

## Study Diffusion of Water to Carbon Fiber /Epoxy Composite

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### Abstract

In present work moisture diffusion properties of the woven fabric carbon/epoxy laminates were determined using weight gain, experiments over a temperature range of 30 °C to 60 °C. The laminate-shaped fiber reinforced composites were manufactured by using epoxy resin (Epon 828) cured with TETA (tri ethylene tetra amine) reinforced with carbon fiber. The prepared Composite samples were immersed in water for several weeks and moisture content was measured. The diffusivity of the composite was found to obey the Arrhenius relation over the entire range of temperature. Analytical solution to Fick's law is done by build up computer program in Matlab. Good agreement between experiment data and analytical solution of Fick's Law.

**Keywords :** Composite, Diffusion, Laminate, Activation Energy.

### دراسة انتشاريه الماء لمواد متراكبة من الياف الكربون والايوكسي

#### الخلاصة

في البحث الحالي تم دراسة عملية انتشار الماء في مواد متراكبة. تم تصنيعها من راتنج الايوكسي (ايون 828 ) المقسى بالمصلد (TETA) و المسلح بالالياف الكربونية. تم غمر النماذج في الماء لعدة اسابيع وبدرجات حراره تتروح من 30 – 60 درجة سيليزية. فسر السلوك الذي أظهرته عملية الانتشار في النماذج حسب قانون فك ( Ficks-law ) . تم حل معادله (Ficks-law) باستخدام برنامج حاسبه وجد هنالك تطابق بين الدراسه النظرية والتحليليه .

### Nomenclature

$c$	The concentration (mole/liter)
$C_p$	Specific heat (J/g °C)
$D$	Diffusion coefficient (cm <sup>2</sup> /sec)
$E_d$	Activation energy, kJ/mole
$h$	Thickness of lam
inate, mm	
$K$	Thermal conductivity ( kcal/h °C)
$M$	Mass percentage of water absorbed (%)
$R$	Gas constant, j/mol K
$t$	Time (s)
$T$	Temperature, °C

## 1. Introduction

A fiber reinforced plastics (FRP) is a composite material consisting of a network of reinforcing fibers embedded in matrix. In FRP, fibers and plastics with some excellent physical and mechanical properties are combined to give a material with new and superior properties<sup>1</sup>.

Fiber reinforced polymeric composites are currently used in a variety of applications where they could be subjected to mechanical loads or environmental effects such as a wide range of temperatures, moisture, radiation, or aggressive solvent-rich atmospheres.

Moisture absorbed in a polymer matrix can lead to a wide range of effects. Some effects on the polymeric materials are reversible and can be erased on removal of water. Others are irreversible and result in permanent changes in the performance of polymers. Water absorption into polymer materials can cause plasticization and swelling, which are both reversible processes. Water acting as a plasticizer can depress the  $T_g$  of the polymer matrix and reduce the strength and modulus of the adhesive.

Polymeric matrix composites differ from other materials in the sense that low-molecular weight substances such as water may easily migrate even at room temperature, generating a variation of the material's structure, morphology, and composition. This phenomenon occurs only in the matrix or at the fiber-matrix interface since water cannot penetrate the fiber. In many cases, it could lead to an irreversible degradation of the material in the so-called humid aging that includes both chemical aging and physical aging. The epoxy matrices show moisture

sensitivity due to interactions between some polar groups of the macromolecule and the water molecules, which leads to a reduction of both glass transitions temperature and mechanical properties. This sensitivity increases with the increasing degree of cross-linking, and also with the polarity and concentration of the molecular groups. Among epoxy polymers, aromatic amine-cured epoxies show the highest sensitivity.

The aim of this paper is to find a systematic method for investigating and understanding water absorption properties and diffusion coefficients at different temperatures in composite materials.

## 2. Theory

### 2.1) Kinetics of Water Absorption

Diffusion is the process by which matter is transported from one part of the system to another as a result of random molecule can be described in terms of the random molecular motion. In general, diffusion behavior and transport in glassy polymers have been classified according to the relative rate of mobility of the Penetrate and of polymer segments.

According to the one-dimensional Fick's law, the distribution of moisture concentration through-the-thickness of an infinite laminate is a function of time  $t$  and position  $z$  in the thickness direction. It is given by<sup>(2)</sup>

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial z^2} \quad \dots\dots\dots(1)$$

where  $c$  is the concentration of the penetrate,  $t$  is the time,  $z$  is the distance through the plate thickness, and  $D$  is the diffusion coefficient. Various regions are involved during the moisture uptake process in a

polymer/composite. There are at least 3 regions

(i) Initial absorption process, which is linear, is characterized as being a quick process. In terms of diffusion, this is the region during which the concentration gradients are equilibrating and therefore this is a “diffusion controlled” region. Any changes to the environment, for example changing the temperature of the aging water bath will result in a corresponding change in diffusion coefficient and therefore, the rate of uptake will either increase or decrease depending on the direction of temperature change. In terms of free volume, this is a region that is controlled by the “filling up” of the free volume of the polymer. Therefore much of the research papers that focused on measuring strain during moisture uptake noticed little strain being experienced by the polymer during this region.

(ii) The second region is the non-linear region in the Fickian uptake curve. This region is marked by the long time equilibration of concentration gradients. The end result is a stage in which the moisture content essentially remains unchanged over a long period of time. This region therefore marks a transition from the conventional diffusion controlled regime to a chemical equilibrium regime. The chemical equilibrium being established between the liquid phase and the polymer. If the chemical structure of the polymer allows for the existence of specific interactions (example hydrogen bonding) with water, then this region becomes extremely sensitive to external features such as temperature.

(iii) The third region becomes important in the case of composites wherein upon saturation; additional moisture uptake is seen at longer exposure times. At very long exposure times, reinforcements such

as glass can start degrading and this could allow room for further discrepancies.

## 2.2) Pervious Work

Ivanova <sup>(1)</sup> demonstrated that the introduction of water in the polymeric materials causes swelling, which may have introduced swelling stresses into the adhesive system.

Shen and Springer <sup>(2)</sup> used the Fickian model with great success to compute diffusion coefficients and predict uptake profiles for both polymers and unidirectional composites. They have derived an appropriate expression for the calculation of the fractional water uptake as follows:

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

.....(2)

Where  $M_t$  and  $M_\infty$  are mass percentage of water absorbed at time  $t$  and equilibrium, respectively,  $D_t$  is the diffusion coefficients of the less-dense phase, and  $h$  is the thickness of the polymer sheet

However Loos et al. <sup>(3)</sup> observed deviations from Fickian behavior for composites under long term exposure. Micro damage that exists and accumulates in the composite during moisture exposure is usually identified as being the cause for this deviation. In fact, Whitney and Browning <sup>(4)</sup> have indicated that fiber architecture has a major influence on the extent of Non-Fickian behavior. Therefore understanding the moisture uptake phenomenon in composites can prove to be a particularly challenging task. The specific

mechanisms of micro damage are not completely understood.

Jacobs and Jones <sup>(5,6)</sup>, in studies of fiber-reinforced composites, have proposed a diffusion model to describe the kinetics of water absorption in a two-phase material consisting of one dense phase and one less-dense phase. They have suggested that water diffusion in each phase follows the Fickian diffusion process.

According to Jacobs and Jones, the fractional water uptake with time in the polymeric material can be described using the following equation:

$$\frac{M_t}{M_\infty} = V_d \left\{ 1 - \exp \left[ -7.3 \left( \frac{D_d t}{h^2} \right)^{0.75} \right] \right\} + (1 - V_d) \left\{ 1 - \exp \left[ -7.3 \left( \frac{D_l t}{h^2} \right)^{0.75} \right] \right\} \dots\dots(3)$$

where  $D_l$  and  $D_d$  are the diffusion coefficients of the less-dense phase and the dense phase, respectively, and  $V_d$  is the volume fraction of the dense phase.

Maggana and Pissis <sup>(7)</sup> have further modified the Jacobs-Jones model by considering the epoxy resin system as a two-phase system with a homogeneous and nonpolar phase, where the major part of water is absorbed, and a second phase with different density or/and hydrophilic character. By assuming that water diffusion takes place independently in the different phases in accordance with the Fick's second law, Maggana and Pissis have proposed the following equation

$$M_t = M_1 \left\{ 1 - \exp \left[ -7.3 \left( \frac{D_d t}{h^2} \right)^{0.75} \right] \right\} + M_2 \left\{ 1 - \exp \left[ -7.3 \left( \frac{D_l t}{h^2} \right)^{0.75} \right] \right\} \dots\dots (4)$$

Where  $D_l$  and  $D_d$  are the diffusion coefficient of the two phases, and  $M_1$  and  $M_2$  is the mass percentage of absorbed water at equilibrium in phase 1 and 2.

### 3. Experimental work

The material considered for this study was laminate hand lay-ups, which is a carbon–epoxy fabric composite prepared from prepreg by autoclave molding. Unidirectional XA-S carbon fiber, woven tape (340 g/m<sup>2</sup>), 100 mm in width was selected as the reinforcing component of the composite system. The matrix is proprietary diglycidyl ether of bisphenol A (DGEBA) epoxy resin cured with TETA as curing agent product of (Ciba Co.) trade name CY 956.

The curing of the samples was carried out on a Autoclave, the suggested cure cycle is curing temperature is 70 °C , for 1 hour, post curing temperature is 150 °C, for 6 hours, applied pressure is 6 bar.

Details of the fabrication and curing can be found in references <sup>(8)</sup>.

#### 3.1) Diffusion and Permeability of Composite Test

Diffusivity,  $D$  is generally measured by exposing a dry sample to a humid environment and measuring the mass of water absorbed, i.e. the weight gain, as a function of time. The measured weight gain is then fit to the solution to the diffusion equation (Fick's law) to determine  $D$ .

The test was carried out according to ASTM- D570 as follows:

1. The prepared samples were weighed by using digital balance (Sartorius- Germany). Their weight, gave the value  $W_0$ .
2. In order to calculate the water absorbed (up taken) by samples, the samples were immersed in water.
3. The samples were reweighed after the immersion of samples in water.
4. The process was repeated for several weeks and moisture content was determined using the following equation:

$$M(\%) = \left[ \frac{W - W_0}{W_0} \right] * 100 \quad \dots (5)$$

where  $M(\%)$ ,  $W$  and  $W_0$  are the moisture content at a given time, weight of the sample at the time of the measurement and initial weight in grams respectively <sup>(2)</sup>.

The diffusion coefficient is calculated according to Fick's second law, by using equation (6)

5. In order to get an estimate of the diffusion coefficient at different temperature. Experiments were run at four different temperatures namely 60°C, 50°C, 40°C and 30°C.

## 4. Results and Discussion

### 4.1) Isothermal Water Uptake

Isothermal moisture uptake experiments were performed on specimens at different temperatures. Sample weight changes were plotted against time. A typical plot is shown in Figure (1). This is a moisture uptake plot for aging performed at 60°C.

The time axis on the plot has been intentionally plotted as  $\text{hour}^{1/2}$  in order to comply with Ficks law. Three samples were run at this temperature and the standard deviation was found to be insignificant. Moisture content was determined using equation (5)

Figure (2) shows a plot of moisture uptake at all four temperatures. It is

evident from the plot that as temperature increases, the rate of moisture absorption increases and so does the maximum moisture content. An increase in the conditioning temperature significantly reduces the time required to reach the equilibrium moisture content.

The experimental results presented in Figure 1 show that there is an initial linear behavior for all directions and its slope is then independent of both concentration and time, allowing the determination of the diffusion coefficient. The diffusion coefficients determined for the above mentioned four exposure temperatures are summarized in Table1.

**Table 1:** Calculated Diffusion Coefficients for woven fabric carbon/epoxy laminates

Temperature (°C)	Maximum Moisture content (%)	Diffusion coefficient, D (cm <sup>2</sup> /sec)
60	1.32	2.639e-8
50	1.22	1.76e-8
40	1.12	6.865e-9
30	1.02	2.905e-9

### 4.2) Diffusivity vs. Temperature

The above information can then be used to get activation energy for the diffusion process by using a Arrhenius type equation that describes the temperature dependence of the process. This equation is of the following type, <sup>(8)</sup>

$$D = D_0 \exp\left(\frac{E_d}{R}\right) \quad \dots (6)$$

Where  $E_d$ ,  $D_0$ ,  $R$  and  $T$  are the activation energy for diffusion, constant coefficient, universal gas constant and temperature in degrees Kelvin respectively. This equation can

then be reduced into a linear form by taking natural log on both sides. The equation then takes the following form and is plotted to acquire the slope and the intercept.

$$\ln D = \ln(D_o) - \left(\frac{E_d}{R}\right)\frac{1}{T} \dots\dots(7)$$

Figure (3) shows a plot of the above equation indicating the expected linear correlation. The constants of the equation are  $E_d = 622$  KJ/mole and  $D_o = 6.40 \times 10^{-8}$  cm<sup>2</sup>/sec. Other workers reported<sup>(9, 10)</sup> different values for their systems.  $Mt\%$  and the related  $D_o$  and  $E_d$  values depend on several factors such as structural differences and in a particular system on the conditions of curing and sample preparation.

**4.3) Moisture Diffusion Modeling**

In order to compute the diffusion coefficient one has to review the transport problem that exists. It is a combined thermal and moisture transport problem involving both Fourier and Fick's law respectively. However upon examination of the two transport processes, it becomes obvious that the thermal process is extremely fast compared to the moisture transport problem. Mathematically this is represented as follows<sup>(2)</sup>,  $(k/\rho C)/D$  which is the ratio of the thermal to the moisture transportation speed is approximately  $10^6$ .  $k$ ,  $\rho$ ,  $C$  and  $D$  are the thermal conductivity, density, specific heat and diffusion coefficient respectively. Therefore we tend to concentrate only on the moisture diffusion problem and neglect the temperature transport problem. This process is usually described by a differential mass balance, often called Fick's second law of diffusion, which in the one-dimensional case may be written as equation (1).

In order to determine the moisture distribution in a composite specimen, boundary conditions have to be specified in addition to equation (1). It can be assumed that at the initial time  $t_0$ , concentration  $c$  is equal to zero everywhere inside the plate. However, on the surfaces, the moisture concentration is different than zero, which corresponds to the fact that these surfaces are subjected to diffusion from the surrounding environment. The magnitude of the initial concentration  $c_i$  on the surfaces can only be determined from an experiment. However, if the magnitude of  $c_i$  is known, the changes of concentration  $c$  with time can be quite easily determined from equation (1).

$$\frac{\partial c(z,t)}{\partial t} = D \frac{\partial^2 c(z,t)}{\partial z^2}$$

At  $0 < z < h$  and  $t > 0$ ;  
 $c(z, t) = c_i(z)$ ,  $0 \leq z \leq h$  and  $t < 0$ ;  
 $c(z, t) = c_\infty$ ,  $z < 0$ ,  $z > h$  and  $t > 0$   
 .....(8)

The solution of the above partial differential equation is<sup>(11)</sup>

$$\frac{c - c_o}{c_\infty - c_o} = 1 - \frac{4}{p} \sum_{n=0}^{\infty} \frac{1}{(2n+1)} \sin \frac{(2n+1)pz}{h} \exp\left(-\frac{p^2(2n+1)^2}{h^2} Dt\right) \dots\dots(9)$$

where  $c_o$  is the initial moisture concentration and  $c_\infty$ , the saturation moisture concentration. The average moisture concentration through the thickness of the specimen can be computed as

$$\bar{c} = \frac{1}{h} \int_0^h c(z,t) dz = c_o + (c_\infty - c_o) \left[ \dots \right]$$

$$1 - \frac{8}{p^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{p^2(2n+1)^2}{h^2} Dt\right) \dots\dots (10)$$

The following expression is commonly used<sup>(8, 12, 13)</sup>

$$\frac{c - c_o}{c_{\infty} - c_o} = \frac{M - M_o}{M_{\infty} - M_o} = \left(1 - \frac{8}{p^2}\right) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{p^2(2n+1)^2}{h^2} Dt\right) \dots\dots(11)$$

where  $M_0$  is the initial moisture concentration, which is null in this study, and  $M_{\infty}$  is the maximum quantity of the diffusing substance at infinite time. For short times, when  $M \leq 0.5M_{\infty}$  .....(12)

Equation (12) can be well approximated by

$$\frac{\bar{c}}{c_{\infty}} = \frac{M}{M_{\infty}} = \frac{4}{\sqrt{p}} \left(\frac{Dt}{h^2}\right)^{1/2} \dots\dots (13)$$

It is usual to plot  $M/ M_{\infty}$  against the square root of time and the linearity of the curve in its initial portion can be considered as a validity criterion for the Fick's law. In order to predict the concentration gradient within the woven fabric carbon/epoxy laminates, the moisture content at saturation  $c_{\infty}$  and the diffusivity  $D$  must be determined. Moisture uptake tests are performed to measure these parameters<sup>(14, 15)</sup>. The set of two parameters ( $c_{\infty}$ ,  $D$ ) given in Table 1.

Analytical solutions based on Fick's law are done by build up computer program in Mat lab version 5.3.<sup>(16)</sup> The solid lines in Figure (2) are the predictions based on equation (9) for the uptake at different exposure temperatures. As one can see the moisture uptake for woven fabric carbon/epoxy laminates does obey Fick's Law. Good agreement

between experiment data and analytical solution of Fick's Law.

**5. Conclusions**

Experimental results clearly confirm that the diffusion process within the woven fabric carbon/epoxy laminates is in agreement with the Fick's law. Diffusion coefficient of the samples was determined at different temperatures. The results showed that diffusion coefficient increases as temperature rises, indicating that the time required to reach the saturation level decreases as temperature is increasing. The results show that diffusivity,  $D$  is well represented by the Arrhenius law, with  $D_0=6.40e-8$  cm<sup>2</sup>/sec and  $E_d = 622$  kJ/mol over a wide range of temperatures. Diffusivity was determined by fitting weight gain or loss data to the solution of the diffusion equation.

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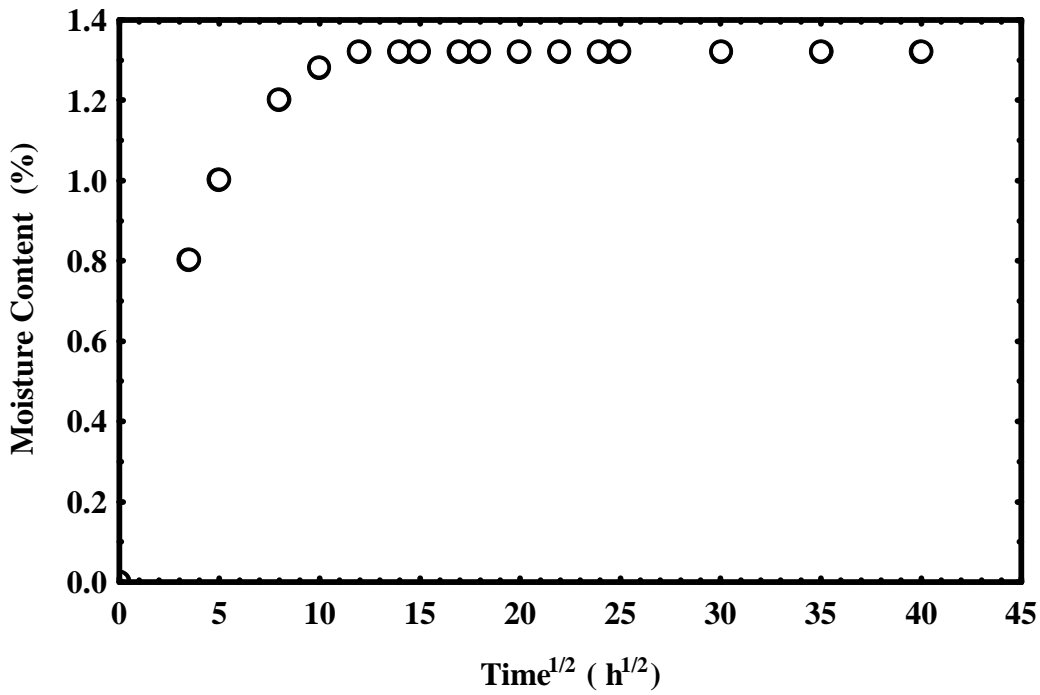


Figure 1: Moisture uptake at 60°C for woven fabric carbon/epoxy laminates

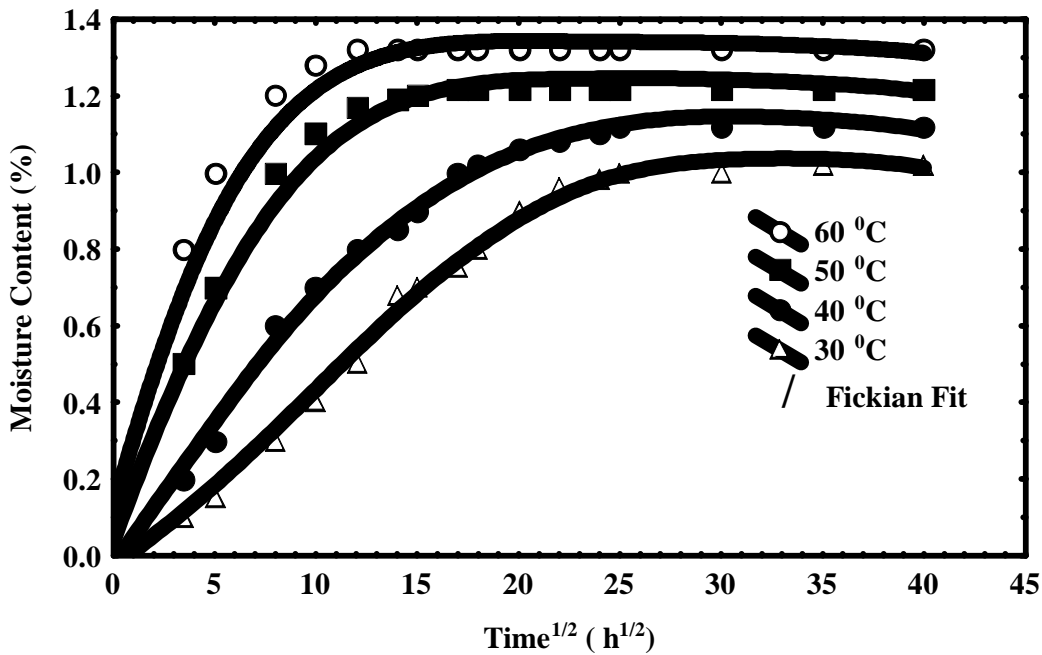


Figure 2: Temperature dependence on moisture absorption in woven fabric carbon/epoxy laminates

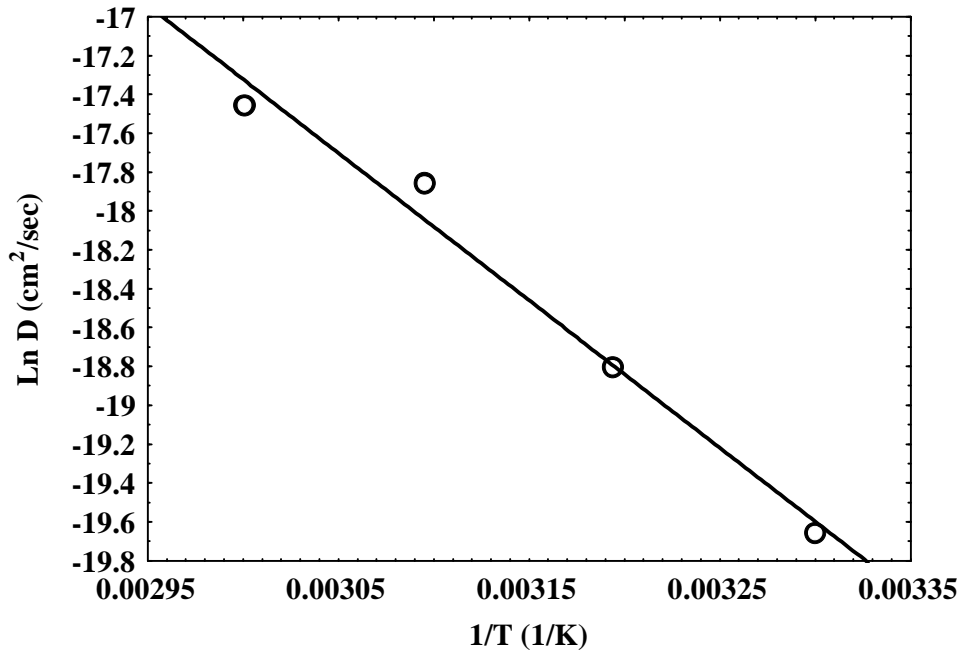


Figure 3: Arrhenius plot of diffusion coefficients for woven fabric carbon /epoxy laminates