# EFFECTS OF SEA WATER ON GLASS / EPOXY AND KEVLAR/EPOXY COMPOSITE MATERIALS

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## الملخص

إن استخدام المواد المركبة المصنعة من المواد البلاستيكية المعززة بالألياف الصناعية دخل في العديد من التطبيقات الصناعية خاصة الصناعات البحرية التي تحتاج إلي مواد تتحمل الصدأ والعوامل البيئية الصعبة. وعليه فإن معرفة سلوك هذه المواد في مثل هذه الظروف يعتبر مهما جدا لهده الصناعات. يقدم هذا البحث دراسة تحليلية و عملية على نوعين من المواد المركبة ، النوع الأول هو مادة الإبوكسي البلاستكية المعززة بالألياف الزجاجية و النوع الثاني هو مادة الإبوكسي المعززة بألياف الكفلر وذلك لمعرفة خواصها الميكانيكية ومقدرتها على امتصاص ماء البحر عند درجات الحرارة العالية. ولقد لوحظ من خلال التجارب أن المادتين قد امتصتا كمية كبيرة من الماء.كما تم اختبار مقاومة الانحناء للعينات وهى مبللة و عند درجات حرارة مختلفة ولقد تبين أن معامل الصلادة يقل كلما زادت درجة الحرارة و أن هذا الانخفاض يزداد بصورة كبيرة بعد درجة الحرارة الانتقالية (الزجاجية) للمادة.

## ABSTRACT

Composite materials are being widely used in applications including marine industry where specific properties and corrosion resistance are required. Many applications have been mentioned for pipes systems on ships, offshore platforms and also for coastal engineering plant such as power stations and desalination installations. However, it was recognized that the optimum use of composite materials would be strengthened by more information on the durability of composite materials in such environment. In this paper, analytical and experimental investigations have been carried out on glass / epoxy and Kevlar / epoxy composite laminates in sea water at elevated temperatures. Both materials absorbed a considerable amount of water which caused degradation of physical and chemical structure of the material. Flexure Young's moduli for dry and wet samples were measured at elevated temperature using three bending test method. It was found that the moduli exhibited a considerable reduction above the glass transition temperature.

**KEYWORDS**: Glass; Kevlar; Epoxy; Glass transition temperature; Degradation; Water absorptions; Young's modulus; Plasticization; Swelling; Composites.

## INTRODUCTION

Composite materials are a heterogeneous combination of two or more materials (reinforcing fibers & matrix), differing in form or composition on a macroscale. The combination results in a material that maximizes specific performance properties. The constituents do not dissolve or merge completely and therefore normally exhibit an interface between one another. In this form, both reinforcing fibers and matrix retain their physical and chemical identities, yet they produce a combination of properties that

cannot be achieved with either of the constituents acting alone [1]. Composites are commonly classified based on the type of matrix used: polymer, metallic and ceramic. In fiber - reinforced composites, fibers are the principal load carrying members, while the surrounding matrix keeps them in the desired location and orientation. Matrix also acts as a load transfer medium between the fibers, and protects them from environmental damages due to elevated temperatures, humidity and corrosion. The principal fibers in commercial use are various types of glass, carbon and Kevlar. E-Glass has good tensile strength, low tensile modulus. It is available in many forms and widely used in commercial and industrial products. -Glass has high strength and modulus. It has been used in aerospace and high performance pressure vessel applications. Kevlar fiber has very good strength and excellent tensile modulus, very low density (one-half of glass fiber) and excellent impact properties. There are many resins can be used as a thermosetting matrix such as polyester, vinyl ester, and epoxy. The epoxy resins are the wide range of resins available. It has superior mechanical properties such as fatigue performance, heat resistance and good chemical resistance [1].

Composites materials are being widely used in applications where high specific properties and low maintenance are required. The corrosion of metallic materials in contact with sea water causes problems and for these applications composite materials are increasingly being applied. One aspect which requires a thorough understanding is the wet aging of composite materials at elevated temperatures and the marine industry has devoted considerable effort to this area [2, 3]. The effect of aqueous environments on polymer matrix composites has been well documented over the last thirty years and recently been reviewed by Carol and Schutt [4]. Water is able to enter the composite by diffusion through the resin matrix. The effect of water absorption on the resin causes a swelling to it, which can produce internal stresses [5]. Absorbed water also plasticizes the resin, leading to a reduction in glass transition temperature and thus the high performance of composite. It hydrolyses the resin due to the chemical reaction between molecules of water and resin resulting in a soluble compound out from the matrix. [5, 6]

The effect of water absorption depends particularly on the type of fiber. Fibers such as carbon are not significantly affected. However, other fibers like glass and Kevlar are influenced by water absorption even at low exposure levels. This effect increases in the presence of high temperatures.

The kinetics of water absorption is a complex phenomenon and depends on the molecular interaction between water and resin. In normal absorption, the mechanism can be described using the Fickian Model [7], in which the rate of water absorption increases with temperature, but the maximum amount of water absorbed is dependent on temperature and relative humidity if the materials is exposed to humid air. In anomalous absorption, the diffusion mechanism is non Fickian behavior and can be described by other models such as Langmuir model [8]. Water absorption causes a swelling to the resin, resulting in plasticization of the resin. The swelling and plasticization phenomena have been studied extensively in literature. Xiao and Shanahan [6] studied the behavior of isothermal water uptake and the swelling behavior of epoxy resin below its glass transition temperature. They concluded that the swelling induction by hydrothermal again was not fully reversible, particularly at high temperatures. Jones [9] stated that the plasticization of the matrix occurs when water interacts with the resin through polar interactions and hydrogen bonding and causes an increase in free volume. As a result,

the glass transition temperature of the resin is reduced at a rate of approximately 20 K for each 1 % of water absorbed.

High temperatures cause an extensive thermal degradation to the mechanical properties including the elastic modulus and strength. The response of the composite to elevated temperature can be characterized by determining the mechanical properties at different temperatures [2]. At low temperature, glass state region, the modulus shows a slightly decrease. At glass transition temperature, the matrix goes from glassy to rubbery state and modulus exhibits considerable reduction. At high temperature, rubbery state, the matrix undergoes rapid relaxation and the modulus exhibits another slight reduction. Haque and Hossain [10] investigated the effects moisture and temperature on the mechanical properties at high strain rate. They concluded that the failure stress, failure strain and modulus degraded at elevated temperatures.

The purpose of the present work was to study the influence of both sea water and temperature on glass/epoxy and Kevlar/epoxy composite laminate.

## EXPERIMENTAL WORK

The materials adopted for this study are two composite laminates, based on E-glass fiber and Kevlar fiber $\pm 45^{o}$ reinforced with epoxy resin. Both composite laminates were manufactured with hand lay up method with volume fraction of 0.5 and dimensions of 300 x 300 x 3mm. Five specimens with dimensions of 15 x 150 mm were cut at an angle of $\pm 45^{o}$ to the direction of the fiber from each type. All specimens were milled to their final dimensions using ASAX universal milling machine.

### Water absorption test

Before investigating the flexure modulus of the two composites, all the specimens were conditioned by immersion in sea water at 95 $^{o}$C, in a small stainless steel tank provided by an electric heater, until saturation time was achieved as indicated by no further change in weight. The use of this fairly high temperature enabled saturation to be achieved in a matter of days.

To measure the rate of water uptake, several specimens with dimensions of 50x50 mm were cut form each composite laminate. Water absorption was measured by periodically removing samples from the water tank, weighing, and returning them. To check whether any leaching of material had been take place, some additional samples were dried at 100 $^{o}$C after weighing then reweighed to ensure whether there had been any weight change. No significant effects were observed. The percentage of water absorption content can be found from the change in mass of the samples before and after immersing in the sea water as:

$$\overline{M} = \frac{W_w - W_d}{W_d} \, X \, 100 \qquad\qquad (1)$$

Where: $W_w$ and $W_d$ are wet and dry weights of the specimen respectively.

### Axial Flexure Young's Modulus Test

In order to characterize the influence of composite laminates to elevated temperatures at dry and hot conditions, three point bending tests were carried out at constant load at a range of constant temperatures. The experimental rig used, shown in Figure (1) consists of a small temperature controller hot chamber containing two small

supports spaced at 120 mm [11] and fixed on steel base. The assembly was provided with a displacement transducer (LVDT) to measure the deflection of the loaded spacemen. After achieved thermal equilibrium at each test temperature, a constant load was applied at the center of the span and deflection noted after 100 seconds. For dry specimens, the same sample was used for a range of test temperature. Where as the wet specimens were immersed in water at 95 $^{o}$C prior to the test then wrapped in plastic film to minimize water loss during the test. One sample was used for each test temperature. It was observed that the applied load should be low enough to produce a proportional relationship between the load and displacement. Each test was repeated five times and the values of the deflection were taken as the mean value of these tests. The axial Young's modulus then can be calculated by the following formula [12]:

$$E = \frac{F\,l^3}{48\,I\,y} \tag{2}$$

Where: F is applied load (N), $l$ is the span length (mm), $I$ is the moment of inertia (mm$^4$), and y is the deflection
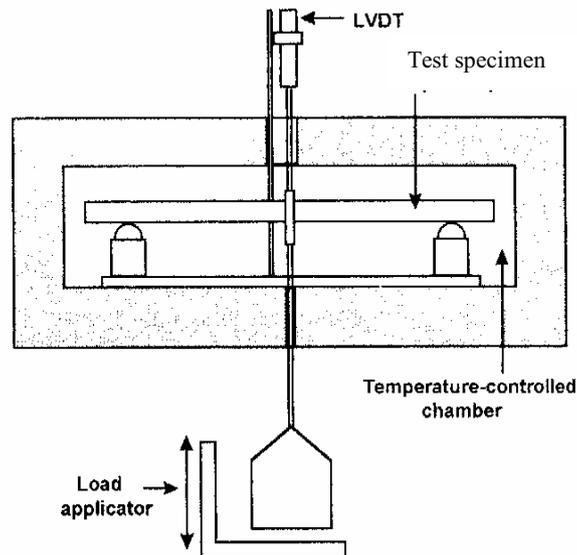


**Figure 1: Schematic diagram for apparatus for measurement of flexural axial modulus**

## PREDICTION OF THE YOUNG'S MODULUS OF THE MATRIX

The matrix modulus can be predicted theoretically by the following equations.

$$
\left.
\begin{aligned}
E_{11} &= E_f V_f + E_m V_m \\[6pt]
E_{22} &= E_m \frac{1 + \xi_{22}\eta_{22}V_f}{1 - \eta_{22}V_f} \\[6pt]
G_{12} &= G_m \frac{1 + \xi_{12}\eta_{12}V_f}{1 - \eta_{12}V_f} \\[6pt]
v_{12} &= v_f V_f + v_m V_m
\end{aligned}
\right\} \tag{3}
$$

Where: the parameters $\eta_{22}$ and $\eta_{12}$ are called halpin-Tasi parameters and can be calculated by the following equations [7] :

$$\eta_{22} = \frac{(E_f / E_m)}{(E_f / E_m) + \xi_{22}} \quad \text{and} \quad \eta_{12} = \frac{(G_f / G_m) - 1}{(G_f / G_m) + \xi_{12}} \tag{4}$$

Obviously, the parameters $\xi_{11}$ and $\xi_{12}$ take different values, which can be deduced or fitted when modeling a particular property. Hull [13] demonstrated that these parameters often take values 0.2 and 1 for. $\xi_{11}$ and $\xi_{12}$ respectively. Table (1) shows the parameters which were used to model the elastic constant of the laminates.

**Table 1: Materials properties used to model the elastic constants [13]**

| Parameter | Kevlar fiber | Glass fiber | Epoxy risen | Glass / epoxy | Kevlar/epoxy |
|---|---|---|---|---|---|
| Young's modulus (E) | 130 GN/m$^2$ | 76 GN/m$^2$ | 3.5 GN/m$^2$ | --- | --- |
| Volume fraction ($V_f$) | --- | --- | ----- | 0.6 | 0.5 |
| Poisson's ratio ($v$) | 0.21 | 0.25 | 0.33 | 0.57 | 0.42 |
| Fibre orientation ($\theta$) | -- | --- | --- | $\pm 45^o$ | $\pm 45^o$ |

The reduced stiffness constants of unidirectional ply were calculated [2] by:

$$Q_{11} = \frac{E_{11}}{1 - v_{12}v_{21}} \;\; ; \;\; Q_{22} = \frac{E_{22}}{1 - v_{12}v_{21}} \;\; , \;\; Q_{12} = v_{12}Q_{22} \;\; ; \;\; Q_{66} = G_{12} \tag{5}$$

The above reduced stiffness constants were transformed to obtain the corresponding values in coordinate system of the laminate, equivalent to a rotation of ($\theta$). Therefore, the transformed reduced stiffness constants were obtained by using the following equation [13]:

$$[R] = \begin{bmatrix} \cos^2\theta & \sin^2\theta & 2\cos\theta\sin\theta \\ \sin^2\theta & \cos^2\theta & -2\cos\theta\sin\theta \\ -\cos\theta\sin\theta & \cos\theta\sin\theta & \cos^2\theta - \sin^2\theta \end{bmatrix} \tag{6}$$

This is lead to:
$$\left. \begin{aligned} \overline{Q}_{11} &= Q_{11}c^4 + 2(Q_{12} + 2Q_{66})s^2c^2 + Q_{22}s^4 \\ \overline{Q}_{12} &= (Q_{11} + Q_{22} - 4Q_{66})s^2c^2 + Q_{12}(s^4 + c^4) \\ \overline{Q}_{22} &= Q_{22}c^4 + 2(Q_{12} + 2Q_{66})s^2c^2 + Q_{11}s^4 \\ \overline{Q}_{66} &= (Q_{11} + Q_{22} - 2Q_{12} - 2Q_{66})s^2c^2 + Q_{66}(s^4 + c^4) \end{aligned} \right\} \tag{7}$$

The elastic constants of the laminate were evaluated as follows:

$$E_y = \overline{Q}_{11}\,(1 - \nu_{yx}\,\nu_{xy})$$

$$E_x = \overline{Q}_{22}\,(1 - \nu_{yx}\,\nu_{xy})$$

$$G_{xy} = \overline{Q}_{66} \tag{8}$$

$$\nu_{yx} = \frac{\overline{Q}_{12}}{\overline{Q}_{22}}$$

$$\nu_{xy} = \frac{\overline{Q}_{12}}{\overline{Q}_{11}}$$

The above equations were implemented in Visual Basic program to predict the elastic constants in equation (8). To predict the flexural young's modulus of the composite laminates, first of all, the axial modulus should be decremented experimentally as described previously, and then by comparing these results by the modeled values, it is possible to find the corresponding flexural modulus of matrix,

## RESULTS AND DISCUSSIONS
### Water absorptions

Figure (2) shows experimental result for water absorption of Kevlar/ epoxy and glass/epoxy specimens after immersion at 95 $^o$C in period of 625 hours. It can be seen that the both curves are linear with square root of time from the beginning to percent water content of 1.29 % and 0.65 % for Kevlar/epoxy and glass/epoxy specimens respectively, following the Fickian behavior. This linearity suggests that the water absorption is predominantly diffusion in this region.
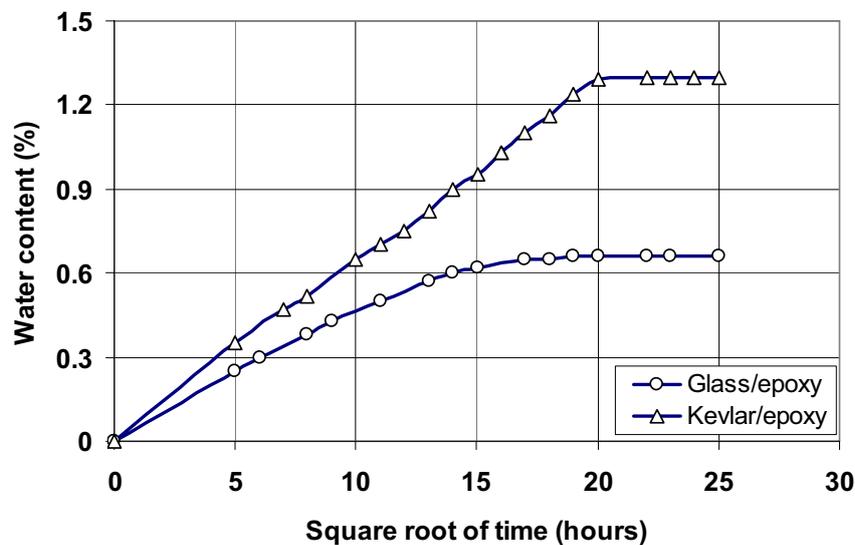


**Figure 2: Water absorbed curves for Glass and Kevlar reinforced epoxy laminates at 95 $^o$C in sea water**

After this region, the curves become none linear because the specimens began to fill with water and absorption rate became very slow and approximately constant. Adamson [14] demonstrated that the final equilibrium may not be achieved for perhaps years in this region due to the difficulty with which water enters the highly cross-linked micro-gel particles or micelles within the resin. However, the rate of absorption can be accelerated by increase the absorption temperature [2].

It can be noted that the percentage of the water content of the Kevlar / epoxy composite is two times higher than Glass/ epoxy composite due to the nature of the polymer fiber which is susceptible to water absorption controlled by temperate. This observation agrees with observation of Khatibi et. al. [15] who observed three to five times lowers absorption rates in Glass reinforced polymer laminates than Kevlar reinforced polymer laminates. This is due to the fact that the water absorption of Kevlar fiber is significant compared to carbon and glass fibers. However, since the water absorption can only access at free edges.

Figures (3) and (4) show flexure moduli against temperature for dry and wet conditions Kevlar and glass epoxies laminates respectively. Both Figures show an increased rate of fall in modulus at high temperature corresponding to the glass transition temperature of the laminates.
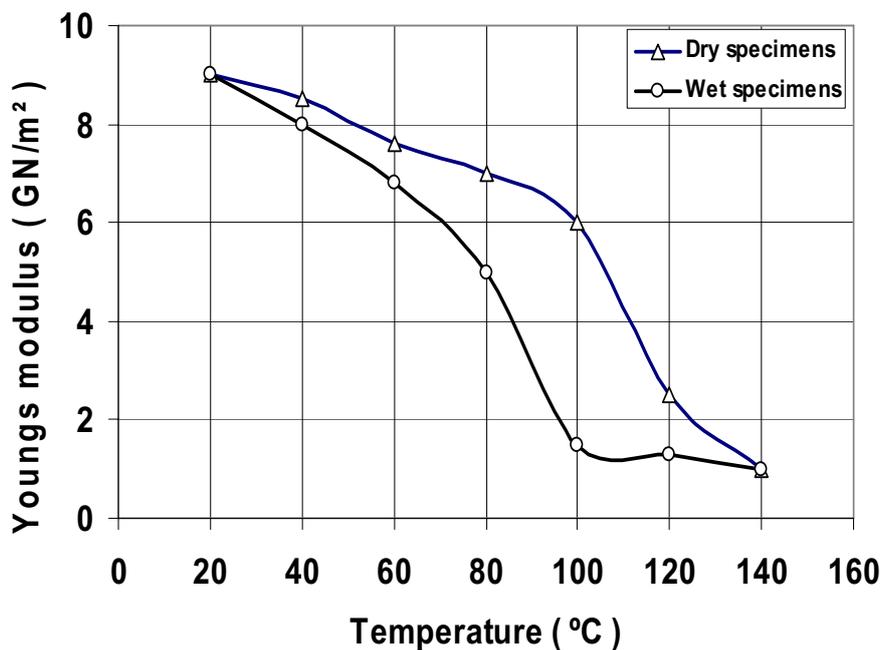


**Figure 3: flexural Young's modulus versus temperatures for Kevlar/epoxy laminate**

After the glass transition temperature, the curved significantly displaced downwards. At moderate temperatures (below transition temperature) both dry and wet curves have a similar response to increase temperature. At about 60 $^o$C for glass/ epoxy specimens and 20 $^o$C for Kevlar/epoxy, the curves diverge due to lower transition temperature of the plasticized wet specimens. At high temperature (approximately 140 $^o$C) the two curves meet where the dry and wet specimens exhibit the same values. This convergence is probably related to the effect of the very high temperature on the wet specimens which become dry and may recover some of their stiffness.

It can be seen that the two composites show a significant shift of about 30 $^o$C in transition temperature with water absorption. The Kevlar /epoxy and glass / epoxy specimens show dry transition temperatures of 100 $^o$C and 120 $^o$C respectively. These values fall to about 80 $^o$C on water absorption. These values of transition temperatures are within the range of values which presented by Harris [16].
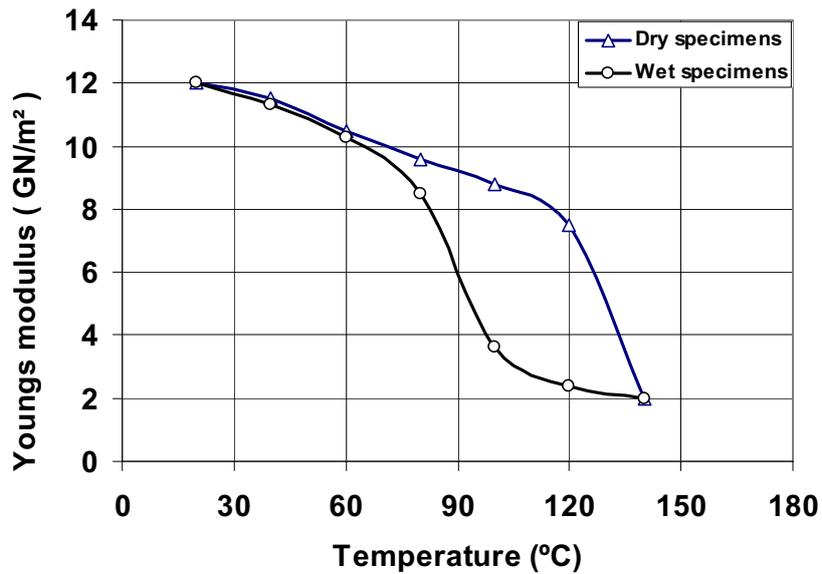
**Figure 4: flexural Young's modulus versus temperatures for glass/epoxy laminate**

Figure (5) shows estimated values of flexural young's modulus of the epoxy resin, back calculation (modeled results) from the laminate modulus in principle axis using the equations described above. The curve shows the effects of plasticization and swelling of the resin due to the effect of water absorption. The plasticization and swelling reduced the transition temperature of the resin from 110 $^o$C to 80 $^o$C. When water diffuses in the resin, some of water began to occupy polymer free volume, cause no swelling, while some of water disrupts interchain hydrogen bonds, causing swelling by hydrogen bonding with resin resulting in plasticization of the resin [6]
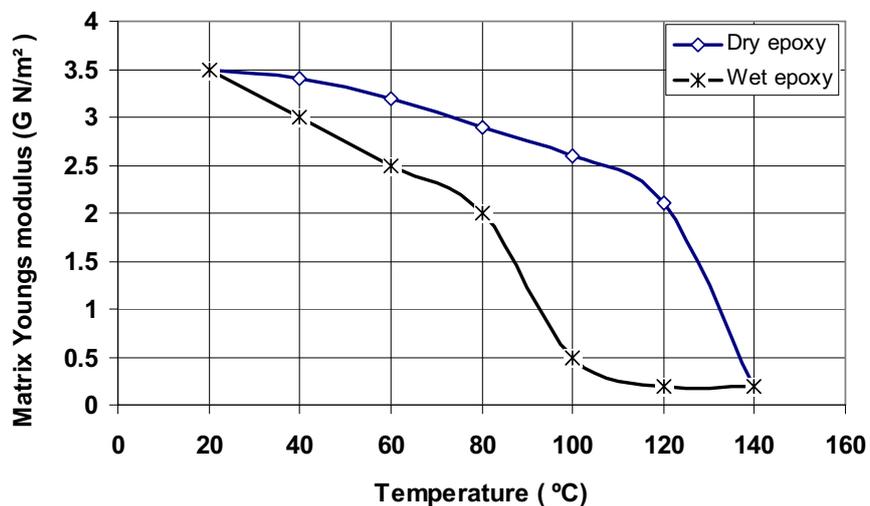


**Figure 5: matrix modulus versus temperatures for the epoxy resin**

The curve follows the same behavior of the curves of axial modulus in Figure (3). At room temperature, the two moduli have same values (about 3.5 GN/m$^2$) and then diverge due to the effect of temperature to meet again at about 140 $^o$C. Similar observation was made by Geoff et al [2] for epoxy, vinyl ester and phenol resins.

## CONCLUSION

- Sea water absorption tests at 95 $^{\circ}$C on Kevlar/epoxy and glass/epoxy composite specimens showed that both materials absorbed a considerable amount of water which caused degradation of physical and chemical properties of the material.
- The axial flexural modulus was found to be reduced gradually by temperature below the glass transition temperature. This reduction was increased considerable above the glass transition temperature.
- The glass transition temperature of the epoxy resin was found to be decreased by about 30 $^{\circ}$C at wet condition.
- The plasticization and swelling phenomena, due to water absorption, have considerable effect on the degradation of the Kevlar and glass / epoxy composite laminates.

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## NOMENCLATURE

| | |
|---|---|
| c, s | $\text{Cos}\theta$ and $\sin\theta$ |
| $E_{11,}\ E_{22},\ G_{12}$ | Longitudinal, transverse and shear moduli in principal directions. |
| $E_f,\ E_m$ | Fibre and matrix Young's moduli. |
| $E_2,\ G_2$ | Effective transverse and shear moduli in principal directions. |
| F | Applied load (N) |
| $G_f,\ G_m$ | Fibre and matrix shear moduli. |
| I | Moment of inertia ($\text{mm}^4$) |
| l | Span length (mm) |
| $\overline{M}$ | Water absorption rate |
| [R] | Transformation equation. |
| $Q_{11}, Q_{22}, Q_{12}, Q_{66}$ | Reduced stiffness of the undamaged ply. |
| $\overline{Q}_{11}, \overline{Q}_{22}, \overline{Q}_{12}, \overline{Q}_{66}$ | Transformed reduced stiffness. |
| $V_{f,}\ V_m$ | Fibre and matrix volume fractions. |
| $v_{12}, v_{21}$ | Poisson's ratios in principal directions. |
| $v_f,\ v_m$ | Poisson's ratio for glass fibre and matrix. |
| $v_{xy}\ v_{yx}$ | Poisson's ratio in x and y directions |
| Y | Deflection |
| $W_w$ and $W_d$ | Wet and dry weights of the specimen. |