

Diffusion of various liquids to tubular shaped fiber reinforced composites

Hussein Ali Hamid AL-Abdly ^{*}, Najat j. Salah ^{}, Adnan A. AbdulRazak ^{ID}, and Hassen Sh. Majdi ^{*}**

Received On :27/9/2005

Accepted On:7/10/2007

Abstract

In present work tubular –shaped fiber reinforced composites were manufactured by using two types of resins (Epoxy and unsaturated polyester) and separately reinforced with glass, carbon and kevlar-49 fibers (filament and woven roving), hybrid reinforcement composites of these fibers were also prepared. The fibers were wet wound on a mandrel using a purposely designed winding machine, developed by modifying an ordinary lathe, in winding angle of 55° for filament. Various liquids were allowed to diffuse into the composite samples, where all composite samples were immersed in water, HCl (0.5N, 1N) and NaOH (0.5N, 1N). The exhibited behaviors were mainly explained in accordance to Fick’s –law. However, there were few case of anomalous behavior observed.

The observed difference in diffusion rate for acidic and basic solutions may be explained in terms of different permeability of OH⁻ and H⁺ ions in the composite samples. This permeability was also found to be affected by the debonding process which might be initiated by the liquid penetration. Diffusion coefficients were also deduced and their relatively higher values are indicative for some damage mechanism taking place in the composite and not the pure matrix. UP composite exhibited higher values than EP composite which suggest that higher damage has taken place in UP-composite.

Keywords: diffusion, tubular shaped, composites

() 49-

55⁰

NaOH (1,0.5) HCL (1,0.5)

(Ficks-law)

H⁺ () OH⁻

()

Nomenclature

b	Thickness of samples
C	Carbon fiber
D	Diffusion coefficient
D_0	Permeability index
E_a	Activation energy of the diffusion process
E_p	Epoxy resin
F_x	The flux in the x-direction
G	Glass fiber
k	Constant
K	Kevlar fiber
M_t	Relative weight gain
M_∞	Equilibrium relative weight gain
n	Constant
PVA	Poly vinyl acetate
R	The gas constant
Up	Unsaturated poly ester

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 properties¹.

Polymers which are the matrix phase in composites are permeable, whilst ceramics, glasses and metals are generally impermeable, this may seem a disadvantage in fiber – reinforced composite which cause weakening, however in some cases permeability is an advantage, and one particular area where this is so in the use of polymers in drug delivery systems.

The broad subject of interactions between polymeric composite materials and liquids or vapor environments has been and currently is the theme of numerous

studies. Most of them can be classified into three topics representing three conceptual approaches. The first focuses on the actual mechanisms of penetration, where emphasis is given to questions related to transport kinetics and to diffusion processes. The theme of the second topic is the studying of dimensional response of the composite, termed hygroelasticity, where one is confronted with questions such as how many the structures swells, and what is the magnitude of the internal stresses which develop in it. The third topic is concerned with the deterioration of the original properties due to the attack of moisture and in investigates the environmental effect on the residual properties.

The aim of this paper found a systematic method for investigating and understanding these phenomena in composite materials is to initially define and characterize theme in the

un-reinforced polymeric matrix. There after additional effects contributed by the presence of the reinforcement and of the interface appear clearly.

2. Theory

During its service life time a composite material comprising a fibrous reinforcement and an organic resin matrix will absorb moisture and other solution from its surroundings. With an organic reinforcing fiber the amount of water or others absorbed will depend primarily upon the chemical nature of the resin matrix and the environment to which it is exposed. With an organic reinforcing fiber moisture can also taken up by the fiber itself².

2.1 Mechanisms of liquid penetration.

2.1.1 Liquid transport in the matrix phase

Matrices for advanced composite materials usually comprise cross linked polymers with high glass transition temperatures, so that the polymer under the variable service conditions is mostly in its glassy state. It is there fore relevant to examine liquid transport in glassy polymers (diffusion). It has been shown that the cross-linked resins exhibit more complicated behavior. This is partly, but not entirely, because liquid sorption occurs with the loss of organic matter by leaching, the absorption curve then resembles a Fickian on behavior but usually the first plateau is followed by a Fick's second law of diffusion^{3,4,5,6}.

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. The motion of a single molecule can be described in terms of "random walk" picture.

It is possible, statistically, to calculate the mean- square distance it has traveled in a given time interval, but is impossible to predict in what direction a given molecule will have moved in that time⁷. 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.

Such classification produces three basic categories of behavior as follows:-

Case I, or Fickian diffusion, in which, the rate of diffusion is much less than that of the polymer segment mobility. Sorption equilibrium is rapidly established, leading to time-independent boundary conditions which exhibit no dependence or swelling kinetics.

Case II (or super case II), the other extreme in which diffusion and penetrate mobility are much greater compared with other relaxation processes, sorption processes are strongly dependence on swelling kinetics.

Case III Non- Fickian, or anomalous diffusion which occurs when the penetrate mobility and polymer segment relaxation are comparable.

This diffusion is related to the fact that the polymers in which it is observed are hard or glassy, and it vanishes at and above the glass transition temperature⁸. Case I (Fickian) and case II can be viewed as the two limiting types of transport processes with anomalous diffusion being between them. They can be distinguished by the shape of the sorption time curve represented by:

$$\frac{M_t}{M_\infty} = Kt_n \tag{1}$$

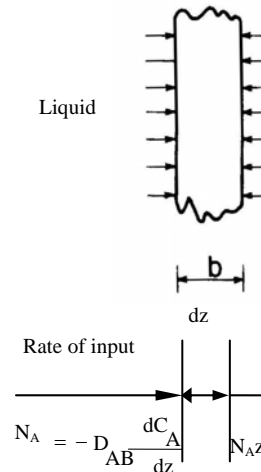


Fig 1 A schematic presentation of specimen exposed on both sides

Where M_t is the relative weight gain at time t , M_∞ is the equilibrium relative weight gain, K and n are constants.

For Fickian systems: $n = \frac{1}{2}$, while for case II, $n = 1$ (and for super case II, $n > 1$). For anomalous systems $\frac{1}{2} < n < 1$.

For Fickian uptake by a specimens of thickness b exposed on both sides to the same environment, as shown schematically in Fig (1), mass uptake is related to time by the following equation⁵.

$$\frac{M_t}{M_\infty} = \frac{4}{b} \left(\frac{Dt}{\pi} \right)^{1/2} \quad (2)$$

Where D is the diffusion coefficient.

2.1.1.1. Fickian diffusion

Fick's First law is the fundamental law of diffusion It states that the flux in the x-direction (F_x) is proportional to the concentration gradient ($\partial c / \partial x$)

$$F_x = -D \left(\partial c / \partial x \right) \quad (3)$$

Flux is the amount of substance diffusing across unit area in unit time and D is the diffusion coefficient. The first law can only be directly applied to diffusion in the steady state, that is, where concentration is not varying with time⁹.

Fick's second law of diffusion describes the unsteady state and it can be expressed by the flux gradient are obtained for Cartesian coordinate by differentiation equ. (3), for example:

$$\partial F_x / \partial X = -D \partial^2 C / \partial X^2 \quad (4)$$

So that for (x,y,z) direction:

$$\frac{\partial c}{\partial t} = -D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \quad (5)$$

Equ. (5) is known as Fick's second law of diffusion. Under circumstances where diffusion is limited to the x- direction it simplifies

$$\frac{\partial C}{\partial t} = -D \frac{\partial^2 C}{\partial x^2} \quad (6)$$

However if D depends on the concentration of the diffusion and hence, on location, it may be written as:

$$\frac{\partial c}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial c}{\partial x} \right) + \frac{\partial}{\partial y} \left(D \frac{\partial c}{\partial y} \right) + \frac{\partial}{\partial z} \left(D \frac{\partial c}{\partial z} \right) \quad (7)$$

Some of the characteristic features of Fickian diffusion are as follows:¹⁰ both sorption and desorption curves as functions of the square root of time are linear in the initial stage.

1. Above the linear portion both absorption and desorption curves are concave to the abscissa.
2. The sorption behavior obeys the film thickness scaling law, i.e. reduced sorption curves for films of different thicknesses b are all superimposable.

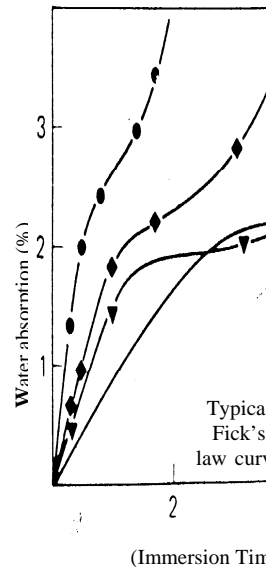


Fig (2) Resin water ab

3. When D is constant the absorption and the desorption curves coincide over the entire range of t.
4. The temperature dependence of D can be expressed by the Arrhenius relation.

$$D = D_0 \exp(-E_a/RT) \quad (8)$$

Where the pre-exponential term, D_0 , is the permeability index, E_a is the activation energy of the diffusion process and R is the gas constant.

The liquid diffusion coefficient, for example, may be determined readily by exposing a thin dry specimen (after recording its dry weight) to a constant liquid environment, monitoring and plotting its weight gain versus $t^{1/2}$. Such results for an epoxy resin are demonstrated in Fig. (2) The diffusion coefficient is then calculated by

$$D = \pi \left(\frac{kb}{4M_\infty} \right)^2 \quad (9)$$

Where: D_i = Diffusion coeff., b = Thickness of samples,

M_∞ = Max. Weight gain, k is the slope of the linear portion of the plot of M_t versus $t^{1/2}$. This experiment obviously assumes one-dimensional penetration and therefore a thin specimen (compared with the other dimensions) should be employed to minimize the edge effect².

Fig (3) presents schematic description of the manger sorption anomalies that have been reported, they are:

1. Pseudo Fickian behavior; the sorption and desorption curves when plotted against $t^{1/2}$ show anomalously short initial linear portions, and /or the sorption curves depart from film thickness scaling law.
2. Sigmoid behavior: the sorption curves are sigmoid in shape with a simple inflection point at about 50% equilibrium sorption. The initial rate of desorption then becomes slower and the curves cross.
3. Two – stage sorption behavior: The initial uptake is rapid and a linear function of $t^{1/2}$. The sorption curve then approach a quasi-equilibrium followed by a slow approach to a final true equilibrium.

As far as composite materials are concerned the most striking phenomenon with regard to the anomalous behavior is diminishing or even completes disappearance with the introduction of the reinforcement. Considering the complexity of the sorption behavior of the bulk resin, the almost classical Fickian behavior of the composites comes as a surprise and represents a welcome simplification.

An explanation drawn by analogy with the size dependence of relaxation controlled diffusion effects, suggests that the matrix sections between the fibers and, therefore, the path length are too small, hence the contribution of the relaxation controlled behavior disappear¹¹.

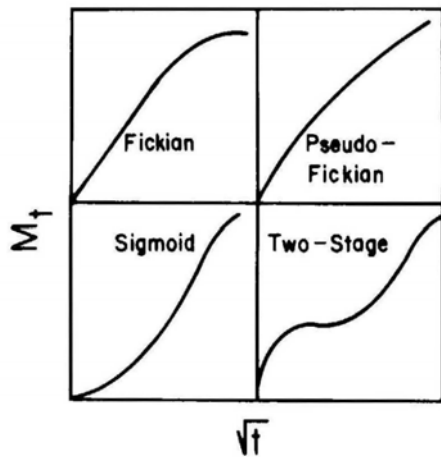


Fig (3) A schematic presentation of some major sorption anomalies

2.1.1.2. Mechanism of Liquid Penetration in Composites

Liquid penetration into composite materials is conducted by one major mechanism, namely diffusion. This mechanism involves direct diffusion

of liquid molecules into the matrix and, to a much lesser extent, into the fibers. It depends on the angle between the penetration direction and the fibers, the angular dependence resulting from the variation with the angle of the matrix cross-section available for direct diffusion.

The other common mechanisms of liquid penetration into composite materials are capillarity and transport by micro cracks. Each of them becomes active only after the occurrence of specific damage to the composites. Frequently, that damage, which enhances liquid penetration by activating those additional mechanisms, is in itself a direct consequence of the exposure of the composite to liquid. The capillarity mechanism involves flow of liquid molecules along the fiber-matrix interface followed by diffusion from the interface into the bulk resin. It is not active unless de-bonding between

the fibers and the matrix has occurred, often as a result of liquid attack at the interface.

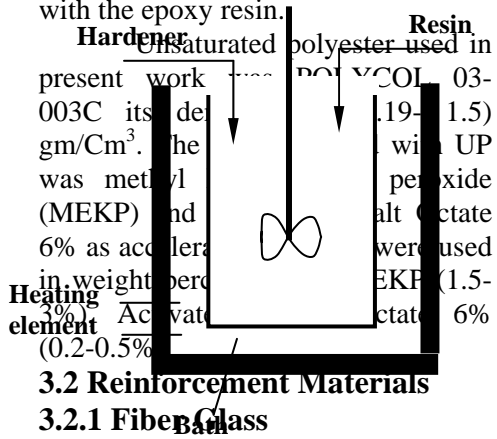
Transport of liquid by micro cracks involves both flow and storage of liquid in micro cracks or other forms of micro damage which result from environmental effects or from service conditions. The activation of these mechanisms is distinguished in increasing both the rate and the maximum capacity of liquid absorption in an auto-accelerative manner.^(9, 10)

3. Experimental Work

3.1 Materials

The materials used in the present work as a matrix were: Epoxy resin and unsaturated polyester resin and the material used as reinforcements were fibre glass (type E), Kevlar-49 fiber, and carbon fiber (HS).

The resin used in present work was Epoxy (Cy- 223), its density was (1.3-1.4) g/cm³ and Mwt = 380 g/g mole, The hardener used was HY 956 (Diethylene tri amine), it is liquid, with a density is ranging from (1.15-1.25) gm/cm³, it was added to the resin, thus the chemical bonding and cross linking was formed with the epoxy resin.



3.2 Reinforcement Materials

3.2.1 Fiber Glass

In the present work "E" glass was used, it has good strength, stiffness, electrical and weathering properties.

Its chemical composition is shown in the following table, and it was used as continuous filament.

Table (1) Chemical composition of glass fiber

SiO ₂	Al ₂ O ₃	CaO	MgO	Na ₂ O K ₂ O	Ba ₂ O ₂
52.4	14.4	17.2	4.6	0.8	10.6

3.2.2 Kevlar fibers

In the present work woven roving Kevlar- 49 (0°-45°) was used and its surface density was (340g/m²).

3.2.3 Carbon Fiber

HST carbon fiber was used as woven roving (0°-90°), and its surface density was 225g/m².

3.3 Experimental Apparatus

Experimental apparatus consists of the followings:

3.3.1 Resin Bath

It is a tank equipped with thermostat electrical heater; it was used for preparation of the resin. A mixer of helical ribbon type with 1500 rpm used for a continuous mixing of viscous liquid, the specifications of this mixer were: RPM is 1500 (rpm used), type is helical ribbon. Resin bath and mixer are shown in Fig (4).

3.3.2 Mandrel

There are several factors affecting the selection of mandrel materials. These factors include the number and size of the moldings to be produced, the type and finishing requirements of the products as well as the molding process itself.

The mandrel used during the course of this work was fabricated from low carbon steel coated with a thin layer of nickel chrome to give the required impact resistance, strength, smooth and shiny surface.

The dimensions of mandrel was L= 160 Cm and D_o = 16 Cm.

3.4 Winding Machine

Filament winding was used to fabricate the structural cylindrical samples, based on polymer matrix-fibrous composite; these samples were fabricated using a modified winding machine shown in fig (5). The fabrication steps were as follows:

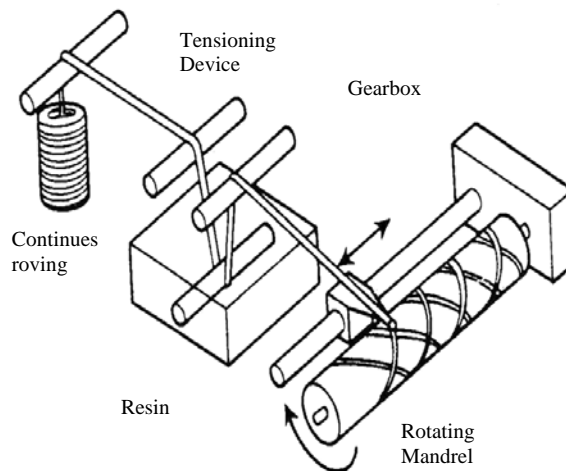


Fig 5 Schematic of Modified Winding Machine

3.4.1 Preparation of Mandrel

The mandrel was coated with a thin homogenous layer of honey wax for 15 minutes, then it was polished with a dry piece of cloth, after that the mandrel was sprayed with PVA solution three times at interval of 15 minutes.

3.4.2 Winding Process

After the preparation of the resin with the specification mentioned in section (3.1), by using the resin bath, the winding process was carried out using the winding machine as follows:

The fiber is usually wetted before winding and laid down under tension, then impregnation or soaking of the filaments, woven fabrics (tapes) was carried out by passing them through the resin bath at low speed and at constant rate to ensure sufficient saturation of fibrous with the resin. After leaving the resin bath, the reinforced fiber were passed over tensioning devices; to keep the required tension; after which the fibers were wound onto the mandrel, a part-layer after layer with preset tension. The mandrel can make one or two rotational movements and with a thread guide, an inverted translational or rotational movement, this permits to control the reinforcement laying scheme both within one and the same layer and through the thickness of article, by varying the angle of filament or tape placement.

The winding angle ($55^{\circ} \pm 2^{\circ}$) was determined by the relative speeds of the lateral movement of the traverse and rotation of the mandrel and the diameter of the mandrel.

The samples were kept in the mandrel for 48 hrs before they were drawn from the mandrel. The winding process is shown schematically in Fig (5)

3.5 Preparation of Samples

The following samples were prepared:

3.5.1 Resin with One Type of Fiber

Samples with single fiber were used with volume fractions of 50% as follows:

3.5.2 Hybrid Samples

Samples with more than one fiber were used with volume fractions of 50% as follows:

The following diagram illustrates the possibilities of having more than one hybrid compound

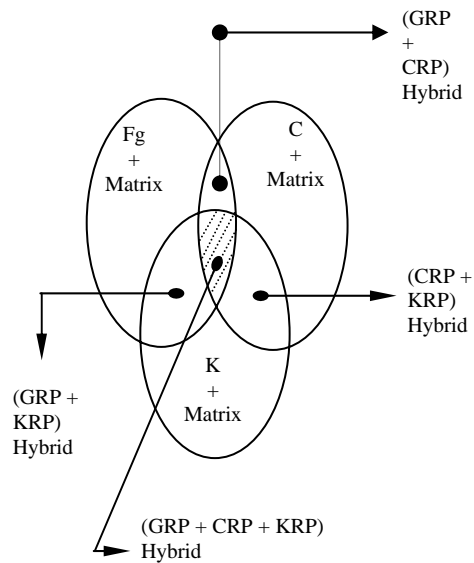


Fig. (6) Schematic shown the possibility of making hybrid composites

Where:

GRP: Glass reinforced plastic

CRP: Carbon reinforced plastic

KRP: Kevlar reinforced plastic

C: Carbon fiber + Glass fiber

K: Kevlar fiber

Eg: "E" Glass fiber

Epoxy + Kevlar fiber -49

UP

3.6 Diffusion and Permeability of Polymer test

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

1. The prepared samples were weight by using digital balance (Sartorius-Germany). Their weight, gave the value m_1 .
2. In order to calculate the water or different types of solution absorbed (up taken) by samples the samples were immersed in water, acid (HCl) with concentration of (0.5N) and (1N) while other samples immersed in (0.5N), (1N) NaOH solutions.
3. The samples were reweighed after the immersion of samples in water, and other solution acids or bases and this gave the values of (m_2).
4. The process was repeated for several weeks and the percentage of absorption was calculated as follows:

$$\left(\frac{m_2 - m_1}{m_1} * 100\% \right), \quad \begin{matrix} m_1 = \text{initial weight} \\ m_2 = \text{final weight} \end{matrix} \tag{10}$$

The diffusion coefficient is calculated according to Fick's second law, by using equation (9)

4. Results and discussion

Because of their nature matrix materials can have a comparatively rapid uptake of environmental agent such water or other liquids due to diffusion processes which occurs into fiber reinforced composites comprising glassy cross linked resin matrices such as epoxy or unsaturated polyester resins are experimentally shown to be Fickian (or anomalous Fickian), and to governed by a diffusion coefficients¹¹.

In present work the diffusion process was studied by the immersion of composite samples in water, hydrochloric acid with (0.5N, 1N) and sodium hydroxide with (0.5N, 1N) Solutions.

Fig (7, 8, 9) shows the relation between weight gain percentage of water with square root of soaking time for EP composite samples immersed in water for nine weeks for different types of reinforcement it is clear from Fig (7) for single fiber that epoxy reinforced with Kevlar fiber has a higher value of absorbed water than that reinforced with glass fiber because Kevlar fiber is a polyamide (organic fiber) as mentioned above.

From Fig (8) for hybrid composite, it is clear that the hybrid with (G + K) fibers have higher value of absorbed water, then that with (K +C) fibers and finally with (G + K + C).

Fig. (9) shows the comparison between that reinforced with single fiber and the hybrid composite, it is clear that the higher value was for (+ K_ > (+ G + K) > (+ K + C) > (+ G) > (+ G + K + C).

Fig (10, 11, and 12) show the relation between weight gain percentages with square root of soaking time for UP composite samples immersed in water for nine weeks for different type of reinforcement.

It is clear form Fig (11) for single fiber that UP reinforced with Kevlar fiber has a higher value of absorbed water than that reinforced with glass fiber.

Fig (12) show that UP reinforced with (G + K) hybrid has higher value than the hybrid with (K + C) an finally than that within (G + K + C) fibers from Fig (12) it is clear that the higher was for up reinforced with Kevlar has a higher value and > (+ G + K) > (+ K + C) > (+ G) > (+G+K+C).

It has been concluded from the figure above that the behavior of diffusion process was obey the fickion diffusion and this can be summarized by, both aborpsion and desorption curves as function of (t)^{1/2} are linear

in the initial stage, then above the linear portion both absorption and desorption curves are concave to the abscissa, and the sorption behavior obeys the film thickness scaling law¹¹.

Figs (13,14,15) shows the relation between weight gain percentage with square root of soaking time for EP composite samples immersed in (NaOH) solution with 1N and 0.5N concentrations respectively.

It is clear from Figs (13,14,15) for single fiber that the higher value was for EP reinforced with Kevlar fiber from Figs (14, 17) for hybrid composites, it is clearly seen that the samples with (G + K) fibers have higher value then with (K + C) and finally for (G + K + C) hybrid.

From Figs (15, 18) it is clearly shown that the order of highest value was for EP reinforced with (+ K) > (+ G + K) > (+ K + C) > (+G) > (+ G + K + C).

Form the figures above, it can be concluded that the rate of diffusion was concentration dependent because the samples immersed in NaOH with (1N) have absorbed higher value of solution than that immersed in (0.5N), and this agrees well with Fick's first law.

Figs (19 to 24) shows the relation between weight gain percentage with square root of soaking time for Up composite samples immersed for nine weeks in NaOH solution with (1N) and (0.5N) concentrations respectively.

Figs (19, 22) shows that up reinforced with Kevlar fiber has a higher value than that reinforced with fiber glass.

Fig (20, 23) for hybrid composite samples, it is clear that the hybrid with (G + K) has a higher value than that with (K +C) and

finally than that with (G + K + C) hybrid.

It is clearly seen form fig (21, 24) that the order of highest value was for Up composed of (+ K) > (+ G + K) > (+ K + C) > (+ G) > (+ G + K+C).

The same conclusion that for epoxy composites samples was applied for up composite samples.

Fig (25 to 30) shows the relation between weight gain percentage with square root of soaking time for EP composite samples immersed in HCl solution with 1N and 0.5N concentrations respectively.

Form Fig (25, 28) it is clear that EP reinforced with Kevlar fiber has higher value than that reinforced with fiber glass.

It is clearly seen from Fig (26 to 29) that the higher value of weight gain was for samples composed of (EP + G + K) then (EP+K+C) and (EP + G + K + C).

Fig (27, 30) shows that the order of highest value was (+ K) > (+ G + K) > (+ K + C) > (+ G) > (+ G + K + C).

It can be concluded form figures above that the samples immersed in 1N HCl have higher weight gain absorbed than that immersed in 0.5N HCl, and here the fickian behavior mechanism was applied here.

Fig (31 to 36) shows the relation between weight gain percentage with square root of soaking time for Up composite samples immersed in HCl solution with 1N and 0.5N concentrations respectively.

It is clear from Fig (31, 34) that Up reinforced with Kevlar fiber has a higher value than that reinforced with glass fiber.

Fig (32, 35) for hybrid samples shows that up hybrid composite with (G +K) fibers has a

higher value than that with (K +C) and finally with (G + K + C) fibers.

It is clearly seen from Fig (33, 36) that the order of highest value was (Up + K) > (Up + G + K) > (Up + K + C) > (Up + K) > (Up + G + K + C).

Also here for Up composites and as clearly seen from figures above that the Fickian behavior mechanism was applied here.

The Diffusion coefficient was determined experimentally by using

Sampl es	H2O	NaOH (0.5N)	NaOH (1N)	HCl (0.5 N)	HCl (1N)
Up + K	0.52	0.62	0.87	0.54	0.85
Up+G +K	0.48	0.6	0.84	0.5	0.74
Up+K +C	0.42	0.59	0.76	0.45	0.71
Up+G	0.4	0.52	0.74	0.42	0.58
Up+G +K+C	0.18	0.38	0.43	0.27	0.31

the equation $D = \pi \left(\frac{kb}{4M\infty} \right)^2$ and k is the slope of weight gain versus $t^{1/2}$ plot.

The calculated values of diffusion coefficient was show in table (2) and (3) for EP composite and Up composite respectively it is clearly seen from table (5.5) that the order of highest value from EP composite samples immersed in water was for (EP + K) > (EP + G + K) > (EP + K + C) > (EP + G) > (EP + G +

Samples	H2O	NaOH (0.5N)	NaOH (1N)	HCl (0.5 N)	HCl (1N)
Up + K	0.69	0.74	0.94	0.71	0.93
Up+G+K	0.67	0.7	0.92	0.68	0.83
Up+K+C	0.6	0.63	0.8	0.62	0.66
Up+G	0.42	0.54	0.78	0.44	0.61
Up+G+K +C	0.32	0.44	0.67	0.32	0.36

K + C).

And Also from table (2) it is clear that the order of highest value for EP composite samples immersed

in NaOH solution with 0.5N, 1N was also in the same order that for water. And also it is clear from table (2) that the order of highest value for EP composite samples immersed in HCl solution with (1N, 0.5N) was also in the same order it is clear also from table (2) that the higher diffusion coefficient was obtained when NaOH (1N) solution was used and then for HCl (1N) then for NAOH (0.5N), then HCl (0.5N) and finally for water.

Table (2) Values of diffusion coefficient ($m^2 \cdot sec^{-1}$) for EP composite samples immersed in different solutions

Table (3) show the values of diffusion coefficient for Up composite samples, it is clearly seen that the same order of values that for EP composite samples was obtained, but the value of diffusion coefficient of Up composite samples was larger than the value of Ep composite samples.

Table (3) Values diffusion coefficient ($m^2 \cdot sec^{-1}$) for UP composite samples immersed in different solutions

The exposure of composites to water, acids and alkali solution induced modifications of the mechanical properties and the morphology of the polymeric samples, this is due to that the sorbed liquid act as both plasticizer and crazing agent, deteriorates the mechanical integrity of the resin matrix, this deterioration or degradation of composite materials under the influence of an aggressive environment can result from a number of factors ¹⁵.

- 1 1- Loss of strength of reinforcing fibres by stress corrosion.
- 2 2- Loss of bond strength through degradation of the interfacial fiber/matrix bond.
- 3 3 - Chemical degradation of the matrix.

- 4- Accelerated degradation caused by the combined action of temperature and chemical environment.

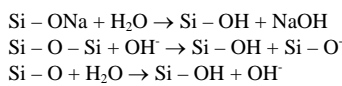
This damage mechanism can be discussed by (i) the capillary flow of liquid along the fiber – matrix interface; and (ii) the diffusion through cracks, pores or small channels present in the material. These two mechanisms are active in addition to the diffusion.

Debonding process starts immediately upon exposing the composites to liquids. The debonding enhances liquid penetration by capillary flow along the interface¹⁵.

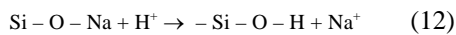
The chemical effects of various solutions on the reinforcement can be demonstrated by the example of glass fibers. It is established that degradation of glass in the presence of solution occurs mostly where the former contains alkali ions. Equation (11) presents a sequence of reactions leading to cleavage of silicon- oxygen bonds and to their conversion to

Solution		Temp. °C	Time /hr	Effect on breaking strength
10%	HCl	71	10	Degraded
10%	NaOH	99	10	Degraded
40%	NaOH	21	100	Degraded

hydroxysilane⁸.



And in acidic solution the effect is usually attributed to a hydrogen ion exchange process of the form:



The overall reaction, which is autocatalytic due to the gradual increase in the pH level, results in degradation and flaw formation at the glass fiber surface, and in significant strength reduction. With carbon fibers, for example, arrange of active

functional group like – CO₂H, – C – OH and – C = O are produced by various oxidative surface attack such as in hydrochloric acid or sodium hydroxide. With Kevlar fiber, it has been seen that Kevlar fibers on prolonged exposure to certain acid as hydrochloric acid may be affect the fibers generally speaking; strong acids and strong bases may affect Kevlar fiber at high temperatures and high concentrations¹⁶. This effect shown in table (4)

Table (4) The effect of acid, base on Kevlar fiber

Also the presence of the amide groups at regular intervals along the main chain backbone facilitates extensive hydrogen bonding between the adjacent chain, consequently high crystallinity and a high degree of internal stability is achieved. The functional groups which from chemical bonds directly or through saline and others with resins, are liable to hygrothermal chemical attack, and to interfacial degradation¹⁷

In addition to the chemical bonding, the physical morphologies of the constituents at their interface determine the type of physical bonding which is formed, and whose strength is sensitive to physical processes such as the build – up of destructive internal swelling stresses⁽¹⁾

Finally, the chemical source of the hygrothermal ageing of the matrix also depends on its chemical composition. Thus, epoxy resins are generally hydrolysis – stable, and although indications of liquid – induced conversion of the cross linked structure do exist, their durability depends mostly on physical processes such as crazing, contrarily, polyesters are hydrolysis – prone resins due to the ester groups which are highly susceptible to saponification¹⁸.

5. Conclusion

It can be concluded from all the figures above and the value of diffusion coefficient that:

1. The immersion of samples in (NaOH) have a higher effect than (HCl) this is due to the diffusion of OH^- was found to be greater than that of H^+ in composite samples
2. The diffusion occurs because that the debonding process in composite starts immediately upon exposing the samples to solutions. The debonding enhances liquid Penetration by capillary flow the interface accounting for the relatively high liquid concentration at the interfacial region
- 3- It is clear that the type of fibers effect on the rate of diffusion of such resin.
3. It is clear that composite with Up resin matrix has a higher values of weight gain for several solutions than that composite with EP resin matrix.
4. The higher values of diffusion coefficient in the composite are indicative of a damage mechanism occurring typically in the composite and not in the pure matrix, from this it is clear that Up composite samples damaged larger than EP composites.

References

1. B. John, "Introduction to Engineering Materials" 2nd Edition, Macmillan Pub. Ltd, ISBN, London, (1985).
2. W. W.Wright "Composites", July, (1981).
3. Abeysinghe et al., "Polymer", 23 (1982).
4. Peeyush Bhargava1, Kathy C. Chuang, Kenway Chen, and Alan Zehnder "Moisture Diffusion Properties of HFPE-II-52 Polyimide " Accepted by Journal of Applied Polymer Science, April'2006 www.people.ccmr.cornell.edu
5. Haleh Ardebili, Craig Hillman, Marjorie Ann Erickson Natishan, Patrick McCluskey, Michael G. Pecht,

and Dave Peterson " A Comparison of the Theory of Moisture Diffusion in Plastic Encapsulated Microelectronics With Moisture Sensor Chip and Weight-Gain Measurements " IEEE Transactions on Components and Packaging Technologies,25,1, (2002)

www.dfrsolutions.com/Articles/2002_Diffusion_Hillman.Ardebili

6. J. L. ABOT, A. YASMIN AND I. M. DANIEL"

Hygroscopic Behavior of Woven Fabric Carbon-Epoxy Composites "Journal of Reinforced Plastics and Composites, 24, 2,(2005).

http://mae.ucdavis.edu/vlasaponara/moisture_paper.pdf

7. Lydersen, "Mass Transfer in Engineering Practice", John Wiley & Sons, Chichester (1979).

8. J. Comyn, "Polymer Permeability" Elsevier Applied Science Pub., London, (1985).

9. R. B. Bird, "Transport Phenomena", John Wiley & Sons, (1976).

10. J. R. Backhurst & J. H. Harker "Chemical Engineering", vol.1, 3rd ed., Pergamon Press.

11. J. Crank, "The Mathematics of Diffusion" 2nd ed. Oxford University press, London. (1975).

12. J. Comyn, "Polymer Permeability" Elsevier Applied Science Pub., London, (1985).

13. G. Pritchard & S. D. Speaker, "Composites" UK., 18, 3, (1987).

14. A Mazar et al., "Polymer Engineering Science, 18, 341,(1974).

15. G. Eckold, "Design & Manufacture of Composite Structure", McGraw-Hill inc., Engl&, (2000).

16. Dupont information Bulletin, No.K-4 E.I Dupont de nemour & C. Inco, (1979).

17. D. H. Kaelble et al., "Journal of Adhesion" 8, 12, (1976).

18. A. L. Glass & J Smith, "Journal of Paint Technology", 39 (1976).

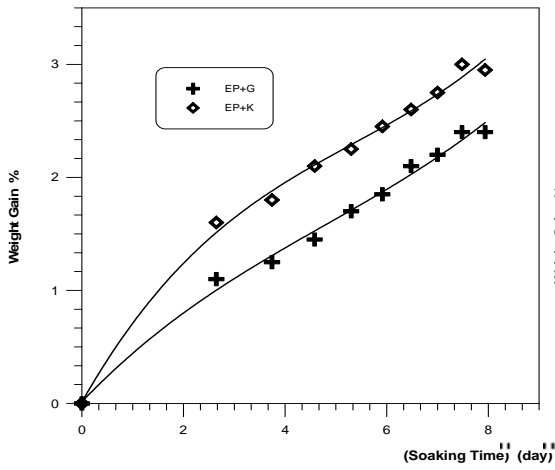


Fig (7) Weight gain % as a function of $t^{1/2}$ for EP composites (single) immersed in H₂O

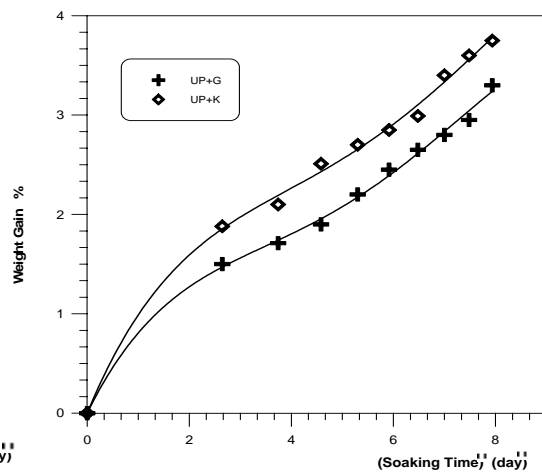


Fig (10) Weight gain % as a function of $t^{1/2}$ for UP composites (single) immersed in H₂O

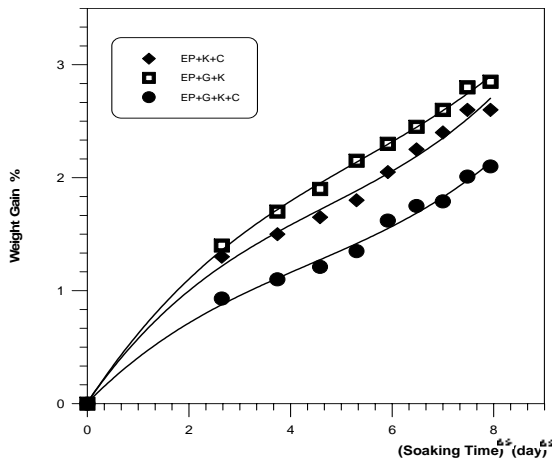


Fig (8) Weight gain % as a function of $t^{1/2}$ for EP composites (hybrid) immersed in H₂O

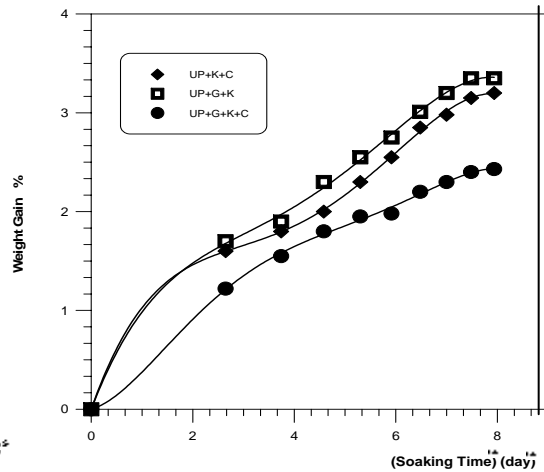


Fig (11) Weight gain % as a function of $t^{1/2}$ for UP composites (hybrid) immersed in H₂O

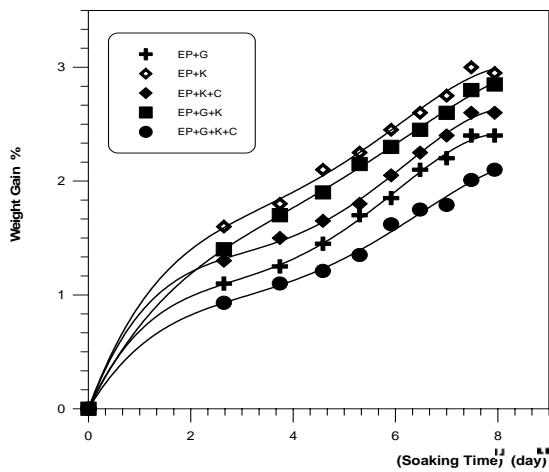


Fig (9) Weight gain % as a function of $t^{1/2}$ for EP composites (single, hybrid) immersed in H₂O

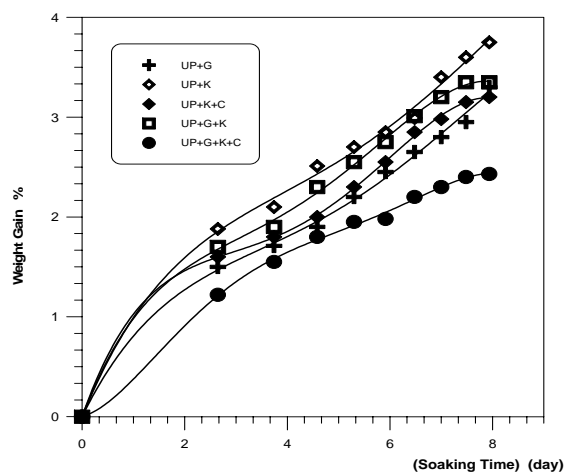


Fig (12) Weight gain % as a function of $t^{1/2}$ for UP composites (single, hybrid) immersed in H₂O

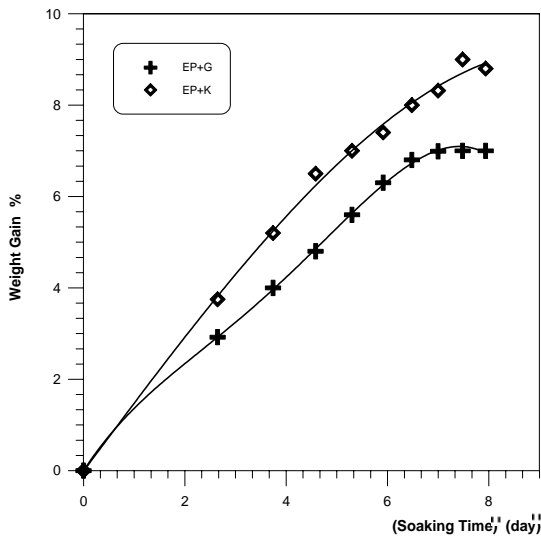


Fig (13) Weight gain % as a function of $t^{1/2}$ for EP composites (single) immersed in NaOH (1N)

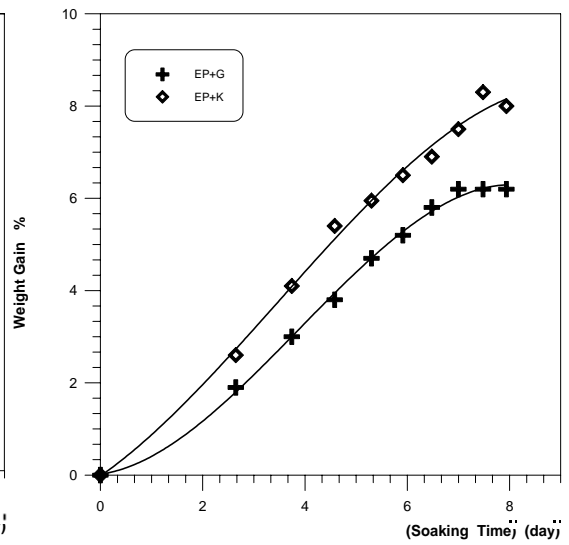


Fig (16) Weight gain % as a function of $t^{1/2}$ for EP composites (single) immersed in NaOH (0.5N)

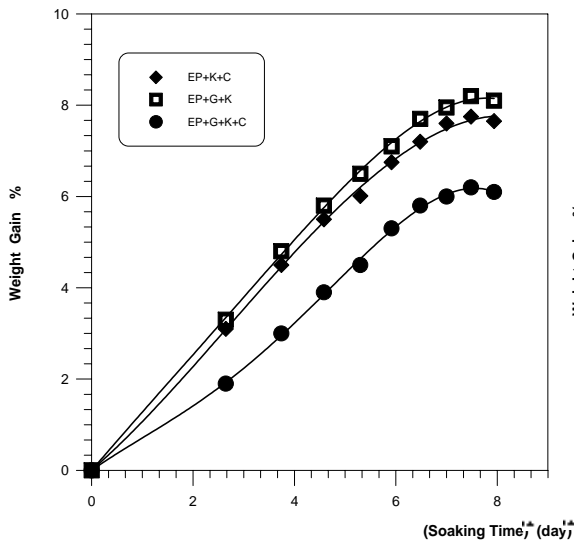


Fig (14) Weight gain % as a function of $t^{1/2}$ for EP composites (hybrid) immersed in NaOH (1N)

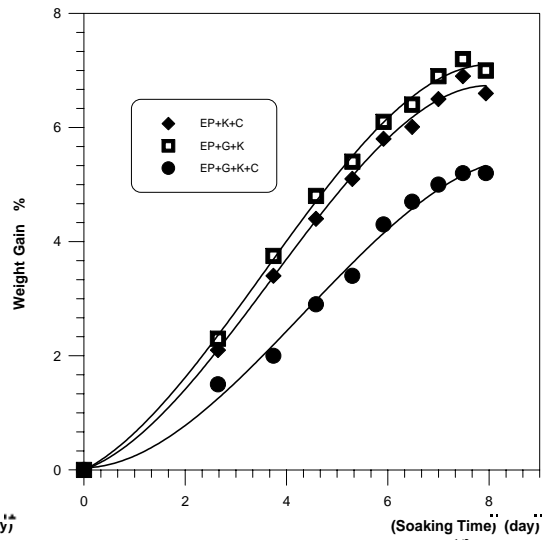


Fig (17) Weight gain % as a function of $t^{1/2}$ for EP composites (hybrid) immersed in NaOH (0.5N)

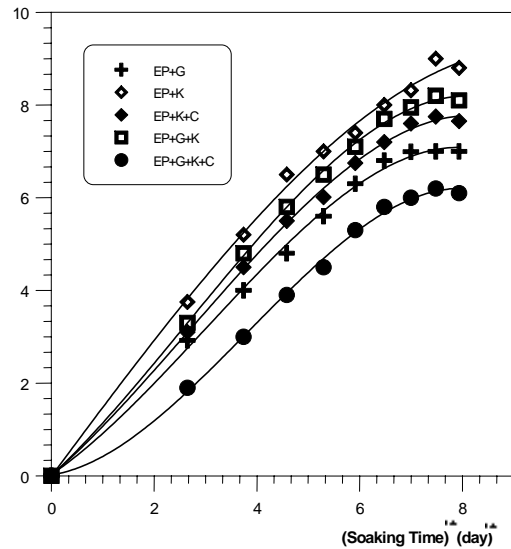


Fig (15) Weight gain % as a function of $t^{1/2}$ for EP composites (single, hybrid) immersed in NaOH (1N)

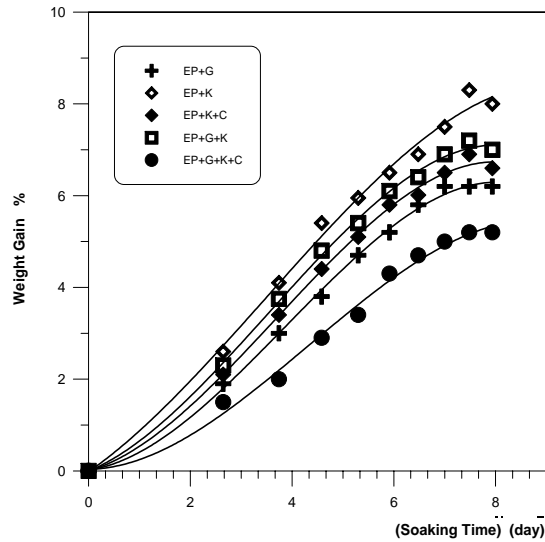


Fig (18) Weight gain % as a function of $t^{1/2}$ for EP composites (single, hybrid) immersed in NaOH (0.5N)

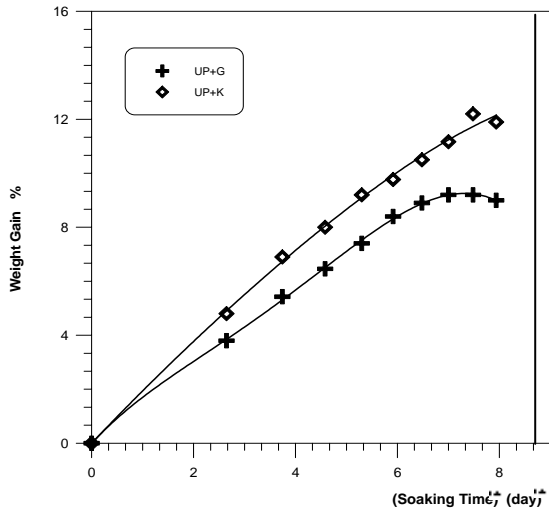


Fig (19) Weight gain % as a function of $t^{1/2}$ for UP composites (single) immersed in NaOH (1N)

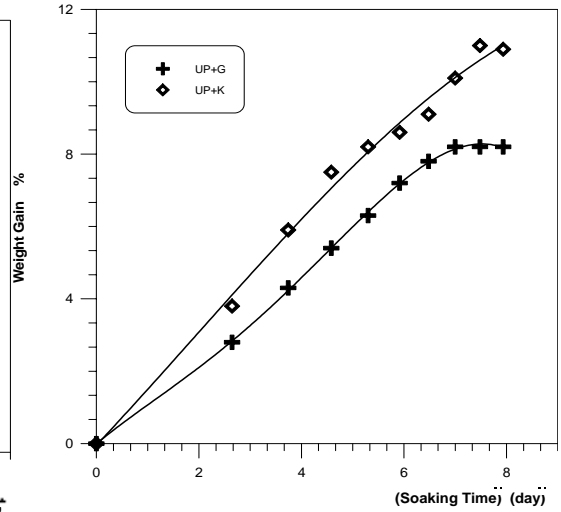


Fig (22) Weight gain % as a function of $t^{1/2}$ for UP composites (single) immersed in NaOH (0.5N)

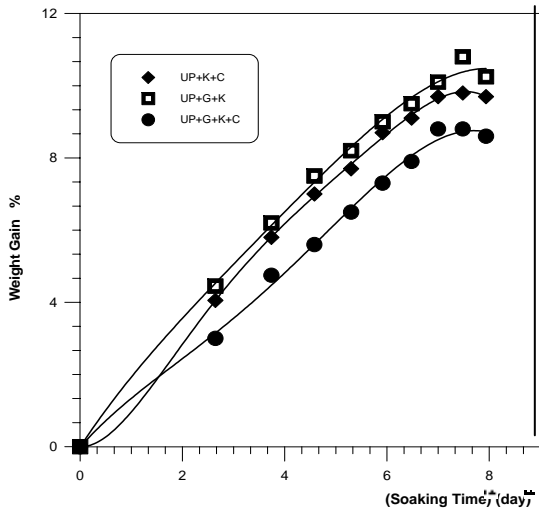


Fig (20) Weight gain % as a function of $t^{1/2}$ for UP composites (hybrid) immersed in NaOH (1N)

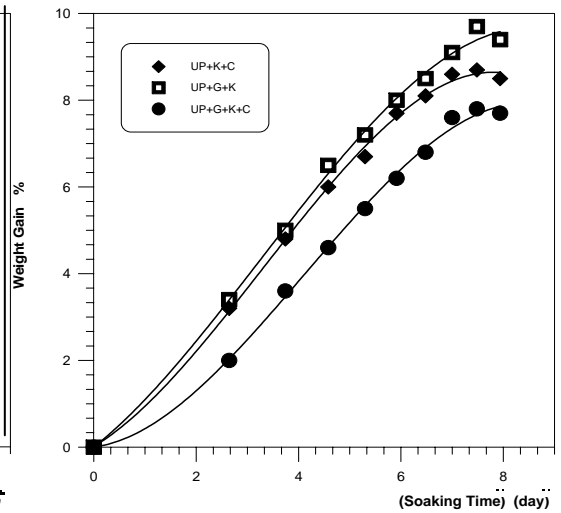


Fig (23) Weight gain % as a function of $t^{1/2}$ for UP composites (hybrid) immersed in NaOH (0.5N)

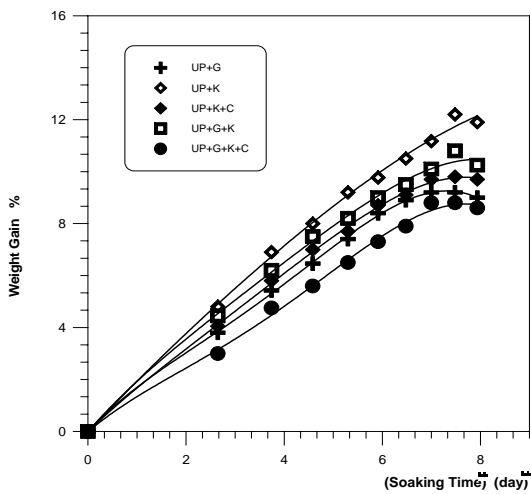


Fig (21) Weight gain % as a function of $t^{1/2}$ for UP composites (single, hybrid) immersed in NaOH (1N)

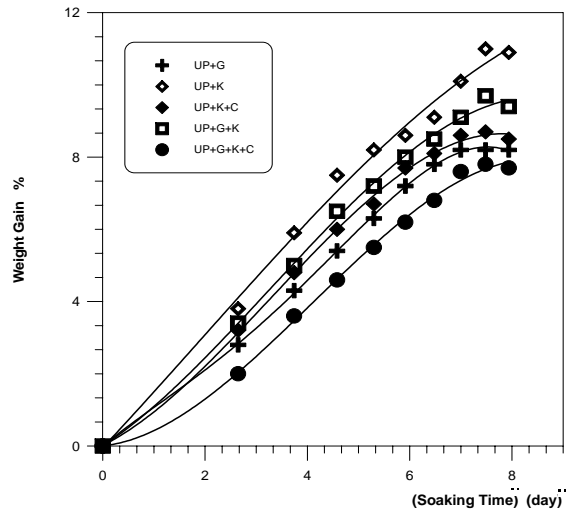


Fig (24) Weight gain % as a function of $t^{1/2}$ for UP composites (single, hybrid) immersed in NaOH (0.5N)

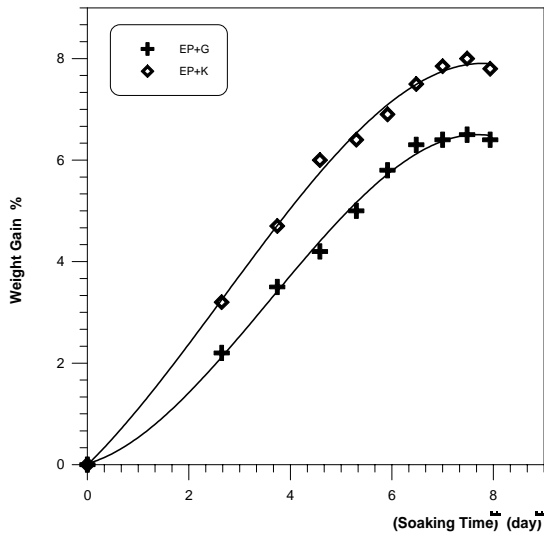


Fig (25) Weight gain % as a function of $t^{1/2}$ for EP composites (single) immersed in HCl (1N)

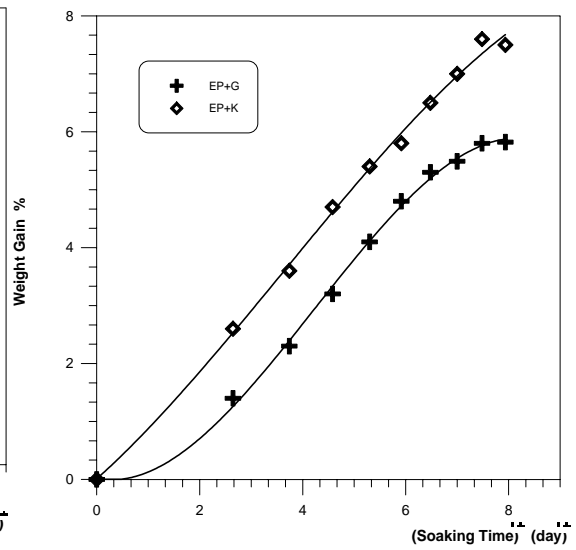


Fig (28) Weight gain % as a function of $t^{1/2}$ for EP composites (single) immersed in HCl (0.5N)

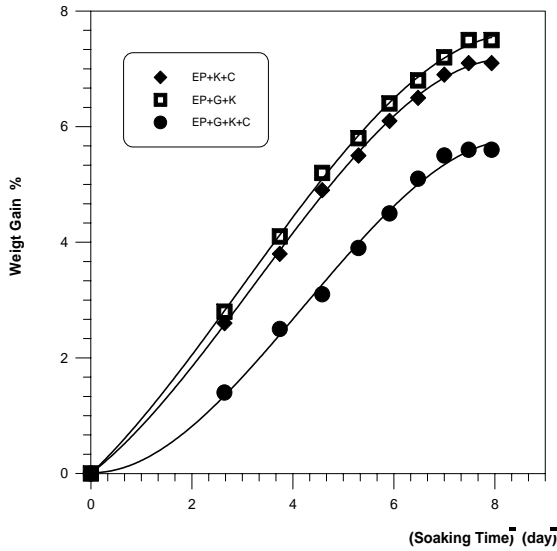


Fig (26) Weight gain % as a function of $t^{1/2}$ for EP composites (hybrid) immersed in HCl (1N)

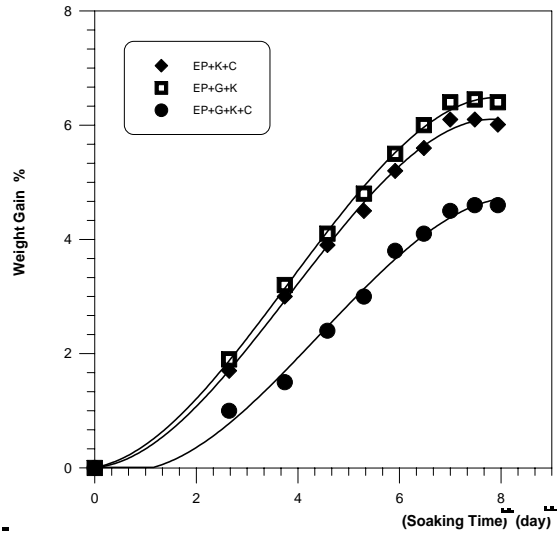


Fig (29) Weight gain % as a function of $t^{1/2}$ for EP composites (hybrid) immersed in HCl (0.5N)

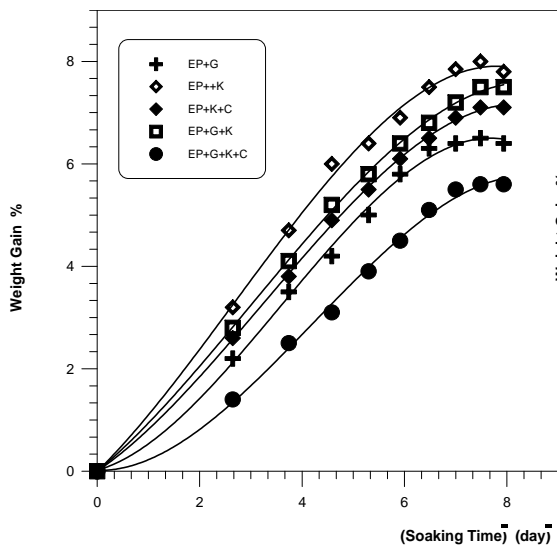


Fig (27) Weight gain % as a function of $t^{1/2}$ for EP composites (single, hybrid) immersed in HCl (1N)

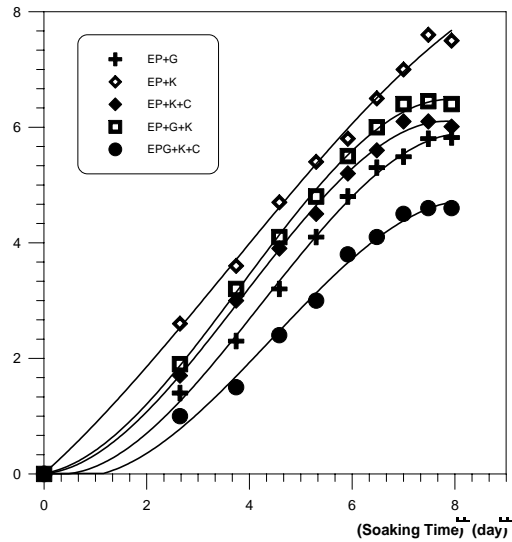


Fig (30) Weight gain % as a function of $t^{1/2}$ for EP composites (single, hybrid) immersed in HCl (0.5N)

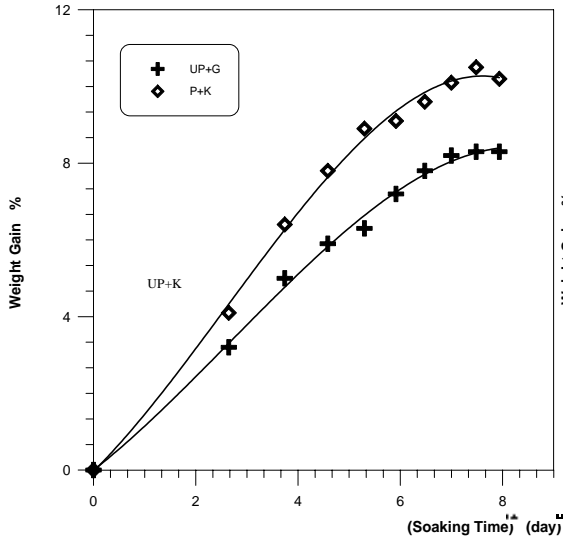


Fig (31) Weight gain % as a function of $t^{1/2}$ for UP composites (single) immersed in HCl (1N)

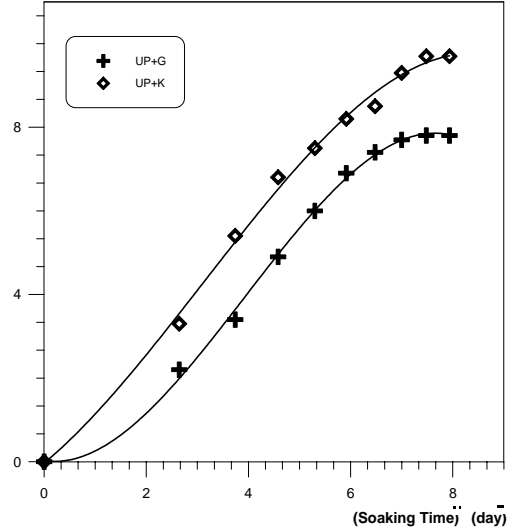


Fig (34) Weight gain % as a function of $t^{1/2}$ for UP composites (single) immersed in HCl (0.5N)

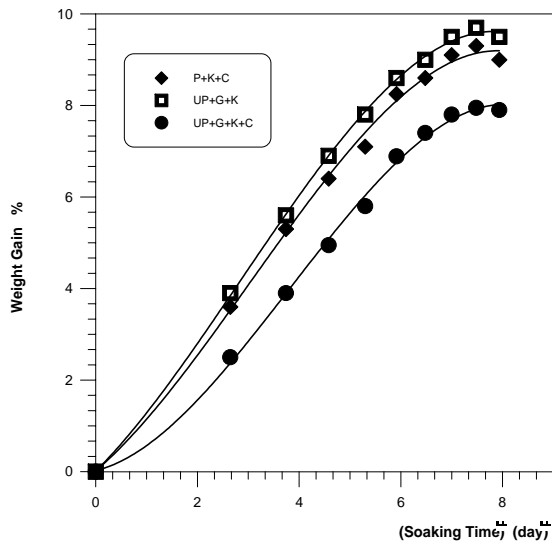


Fig (32) Weight gain % as a function of $t^{1/2}$ for UP composites (hybrid) immersed in HCl (1N)

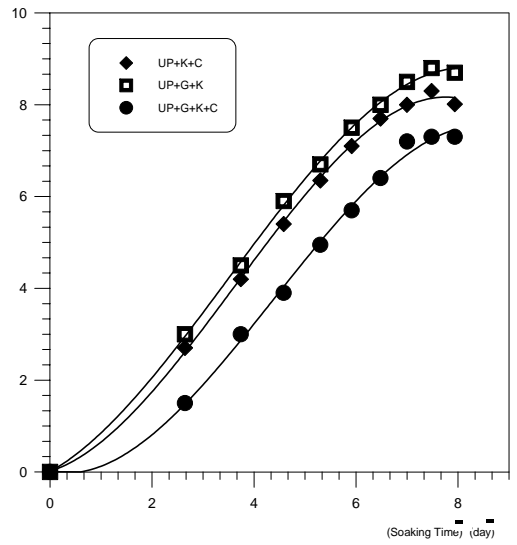


Fig (35) Weight gain % as a function of $t^{1/2}$ for UP composites (hybrid) immersed in HCl (0.5N)

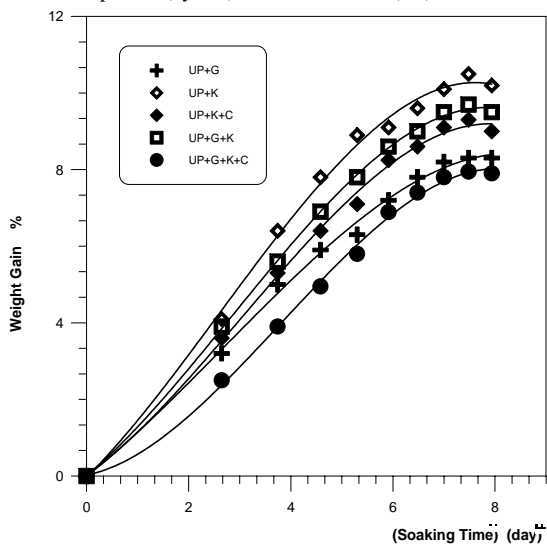


Fig (33) Weight gain % as a function of $t^{1/2}$ for UP composites (single, hybrid) immersed in HCl (1N)

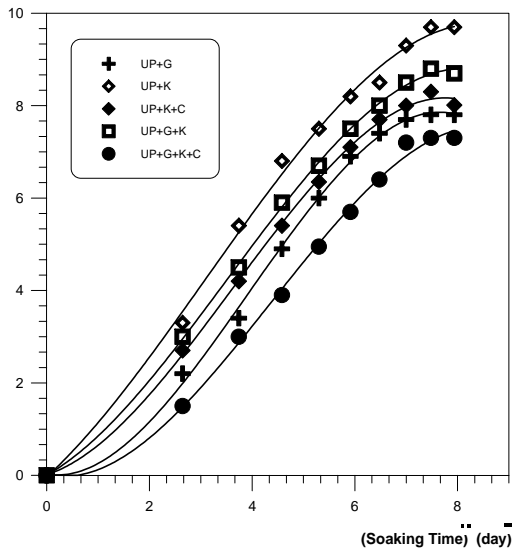


Fig (36) Weight gain % as a function of $t^{1/2}$ for UP composites (hybrid) immersed in HCl (0.5N)