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MECHANICAL BEHAVIOR OF HYGROTHERMALLY CONDITIONED FRP COMPOSITES AFTER THERMAL SPIKES

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ABSTRACT

The effect of absorbed moisture on the mechanical properties of E-Glass/Epoxy composite was investigated. It is now well known that the exposure of polymeric composites in moist environments, under both normal and sub-zero conditions, leads to certain degradation of its mechanical properties which necessitates proper understanding of the correlation between the moist environment and the structural integrity. Environments similar to several that in real life, like marine environments, the high temperature excursions (thermal spikes) experienced by the undercarriage of VTOL aircraft, or even natural weathering conditions were tried to be regenerated and an attempt was made to understand their impact on the fiber-matrix adhesion property. The tensile and bending properties were determined under hydrothermal conditions and the effect of thermal spike on the inter-laminar shear strength (ILSS) values of the composite under different conditions were also discussed. The changes in glass transition temperature (T_g) and investigations through scanning electron microscopy (SEM) showed that E-Glass/epoxy composites quite sensitive to environmental conditioning.

INTRODUCTION

For their several significant advantages, the composites structures are fast gaining their popularity as an effective structural component over their metallic counterparts. In recent years the glass fiber reinforced polymers (GRP) , specially glass/epoxy composites are widely applied in several civil engineering applications ranging from seismic retrofit of columns and strengthening of walls, slabs, to new building frames and even bridges. It is also well known that there is a degradation of material property during its service life, as it is often subjected to environments with high temperature and humidity or having a sharp rise and fall of temperature (thermal spikes). The deterioration that occurs is FRP during the service life is in general, linked to the level of moisture that is absorbed. The absorption of moisture can be attributed largely to the affinity for moisture of specific functional groups of a highly polar nature in the cured resin. The absorption of moisture causes plasticization of the resin to occur with a concurrent swelling and lowering the glass transition temperature of the resin. This adversely effects the fiber-matrix adhesion properties, resulting debonding at fiber/matrix interfaces, micro-cracking in the matrix, fiber fragmentations, continuous cracks and several other phenomena that actually degrades the mechanical property of the composites.

There has been several efforts made by many researches in the last few decades, to establish a much needed correlation between the mechanical property of the material, and the moist environment , or similar hydrothermal (or hygrothermal) environments with thermal spikes that effects the moisture intake in a composite. The focus of research has been concentrated to understand the change that takes place at the bonding interface between the fiber and matrix as it is of prime importance due to its link to the stress transfer, and distribution of load and it also governs mechanisms of damage accumulation and propagation. Many techniques have been devised to access such interfacial properties. Tensile properties, interlaminar shear strength (ILSS) which can be determined by the Three point bend test, gives a good account of this at a bulk scale. However there are several other micro (or macro) approaches that have also come out in recent time like microbond technique, single fiber fragmentation

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techniques, microdebond or microindentation technique.

In this work the simulated test conditions correspond to aerospace applications (where the exhaust fumes subject the material to severe thermal spike and then its exposure to moisture -rain or clouds), marine application (where the material is exposed to severe humidity conditions), and sub-zero temperature applications (where the moisture freezes to ice) were tried to be created and their effect on the mechanical property was studied.

EXPERIMENTAL

The investigations were carried out with woven cloth glass fiber and epoxy resin. From literature, it is seen that the optimum mechanical properties of FRP composites for a variety of structural applications is obtained at a fiber/matrix ratio of 60:40. With this in mind specimen conforming to this ratio were prepared. The FRP composites used for the present investigations were prepared by the conventional hand lay up process. As per ASTM standards, 16 plies were used to prepare each composite specimen. Curing of the fiber reinforced epoxy was made possible by use of a hardener amounting to 5 % by weight of the total resin matrix, which required a period of 24 hours to harden.

The specimen thus prepared were exposed to several moist thermal environments. The moisture absorption in the composite specimen were measured after different exposure time and were then subjected to suitable characterization procedures.

The hygrothermally treated specimen were subjected to the three point bend test. The test specimen had been prepared according to the specified relations amongst the various dimensions. The final specimen measured 45 mm X 6 mm. The three point bend tests were carried out using INSTRON. The three point bend test results can be taken as indications of the interlaminar shear strength of the composites after they had been hygrothermally treated. For the purpose of comparison, the tests were performed with different loading speeds. Loading was done at two different crosshead speeds. In order to study the thermal effects on the damage mechanisms, a different set of specimen were subjected to a thermal spike at a high temperature. Two series of composites were used in this case, one of which was hygrothermally conditioned at boiling point of water and nearly absolute relative humidity, while the other was immersed in a hot water bath, the temperature of which was controlled at 90^o C. Then the variation of ILSS values due to the effect of thermal spikes were investigated.

The degradation in mechanical properties related to glass transition temperature had been characterized using DSC techniques. Damage such as debonding at fiber/matrix interfaces and continuous cracks are investigations through scanning electron microscopy (SEM).

RESULTS & DISCUSSIONS

The aim of this work is to investigate the absorption of moisture in E-Glass / Epoxy composites under both normal and sub-zero conditions to understand the overall effect of moisture absorption on the mechanical property under different thermal and environmental conditions.

Theory of Moisture Absorption :

Weight gain of the preconditioned specimens was carefully monitored by weighing multiple specimens periodically, with precautions taken to remove the surface moisture by wiping them before weighing. Percentage weight gain was determined as

$$M = \frac{(\text{ Weight of specimen} - \text{Weight of dry specimen })}{(\text{ Weight of dry specimen })} \times 100 \qquad (1)$$

As the natural process of moisture absorption in epoxy matrices is normally very slow, so Fick's second law for a concentration independent moisture diffusion process for a long period of exposure in the solution can be approximated [6] as

$$M = \{ 1- 8/\pi^2 \exp(-\pi^2 D\, t /h^2)\}\, M_m \qquad (2)$$

where D, t, h, M_m are the composite diffusion coefficient, time at maximum moisture content , specimen thickness, and maximum moisture content respectively. Assuming that the moisture absorption process follows Fick's law, the apparent diffusivity, D, can be determined as [3]

$$D = \pi\, (h/4\, M_m)^2\{(M_2 – M_1)/(\sqrt{t_2} - \sqrt{t_1})\}^2\, (1+ h/L_e + h/w)^{-2} \qquad (4)$$

where L_e and w length width of the test-specimen respectively, and M_1, M_2 are moisture contents at time t_1 and t_2 respectively.

Conditions Affecting Moisture Absorption:

The deterioration that occurs in composite structures during its service is linked with the level of moisture that is absorbed. Its usually confined to the resin matrix in case of glass fibers unlike its counterparts of aramid family. The way moisture is absorbed is dependent upon many factors. The factor that features most is that of climatic exposure, that is the severity of exposure to humidity and temperature .

The moisture gain is plotted against the square root of time for the E-Glass/Epoxy composite (60 : 40) (fig.1). It can be observed that initially, there is almost a linear increase in the equilibrium moisture content, and gradually it approaches to a constant saturation level, as observed by other previous researches [3, 2]. The variation of moisture content indicates typical Fickian diffusion behavior. The fact that moisture content gradually increased and then becomes almost constant manifests that the mechanism of weight change is different beyond the saturation time. Until the saturation time is reached the water absorption and matrix dissolution occurs simultaneously, and after that the rate of water absorption is gradually decreased, however the matrix dissolution continued to occur at a constant rate.

Water equilibrium concentration is expected to be independent of temperature and packing density . However the increase in equilibrium moisture content is observed in overall lower fiber volume content and greater resin rich surfaces [7]. Researches [3] have also studied that the use of chopped stand mat layers due to their smoother surface finish, can only accelerate the degradation kinetics due to better solution absorption at the surface. Since free segmental motion is restricted to a large extent in a chemically cross-linked polymers microvoids develop, that acts as sites for water absorption and further capillary action and wicking action with the solution clustering more readily along the individual fibers which intrinsically encourages water clustering in the less densely packed sites [8].

Moisture Absorption at Different Environments:

The structural integrity of a composite structure is chiefly decided by the adhesion characteristics of the fiber and the matrix. Many attempts are made to develop techniques to measure the fiber-matrix adhesion level [1] for last few decades. The previous investigators [2] have shown that the degradation of mechanical property has manifested itself through the decrease in strength at the fiber-matrix interface, which gives rice to the degradation of the material.

Researches have given simulated accelerated thermal cycles [3] so as to mimic the rise and fall of temperature through the day. As shown in the figure below (fig. 2), the minimum temperature selected corresponds to the average minimum temperature at night, the rise shows the day time increase in temperatures, the plateau for the time during the entire day, the fall is to ape the lowering of temperature at night. Exposure of composite structure in marine environments have also been simulated [3] which studies the effect marine parameters on the structural integrity of the composite. Studies been also carried out to study the effect of prolonged natural weathering [3]. All this environmental conditions affects the moisture absorption in composite structures in its own unique way that induces a certain level of stress within itself the effect of which is to be critically considered.

Fig.1: Effect of Time on Moisture Pick-up

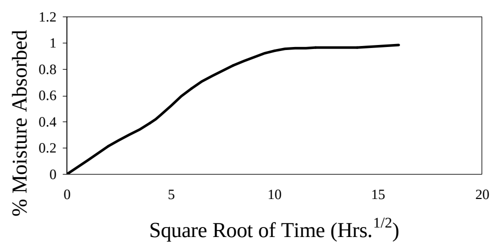
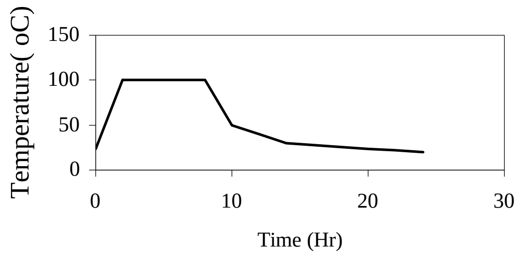


Fig. 2 Simulation of Accelerated thermal cycling



Effect of Moisture on Tensile Property Retention:

Several efforts have been put in to understand the effect of moisture absorption on Mechanical property [5,7]. Hamada et.al has given several correlations for measuring various tensile parameters based on their detailed studies on the mechanical property of GRP under the effects of water environment. It was shown (fig. 3) that the tensile elastic modulus is linearly decreased till the net weight gain (M_g) reaches to the saturation level approximately at 1.9 % , beyond which the tensile elastic modulus keeps a constant value. It is well known that the tensile elastic modulus of the composite material is represented by the rule of mixture. It is assumed that the tensile elastic modulus of a glass fiber is not decreased due to the water absorption, thus the decrease of the tensile elastic modulus below 1.9 % of M_g may be caused by the decrease of that of the matrix due to the moisture absorption. In Fig. 4 the relationship between the tensile strength and M_g is shown. The tensile strength is linearly decreased against M_g. This tendency differ from the tensile elastic modulus as shown in Fig. 3. Therefore, it seems that the absorbed moisture has far greater effect on the tensile strength than on the tensile elastic modulus. Apparently it seems as if the tensile strength is decreased due to increase of M_g. But the reduction in mechanical properties is not only caused by the plasticization of the matrix due to the water adsorption but also by fiber/matrix interfacial adhesion, possibly including chemical bonding, secondary forces of attraction, residual thermal compression forces and mechanical interlocking friction between the fiber and resin.

Figure 5 shows the relation between the bending elastic modulus and M_g. The bending elastic modulus is linearly decreased below approximately 1.2% , which corresponds to the immersion for the saturation period and above that it keeps almost constant. The M_g at which the bending elastic modulus reaches a constant value is different from that at which the tensile elastic modulus does. It seems that this difference arises since the specimen is subjected to only tensile load in the tensile test, while in the bending test it is subjected to both compressive and tensile load. In Fig. 6, the relationship between the bending strength with shows the similar trend to that of the tensile strength, since the tension failure ultimately occurs at the lower side of the specimen in bending.

From the above results tensile and bending properties can be calculated using the following equations if the reduction in mechanical properties are considered solely due to moisture absorption.

Tensile Elastic Modulus (E_t):

E_t (Gpa) = - 2.73 x M_g (%) + 11.63 $\quad$ ($0 < M_g < 1.92$ %)

E_t (Gpa) = 6.40 $\quad$ ($M_g > 1.92$ %)

Tensile Strength (σ_t):

σ_t (Mpa) = -19.6 x M_g (%) + 110.4

Bending Elastic Modulus(E_b):

E_b (Gpa) = - 2.40 x M_g(%) + 8.86 (0 M_g 1.15 %)
E_b (Gpa) = 6.09 (M_g 1.15 %)

Bending Strength (σ_b):
σ_b (Mpa) = -42.5 x M_g(%) + 215.1

Fig. 3: The Effect Of Moisture Absorption On Tensile Elastic Modulus (Et)

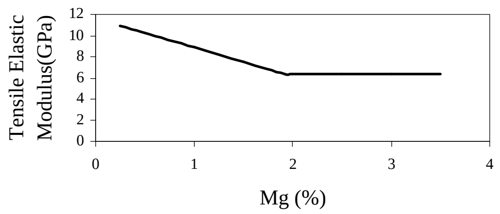


Fig. 4: Effect of Moisture on Tensile Strength (MPa)

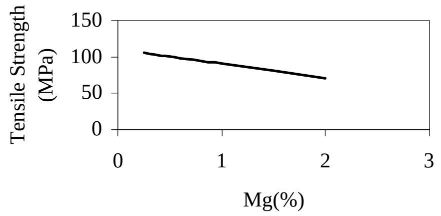


Fig. 5: The Effect Of Moisture Absorption On Tensile ending Elastic Modulus (Eb)

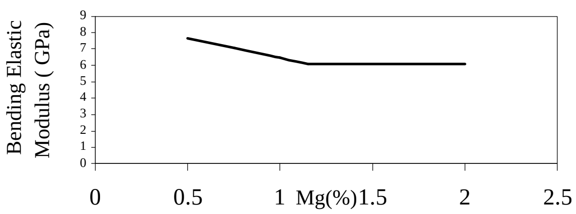
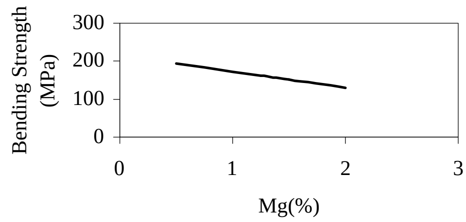


Fig. 6: The Effect Of Moisture Absorption On Bending Strength



Effect Of Frozen Moisture on Interlaminar Sheer Stress:

The study on the absorption of moisture under frozen conditions is also interesting to investigate specially in the context of aviation and aerospace as they often experience such an environment during their voyage. Even the structural parts in the arctic region can also encounter such a condition. Hence the following investigation can prove to be very useful in those conditions.

As discussed earlier there is certain amount of degradation in the mechanical property when the composite is exposed to thermal and moist environment. This also true for sub-zero conditions, and the effect of moisture under frozen conditions can similarly be investigated. In this case the measure of mechanical behavior is observed on the context of interlaminar sheer stress (ILSS). So, the effect on ILSS values were recorded for both plain and frozen moist moistures under same level of moisture content , and plotted against the square root of the exposure time (fig. 7). As shown in the figure, except in the initial period of exposure, the shear strength of the specimens with frozen moisture was lower than that of plain moist specimen with the same time of exposure. This may due to the increase in swelling stresses, due to the volume expansion of moisture during freezing. The initial exception may be due to the strain-free state of the composite, as the swelling stress developed due to the freezing of moisture might have released the residual strains induced during the cooling of the composite from its curing temperature [4].

Fig. 8 shows the effect of loading speed on the ILSS values of frozen moist composites, plotted against the square root of conditioning time. The overall nature of the curve shows that the ILSS values for the lower loading speed is lower than that for the higher loading speed for the same time of exposure. The more detrimental effect for the lower loading speed may be due to the greater time available for the absorbed moisture to diffuse through the debonded gaps into the stress-concentrated area, consequently causing further deterioration of the fiber-matrix interface and/or matrix itself during the testing.

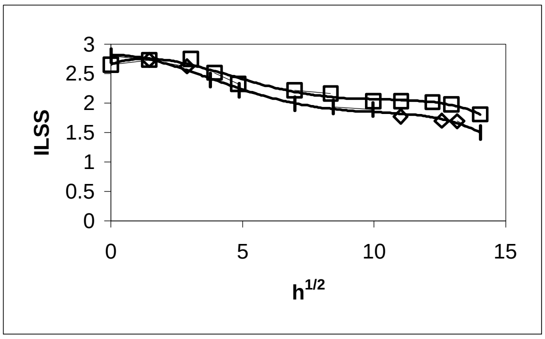


fig. 7 Effect on ILSS values for composites exposed to both plain and frozen moist moistures

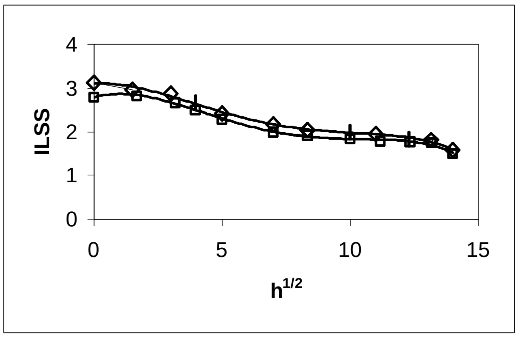


Fig. 8 Effect of conditioning time on frozen composites for different crosshead speeds

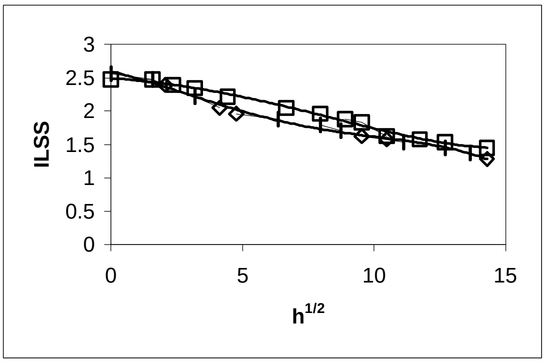


fig. 9 Effect of thermal spikes on the ILSS values of hygrothermally conditioned composite specimens

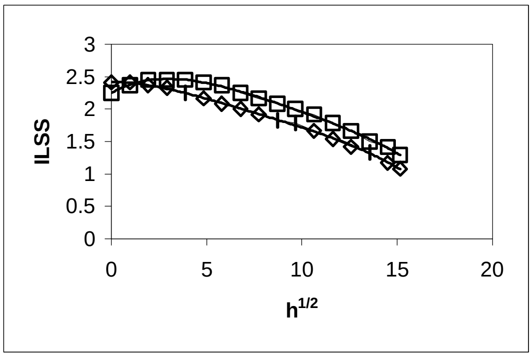


fig. 10 Effect of thermal spikes on the ILSS values of composites conditioned by immersing in boiling water

Fig. 9 and 10 were drawn to investigate the effect the effect of thermal spikes on the ILSS values of composite specimens hygrothermally conditioned at boiling point of water and near absolute humidity, and conditioned by immersion in hot water at boiling temperature, respectively. These figures show that the overall effect of the thermal spikes is adsorption of absorbed moisture, and thereby an increase in ILSS values compared with those conditioned specimens without thermal spikes. However, some deviations at the very commencement are observed for both the curves (fig 10 and 11). This may be due to the higher amount of residual stresses in the composites. For the specimens without thermal spikes hygroscopic (swelling) stresses which are being developed during the conditioning counteract the curing stresses, resulting in a lower amount of resultant residual stresses, as these stresses are opposite in nature [5]. This can explain the higher ILSS values of plain conditioned specimens at the initial periods of exposure compared with that of conditioned specimens with thermal spikes.

Effect Of Absorbed Moisture On Glass Transition Temperature

The glass transition temperature, T_g , of a polymer is the temperature above which it is soft and below it is hard. For Epoxy resins, T_g is the temperature at which the polymer goes from glassy to a rubbery solid. Practically in case of resins it is a temperature region rather a single point. At T_g ,a very rapid change in property takes place, so it is very difficult to estimate it precisely.

It is an accepted theory [8] that at and below the glass transition temperature 1/40 of the total volume of the material is free volume. Taking this into consideration, T_g will be lowered when a polymer is mixed with a miscible liquid having more free volume, such that the diluent-polymer solution will contain more free volume at any given temperature. As a result , the polymer must be cooled to a lower temperature in order to reduce its volume to 1/40 of the total volume of the diluent-polymer combination. This is the process which occurs when moisture absorption takes place in to the exposed resin.

Based on this, Bueche et.al [9] derived the following expressing for T_g a plasticized system

$$T_g = \frac{\alpha_p V_p T_{gp} + \alpha_d (1 - V_p) T_{gd}}{\alpha_p V_p + \alpha_d (1 - V_p)} \tag{5}$$

where,

T_{gp} = glass transition temperature of the polymer,
T_{gd} = glass transition temperature of the diluent,
α_p = expansion co-efficient of the polymer,
α_d = expansion co-efficient of the diluent,
V_p = volume fraction of the polymer.

In terms of the percentage weight gain in the polymer, M

$$V_p = [\, 1 + \rho_p / \rho_d \{ (0.01)M \}]^{-1} \tag{6}$$

Surface morphology

The following microphotographs shows the effect of moisture absorption in glass/epoxy composites. As discussed earlier the moisture results in the loss of adhesion between the fiber and the matrix as can be seen from Fig. 13. The degradation of epoxy matrix in case of an aged specimen , is as shown in Fig. 14, the out crop in of epoxy matrix is clearly visible in the micrograph.

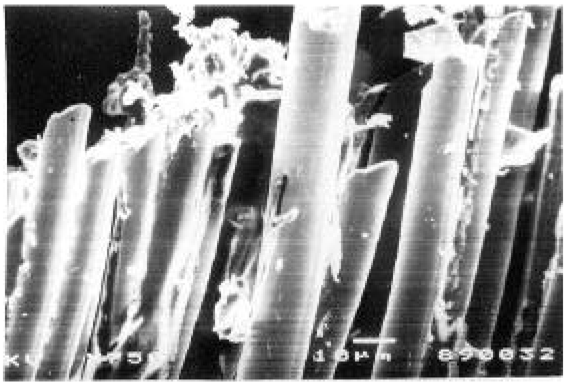


Figure 13 : Loss of adhesion between the fiber and the matrix

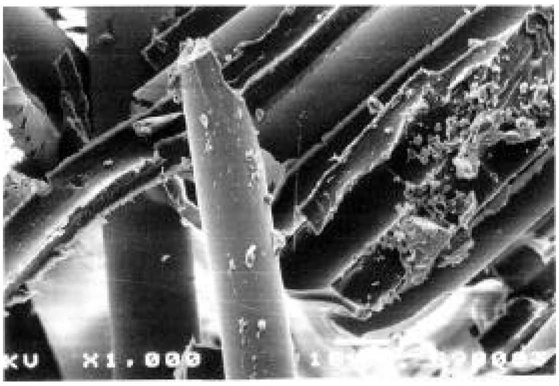


Figure 14 : Out crop of epoxy polymer in case of the aged specimen

CONCLUSION

The effect of moist environment on the mechanical properties of Glass/Epoxy composites were investigated. The following conclusions may be drawn for this study :

Moisture, in both normal and frozen conditions, has detrimental effect on the mechanical properties of glass/epoxy composites, however the extent of damage is more severe in case of frozen moisture.

Debonding at the fiber/matrix interface in a fiber bundle is caused after the amount of absorbed moisture reaches to a saturation level, and as a result the tensile elastic modulus remains constant.

The tensile strength below the amount of saturated moisture is decreased by the plasticization of the matrix and above that it is related to the interfacial degradation.

The higher loading speed result in less deleterious effect on ILSS values of glass/epoxy composites with frozen conditions.

Thermal spike at high temperature of hygrothermally conditioned composites may result in only desorption of absorbed moisture and thus result in less deterioration of ILSS values.

REFERENCES

1. Herrera-Franco, P.J., and Drzal, L.T., (1992) "Comparison Of Methods For The Measurement Of Fiber/Matrix Adhesion In Composites", *Composites.* 23. No. 1 ,2-27.

2. Schutte.C.L (1994) "Environmental Durability Of Glass-Fiber Composites", *Materials Science and Engineering*, R 13, 265-324

3. Shi Zhang, et. al. (2000) "Evaluation Of Property Retention In E-Glass / Vinylester Composites After Exposure To Salt Solution And Natural Weathering", *Journal of Reinforced Plastics and Composites,* 19, 704-730.

4. B.C.Ray, Biswas A.,Sinha P.K., (1992) "Freezing And Thermal Spikes Effects On Interlaminar Shear Strength Values Of Hygrothermally Conditioned Glass fiber/Epoxy Composites", *Journal of Materials Science Letters* ,11, 508-509.

5. Singh S.K., Singh. P.K., and Rao, R.M.V.G.K. (1991) "Hygrothermal Effects On Chopped Fiber/Woven Fabric Reinforced Epoxy Composites. Part A: Moisture Absorption Characteristics", *Journal of Reinforced Plastics and Composites*, 10, 446-456.

6. Crank, J.,(1956) *Mathematics Of Diffusion,* Oxford University Press.

7. Shen C.H., and Springer, G.S., (1976) "Moisture Absorption And Desorption Of Composite Materials*", Journal of Composite Materials,* 10, 1-20.

8. C.E. Browning, Husman, G.E., and Whitney J.M., (1977) "Moisture Effects In Epoxy Matrix Composites" *Composite Materials : Testing and Design (Fourth Conference)*, 481-496.

9. Bueche, F. and Kelly, F. N., (1972) "Modeling Of Glass Transitional Temperature for Composites", *Journal of Polymer Science* 6, 552-554.