the matrix epoxy start to take place in the form of entanglement of polymer molecules, i.e., crosslinking occurs. When crosslinking occurs, the epoxy shrinks (chemical shrinkage). The resulting deformation of a unidirectional composite in the transverse direction is much larger than in the longitudinal direction. Therefore, within laminate the deformation of one ply is constrained by the other plies with different fibre orientation and hence residual stresses are built up in each ply. However, since most cross-linking takes place at the highest temperature, called the cure temperature, the epoxy can be still viscous enough to allow complete relaxation of the residual stress. Thus, the cure temperature can be taken as the stress-free temperature, as long as almost all cure takes place at the cure temperature. In reality, however, the stress – free temperature will vary with the cure process employed because the property change during cure is very much time-dependent [3]. It has been reported [2] that the residual stress – free temperature is lower than the curing temperature.

Effect of loading speed on environmentally conditioned glass/epoxy composite is investigated by Ray [67]. It is observed that the hygrothermally conditioned glass fibre/epoxy composite is sensitive to loading speed. Further freezing treatment of absorbed moisture results in further damaging effects and these damaging effects are more evident at lower loading speed.

The most important conclusion is that the hygrothermal stresses are analogous to thermal stresses: the effect is dilatational, there exists co-efficient of hygroscopic expansion, β_i , is

analogous to the co-efficients of thermal expansion, α_i , and the induced stresses are self-equilibrating across the laminate thickness [3].

Strength and Stiffness Properties

It is observed that room temperature properties may be significantly altered by water absorption [47,68-69]. Joshi [62] has reported the effect of moisture on the mechanical properties of composites (carbon fibre – reinforced epoxy resins) which are measured at room temperature and at elevated temperature. Initially increase of about 10% in the interlaminar shear strength (ILSS) value were recorded with 0.1 weight % absorbed moisture, then the ILSS decreased by 25% (from 115 MPa to 90 MPa) when the composite had absorbed a maximum amount of moisture (approximately 2%). Ray [70] studied the effect of freezing and thermal spike on hygrothermally conditioned specimen and reported that the frozen moisture is more detrimental for interlaminar shear strength of glass/epoxy composites as compared to only moisture. Thermal spike at 250°C results in desorption of absorbed moisture as a consequence of which less detrimental effects of absorbed moisture were observed. Lassila et al. [71] reported that flexural strength of specimens with 45 vol% fraction E-glass fibers varied from 759 to 916 MPa in dry conditions whereas Water-stored (exposed to 30 days) specimens showed flexural strengths of 420–607 MPa. Wan et al. [72] studied moisture absorption desorption and its effect on mechanical properties of 3D braided carbon fibre– epoxy (denoted as C3D/EP) and unidirectional carbon fibre–epoxy resin (CL/EP) composite, their results are illustrated in table 1.

Chu et al. [73] studied the effect of water sorption on mechanical performance pultruded E-glass/vinylester composites. For woven glass/epoxy reinforced polymer laminates with 1.29% absorbed moisture, delamination load-carrying capability reduced to 40% [74].

It is, in general, observed that the mechanical properties degrade when subjected to moisture and temperature environments. However, these material data have direct relevance to design applications; they need further investigation.

Other Environmental Effects

During the service life of a military aircraft there may be situations in which certain areas of structure are subjected to rapidly high temperature excursions (thermal spikes). For example, this may be caused by ground–reflected engine efflux experience by VTOL aircraft [42].

Measurement of the variation of the weight of carbon fibre/epoxy composite laminates during the tests indicates a change in the moisture kinetics resulting in increased moisture equilibrium levels at spike temperature upto 175° C. The spiking at a temperature range between 200–300°C shows a marked loss of laminate weight. This may not be attributed to the loss of water alone. Permanent damage such as cracking in the matrix is evident in some cases [75]. It is concluded that the deterioration is probably caused by thermal spiking through exposure to the engine efflux, and that the damage subsequently propagated by acoustic fatigue.

Ray [76] investigated the effects of thermal shock (i.e.+80°C to -80°C and -80°C to +80°C temperature) on interlaminar shear strength of kevlar/polyester composite. The experimental results revealed that both type of environment resulted in damage in interfacial bonding and which leads to the loss in interlaminar shear strength of the composite. While in another investigation [77], thermal shock (+80° C to -80° C temperature) resulted in improvement in flexural modulus of kevlar polyester composite. Thermal shock conditioning on glass/epoxy composites [78] resulted in improvement in ILSS for given durations (i.e.5, 10, 15, and 20 min.) except for 5 min. conditioning time.

When exposed to rapid high-intensity heating, organic-matrix composite structures display a marked reduction in load-carrying capability due largely to the pronounced degradation in mechanical properties (ultimate strength, elastic moduli, ductility, etc.) at temperatures above 200° C [79]. Other adverse effects of elevated temperature exposure include ablation of critical load-bearing components and high stress intensification which may accompany localized burn through. In addition, severe thermal stresses may be induced in regions subjected to concentrated heating and increase the likelihood of failure [32].

Radiation dose upto thousands of Megarads do not appreciably degrade the tensile strength or modulus of polymer/graphite composites, if the irradiation takes place in the absence of oxygen; there is a slight decrease in the transverse shear strength [80]. Irradiation in the presence of oxygen is considerably more damaging to the material than in an oxygen-free environment. Even small amount of residual oxygen in a relatively oxygen-free environment have a significant effect. The effect of radiation on the carbon fibre alone is not great. Epoxies undergo additional crosslinking reactions as well as chain scission.

Ray [81] experimentally investigated the effects of ultra-low freezing and thawing of glass-polyester composites for varied weight fraction constituents at different loading rates.

Loading rate sensitivity is strongly evident at lower range of crosshead speed (0.5 to 50 mm/min) and ILSS values are found to increase in all situations with more loading speed in the range. Loading rate sensitivity seems to be controlled by the area of interfaces and the percentage of polymer matrix phase present in composites [5]. The effects of changing seawater temperature during immersion ageing of glass/epoxy and glass/polyester composites have been investigated by Ray [82]. The measured shear strength was higher at all points of the cyclic environment at higher crosshead speeds. A fall in ILSS was noticed for both the composite systems. It was also observed that the reduction in shear strength was dependent on the volume fraction of fibres. Kalfon et al. [83] studied the combined effects of non-uniform heating and moisture in glass and carbon fiber-reinforced epoxy laminates. They found that delamination damage in a form of bulging occurs only in the presence of a threshold level of moisture of about 1 wt%. This threshold level corresponds to the critical moisture content found to produce major mechanical property reduction and interlamina separation.

Failure Mechanisms

Composite materials are complex structures which may fail by a number of mechanisms which are not encountered in more homogeneous materials. The possible failure modes are dominated by the fibre fracture and the shear and tensile failure of the matrix. The study of load transfer between a fibre and the matrix has been carried out by Cox [84], who has analyzed the stress transfer around a single discontinuous fibre embedded in a matrix. This has come to be called the shear-lag theory. Galoitis et al. [85] have experimentally confirmed these predictions. The basic assumption of the shear – lag theory is that all the tensile loads are carried by the fibre and all the shear loads are carried by the matrix, although in practice the matrix surrounding the fibre also experiences some tensile stresses. The load transfer into the fibre from the matrix occurs over a length of fibre commonly called the ineffective length, which is defined when some proportion of the remote fibre load is reached.

It is often impossible to be certain of the failure mechanism involved of composite materials. Thus discrimination has to be searched explained and established between the various failure mechanisms. The possible failure modes range from simple loss of structural stiffness due to gross inelastic deformation (e.g. yielding), through a reduction in load – carrying capacity, to localized deformation and damage growth (e.g. delamination) to the complete loss of load –

carrying capacity by gross macroscopic deformation and separation (e.g. fracture). Thus, the failure can be gradual or rapid and may or may not be catastrophic in nature [86]. The acoustic emission technique has been utilized to obtain information on various mechanisms involved in the composite failure process. Initially the frequency analysis of the acoustic signals has been used and giving way progressively to the amplitude analysis to examine failure mechanisms [87]. Most authors suggest that weak signals and hence low amplitude can be expected from the microcracking of the matrix resin, medium values for interfacial failure and high amplitude for fibre breaks [88]. But Valentin et al. [89] have reported the highest amplitude signals correspond to the matrix cracking parallel to fibres, whereas the fibre failure results in smaller amplitude emissions because of the dimensions of the fibre for carbon fibre / epoxy composites.

As stated by Wells [90], a composite material can suffer any of the modes of failure of its constituents together with a few more arising from their combination. It is for these reasons that the basic fracture mechanics equation for the onset of crack growth is affected independent [91] of both sides of the equation. The fracture mechanics equation is

$$G = G_c \dots\dots\dots(19)$$

Where G denotes the crack-driving force (units of energy per unit area of crack extension) and G_c is the energy dissipated at the crack tip (per unit area) during an increment of crack advance.

Just as for metals, it can be assumed that failure in a fibre composite emanates from small, inherent defects in the material [86]. These defects may be broken fibres, flaws in the matrix, and debonded interfaces. It can be considered that the longer the fibre the greater the probability that a critical defect exists which may cause individual fibre breakage at loads well below the average fibre strength of the composites. After a single fibre breaks, more fibre breakages would occur resulting in debonding and separation of the fibre and matrix due to weakening owing to the single fibre breakage. Defects in the matrix may also lead to yielding and fracture of the matrix between fibres. This will create further stress concentrations at the fibres and fibre/matrix interfaces. Thus, at relatively low load levels small cracks are likely to occur that will have a size of the order of the fibre diameter or the fibre spacing.

Even after microcracks coalesce to form an identifiable crack-line flaw, the size of the damage neat the crack tip will still be small relative to the crack length and other dimensions of the body. Hence, qualitatively, the same failure mechanism (e.g. fibre breakage, debonding and matrix yielding or cracking) will always be important in the fracture process. This will be true whether

the composite is composed of uniaxially or multiaxially oriented fibres. These failure mechanisms can be characterized in terms of energy absorption processes. Theoretical estimation of the energy absorption per fibre associated with each of these has been compiled by Phillips et al. [86]. A brief qualitative description relevant to a microcrack running transverse to the fibres is shown conceptually in Fig.2.

Fig.2 shows several possible local failure events occurring prior to the fracture of a fibre composite. At some distance ahead of the crack, the fibres are intact. In the high stress region near the tip, they are broken although not necessarily along the crack plane. Immediately behind the crack tip fibres pull-out of the matrix, absorbing energy if the shear stress at the fibre/matrix interface is maintained while the fibres are pulled out. Theoretical treatments of the mechanics of the fibre / matrix interface have been presented by several investigators [92-94].

In some bonded composites, the stresses near the crack tip could cause the fibre to debond from the matrix before they break. When total debonding occurs, the strain energy in the bonded length of fibre is lost to the material and is dissipated as heat [86]. The fibre 'stress - relaxation', a variation of the debonding model, estimates the elastic energy that is lost from a broken fibre when the interfacial bond is not destroyed. It is also possible for a fibre to be left intact as the crack propagates. This process, known as 'crack bridging', can also contribute to the toughness of the material. The analysis of debonding and crack bridging for brittle fibres in a perfectly plastic material has been carried out by Piggott [95].

A model developed by Kanninen et al [86] treats the composite material as heterogeneous when it is essential and as an anisotropic continuum only where it is permissible. The approach can be linked conceptually to the well-established singular perturbation and matched asymptotic expansion techniques of fluid mechanics. Here, a flaw is divided into distinct 'inner' and 'outer' regions. In each of these regions, the material is modeled in different ways. The inner region, which either contain the tip of a macroscopic crack or, an entire microscopic crack, is considered on the microscopic level and treats the material as being heterogeneous. This region is referred to as the local heterogeneous region (LHR). The outer region surrounds the crack tip region and treats the material as a homogeneous orthotropic continuum. A typical LHR model is shown in Fig. 3 which depicts a unidirectional fibre composite.

The proper application of fracture mechanics to composite materials is one that can take account of the applied loading, the geometry of the structure and the environmental effects while reflecting the properties of its constituents and its micro-structural design.

Fibre/Matrix Interface Behavior

Characterization of Fibre / Matrix Interfaces

The bond between the fibre and the matrix is of prime importance to the performance of composite materials, since this controls stress transfer to the fibres and stress distribution between fibres. This interface bond is not only significant to the strength and stiffness of the composite, but it also governs mechanisms of damage accumulation and propagation [96]. It thus plays a central role in a fibre composite. But it is surprising, that still very little is known about it. Earlier work has suggested that the role of the interface is only secondary for a composite which has aligned fibres and which are very long, when the stress is in the fibre direction [97]. However, toughness, shear strength and compression strength are highly dependent on the interface, and the bond at the interface has to be strong for the shear and compression strengths to be good [95, 97-99]. Current interest is in producing composite systems in which the fibres and the resin matrices to give the desired optimum properties by adjusting the fibre/resin interface. Adjustment may take the form of novel sizes, coating or surface treatment. The effect of fibre surface treatment on the mechanical properties of carbon fibre-reinforced composites has been well documented [100].

The strength of the fibre/resin interface is a key property when investigating the macromechanical behavior of composite, since it is a measure of the integrity of the interface. Accurate evaluation of this parameter has until now been very difficult although there has been keen interest for many years. Grey [101] had reported 16 different tests for evaluating bond strength and concluded that of these only six out of these sixteen tests, including single fibre pull-out, come close to the requirement for a satisfactory test method. All these techniques involve pulling the fibre from the matrix, although Mandell et al. [102] have proposed a fibre push-out test but it requires a number of refinements before it could guarantee reproducibility. The major drawback for all these tests is that they only produce a value for the pull-out force from which the mean interfacial shear stress, τ , for the length of the embedded fibre may be calculated using the following relation:

$$T = \frac{F}{\pi dl} \dots\dots\dots(20)$$

Where F is the debonding or first peak force and πdl is the interface area, where d is the fibre diameter and l is the embedded length.

But this does not provide a value for the maximum interfacial shear stress, which corresponds to the strength of the interfacial bond, and is a key parameter in adjusting the fibre / resin interface for optimum composite performance [103]. The load transfer into the fibre from the matrix occurs over a length of fibre commonly called the ineffective length. The shear stress is calculated from the above equation for a fibre whose embedded length is greater than this ineffective length, then the shear strength will be underestimated. This is because a length of fibre is included over which little stress transfer takes place. Thus the smaller the embedded length the greater will be the estimate of the shear stress. Extending this argument the maximum shear stress will be obtained when the embedded length tends to zero. Pitkethly et al. [103] have presented a method whereby the maximum interfacial bond shear stress may be evaluated from the simple measurement of the pull-out force and fibre dimensions. Additional information may also be obtained concerning the interface morphology, like interface shear modulus and the interface thickness which will be of use in micromechanical modeling of the interface region. This is currently the subject of further investigation.

Marshall et al. [104] have designed a ‘micro-composite’ single fibre pull-out test to permit the visual observation of events at the fibre/matrix interface and the collection of detailed mechanical data as interface debonding and fibre pull-out occur. Several characteristics displayed by the load/displacement measurements have been directly correlated with observed events such as fibre Stick-slip [105] and interfacial frictional effects. The linear relationship between debonding force and embedded length (Fig.4) indicates a failure mechanism of simultaneous yielding of an interface having a uniform stress distribution.

Environmental Effects on Fibre / Matrix Interface

Mechanical properties of fibre – reinforced polymeric composites degrade upon exposure to various environmental factors including hydrothermal (immersion in water) and hygrothermal (contact with water vapor) exposures [4,106]. Moisture can affect each of the three phase in a composite, namely, the fibre, the matrix and the interfacial zone. The contribution of each phase of any observed change in mechanical properties depends upon the direction of applied stress in

relation to fibre orientation. Changes in fibre strength should influence the longitudinal tensile strength of the composite, whereas changes in the matrix and/or the interfacial zone influence the off – axis and shear strength of the composite. It is generally believed that a major mechanism of shear strength reduction is partially debonding or weakening of the interfacial bond [107].

It is also reasonable to assume that the interfacial shear strength is the net result of a number of contribution to the fibre / resin adhesion, possibly including chemical bonding, secondary forces of attraction (Van der Waals, H-bonding, acid–base interactions etc.), residual thermal compression forces due to differential shrinkage, and mechanical locking friction between the fibre and the resin. Moisture may penetrate into composite materials by diffusive or capillary processes [108-110]. The former involves direct diffusion of water molecules into the matrix, while the capillary mechanism depends on movement of water molecules along the fibre/matrix interfacial areas followed by diffusion from the interface into the resin.

An experimental method, called the ‘micro–bond’ technique, for direct measure of the interfacial adhesion between a fibre and a resin matrix has been developed [111], which is demonstrated in Fig. 5. The technique involves application of micro-droplets of resin (30-200 μm long) onto a single fibre, followed by measurement of the force required to pull out or debond the fibre from each droplet. This technique has been applied successfully to various fibre/resin systems and to study the consequences of fibre surface treatments [105]. Later, Gaur et al. [107] have used the micro-bond technique to investigate the effect of environmental exposure on the interfacial shear strength of E-glass/epoxy and Kevlar/epoxy systems.

Gaur et al. [107] have reported that the technique is effective in isolating and evaluating the effects of environmental exposure on interfacial shear strength in composites. The complications of resin deterioration and cohesive failure can be circumvented due to the small dimensions involved in the method. They have found that upon hydrothermal aging at 88⁰ C temperature, the bond strength decreases rapidly at first, and further ageing does not produce any further reduction, implying that there are certain components of interfacial adhesion which are unaffected by hydrothermal ageing. Upon vacuum drying the aged specimens, bond strength is completely regenerated for both untreated and surface modified Kevlar–49 /Epon–828 system. This may be due to reduction of compressive forces caused by swelling of the crosslinked epoxy network and, consequently, is completely reversible. However, partial regeneration for E-glass/Epon828 of the bond strength reduction because of drying is the result of either irreversible

hydrolysis of chemical bonds or breakdown of secondary forces of attraction, and therefore only partial regeneration is observed.

The shear strength of the epoxy is known to suffer a substantial loss on hydrothermal ageing [4]. This could change the locus of failure from the interface and produce cohesive failure in the epoxy, particularly in composites that have greater interfacial adhesion due to fibre surface treatments [112-113]. The mechanical properties of epoxy composites, including interfacial shear strength, may continue to deteriorate for up to several years, although most of the reductions are observed within a few hours [114]. The short term reductions are related to diffusion and capillary processes, whereas the long term reductions are attributed to leaching out of low molecular weight uncrosslinked epoxy molecules and slow dissolution of fibre surface treatments.

Remarks

The measured critical surface tensions of all plastics (18–50 dyn/cm) are well below the surface tension of water (72.8 dyn/cm); therefore, all plastic surfaces are hydrophobic. The hydrothermal diffusion usually takes place in presence of thermal and moisture gradients. In many cases water absorption obeys Fick's Law, and diffusion is driven by the moisture concentration gradient between the environment and the materials producing continuous absorption until saturation is reached. The rate of diffusion increases rapidly with the rise of temperature. The concentration gradient of moisture is developed due to non-uniform distribution of moisture. The presence of imperfection and internal stresses also accelerates the process of diffusion. The water absorbed is not usually in the liquid form but consists of molecules or groups of molecules linked by hydrogen bond to the polymer. In addition, liquid water can be absorbed by capillary action along any crack which may be present or along the fibre-matrix interface. Experimental evidence indicates that for most of polymeric composite materials the hydrothermal behavior is Fickian nature. Thus, the absorption and desorption curves when plotted against time are always concave towards the time axis and asymptotically reach the equilibrium value. But, the diffusion behavior of glass polymer does not obey the Fick's law. Non-Fickian behavior is also a material characteristic. The deviation from Fick's law becomes more pronounced at an elevated temperature and for materials immersed in liquids.

Today more and more structural components are either being designed with polymeric composites or being replaced from their metallic counterparts by composites. The hygroscopic nature of polymeric systems, however, necessitates a complete understanding of the interaction between structural integrity and moist environment. Research reports published in the last two decades have already established the fact that there is a certain amount of degradation of mechanical properties, especially shear, flexural, compression and $\pm 45^\circ$ axial tensile strengths when the polymeric composites are exposed to thermal and moist environment. Research developments on the hygrothermal response of laminated polymeric composites have shown that absorbed moisture reduces the glass transition temperature of a polymeric composite and also causes plasticization of it, resulting in the reduction of the composite strength properties dominated by matrix characteristics.

Interfacial durability is a primary factor because environments to which the FRP composites are exposed during service can degrade interfacial adhesion as well as properties of the materials as a whole [115]. The design and development of glass, carbon and aramid organic fibres reinforced polymeric composites is the beginning of an era of new light weight and durable structural materials. The precise mode of failure of composite is a function of the status of environmentally conditioned interfaces and time of exposure, thus complicating the prediction of its performances and behavior. The uncontrolled and non-uniform degradations at micro- and macro-levels manifested in the interphase because of different environmental conditions during service life. These may restrain its uses in the short term and also in the long term reliability of the material. An urgent need exists here to evaluate and assess the character and the chemistry of the interfacial region by the advanced resolving techniques, unless otherwise the full potential of FRP may not be realized and explored in service life.

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REFERNCES

1. R.B. Pipes, J.R. Vinson, and T.W. Chou, *J. Compos Mater*, **10**,129 (1990).
2. H.T. Hahn, *J. Compos Mater*, **10**, 266 (1976).
3. S.W. Tsai, and H.T. Hahn, *Introduction to Composite Materials (Ed.)*, Technomic Publishing Company, Inc. Lancaster, Pennsylvania, USA (1980).
4. G.S. Springer, *Environmental Effects on Composite Materials (Ed.)*, Technomic Publishing Company Inc., West Post, USA (1981).
5. B.C. Ray, *J.Colloid Interface Sci.*, **298**, 111 (2006).
6. I. Cerny, R.M. Mayer, *Compos Struct*, **92**, 2035 (2010).
7. I.N. Ermolenko, I.P. Lyublner and N.V. Gulko, *Chemically Modified Carbon Fibers and their Application (Ed.)*, VCH Publishers, Inc. New York, USA (1990) .
8. W. Watt and B.V. Perov, *Handbook of Composites (Ed.)*, **1**, Amsterdam, North Holland (1985).
9. D. W. McKee, C. L. Spiro, and E. J. Lamby, *Carbon*, **22**, 285 (1984).
10. E. Fitzer, W. Frchs, and M. Heine, *Carbon*, **24**, 387 (1986).
11. G.M. Jenkins, and K. Kawamura, *Polymeric Carbons Carbon Fibre, Glass and Char (Ed.)*, Cambridge University Press, London (1976).
12. D. A. Baker, T. G. Rials. *J Appl.Polym.Sci.* **130**, 713 (2013).
13. C.D.Warren, F.L. Paulauskas, F.S. Baker, C.C. Eberle, A Naskar. Proceedings of the SAMPE Fall Technical Conference, Memphis, TN, USA, September 2008.
14. S.M. White, J.E. Spruiell, F.L. Paulauskas, Proceedings of the International SAMPE Technical Conference, Long Beach, CA, USA, May 2006.
15. F.S. Baker, D.A. Baker, N.C. Gallego, Carbon fiber from lignin. Proceeding, Carbon 2010, Clemson, SC, July 11–16, 2010.
16. F.S. Baker, D.A. Baker, N.C. Gallego. Proceeding, SAMPE '10 Conference and Exhibition, Seattle, WA, May 17–20, 2010.
17. W. Watt, and B.V. Perov, *Handbook of Composites – Strong Fibres*, **1**, Elsevier Science Publishers, Amsterdam, Netherlands (1988).
18. M.S. Aslonova, *Glass Fibers (Ed.)*Kkhimia, Mosco (1979).

19. G.D. Andrievskala, *High Strength Oriented Glass Reinforced Plastics (Ed.)*, Nauka, Moscow (1966).
20. J.I. Kroschwitz, H.F. Mark, N.M. Bikales, C.G. Overberger, *Encyclopedia of Polymer Science and Engineering (Ed)*, Vol. 6, John Wiley Sons, New York, USA (1986).
21. D. Feldman, *Prog. Polym. Sci.*, **15**, 603 (1990).
22. C.V. Cagle, *Handbook of Adhesive Bonding (Ed.)*, McGraw Hill Book Company, New York, USA (1973).
23. G.M. Odegard and A. Bandyopadhyay, *J. Polym. Sci. Part B Polym. Phys.* **49** (24) 1695 (2011).
24. Y Martinez-Rubi, B Ashrafi, J Guan, C Kingston, A Johnston, B Simard, V Mirjalili, P Hubert, L Deng, and R J Young. *Appl. Mater. Interface Sci.* **3**, 2309 (2011).
25. H.W. He, K.X. Li, J. Wang, G.H. Sun, Y.Q. Li, J.L. Wang. *Mater Des.* **32**:4521 (2011).
26. Y. Nakamura, M. Yamaguchi, m. Okubo, T. Matsumoto. *J Appl Polym Sci* **45**:1281 (1992).
27. V. Fombuena, L. Bernardi, O. Fenollar, T. Boronat, R. Balart. *Mater. Des* **57**:168 (2014).
28. M.D. Samper, V. Fombuena, T. Boronat, D. Garcia-Sanoguera, R. Balart. *J Am Oil Chem Soc* **89**:1521 (2012).
29. T. Takahashi, K.I. Hirayama, N. Teramoto, M. Shibata. *J Appl Polym Sci* **108**:1596 (2008).
30. V. Stannett and J.L. Williams, *J. Polym. Sci. Part C: Polym Symposia*, 10, **45** (1965).
31. E Sacher, J.R. Susko, *J. Appl. Poly Sci.* **27**, 3893 (1982).
32. G.S. Springer, *Environmental Effects on Composite Materials (Ed.)*, **3**, Technomic Press, West Pork, USA 1988.
33. J. Crank, G.S. Park, *Diffusion in Polymers (Ed.)*, Academic Press Inc. London 1968.
34. M.J. Adamson, *J. Mater. Sci.* **15**: 1736 (1980).
35. C.J. Tsenoglou, S. Pavlidou, C.D. Papaspyrides. *Compos.Sci.Technol.* **66**: 2855 (2006).
36. A Naceri. *Strength Mater* **41**:444 (2009).
37. A. Fick, *A. Ann Physik Chemic*, 170, 59 (1855).
38. J.P. Fourier, *TheorreAnalytique de la charendon*, Paris 1822, English Translation by Freeman, A., Dover publication, New York, 1955.

39. J.S. Vrentas and J.L.Duda, *J. Appl. Poly. Sci.*, **22**, 2325 (1978).
40. H Fujita, 1961, Fortschr.Hochpolym.-Forsch.,Bd.3 ,S.1
41. C. H. Shen and G.S. Springer, *J. Compos. Mater.***10**: 2 (1976).
42. T.A. Collings and D.L. Mead, *Composites*, **19**:81 (1988).
43. J.M. Whitney, and C.E. Browning, ASTM STP 658, ASTM, Philadelphia, PA, USA (1978).
44. H.G. Carter, and J.G. Kibler, *J. Compos. Mater.***12**, 118 (1978).
45. R. Delasi, and J.E. Whiteside, Effect of Moisture on Epoxy Resins and Composites, Advanced Composite Materials – Environmental Effects, Vinson, J.R., (Ed.) ASTM – STP 658 (1978).
46. H.U. Rsshid, Ph.D Thesis, University of Sheffield, 1978.
47. W.W.Wright, *Composites*, **12**, 201 (1981).
48. P. Bonnian,and A. R. Bunsell, *J. Compos. Mater*, **15**, 272 (1981).
49. S.M. Copley, RAE TR 82010, Royal Aircraft Establishment, Farnborough, UK, 1982.
50. T.A. Collings, and S.M. Copley, *Composites*, **14** ,180 (1983).
51. G. Prichard and S.D. Speake, *Composites*, **18** , 227 (1987).
52. A.R. Berens and H.B. Hopfenberg, *Polymer*, **19**, 489 (1978).
53. W.E. Douglas, J.S.Ghotra, D Ho, and G Pritchard, *Br. Polym. J.*, **16**, 139 (1984).
54. J.M. Whitney, and C.E. Browning, ASTM STP 658, ASTM, Philadelphia, PA, USA (1978).
55. L.R. Bao and A.F. Yee , *Polymer*, **43**, 3987 (2002).
56. V.L. Saponara, *Compos Structs* **93**, 2180 (2011).
57. L.R. Grace and M.C. Altan, *Composites: Part A* **43**, 1187 (2011).
58. M. Blikstad, P.O.W. Sjoblom, and T.R. Johannesson *J. Compos Mater*, **18** 32 (1984).
59. M.E. Gurtin, and C. Yatami, *J Compos Mater*, **13**,126 (1979).
60. J. Crank, The mathematics of diffusion, 2nd edition, Oxford university press, Oxford, 1975.
61. P.C. Upadhayay, and J. Misra, *J. Reinf. Plast Comp*, **9**, 335 (1990).

62. Om K. Joshi, *Composites*, **14**, 196 (1983).
63. C.E. Browning, *Polymer Eng. Sci.* **18**, 16 (1978).
64. L. Banks and B. Ellis, *Polymer Bulletin*, **1**, 377 (1979).
65. Kelley F. N. and Bueche F, 1961 *J. Polym. Sci.* **50**, 549.
66. R.C.Novak. and M.A.DeCrescente, *J. Engineering for Power*, **92**, 377 (1970).
67. B C Ray, *Mat.Sci.Eng.A*, **379**, 39 (2004).
68. C.Y. Lundemoand and S.E. Thor. *J. Compos Mater*, **11**, 276 (1977).
69. A. Mazor.,L.J. Broutman and B.H. Eckstein., *Polymer Engg. Sci.*, **18**, 391 (1978).
70. B.C. Ray, A. Biswas and P.K. Sinha, *J.Mat.Sci.Lett.*,**11**, 508 (1992).
71. L V J Lassila,T Nohrstrom, P K Vallittu, *Biomaterials*, **23**, 2221 (2002).
72. Y.Z. Wan , Y.L. Wang , Y. Huang , F.G. Zhou , B.M. He, G.C. Chen, K.Y. Han, *Compos Sci Technol* **65** 1237(2005).
73. W Chu, V M Karbhari, *J.Mater.Civil.Eng.*,**17**, 63 (2005).
74. M K Bhuyan, M S Bhuyan, J I Rodri'guez-De'vora,and M Yanez, *J. Compos.Mater.* , **47**, 3421 (2013).
75. T.A. Collings. and D.E.W.Stone, *Compos Struct*, **3** , 41 (1985).
76. B C Ray, *J.Mat.Sci.Lett.***21**,1391 (2002).
77. B C Ray, *J.Mat.Sci.Lett.***22**, 201 (2003).
78. B C Ray, *Mat. Lett.*,**58**, 2175 (2004).
79. G.A. Pering, P.V. Farrell and G.S. Springer, Degradation of Tensile and Shear Properties of Composites Exposed to Fire or High Temperature, In: Springer, G.S. (ed.), *Environmental Effects on Composite Materials*, pp. 145-159, Technomic Publishing Company Inc (1981).
80. J.D Memory, R.E. Fornes, and R.D. Gilbert, *J. Reinf. Plast.Compos.***7**, 33 (1988).
81. B C Ray, *J.Reinf.Plast.Comp.***24**,1771 (2005).
82. B C Ray, *J.Appl.Poly.Sci.*,**100**, 2289 (2007).
83. E Kalfon, H Harel, G Marom, E Drukker, A K Green, I Kressel, *Polym Compos*, **26**, 770 (2005).

84. H.L.Cox, *British J Appl. Phys.*, **3** 72 (1952).
85. C. Galiotis, R.J.Young, P.H.J. Yeung. And D.N. Betcheldor, *J. Mater Sci.* **15** 3640 (1984).
86. M.F Kanninen, E.F. Rybicki and W.L.Griffith, ASTM STP 617 (1977).
87. J. Molt and P.J. Wrothingotn., *Int. J Fatigue*, **3**,31 (1981).
88. R.G. WHITE and M.Treatout, *Composites*, **10** ,101 (1979).
89. D.Valentine, Ph.Bonniau, and A.R. Bunsell, *Compoistes*, **14**,345 (1983).
90. A.A.Wells, *Composites*, **3** ,112 (1972).
91. C. Zweben, ASTM STP 521, 65 (1973).
92. D.C. Phillipsand A.S.Tetelman, *Composites*, **3**,216 (1972).
93. G.A.Cooper, A.Keely, ASTM – STP 452 90 (1969).
94. A. Kelly, *Proc. Royal Soc.*, A319 95 (1970).
95. M.R. Piggott, *J. Mater. Sci.*, **5** ,669 (1970).
96. B C Ray, S.Sethi, Mechanical Behavior of Polymer Composites at CryogenicTemperatures. In: Polymers at Cryogenic Temperature, edited by Kalia S, Fu S Y, Springer Berlin Heidelberg, Germany, 2013.
97. M.R.Piggott, Load Bearing Fibre Composites (Ed.) Pergamon, Oxford (1980).
98. B. Harris, P.W.R Beaumont and E.M. deFerran., *J. Mater. Sci.*,**6**, 238 (1971).
99. N.K.Hencox, *J. Mater. Sci.*, **10** , 234 (1975).
100. N.J Wadsworth, and I. Spilling, *British J. Appl. Phys.*, **1**,1049 (1968).
101. R.J.Grey, *Int. J. Adhes Adhes*, **3** , 197 (1983).
102. J.F.Mandell, J.H.Chen, and F.J.McGarry, *Int. J. AdhesAdhes*, **1** ,40 (1980).
103. M.J.Pitkethly, and J.D.Doble, *Composites*, **21** ,389 (1990).
104. P Marshall and J. Price, *Composites*, **22**, 53 (1991).
105. R.F.Cook, M.D.Thovlesss, D.R Clarke, and M.C. Kroll, *Scripta Metallurgica*, **23**, 1725 (1989).

106. G. Lubin, Handbook of Composites (Ed.) Van Nostrand Reinhold Co., New York, USA 1982.
107. U. Gaur and B. Miller, *Polym Compos*, **11**, 217 (1990).
108. G. Marom and L.J. Broutman, *Polym. Compos.*, **2**, 132 (1981).
109. M. Mijovic and K.F. Lin, *J. Appl. Polym. Sci.*, **30**, 2527 (1985).
110. H.D. Kaelble, P.J. Dyness, and L. Maus, *J. Adhesion*, **8**, 121 (1976).
111. Miller. B., Muri. P and L. Rebenfeld, *Compos. Sci. Technol.*, **28**, 17 (1987).
112. L.T. Drzal, M.J. Rich, and M.F. Koeng, *J. Adhesion*, **18**, 49 (1985).
113. A. Benatar and T.J. Gutowski, *Polym. Compos.* **7**, 84 (1986).
114. J.L. Koeng and H. Emadipour, *Polym. Compos.*, **6**, 142 (1985).
115. B.C. Ray, D. Rathore. *Adv. Colloid Interface Sci.* <http://dx.doi.org/10.1016/j.cis.2013.12.014>.