

# **A Recent Understanding on Theories of Moisture Ingression and its Effect on FRP Composites**

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## **Abstract**

Nowadays fiber reinforced polymer (FRP) composites are in massive demand for applications in diversified fields owing to their unique combination of properties. Despite numerous advantages over conventional metallic materials, polymeric composites suffer from the limitation of being susceptible to degradation when exposed to harsh environmental attacks. During their fabrication, storage and service period, components made up of these polymeric materials are subjected to heat and moisture, when operating under changing environments. Such environmental exposures affect the reliability and predictability of the short term as well as the long term properties and also the in-service performance of these components. The fiber/matrix interphase plays a key role in deciding the moisture diffusion kinetics as well as response of the FRP composites to different environments. Although moisture uptake theory and mechanism in polymeric composites has been an active area of research for last few decades, but still accurate predictability of moisture absorption kinetics is under question due to complex sorption kinetics and scattered experimental data.

**Keywords:** Polymer Composites, Hygrothermal Ageing, Thermal Spike, Moisture uptake kinetics, Interphase, Adhesion, Mechanical Properties, Inter-laminar shear strength.

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## 1. Introduction

In recent times, fibrous polymeric composites have received increased attention for a wide range of applications ranging from ladder rails to aircraft wings, from sports goods to space craft frames, from printed circuit boards to rocket motor cases, owing to their unique combination of properties like low density, high strength to weight ratio, good anti-corrosion properties, fatigue resistance and low manufacturing costs. However, FRP composites encounter a variety of environments during their fabrication, storage and service life, which are capable of causing degradation in their expected in-service performance or even complete failure. In aircrafts and spacecrafts, the body parts are subjected to humid condition caused by clouds or rain whereas in marine and pipeline application where the components are exposed to severe humidity conditions throughout their lifetime.

Moisture absorption in polymeric composites is a complex phenomenon which degrades its reliability and performance [1-3]. Moisture ingress leads to decrease in glass transition

temperature of the composite which adversely affects its elastic modulus and other properties [2-4]. Also, the absorbed moisture causes the fiber/matrix interface to become susceptible to aggressive reactions which result in change in interfacial chemistry, thereby affecting its load transfer characteristics and structural integrity [2]. Hence, there is a need to predict the kinetics of water diffusion in polymeric composites in order to predict their short term as well as long term performance. In addition, in view of the increasing usage of polymeric composite materials in various critical applications, there exists a urgent need to obtain a complete understanding of the relation between their in-service properties and hygrothermal environments to which they are exposed.

It is a well-known fact that polymers are hygroscopic in nature and this necessitates proper understanding of the phenomena occurring during moisture ingress in polymeric composites. This paper is an attempt to bring together the theories and mechanisms of moisture ingress as well as their adverse effect on polymeric composites, scattered in various literatures to provide an improved understanding in the aforesaid subject.

## **2. Diffusion Models**

Over decades, different models have been developed with an aim of accurately predicting the moisture ingress phenomenon in such polymeric composites. Alfrey et.al [5] was the first to propose three distinct types classification of diffusion processes in polymeric materials. This classification was based on the relative rates of diffusion of penetrant molecules and relaxation of polymeric chains. The first category is that of Fickian diffusion in which the rate of relaxation is much higher than that of diffusion. Non-Fickian diffusion comes under the second category in which the rate of relaxation is nearly same as diffusion rate. The third category pertains to a case, where rate of relaxation is much lower than that of diffusion.

Many models have also been proposed to quantitatively describe the moisture absorption characteristics of different FRP systems. Some of the diffusion models relevant to moisture diffusion in fibrous polymeric composites, which have evolved over last few decades, are discussed below.

## 2.1. Linear Fickian Diffusion Model

The simplest model which is applicable to most polymeric composites, was developed by Fick long back in 1855 [6], basing his work on the foundation set by Fourier [7].

Fick's first law of diffusion is based on hypothesis that for an isotropic medium, rate of diffusion through any cross-section is directly proportional to the concentration gradient normal to it and is quantitatively represented as -

$$F = -D \frac{\partial C}{\partial x} \quad (1)$$

However, Fick's second law is considered as the fundamental law of diffusion and can be represented by equation (2) when D is dependent on moisture concentration.

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

However, in case of moisture concentration independent D, equation (2) becomes –

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (3)$$

The most accepted classical solution of Fick's second law for that of a plate, which is given below [8] -

$$\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left[ \frac{-(2n+1)^2 \pi^2 D t}{4h^2} \right] \quad (4)$$

Often, for simplicity, the above equation is often approximated as proposed by Springer [9]-

$$\frac{M_t}{M_\infty} = 1 - \exp \left[ -7.3 \left( \frac{D t}{h^2} \right)^{0.75} \right] \quad (5)$$

Also, the solution for moisture desorption is as follows-

$$\frac{M_t}{M_0} = -\frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{(-1)^n}{(2n+1)^2} \exp \left[ \frac{-(2n+1)^2 \pi^2 D t}{4h^2} \right] \quad (6)$$

When the moisture diffusion is Fickian in nature, the diffusion coefficient is alone sufficient to describe the behaviour of the FRP composite [9]. The diffusion coefficient in this case is independent of concentration of penetrating molecules and can be found out by the following equation –

$$D = \pi \left( \frac{h}{4M_\infty} \right)^2 \left( \frac{M_1 - M_2}{\sqrt{t_1} - \sqrt{t_2}} \right)^2 \quad (7)$$

Typical linear Fickian behaviour is shown in Fig-1, which can be roughly divided into two parts - an initial linear region which is the consequence of concentration independent diffusion coefficient and a saturation region in which no more moisture is absorbed even if the sample is kept in same humid condition for a very long time. Fickian behaviour is reported to be more pronounced when the polymer composites are exposed to humid air and at lower temperatures [10].

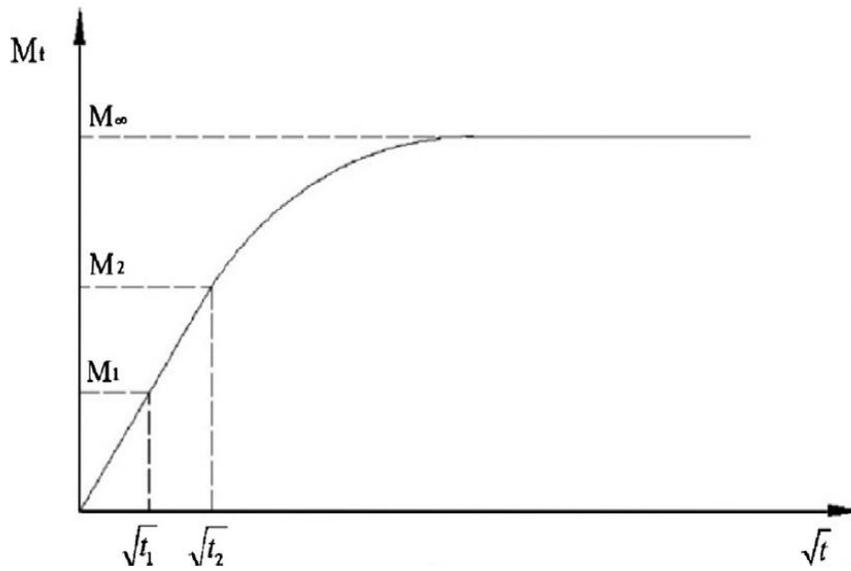


Fig-1: Typical linear Fickian diffusion model [11]

Moisture diffusion in many FRP composites has been reported to follow Fick's law [4, 12-20, 23]. In Fig-2, the gravimetric moisture ingress curve of carbon/epoxy composite is shown, which follows Fick's law.

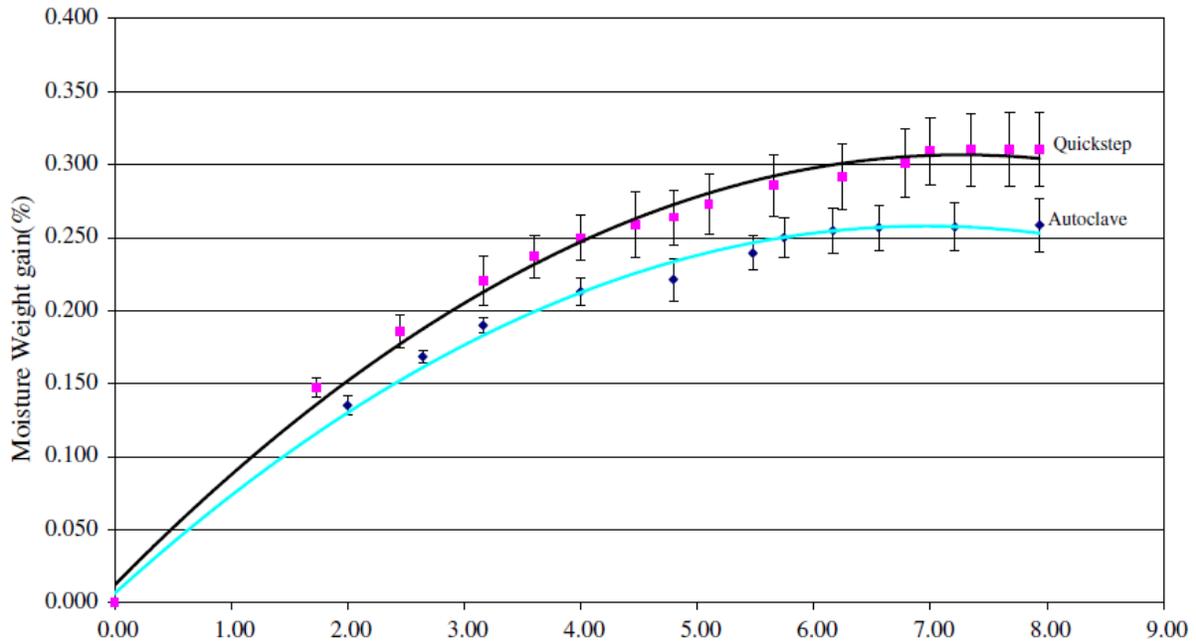


Fig-2: Experimental data fitting with linear Fickian diffusion model of carbon/ epoxy composites aged at 70°C and 85% RH [21]

## 2.2. Deviation from Fickian Behaviour: Non-Fickian Diffusion Models

Glass transition temperature is an important parameter when it comes to study the polymeric systems. Although polymers follow Fick's law of moisture absorption in their rubbery state but, in glassy state, polymers show deviation from Fickian behaviour. Such non-Fickian behaviour is due to different reasons such as negligible swelling of the composites, development of cracks and voids and moisture diffusion along fiber matrix interface [2]. Also, polymer matrix itself has an important role to play in deciding the moisture diffusion behaviour. For example, epoxy resin based composites are usually found to follow non-Fickian moisture absorption kinetics [10].

Different non-Fickian moisture absorption curves observed in polymeric composites are shown in Fig-3.

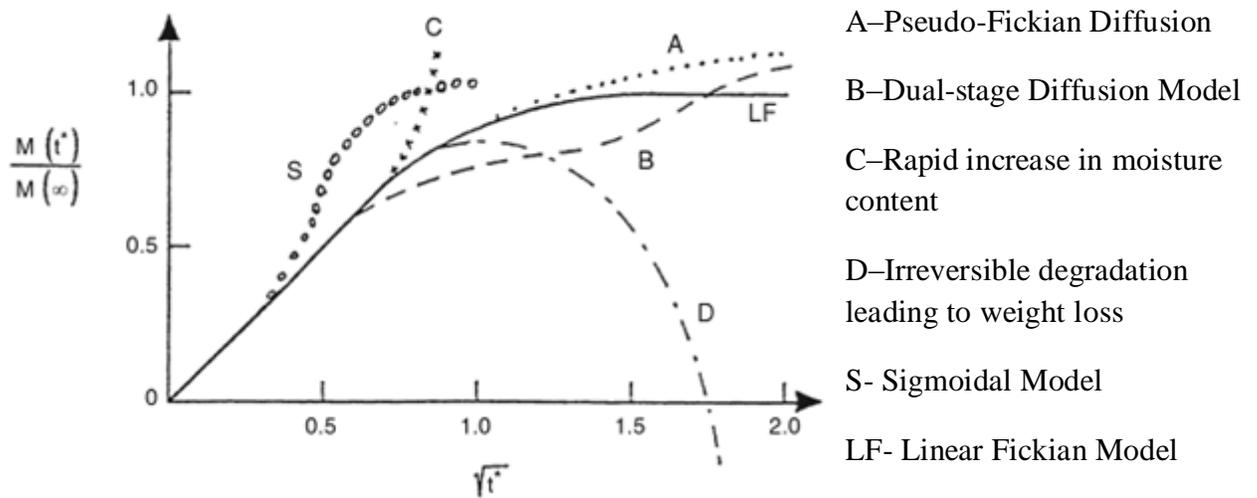


Fig-3: Typical linear Fickian and non-Fickian diffusion models [22]

Curve “A” shows the pseudo-Fickian diffusion in which true equilibrium is never achieved. The curve can be divided into two linear regions – the initial region being similar to Fickian curve and the other region having a lower but non-zero slope. Such behaviour is mostly observed in polymeric composites in which both fiber and matrix absorb moisture, for example - glass/epoxy composites for a variety of humidity and temperature condition [23, 24], glass/epoxy in water at different temperatures [25-27], glass/urethane composite in distilled water at different temperatures [28], glass/polyester composites in water and sea water [29] and so on. But this is not always the case. Many polymeric composites in which the fiber has no role in moisture absorption also show similar behaviour [31, 32]. This might be due to involvement of fiber/matrix interface in moisture absorption. Also, on varying the environment, moisture diffusion kinetics of the same system changes noticeably [23, 27-30].

Curve “C” shows the case of rapid increase in moisture content in the polymer composite, which usually results from induced damage in the material, which might sometimes lead to large deformations, and even failure. Under certain conditions, polymer composites are reported to switch to such kind of irreversible behaviour, although usually they tend to have quite different moisture absorption characteristics [26, 27, 33-36].

Curve “D” accounts for the physical (swelling) or chemical (leaching and hydrolysis) degradation of the composite material which causes weight loss. This irreversible behaviour threatens the loss of structural integrity and might even lead to failure of the composite.

Such behaviour of fibrous polymeric composites has been reported in many literatures [37-40]. In fact, whenever moisture ingress characteristics of a composite material is found to be in resemblance with either curve “C” or “D”, it raises question on the decision of material selection for that particular environment.

Curve “S” represents the sigmoidal type moisture diffusion in the polymer composite and is reported to be related to a moving diffusion front [23, 25, 41, 42].

Many researchers have reported that polymeric composites recover their original strength, either partly or even entirely, on drying [23, 30, 43]. In general, in case of curves “LF”, “A” and “B”, which are associated with reversible changes upon moisture absorption, complete regaining of original strength is possible, but for curves “C” and “D”, permanent loss of strength is observed [3, 22].

### 2.3. Langmuirian Diffusion Model

Langmuirian model, also known as the dual-mode sorption model or the two-phase diffusion model, is based on the assumption that the penetrant molecules are divided into two populations- one consists of the mobile molecules which are dissolved in the matrix and hence are free to diffuse; while the other molecules are locally immobilized as they occupy the micro-voids [44]. However, there exists a possibility of exchange between mobile and bound molecules over time. Langmuirian model of diffusion is a modification of Fick’s law, proposed by Carter and Kibler [44] and can be quantitatively described as -

$$D_{\gamma} \frac{\partial^2 n}{\partial z^2} = \frac{\partial n}{\partial t} + \frac{\partial N}{\partial t} \quad (8)$$

$$\frac{\partial N}{\partial t} = \gamma n - \beta N \quad (9)$$

The solution for the above set of equation is given below-

$$\frac{M_t}{M_{\infty}} = \frac{\beta}{\gamma + \beta} e^{-\gamma t} \left( 1 - \frac{8}{\pi^2} \sum_{h=1}^{\infty} (\text{odd}) \frac{e^{-\kappa_i^2 t}}{i^2} \right) + \frac{\beta}{\gamma + \beta} (e^{-\beta t} - e^{-\gamma t}) + (1 - e^{-\beta t}) ; 2\gamma, 2\beta \ll \kappa \quad (10)$$

For shorter exposure times, equation (11) can be approximated to-

$$\frac{M_t}{M_\infty} \approx \frac{4}{\pi^{3/2}} \left( \frac{\beta}{\gamma + \beta} M_\infty \right) \sqrt{\kappa t}; \quad 2\gamma, 2\beta \ll \kappa, t \leq 0.7\kappa \quad (11)$$

And for longer exposure times, the same equation can be modified as follows-

$$\frac{M_t}{M_\infty} \approx 1 - \frac{\gamma}{\gamma + \beta} e^{-\beta t}; \quad 2\gamma, 2\beta \ll \kappa, t \gg 1/\kappa \quad (12)$$

This model of two-phase diffusion has been adopted by many researchers to explain the moisture absorption kinetics of FRP composites [45-51]. Moreover, Fickian and Langmuirian models could be statistically equivalent in case of certain conditioning environments [1]. However, the Langmuirian model has been reported to be able to accurately predict the moisture uptake of certain systems in certain environments such as carbon/epoxy conditioned in anti-icing additive [52].

A comparison between Fickian and Langmuirian fitting of experimental data of moisture absorption kinetics of glass/epoxy composite is shown in Fig-3 [48]. It can be clearly seen that anomalous Carter-Kibler or Langmuirian fitting gives a more accurate approximation for the observed data than the Fickian fitting.

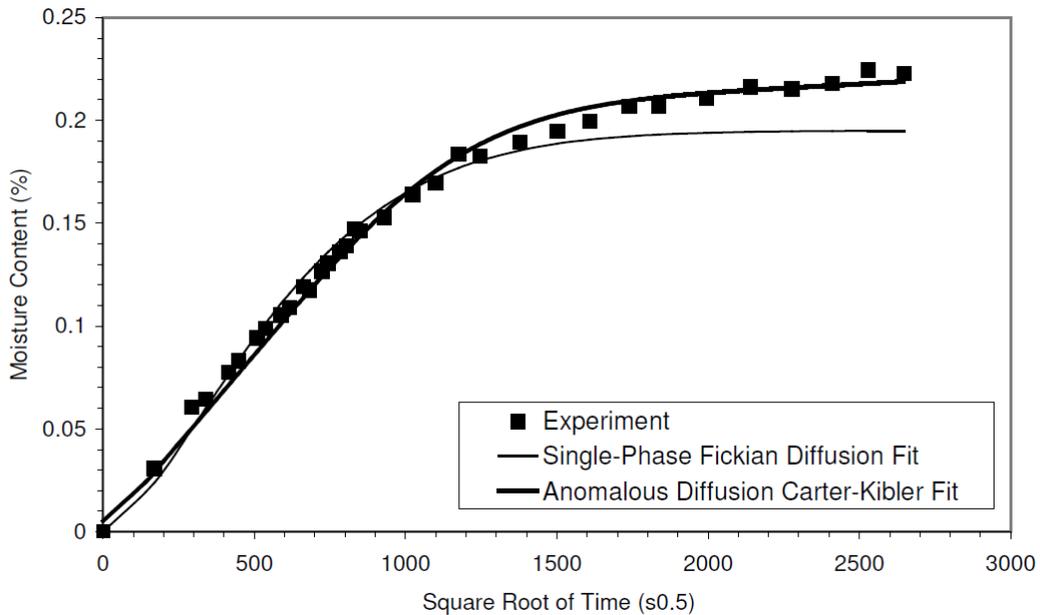


Fig-4: Langmuirian model applied to moisture absorption data of glass/epoxy composite exposed to humid ageing at 70°C and 85% RH [48]

## 2.4. Hindered Diffusion Model

The one-dimensional hindered diffusion model is equivalent to the 1D Langmuirian model [53, 54]. The three dimensional hindered diffusion model of moisture diffusion in polymeric composites is an extended form of the one-dimensional model to incorporate diffusion through multiple surfaces and interaction between water molecules and the polymeric composite. This model can be described by the following equation -

$$D_x^* \frac{\partial^2 n^*}{\partial (x^*)^2} + D_y^* \frac{\partial^2 n^*}{\partial (y^*)^2} + D_z^* \frac{\partial^2 n^*}{\partial (z^*)^2} = \mu \frac{\partial n^*}{\partial t^*} + (1 - \mu)(n^* - N^*) \quad (13)$$

where

$$n^* = \frac{n_t}{n_\infty} N^* = \frac{N_t}{N_\infty} t^* = \beta t$$

$$x^* = \frac{x}{h} y^* = \frac{y}{w} z^* = \frac{z}{l}$$

$$D_x^* = \frac{D_x}{h^2(\gamma + \beta)} D_y^* = \frac{D_y}{w^2(\gamma + \beta)} D_z^* = \frac{D_z}{l^2(\gamma + \beta)} \quad \mu = \frac{\beta}{\gamma + \beta}$$

Moisture absorption in fibrous polymeric composites subjected to hindered diffusion is shown in Fig-5(a). The initial part is linear, after which ‘‘pseudo-equilibrium’’ is attained, where moisture absorption rate slows down noticeably [53]. One can compare this ‘‘pseudo-equilibrium’’ to be equal with the saturation moisture content in case of Fickian diffusion. In case of Fickian diffusion, there is no further increase in moisture content after ‘‘pseudo-equilibrium’’. Hence, it is important to distinguish between the two types of diffusion processes as one might arrive at the incorrect conclusion by assuming the slow moisture uptake rate in hindered diffusion to be Fickian diffusion behavior. Fig-5(b) shows the clear distinction between the two diffusion processes, while fitting with the experimental data of carbon-fiber reinforced bismaleimide composites subjected to distilled water immersion.

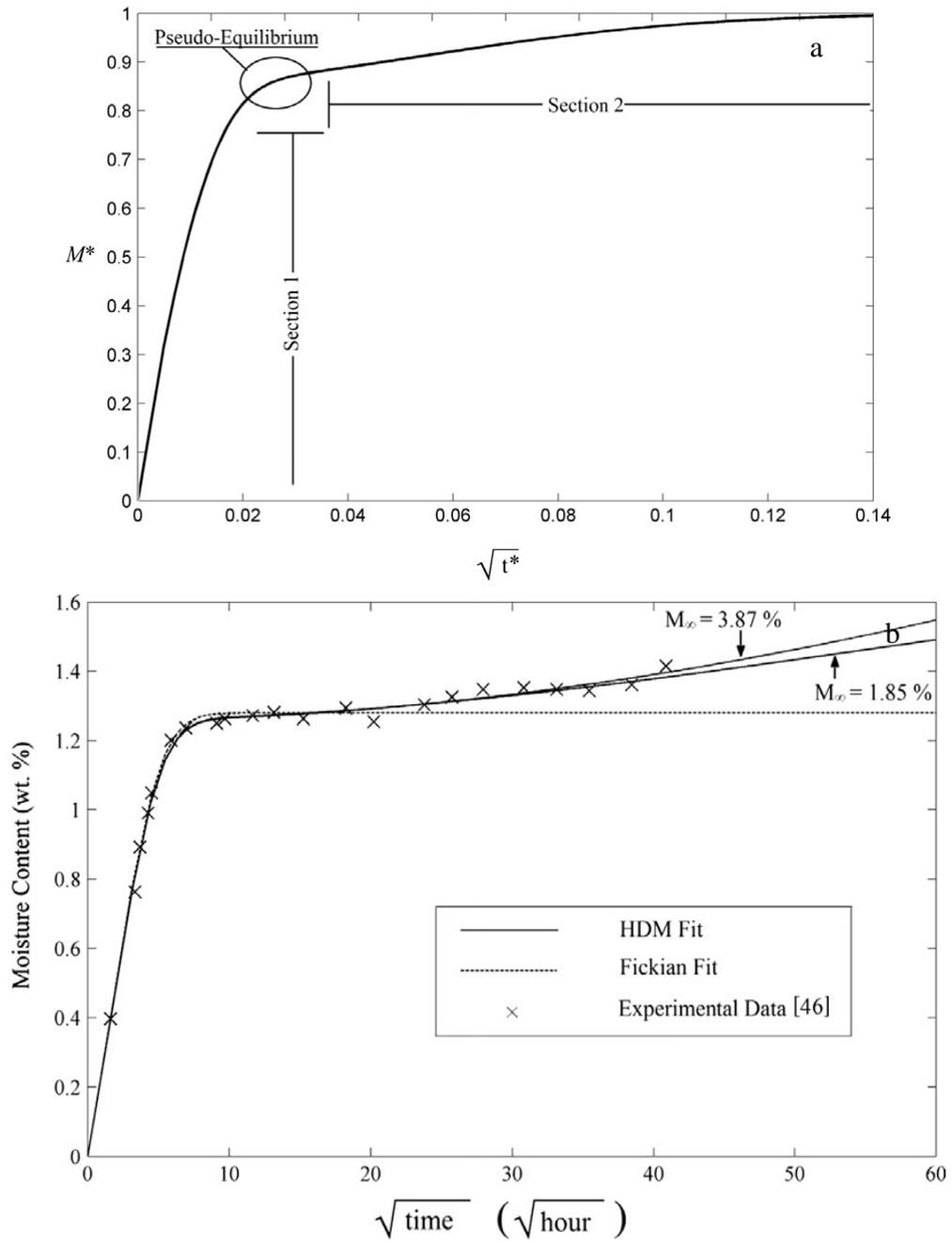


Fig-5: (a) Typical 3D hindered diffusion model and (b) fitting of experimental data of carbon-fiber reinforced bismaleimide composites (immersed in distilled water) with hindered diffusion model and linear Fickian model [53]

## 2.5. Dual-stage Diffusion Model

In Fig-3, Curve “B” shows the dual-stage moisture diffusion model. The dual-stage diffusion model can be quantitatively described by dividing concentration of moisture in the polymeric composite into two parts, namely - the polymer chain relaxation behaviour and the Fickian diffusion behaviour.

$$M_t = M_{t,F} + M_{t,R} \quad (13)$$

The solution to the equation (16) is given by the following equation -

$$M_t = M_{\infty,F} \left\{ 1 - \exp \left[ -7.3 \left( \frac{Dt}{h^2} \right)^{0.75} \right] \right\} + M_{\infty,R} [1 - \exp(-kt)] \quad (14)$$

Equation (14) is plotted in Fig-6, which shows that the two-stage moisture diffusion is the combined effect of the classical Fickian diffusion and polymer matrix relaxation. The initial linear part of the curve is identical to the Fickian curve and hence, it can be said that polymeric relaxation has no influence on it, while polymeric relaxation plays decisive role in determining the second part, in which diffusion rate decreases to attain final saturation moisture level.

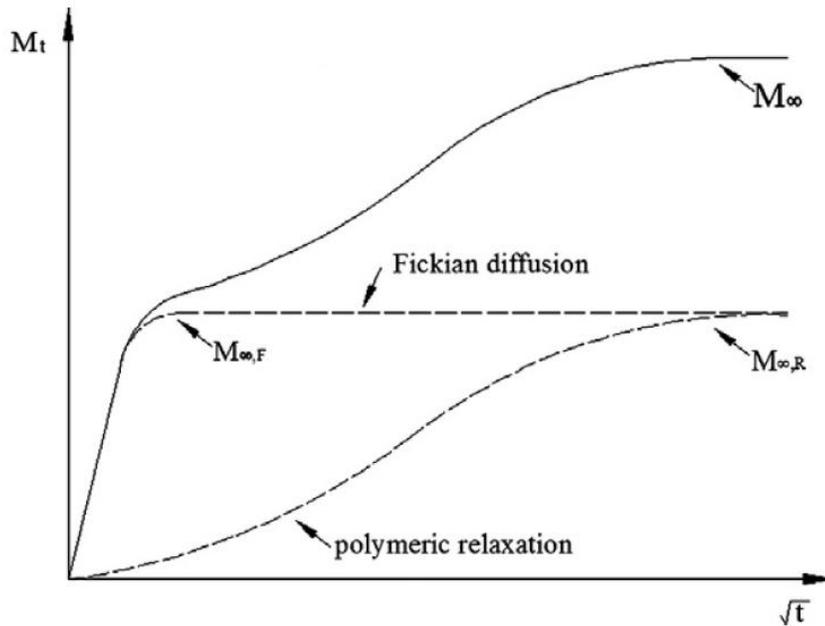


Fig-6: Theoretical moisture uptake curves showing combined effect of Fickian diffusion and polymeric relaxation [57]

Experimental data of some polymeric composite systems, which are reported follow dual-stage diffusion are shown in Fig-7.

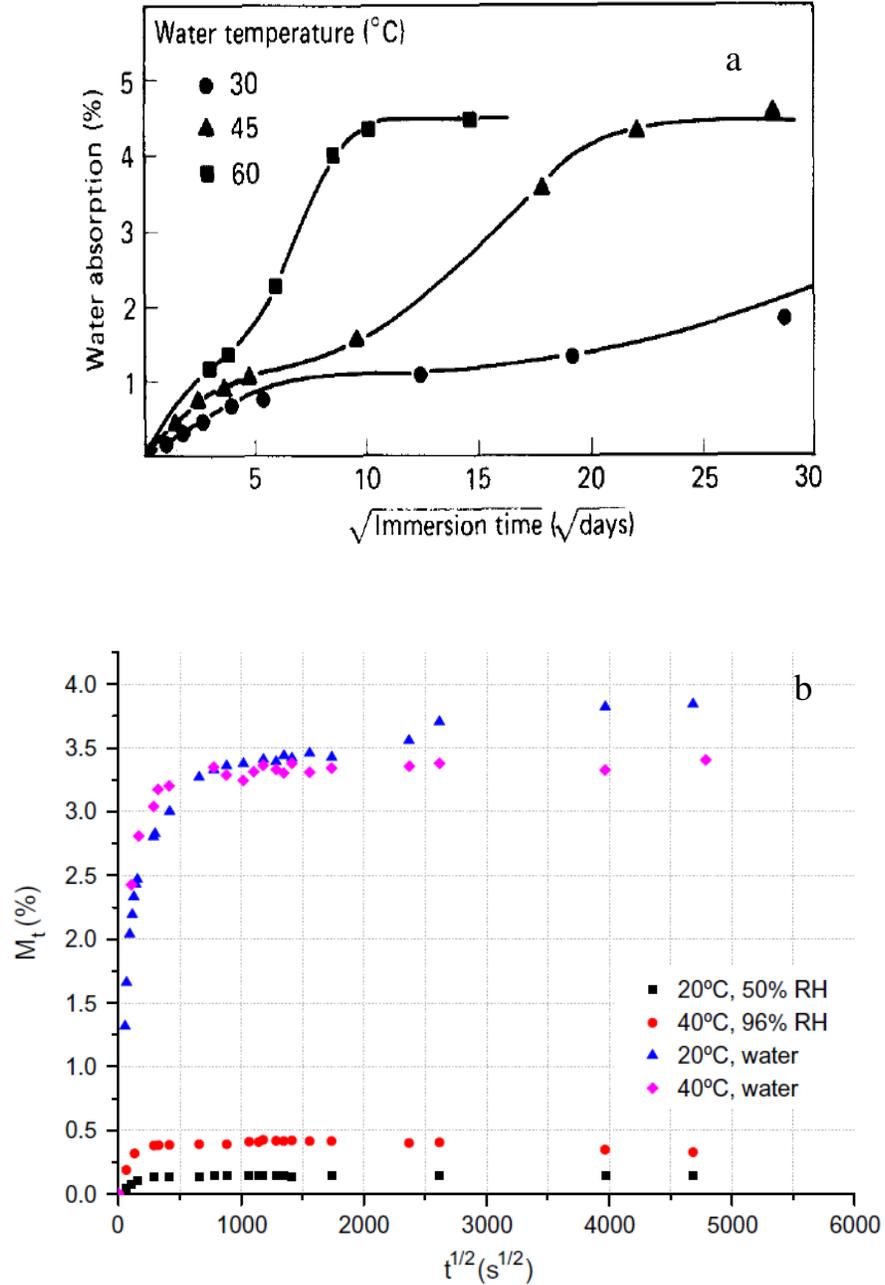


Fig-7: Experimental data following the dual-stage diffusion model in (a) glass fiber reinforced polyester composite, immersed in water [55] and (b) glass fibers reinforced isophthalic polyester composite exposed to water and humidity[56]

### 3. Factors affecting moisture ingress kinetics in polymeric composites

#### 3.1. Effect of Fiber system

On the basis of moisture absorption tendency, fibers can be broadly classified into two groups – permeable and impermeable fibers – as shown in Fig-13.

Glass and aramid fibers are permeable in nature and hence, moisture absorption in polymeric composites containing these fibers is affected by both the fiber and resin. On the contrary, carbon fibers are resistant to moisture absorption and therefore, moisture absorption in carbon fiber reinforced polymer composites depends only on the resin phase.

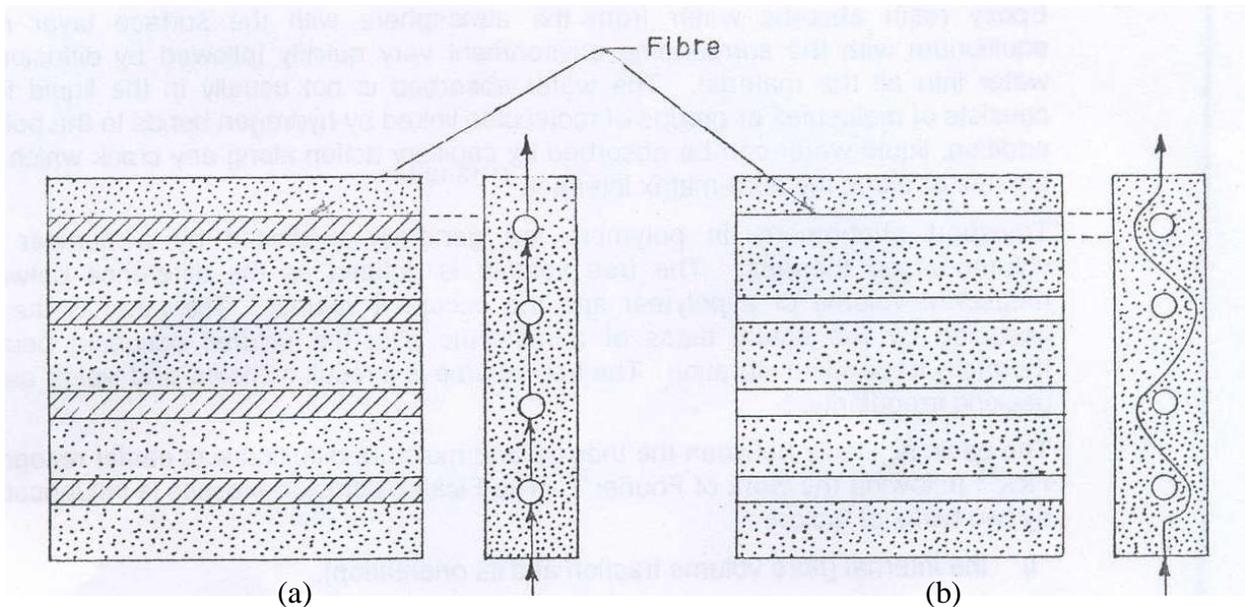


Fig-8: Typical diffusion path in polymeric composites composed of (a) permeable fibers and (b) impermeable fibers [10]

#### 3.2. Effect of resin structure

Proper choice of resin system is of paramount importance in the polymer composites as it decides not only moisture absorption capacity but also the kinetics. Moy et.al [58] has experimentally shown that highly cross-linked epoxy resins absorb less moisture than those

having low cross-link density. Fig-9 shows the significance of epoxy resin structure (functional groups, cross-linking etc.) in deciding moisture absorption characteristics of the system.

Springer [23] showed that on changing the catalyzing agent for the same fiber/matrix system, moisture diffusion kinetics changes.

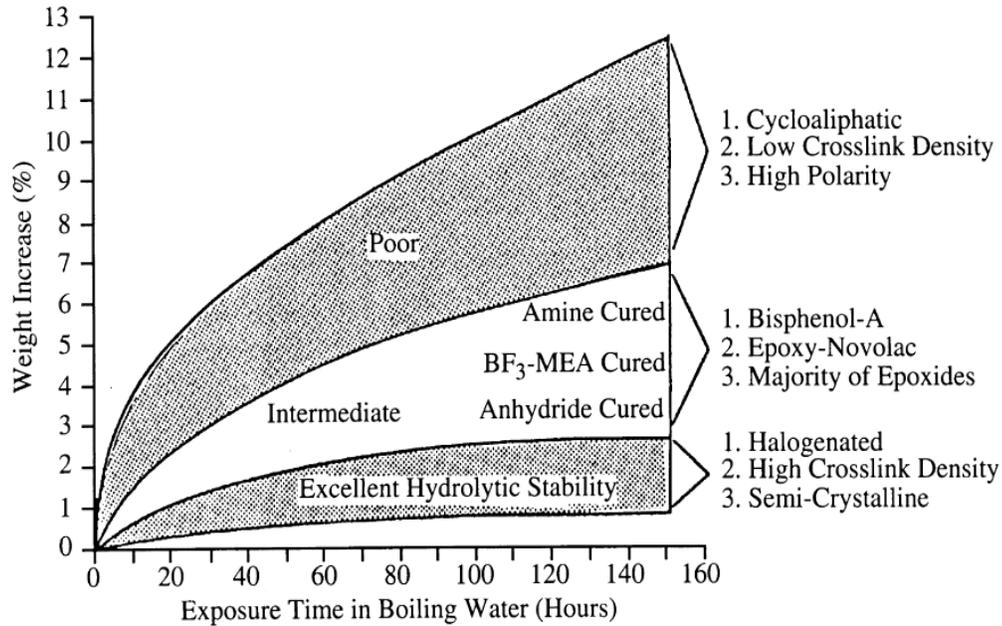


Fig-9: Structure dependence of stability of epoxy resins in boiling water [59]

### 3.3.Effect of interfacial adhesion

Silane coating is usually provided on the surface of glass fibers, which act not only as a protective coating but also as a coupling agent to promote the adhesion with polymer matrix.

The concept behind using silane coupling agents is to utilize chemical reactivity between the inorganic substrate and the organic resin, so as to develop proper adhesion at the fiber/matrix interface.

Fig-10 shows the importance of silanizing agents of glass fibers on the moisture uptake kinetics of the polymeric composites [42]. Three reagents were used for silanization of glass fiber/epoxy composite, namely, 3-aminopropyltriethoxysilane (APTES), 3-aminopropylmethyldiethoxysilane (APDES) and 3-aminopropyl dimethylmonoethoxysilane (APMES). The APMES reagent coupled FRP composite is found to have lowest saturation moisture content, whereas that coupled with APTES agent is found to undergo slowest moisture absorption kinetics.

Hence, it is important to create a healthy interphase/interface so that the threat to durability and reliability of the composite systems is minimized during their in-service performance.

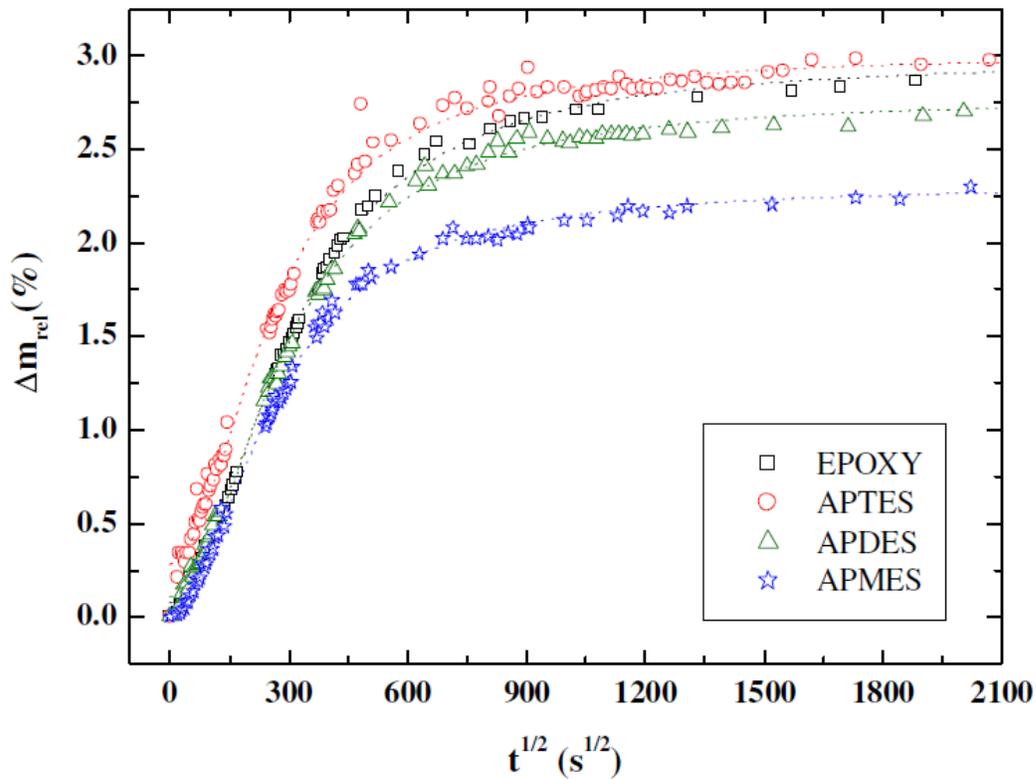


Fig-10: Effect of silanization on the moisture uptake profile of glass fiber/epoxy composites [42]

#### 4. Moisture induced damage mechanisms

Moisture induced degradation of FRP composites is the result of degradation of fibers, polymer matrix and/or the interface/interphase. Different reversible and irreversible chemical, physical and physico-mechanical degradation mechanisms take place as a result of environmental attack.

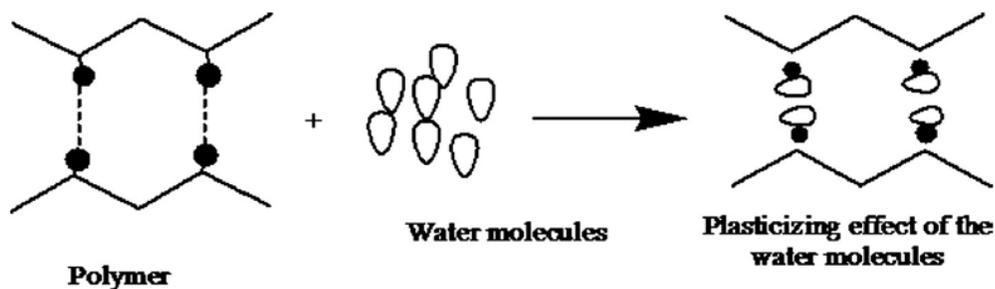


Fig-11: Schematic diagram of plasticization caused by moisture in polymer matrix [60]

When moisture enters the polymer matrix, physical phenomena such as plasticization and swelling occur. In addition, chemical (hydrolysis and debonding) and physico-mechanical phenomena (micro-crack and micro-void formation) also occur in the composite, which can lead to degradation of not only the fibers and the matrix, but also the existing interface/interphase between them [60-72].

Plasticization process is schematically shown in Fig-11, which is the result of interaction of water molecules with polymeric chains. Such interactions interrupt the existing hydrogen bonds in the polymeric matrix [61-63] and create new hydrogen bonds with the polymer matrix. This phenomenon also accounts for the swelling of the polymer matrix occurring due to increase in bond-length between polymer chains.

Microvoid formation in the polymer matrix and at the interface is generally attributed to clustering of water molecules [65-66]. Also, the swelling caused by the absorbed moisture can induce internal stresses in the polymer, which may lead to formation of microvoids or micro-cracks. On the other hand, moisture induced swelling may also relieve residual stresses developed during the curing process.

However, plasticization and swelling are reversible phenomenon, whereas certain degradation phenomena are irreversible in nature such as hydrolysis, leaching, polymer relaxation, micro-cracking and microvoids formation.

Hydrolysis is the phenomena in which side groups are detached from the backbones of the polymeric chains. In general, hydrolysis is considered to be an irreversible degradation mechanism [64], but some literatures report that it is possible to reverse the hydrolyzing effect of diffusing water molecules.

Leaching is another mechanism by which break down of the fiber/matrix interphase region occurs and fibers and polymer get separated.

Composite materials are complex structures which may fail by a number of mechanisms which are not encountered in more homogeneous materials [2]. Hence, the fractographic analysis of FRP composites is crucial in revealing the failure modes induced by moisture ingression. Alawsi et. al [60] studied the influence of exposure time on degradation mechanisms during accelerated humid ageing of E-glass/polyester composites. Fig-13 (a) shows the SEM image of the specimen which was not exposed to moisture, in which strong adhesion between fibers and matrix can be observed. But there is increasing loss of fiber/matrix adhesion with more time of exposure to

humidity, which is highest for 2000 hours. Also, increasing deterioration of polymer matrix is observed as time of exposure was increased.

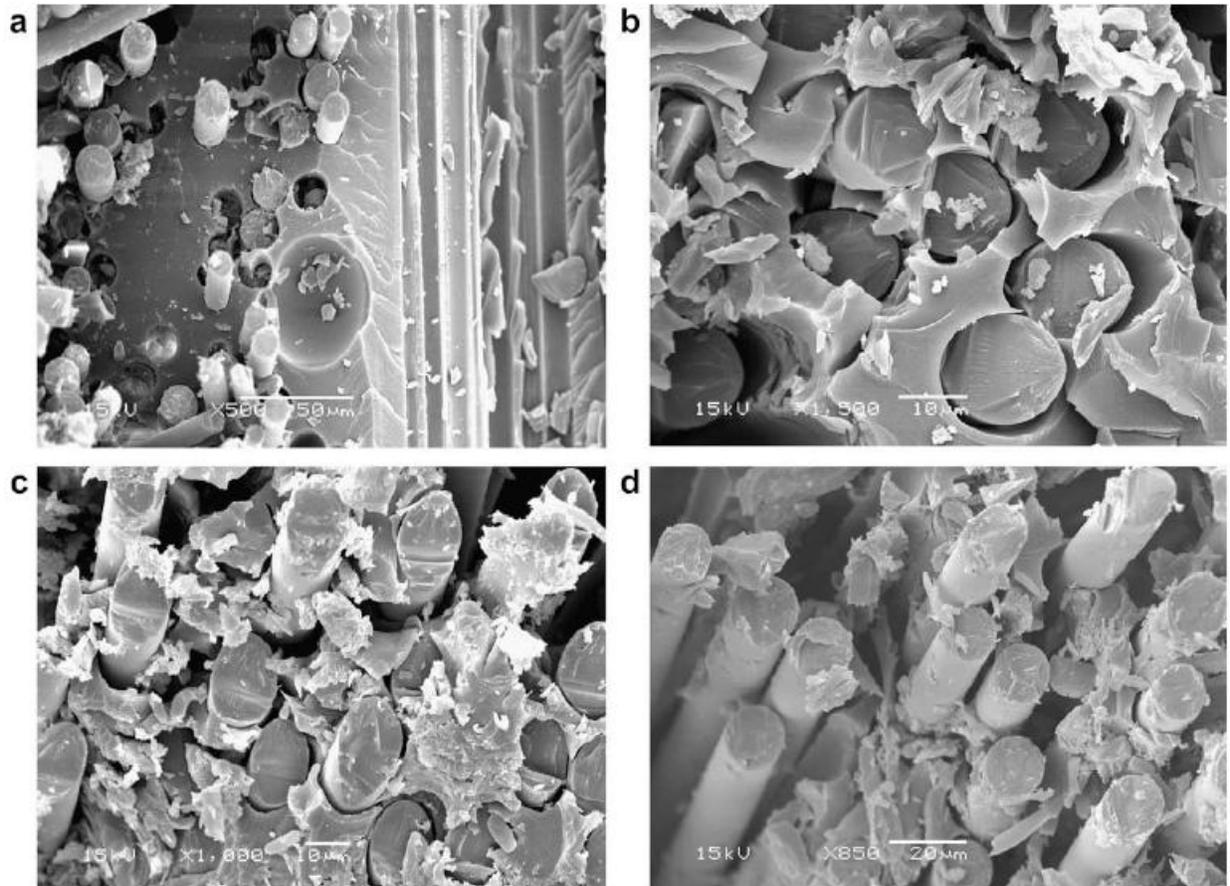


Fig-13: Scanning electron micrographs of fracture surfaces of glass/polyester samples exposed to humid environment for (a) 0 hours (b) 500 hours (c) 1000 hours (d) 2000 hours [73]

Ray [1] studied the effect of moisture ingress on carbon fiber/epoxy composites and observed fiber damage and matrix cracking in samples exposed to humid environment, as shown in Fig-14.

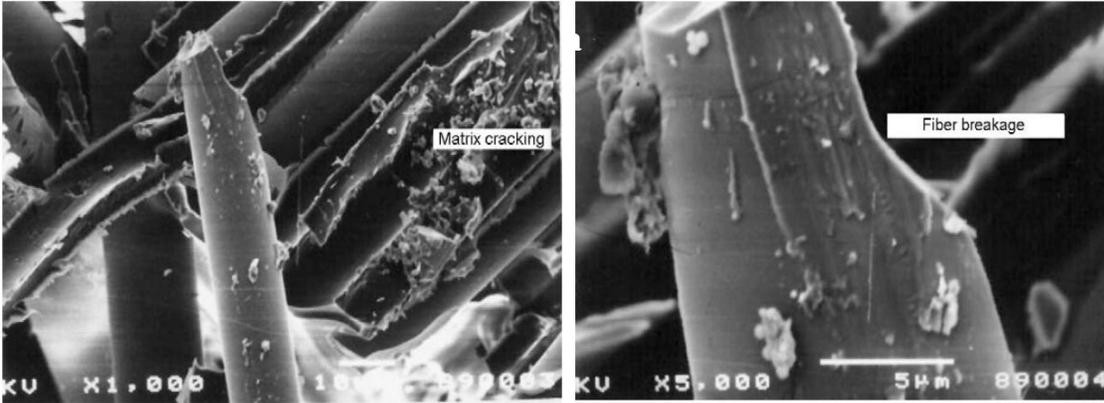


Fig-14: Scanning electron micrographs of carbon/epoxy composites exposed to humidity, showing (a) matrix cracking and (b) fiber breakage [1]

## 5. Degradation of Properties of FRP composites

Plasticization adversely affects the properties of the polymer composite by inducing plastic deformation in the matrix and by lowering its glass transition temperature. Kelley et. al. have reported that there is a drop in glass transition temperature of about 20<sup>0</sup>C for each 1% moisture uptake [74].

Joshi [75] has investigated the effect of moisture on the interlaminar shear strength (ILSS) of carbon fiber/epoxy composites. He reported an initial increase in ILSS of about 10% upto 0.1 weight % absorbed moisture and a subsequent decrease by 25% at maximum moisture of approximately 2%.

The effect of water sorption on mechanical behaviour FRP composites has been investigated by many researchers [76-80]. It was reported that in case woven glass/epoxy composites delamination load-carrying capability was reduced to 40% with 1.29% absorbed moisture [76]. Akay [77] reported that static and fatigue strength of carbon fiber/epoxy composite decreases when subjected to hygrothermal conditioning. Lassila et al. [78] have reported reduction in flexural strength of E-glass fibers reinforced polymer composites when exposed to water for 30 days.

Degradation of mechanical property under hygrothermal conditioning is often attributed to various degradation mechanisms leading to poor interfacial adhesion and change in failure mode due to moisture absorption in the polymeric composite [81-82].

## **6. Remarks and comments**

Fibrous polymeric composites are undoubtedly the most promising material of the present and upcoming century and nowadays more and more structural as well as functional components are being replaced by polymeric composites in lieu of their conventional counterparts. But, unfortunately most of the environments to which they are exposed, have detrimental effects on their in-service performance of these materials, especially moist environments. Although decades of investigation have been concentrated on finding out the behaviour of these materials under the influence of humid environments, but conclusive results are still far away. Hence, there exists a pressing demand to accurately understand the hygrothermal response of polymeric composites, otherwise FRP composites may not exhibit full potential in their service life.

In this article, an attempt has been made to compile scattered literature in the field of humid ageing of polymeric composites in order to gain comprehensive understanding of the kinetics and mechanism of moisture absorption and its deleterious effects. The emphasis has been laid on various moisture absorption models that are being commonly employed to predict the kinetics of humid ageing of FRP composites and their validity and viability in doing the same. The article has also stressed on the operative mechanisms behind the failure of FRP composites exposed to humid environments and their effect on the mechanical properties of these polymeric materials.

In case of rubbery polymers, experimental studies show that moisture absorption kinetics follow Fick's law and an saturation in moisture content is observed, whereas this is not so for glassy polymers. Non-Fickian behaviour is found to be more pronounced when the polymer composites are immersed to water and at higher temperatures. Many such models have been developed by different researchers, of which some widely accepted models are discussed here.

It is an established fact that FRP composites undergo degradation in terms of their mechanical properties such as tensile, compressive, flexural and shear properties [2, 3]. Various physical, chemical and physico-mechanical phenomena such as plasticization, swelling, leaching,

hydrolysis, debonding, micro-crack and micro-void formation are responsible for such degradations. Also, the glass transition temperature is affected by moisture ingress in these composites, which is mostly attributed to the plasticization phenomena. Most importantly, the role of the interface/interphase of the polymeric composite materials is a critical one in sustaining the structural integrity of the system under environmental attack as it decides the stress transmissibility under loading.

## **Acknowledgement**

The authors would like to thank their family members, who have always stood beside them.

## **Nomenclature**

F	Rate of transfer of water molecules per unit area of cross-section of the material ( $\text{kg}/\text{m}^2\text{s}$ )
D	Diffusion coefficient or diffusivity of the moisture in the material ( $\text{m}^2/\text{s}$ )
C	Moisture concentration in the material ( $\text{kg}/\text{m}^3$ )
l	Height of the material (mm)
w	Width of the material (mm)
h	Thickness of the material (mm)
t	Exposure time (s)
M	Percentage moisture content in the material
k	Boltzmann's constant ( $1.38 \times 10^{-23} \text{ J/K}$ )
n	Number density of mobile water molecules ( $\text{molecules}/\text{cm}^3$ )
N	Number density of bound water molecules ( $\text{molecules}/\text{cm}^3$ )

- $\mu$  Dimensionless hindrance coefficient
- $\beta$  Probability per unit time that a bound water molecule becomes mobile ( $\text{days}^{-1}$ )
- $\gamma$  Probability per unit time that a mobile water molecule becomes bound ( $\text{days}^{-1}$ )
- $\kappa$  Characteristic diffusion constant
- I Positive odd integer

### **Subscripts**

x, y, z in x, y and z directions

t at time t

$\infty$  at saturation level

o when concentration dependence is neglected

$\gamma$  for mobile water molecules

F Fickian term

R Resin relaxation term

## References

1. Ray BC. *J Colloid Interf Sci* 2006; 298: 111.
2. Ray BC, Rathore D. *Adv Colloid Interfac* 2014; doi: 10.1016/j.cis.2013.12.014.
3. Ray BC, Rathore D. *Polym Compos* 2014; doi 10.1002/pc
4. Bonniau I, Bunsell AR. *J Compos Mater* 1981; 15;272.
5. Alfrey T, Gurnee EF, Lloyd WG. *J Polym Sci* 1966; C12:249.
6. Fick A, *Ann Physik Chemic* 1855; 170: 59.
7. Fourier J.P., *Theorre Analytique de la charendon*, Paris 1822, English Translation by Freeman, A., Dover Publication, 11.
8. Crank J, Park GS, *Diffusion in Polymers*, Academic Press Inc. London, 1968.
9. Shen CH, Springer GS. *J Compos Mater* 1976; 10: 2.
10. Ray BC, Biswas A, Sinha PK. *Metals Materials and Processes*, 1991; 3: 99.
11. Jiang X, Kolstein H, Bijlaard F, Qiang X. *Compos A* 2014; 57: 49.
12. Loos AC, Springer GS. *J Compos Mater* 1979; 13: 131.
13. Shirrell CD. *Adv Compos Mater Environ Effects*, ASTM STP 1978; 658: 21.
14. Mohlin T. In: Springer GS (ed) *Environmental effects of composite materials*, Technomic, Lancaster, PA, 1984; 3: 163.
15. Loos AC, Springer GS. In: Springer GS (ed) *Environmental effects of composite materials*. Technomic, Westport, CT, 1981: 34.
16. Yoosefinejad A, Hogg, PJ. In: Visconti CI (ed) *Proceedings of ECCM eighth European conference on composite materials*, Naples, Woodhead Publishing, Italy, 1998; 1: 151.
17. Henson MC, Weitsman YJ. *Stress effects on moisture transport in an epoxy resin and its composite*. In: *Proceedings of the third Japan-US conference on composite materials*, Japan Society of Composite Materials, Tokyo, 1986: 775.
18. Althof W. *Proceedings of the 11th National SAMPE Conference*, SAMPE, Azusa, 1979; 11: 309.
19. Nicolais L, Drioli E, Hopfenberg H, Caricati G. *J Membr Sci* 1978; 3: 231.

20. Clark DL. Texas A&M University Report MM 4665-83-16, 1983.
21. Khan LA, Nesbit A, Day RJ. *Compos A*2010; 41: 942.
22. Weitsman Y. *Compos A* 2006; 37: 617.
23. Shen CH, Springer GS. In: Springer GS (ed) *Environmental effects of composite materials*. Technomic, Westport, CT, 1981: .
24. Lo SY, Hahn HT, Chiao TT. In: Hayashi T, Kawata K, Umekawa S (eds) *Proceedings of the fourth international conference on composite materials (ICCM/4)*. Progress in science and engineering of composites, Tokyo, 1982; 2: 987.
25. Yao J, Ziegmann G. *J Compos Mater* 2007; 41: 993.
26. Davies P, Choqueuse D, Mazeas F. In: Reifsnider KL, Dillard DA, Cardon AH (eds) *Progress in durability analysis of composite systems*. Balkema, Rotterdam, 1998: 19.
27. Chateauminois A, Chabert B, Soulier JP, Vincent L. In: Tsai SW, Springer GS (eds) *Proceedings of the eighth international conference on composite materials (ICCM/8)*, Honolulu. 1991: 12.
28. Gao J, Weitsman YJ. University of Tennessee Report MAES 98-4.0 CM, 1998.
29. Lagrange A, Melennec C, Jacquemet R.. In: Cardon AH, Verchery G (eds) *Durability of polymer based composites systems for structural applications*, Elsevier, 1991: 385.
30. Dewimille B, Thoris J, Mailfert R, Bunsell AR. In: Bunsell AR (ed) *Advances in composites materials; Proceedings of the Third International Conference on Composite Materials*, Paris, France. Pergamon, Paris, 1980: 597.
31. Nakanishi Y, Shindo A. In: Hayashi T, Kawata K, Umekawa S (eds) *Proceedings of the fourth international conference on composite materials (ICCM/4)*, Tokyo. ISBS, Beaverton, 1982; 2: 1009.
32. Imaz JJ, Rodriguez JL, Rubio A, Mondragon I. *J Mater Sci Lett* 1991; 10: 662.
33. Gupta VB, Drzal LT, Rich MJ. *J Appl Polym Sci* 1985; 23: 4467.
34. Mohlin T. In: Springer GS (ed) *Environmental effects of composite materials*, Technomic. Lancaster, PA, 1984; 3: 163.
35. Van den Emde CAM, Van den Dolder A. In: Cardon AH, Verchery G (eds) *Durability of polymer based composite systems for structural applications*, Elsevier Applied Science, New York, 1991: 408.

36. Apicella A, Migliaresi C, Nicolais L, Iaccarino L, Roccotelli S. *Composites* 1983; 14: 387.
37. French MA, Pritchard G. In: Cardon AH, Verchery G (eds) *Durability of polymer based composite systems for structural applications*, Elsevier, Amsterdam, 1991: 345.
38. Kootsookos A, Mouritz AP. *Compos Sci Technol* 2004; 64: 1503.
39. Ramirez F, Carlsson L, Acha B. *J Mater Sci* 2008; 43: 5230.
40. Fukuda H. In: Loo TT, Sun CT (eds) *Proceedings of the international symposium on composite materials and structures*, Beijing, 1986: 50.
41. Nicolais L, Apicella A, Del Nobile MA, Mensitieri G. In: Cardon AH, Verchery G (eds) *Durability of polymer based composite systems for structural applications*, Elsevier Applied Science, New York, 1991: 99.
42. Olmos D, Lo'pez-Moro'n R, Gonza'lez-Benito J. *Compos Sci Technol* 2006; 66:2758.
43. Manocha LM, Bahl OP, Jain RK. In: Hayashi T, Kawata K, Umekawa S (eds) *Proceedings of the fourth international conference on composite materials (ICCM/4)*, Progress in Science and engineering of Composites, Tokyo, 1982; 2: 957.
44. Carter HG, Kibler KG. *J Compos Mater* 1978;12: 118.
45. Lee MC, Peppas NA. *J Appl Polym Sci* 1993; 47: 1349.
46. Perreux D, Suri C. *Compos Sci Technol* 1997; 57: 1403.
47. Merdas I, ThomINETTE F, Tcharkhtchi A, Verdu J. *Compos Sci Technol* 2002; 62: 487.
48. Kumosa L, Benedikt B, Armentrout D, Kumosa M. *Compos Part A Appl Sci Manuf* 2004; 35: 1049.
49. Popineau S, Rondeau-Mouro C, Sulpice-Gaillet C, Shanahan MER. *Polymer* 2005;46: 10733.
50. Ferreira JM, Pires JTB, Costa JD, Errajhi OA, Richardson M. *Compos Struct* 2007;78:397.
51. Helbling CS, Kharbari VM. *J Reinf Plast Compos* 2008;27:613.
52. Saponara VL. *Compos Struct* 2011; 93: 2180.
53. Grace LR, Altan MC. *Compos A* 2012: 43: 1187.
54. Grace LR, Altan MC. *Polym Compos* 2013; 34: 1144.
55. Pritchard G, Speake SD. *Composites* 1987; 18: 227.
56. Jiang X, Kolstein H, Bijlaard F. *Mater Des* 2012; 37: 304.

57. Jiang X, Kolstein H, Bijlaard F. *Compos B* 2013; 45: 407.
58. Moy P, Karasz F. *Polym Eng Sci* 1980; 20: 315.
59. Buehler FU, Seferis JC. *Compos A* 2000; 31: 741.
60. Hammiche D, Boukerrou A, Djidjelli H, Corre Y, Grohens Y, Isabelle P. *Constr Build Mater* 2013; 47: 293.
61. Kwei TK. *J Appl Polym Sci* 1966; 10:1647.
62. Nissan AH. *Macromolecules* 1975; 9: 840.
63. Mijovic J, Zhang H. *J PhysChemB*. 2004; 108: 2557.
64. Antoon MK, Koenig JL. *J Macromol Sci R M C* 1980; C19: 135.
65. Ishida H, Koenig JL. *Polym Eng Sci*1978; 18: 128.
66. Lowry HH, Kohman GT. *J PhysChem* 1927; 31: 23.
67. Kim JK, Mai YW, *Engineered interfaces in fiber reinforced composites*, Elsevier, New York, 1998.
68. Plonka R, Mader E, Gao SL, Bellmann C, Dutschk V, Zhandarov S. *Compos Part A- Appl S*2004; 35: 1207.
69. Dibenedetto AT, Lex PJ. *Polym Eng Sci* 1989; 29: 543.
70. Walker P. *J Adhes Sci Technol* 1991; 5: 279.
71. Pisanova E, Mader E. *J. Adhes Sci. Technol.* 2000; 14: 415.
72. Ishida H. *Polym Compos* 1984; 5: 101.
73. Alawsi G, Aldajah S, Rahmaan SA. *Mater Des* 2009; 30: 2506.
74. Kelley FN, Bueche F. *J Polym Sci* 1961;50: 549.
75. Joshi OK. *Composites* 1983; 14: 196.
76. Collings TA. Stone DEW. *Compos Struct* 1985; 3: 41.
77. Akay M. *Composites* 1992; 23:101.
78. Lassila LVJ, Nohrstrom T, Vallittu PK. *Biomaterials* 2002; 23: 2221.
79. Chu W, Karbhari VM. *J Mater Civil Eng*, 2005; 17: 63.
80. Wan YZ, Wang YL, Huang Y, Zhou FG, He BM, Chen GC, Han KY. *Compos SciTechnol* 2005; 65: 1237.
81. Whitney JM, Husman GE. *Exp Mech* 1978; 18: 185.
82. Drzal LT, Madhukar M. *J Mater Sci* 1993; 28: 569.