Study the Effect of Some Solutions on Epoxy Resin & Calculate Diffusion Coefficient of Solution.

Khalil T. Hassan
University of Anbar-Science college

Abstract: Specimen of Epoxy resin have surface area (1cm*1cm) immersed in several individual solvent (0.5% NaoH), (1% NaOH),(2.5% H2SO4), (5%H2SO4),(2.5%HCl), (5% HCl). For long time (three years). The specimen's masses were measured before and after immersion in solutions. Diffusivity and diffusion coefficient of solutions in epoxy resin measured from the relation of the change of specimen weight and the square rout of time.Photograph of the specimen surface have taken by using optical microscope and digital camera. Shoor Hardness test was used to obtain the change of Hardness properties after pot in solvent. The result obtained illustrate the different effect of these solution in the surface of specimen that effect in hardness and diffusion coefficient.

Introduction:-

An epoxy resin is a polymer containing two or more epoxy group rings.
Such groups can be terminal, internal or cyclic structures. They can bond with other molecules, forming large three-dimensional network (figure 1).The most used hardeners are aromatic and aliphatic amine as well as anhydride hardeners. All should be added into the epoxy resin with adequate weight ratio to provide cross-linking. The reaction between aliphatic amines and epoxy groups will usually proceed at room temperature. However, heat is required when rigid aromatic amines or anhydride hardeners are used. The properties of epoxy resins are related to the chemical structure of the cured resin. A greater number of aromatic.Rings results in higher thermal stability and chemical resistance.A lower crosslink density can improve toughness by permitting greater elongation before break.A higher crosslink density can give a higher glass transition temperature and improved resistance to chemical attack. The anhydride-cured system breaks down in strong bases and organic solvents. The Boron Trifluoride-Monoethylene Amine (BF3MEA) -catalyzed system is seriously affected by the organic solvent and long exposure to moisture. Recently, rubber toughened epoxy resins have gained significantly in interest. Small rubber particles scattered in the epoxy resin are believed to improve the fracture toughness of the neat resin [1].

The environment has strong effects on the properties of the polymers. These effects can be classified as reversible effects and irreversible effects.For example, when water diffuses into the matrix it can plasticize and swell the polymer network, decrease the surface free energy and increase the free volume of the polymer [2]
thus inducing a reduction in the glass transition temperature (Tg).
The change in Tg as a function of moisture is shown in figure (2) This process is a reversible process, so the property will recover after drying the material.Long term exposure to moisture can also result in irreversible damage (hydrolysis & microcracing). Hydrolysis may be a primary reason for the weight loss of polymers after long term immersion [3]. Microcracking in the matrix, on the other hand, may contribute to further mechanical property degradation and more water absorption beyond the usual equilibrium level of the undamaged matrix.
When composites are exposed to moisture, water molecules will diffuse into the matrix, passing through the open structure of the

polymer even in the absence of porosity.The uptake of the moisture is a function of the chemistry of the matrix.

Different kinds of resins have different diffusivity and maximum moisture content.

The diffusivity represents the rate of moisture diffusion. The equilibrium moisture content represents the degree of swelling stress. The higher the equilibrium moisture content, the higher the swelling stress is in the materials, the higher the possibility that microcracking and hydrolysis will occur [3].
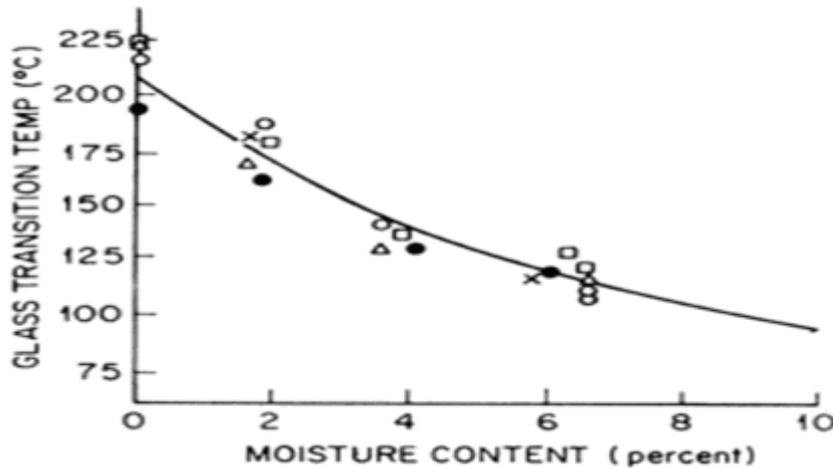
The mechanical properties of composites, especially those matrix dominated properties such as transverse tension strength and [□45] tension strength, have been widely reported to decrease in wet conditions [4]. However, Hale and Gibson [5] reported no property change due to oil exposure. Oil was not absorbed into the particular polymers like moisture was, so the degradation of properties generally occurs when the agent is taken up by the matrix. This tendency depends both on the

size of the molecules of the environmental agent and the interactions with matrix chemistry.

The Experimental studies:

Moisture diffusion into the resin can lead to a reduction in glass transition temperature and softening, which result in the degradation of stiffness and strength.This degradation can be aggravated and nvolve the interface under more severe conditioning. Thus, moisture content and its effects on resin properties are very important for designers.Usually moisture content (weight %) is measured from experiments by theweight gain relative to dry specimens, and plotted as a function of square root oftime

following Fickian predictions.

.

Some composites and neat resins have simple water absorption behavior which fits Fick's second law. Fick's second law states that

$$\frac{\partial M}{\partial t} = D \cdot \frac{\partial^2 M}{\partial Z^2} \quad \text{............(1)}$$

where
D: diffusion coefficient
M: moisture content
t: conditioning time
z: the length in the thickness direction
Moisture absorption curves usually have two characteristics: 1. curves
should be linear initially and 2. the moisture content should eventually reach a
saturation level. The analytical solution of equation (2.) is obtained by the method
of separation of variables and the moisture content varies as a function of time.
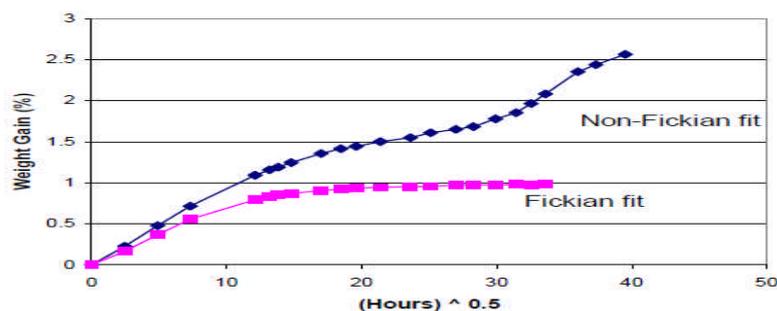
$$M(t) = M_0 + (M_m - M_0) \cdot \frac{4}{h} \cdot \sqrt{\frac{D \cdot t}{\pi}} \quad \cdots\cdots\cdots(2)$$

where
M0: initial amount moisture in the solid
Mm: the saturation moisture content
h: thickness
t: conditioning time
D: diffusivity in direction of the thickness
The time tm required to attain 99.9% of the maximum moisture content can also be expressed as:

$$t_m = \frac{0.678 \cdot s^2}{D} \quad \cdots\cdots\cdots (3)$$

For a material exposed on two sides to the same environment s is equal to the thickness; for a material insulated on one side s is the twice the thickness.
In order to calculate the moisture content and the time required to attain
99.9% of the maximum moisture content, tm,

the maximum moisture M_m and diffusiviity D must be known. Experiments show that the maximum moisture

content (M_m) does not change with the temperature and can be expressed as [6]

M_m = constant (liquid)

M_m = a* (RH%)b

Where RH is the relative humidity. Parameters a and b are materials properties and can be determined through experiment by fitting a line to the data.
The diffusivity D can be obtained by using the value of moisture content for
Two different values of time

$$D = \pi \cdot \left(\frac{h}{4 \cdot M_m}\right)^2 \cdot \left(\frac{M_2 - M_1}{\sqrt{t_2} - \sqrt{t_1}}\right)^2 \quad \cdots\cdots\cdots(4)$$

Which is call second Ficks's law .
However, some composites, especially those which have relatively large
weight gain, have an irregular water absorption curve which indicates that other mechanisms are involved; in the composites, this often is associated with matrix cracking [7-8].

Material and Specimen Preparation
In this study Epoxy resin (Jordon origin) is used to product specimens of dimensions of (1cm), (1cm), (0.2cm) for all specimens. Epoxy mixed in ratio (3:1) with hardener, and after solidification in mold then it has been cut to above dimensions. The weight of specimens have been measured by use digital sensitive balance   Kind (Merrler Toledo Switzer Land)

that sensitive of four digits .The specimens pot in many solutions consist of:
1-(0.5% NaOH)2-(1%NaOH)3-(2.5% H2SO4),4-(5% H2SO4)5-(2.5%HCl)6-(5%HCl).
The specimens weighted in equal periodic times for 3 years, and from knowing the surface area of specimens we can know the surface diffusivity

$$\frac{\Delta m}{A} = \left[\frac{m_2 - m_1}{A}\right] \quad \cdots\cdots\cdots(5)$$

And by second Ficks's law diffusion coefficient obtained.
Pictures of the Specimen surface was taken by use optical microscope and digital camera (Sony kinds) to observe the effect of solution on the epoxy resin.

Results and discussion:-
Fig.(1) presents the uptake of the influence of NaOH solution based of (1%) concentration on the epoxy specimen and fig.(2) illustrate the influence of same solution but (0.5%) concentration. there is no difference between the effects of the two concentrations but the diffusion coefficient of (1%) concentration is higher than (0.5%).Fig.(7) (a)&(b) pictures of the epoxy specimen surface after 3 years (more than 2600 hrs of immersion in solution) illustrate the effect of NaOH solutions on the specimen .We see very clearly that the surface had been affected and increase the holes on it. In both pictures the surface of specimen has whiteness that refers to reduction operations.
Fig(3)and fig.(4) present the uptake of the influence of H2SO4 acid of concentrations (2.5) and (5%) consequently. The effect of H2SO4 acid solution in epoxy resin is very clear especially the solution of (5%) concentration. This effect appears on the surface as deep lines and change the color of epoxy specimen. The color of the specimen surface became yellow. This indicates that there is an oxidation in the chains of epoxy resin. These effects can be shown from pictures (c) and(d) in figure(7). Fig.(5) and fig.(6) illustrate the influence of the HCl acid solution of 2.5% and 55 concentrations on epoxy specimens after immersion in it. Also pictures (e) and(f) in fig.(7) for surface of specimen take by optical microscope. From the figures the HCl acid solution produce less effect comparing to the other solutions since there is no reduction or oxidation operation happened on the epoxy specimen so the specimen still have the origin color but there are deep lines on the surface that mad it not smooth. Table(1) gives the value of diffusion coefficient of these solutions in epoxy specimen obtaining from the second Ficks's

law equation. The results show that epoxy is sensitive for H2SO4 acid especially when concentration increase where the other solutions have less effect on the epoxy especially HCl acid. From figures we note that the gain in weight increases with the time till reach the steady stat at this point epoxy specimen saturated by solution and after along time in solution we see a decreasing in the gain of weight. This decreasing in weight due to degradation in the epoxy chains by the effect of solutions this lead to forming interstitial holes that the solution molecules full it. Degradation operations associated with the decrease in the chemical resistance for the materials that lead to ability to loss compounds start from small polymeric chains happen associated with absorption operation but it slow and separated[9].

References:-

1- Launikitis,M.B., "Vinyl Ester Resins", Handbook of Composites, Edited by lubon, G., 1981, pp. 38-50.

2- Schwartz, M.M. "The influence of Environmental effects", Composite Materials, Properties, Nondestructive, Testing and Repair, 1996,pp.117-119.

3- Schutte, L.C., "Environmental Durability of glass Fiber Composites", Polymer Composites Group, Polymer Division, NIST (1994).

4- Hale, J.M., Gibson, G.A. "Strength Reduction of GRP Composites Exposed to high Temperatures in Offshore Processing Environments" Proceeding of ICCM-11, Gold Coast, Australia, 14th-18th, 1997, pp.526-542.

5- Hale, J.M., Gibson, G.A., "Coupon Tests of Fiber Reinforced Plastics at Elevated Temperatures in Offshore Processing Environments", Journal of Composite Materials, Vol.32,No6/1998, pp. 526-542.

6- Shen, C., Springer, S.G., "Moisture Absorption and Desorption of Composite Materials:, Journal of Composite Materials, Vol. 10, 1976, pp. 2-20.

7- Lundgren, J., Gudmundson, P., "A modeling of Moisture Absorption in Cross-Ply Composite Laminate with Matrix Cracks", Journal of Composite Materials, Vol.32,No6/1998, pp. 2226-2249.

8- Dewilde, P.W., Frolkovic, P., " The Modeling of Moisture Absorption in Epoxies Effects at the Boundaries" ", Composites, Vol. 25, NO. 2, 1994, pp. 119-127.

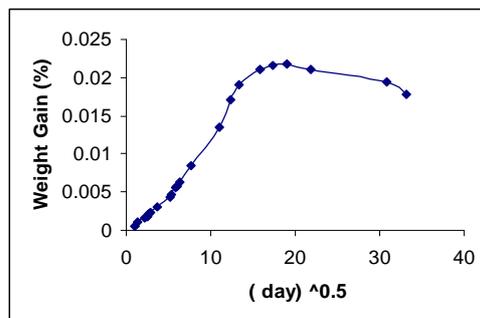9- J. Comyn," Polymer Permeability ", Elsevier Applied Science Pub, London, 1985.

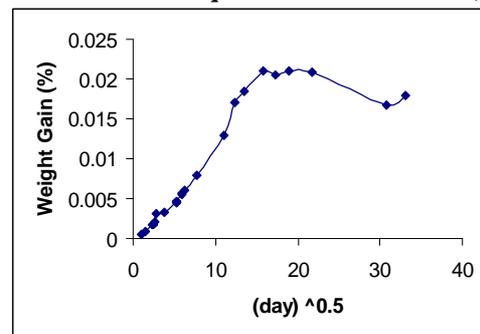**Fig (1) Weight gain as a function of square root of Time for (1%NaOH) solution.**

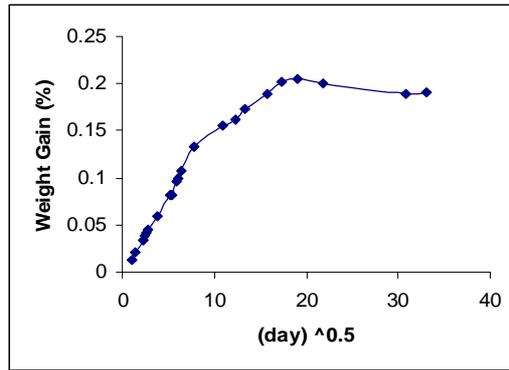**Fig (2) Weight gain as a function of square root of Time for (0.5%NaOH) solution.**

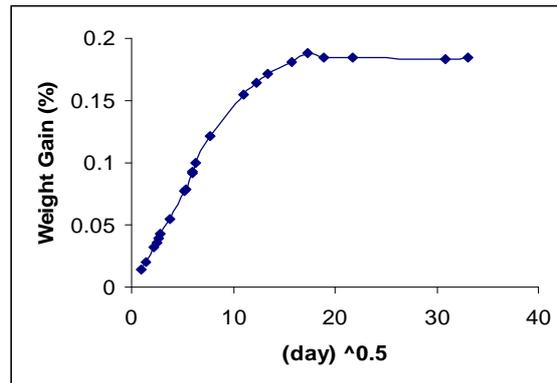**Fig (3) Weight gain as a function of square root of Time for (5%H2So4) solution.**

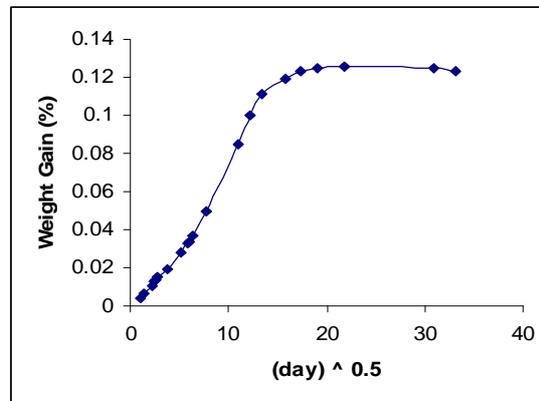**Fig (4) Weight gain as a function of square root of Time for (2.5%H2So4) solution.**

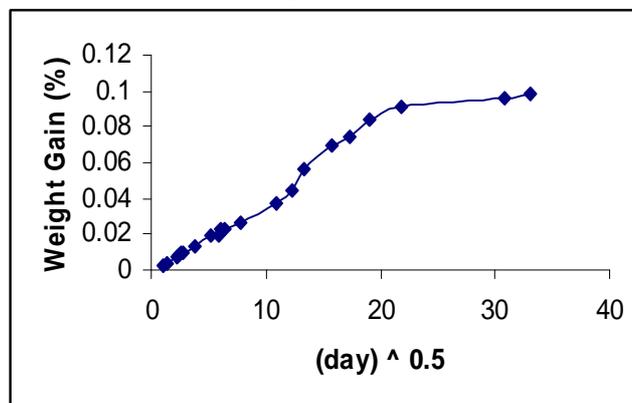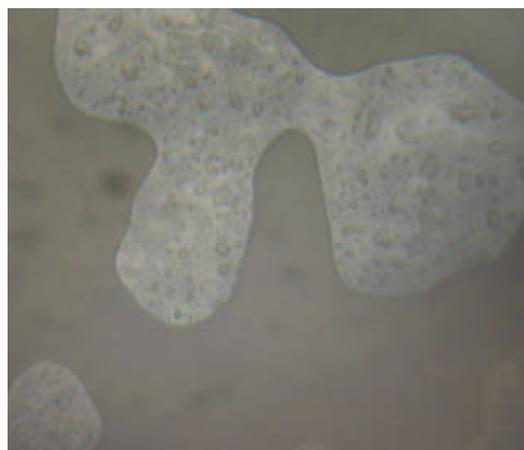**Fig (5) Weight gain as a function of square root of Time for (5%Hcl)   solution.**

Fig (6) Weight gain as a function of square root of time for (2.5%HCl)   solution.

(a) 0.5% NaOH

(a) 1% NaOH

(c) 2.5%H_2SO_4

(d) 5%H_2SO_4

(e) 2.5%HCl

(f) 5%HCl

Fig (7) pictures of the surface of specimen after immersing in on solutions for 3 years.

Table(1) value of diffusion coefficient of solutions in epoxy resin

Diffusion coefficients $*10^{-10}$ (Cm²/sec)					
NaOH (1%)	NaOH (0.5%)	H2So4 (5%)	H2So4 (2.5%)	Hcl (5%)	Hcl (5%)
3.61	2.18	12.56	6.005	5.31	1.3

دراسة تأثير بعض المحاليل على راتنج الايبوكسي وحساب معاملات الانتشار لهذه المحاليل.

خليل ثابت حسان

E.mail: scianb@yahoo.com

الخلاصة:-

في هذا البحث تم غمر عينات مصنوعة من راتنج الايبوكسي ذات أبعاد مساحة مقطع (١سم* ١سم) في محاليل مختلفة كـل علــى حــدة وبتراكيــز مختلفــة وهـي(٠.٥% هيدروكســيد الصـــوديوم)و(١% هيدروكســيد الصـــوديوم)و (٢.٥%وحــامض الكبريتيك)و(٥%وحامض الكبريتيك) و(٢.٥%حامض الهيدوكلوريك)و(٥%حامض الهيدوكلوريك) لفترة زمنية طويلة (ثلاث سنوات) وتم وزن النماذج قبل وبعد الغمر بفترات زمنية مختلفة .تم إيجاد الانتشارية للمحاليل وحساب معامل الانتشار لها من خلال رسم العلاقة بين التغير في وزن العينات والجذر ألتربيعي للزمن .تم التقاط صور لأسطح العينات باستخدام المجهر الضوئي والكاميرا الالكترونية.لقد أظهرت النتائج التأثير المختلف للمحاليل على العينات هذا التأثير ظهر بشكل واضح عل سطوح العينات وعلى قيم معامل الانتشار لهذه المحاليل.