

Effect of the Fiber Orientation on the Sorption Kinetics of Seawater in an Epoxy/Glass Composite: A Free-Volume Microprobe Study

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ABSTRACT: The conventional gravimetric method and positron lifetime spectroscopy have been used to investigate the effect of glass fiber orientation on the diffusion behavior of seawater in epoxy-based composite samples with glass fiber orientations of 0 and 45°. The equilibrium mass uptake of seawater in 45 and 0° orientation composites has been found to be 2.77 and 1.57%, respectively. The diffusion process is non-Fickian in a 45° fiber oriented composite, whereas it is Fickian in a 0° oriented composite. Free-volume data for 45° fiber oriented composites indicates swelling upon the sorption of seawater leading to structural relaxation, and hence the diffusion becomes non-Fickian. On the

other hand, a 0° fiber orientation sample exhibits no swelling, and this suggests that water diffusion to the fiber–resin interface through the resin matrix is impeded by the large number of bonds. A polymer–fiber interaction parameter determined from these results also further supports the idea that interface interaction in a 45° fiber oriented composite is less than that in a 0° fiber oriented composite. Positron and gravimetric results support this argument. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1302–1309, 2008

Key words: composites; diffusion; fibers; interfaces; orientation

INTRODUCTION

Studies on seawater diffusion in marine structures are important because the salinity of seawater aggravates corrosion in these structures. The corrosion is an expensive error for the selection and use of unsuitable materials such as metals and their alloys, which are susceptible to corrosion. To overcome this problem, corrosion-resistant, nonmetallic materials such as polymers and their composites have been tried. In this direction, we find that glass-reinforced polymers are increasingly being tested and tailored for some critical marine components such as masts and submarine propellers.¹ Nowadays, epoxy-based composites are considered better for primary marine structures because an epoxy matrix generally outperforms most other resins in terms of mechanical properties. However, an undesired property of epoxies is that various formulations absorb 1–7% seawater by weight. This has a deleterious effect on the physical properties of the epoxy and can greatly degrade the performance of the epoxy-based composites.² Seawater aging may also strongly affect the polymer matrix through its chemical and physical changes by hydrolysis/leaching or a swelling process, and this

results in debonding at the fiber/matrix interface and thus may reduce the mechanical strength; this might also result in microcracks in the resin structure and hence degrade the properties of the composites as a whole. In glass-fiber-reinforced polymer composites, it is known that bulk glass is susceptible to stress corrosion in the presence of water or water vapor.

It is a well-established fact that the parameters which influence the swelling behavior of the resin matrix are the void content, temperature, presence of the fillers, interfacial adhesion, and diffusing solvent.³ Several investigations have been conducted in the past on the effects of seawater diffusion on mechanical properties such as the loss factor and modulus of fiber-reinforced epoxy composites,⁴ the effect of the interfacial strength of an interlayer E-glass/graphite/epoxy composite (in which damage growth has been studied with increased moisture content as well as increased aging time),⁵ and the effect of the strain rate on the compressive properties under both atmospheric pressure and hydrostatic pressure conditions.⁶ These are only a few of a vast number of reports in the literature. Additionally, we have found work on an apparent shift in the glass-transition temperature upon fiber orientation in epoxy-matrix composites⁷ and orientation effects at a high strain rate that influence the ultimate strength of the composites.⁸ According to Hull,⁹ the glass fiber/resin interface can be

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described as follows. The glass surface has randomly distributed groups of various oxides in addition to SiO₂. These absorb water as hydroxyl groups such as Si—OH and as molecular water attached to the —Si—OH groups. If the oxides are hygroscopic, they become hydrated with water sorption. Because glass absorbs water readily to form a well-bonded surface layer, if the surface stays in contact with water for a long time, the hygroscopic elements can be dissolved, and a porous surface consisting of nonhydrated oxides is then created. If the fiber orientation is changed, this interface profile also changes, and this results in more voids or a porous surface. Although the effect of fiber orientation on seawater diffusion in composites used in marine structures happens to be of significant interest (especially the effect of adhesive bonding of the fiber at the fiber-resin interface on the diffusion process), not many studies have been carried out. This particular aspect is important as it controls the interface profile in terms of voids and pores, the pathways for the diffusion of seawater. Motivated by this, we thought it desirable to take up this investigation to understand the effect of fiber orientation on the sorption kinetics of seawater at the molecular level in epoxy-based composites. This will provide information necessary for end applications such as marine structures with respect to seawater corrosion.

Diffusion is largely dependent on the void content or free-volume holes, which are the open spaces that are present in the amorphous domains of the polymer or epoxy system, and the voids or porous surface at the interface in fiber-reinforced composites.¹⁰ Diffusion of water can also occur from the resin side to the interface. Thomason¹¹ reported absorption enhancement due to void content, particularly at the interface, for a range of epoxy/glass composites exposed to 100% humidity. We know that the free-volume cavities provide pathways for diffusion and help to explain the molecular motion and physical behavior of glassy and liquid states of matter.¹² The free-volume holes and their content in composites can be readily measured with positron lifetime spectroscopy (PLS) because the topology of the composites, which influences the kinetics of seawater transport, can be quantified via PLS in terms of the size and free-volume fraction.¹ Recently, this method has been gaining importance in blends and composites as well. The sorption method,^{13,14} because of its simplicity and range of applicability (diffusivities from 10⁻⁶ to 10⁻¹² cm²/s), is used in this work^{15,16} to understand the diffusion behavior of seawater. Therefore, in this study, we have carried out seawater sorption in epoxy/glass composites with E-glass fibers reinforced in two orientations, 0 and 45°, in the resin matrix through free-volume quantification and sorption kinetics.

EXPERIMENTAL

Sample details

An epoxy resin based on liquid diglycidyl ether of bisphenol A (DGEBA) and a hardener component, triethylene tetraamine (TETA), were combined in a weight ratio of 10 : 1. There were two sets of composites: one with E-glass fibers woven at 0° to the resin matrix [E/G (0°)] and the other with fibers woven at 45° to the matrix [E/G (45°)]. The fiber weight percentage was 60% in both laminated samples. The composites so prepared were cured at room temperature and postcured at 100°C for 3 h. The laminated, multilayered structure was cut into specimens with dimensions of 1.2 × 1 × 0.15 cm³ [E/G (45°)] or 1.2 × 1 × 0.1 cm³ [E/G (0°)] and used in sorption studies followed by PLS measurements.

Seawater sorption measurements

Before the experiment, the samples were dried in an oven at about 70°C (less than the glass-transition temperature of DGEBA/TETA, i.e., 110°C) to desorb the moisture in the samples if there was any. The dry weight of the samples was recorded with a digital balance (Basic BA110 S, Sartorius, Germany) with a precision of ±0.1 mg. The sorption of natural seawater (collected from the Arabian Sea, Mangalore, Karnataka, India, with a salinity of ca. 35% and a density of 1.03 g/cm³) was conducted by the immersion of the samples in a seawater container with an airtight lid, which was kept a room temperature (26 ± 1°C) for a known time. The samples were removed from the container, blotted to remove excess moisture from the surface, and weighed as before. These samples were then used in positron lifetime measurements. This procedure was repeated for a known number of sorption times until the weight gain reached the equilibrium state. Before each immersion, desorption was conducted at 70°C until the original weight of the sample was regained.

Brief description of PLS

The basis of PLS involves the injection of positrons from a radioactive source (²²Na) into the material under study. Positrons thermalize very rapidly through interactions with the molecules and annihilate with electrons of the medium. A positron can annihilate from different states in a molecular medium. In polymers, it can form a bound state called positronium (Ps). Ps exists in two states, depending on the relative spin of the positron-electron pair. *para*-Positronium (*p*-Ps) with antiparallel spins has a lifetime of 125 ps and annihilates with the emission of two γ photons. *ortho*-Positronium (*o*-Ps) with parallel spins has a longer lifetime and annihilates in

free space into three γ photons with a lifetime of 140 ns. However, in a molecular medium, *o*-Ps annihilates predominantly via a fast channel, which is called pick-off annihilation (a positron of *o*-Ps annihilates with an outside electron from the medium having the opposite spin), by two γ -photon emissions, and its lifetime is reduced to a few nanoseconds. The *o*-Ps pick-off lifetime therefore is a measurable parameter that depends on the overlap of the Ps wave function with the wave function of the electrons of the medium. *o*-Ps is localized in free-volume cavities as positrons do in defects before annihilation. Therefore, the *o*-Ps lifetime is a measure of the free-volume cavity size, and in terms of probability, the *o*-Ps intensity is a measure of the relative number of these cavities. The larger the cavity size is, the smaller the overlap is of the wave functions and the longer the *o*-Ps lifetime is.¹⁷ The formation of *o*-Ps and its yield in polymers are determined by the positron lifetime measurement.¹²

Positron lifetime measurements

Positron lifetime measurements in the composites were carried out with a standard fast-fast coincidence system with conically shaped BaF₂ scintillators coupled to photomultiplier tubes of the XP2020/Q type with quartz windows as detectors. The coincidence spectrometer had a time resolution of 220 ps. The source-sample sandwich geometry was used for positron lifetime measurements. The typical lifetime spectrum accumulation time was around 2 h with a 17- μ Ci Na²² positron source, which provided good counting statistics with more than 10⁶ counts under the spectrum. All measurements were made at room temperature. The instrumental time resolution (sum of three Gaussians) and source correction terms were obtained from the lifetime spectrum measured with a well-annealed aluminum sample and with the program Resolution.¹⁸ The lifetime spectra so acquired were analyzed into three lifetime components with the PATFIT-88 computer program,¹⁸ which gave acceptable κ^2 values and standard deviations. More details on the instrumentation and spectrum analysis can be found elsewhere¹⁹

RESULTS AND DISCUSSION

Seawater diffusion results

Sorption results are plotted and shown in Figures 1 [E/G (45°)] and 2 [E/G (0°)]. A plot of Q_t versus the square root of the sorption time ($t^{1/2}$) is generally called the sorption curve; Q_t is the M_t/M_∞ ratio, where M_t is the moisture uptake at time t and M_∞ is the equilibrium moisture uptake. The diffusion coefficient (D) of seawater was calculated from the initial

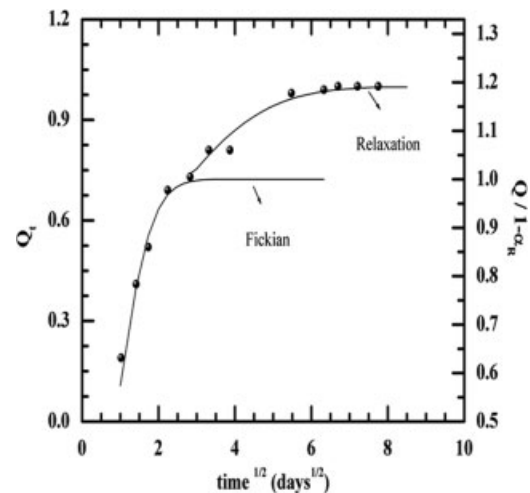


Figure 1 Variation of Q_t and $Q_t/(1 - \alpha_r)$ as a function of $t^{1/2}$ in E/G (45°).

portion of the respective sorption curves with the use of the square root of time law or Stefan's approximation,^{14,20} which is expressed as follows:

$$Q_t = 4(Dt/\pi L^2)^{1/2} \quad (1)$$

where L is the sample thickness and t is the sorption time. Accordingly, for short times (up to $M_t/M_\infty = 0.5$), the amount of the substance diffused is proportional to $t^{1/2}$ under the approximation that D is constant. M_t/M_∞ was evaluated according to the following equation:

$$Q_t = (W_t - W_d)/(W_\infty - W_d) \quad (2)$$

where W_t is the weight of the sample soaked in seawater for time t , W_d is the weight of the dry sample, and W_∞ is the equilibrium weight. Furthermore, we invoked Crank's solution to Fick's second law of diffusion equation¹⁵ to understand the sorption mechanism:

$$Q_t = \left\{ 1 - \sum 8/\pi^2 (2n+1)^2 \times \exp[-D(2n+1)^2 \pi^2 t/L^2] \right\} \quad (3)$$

where n is a positive integer.

This solution holds true for the conditions of an infinite plane sheet maintained at a constant concentration. D can also be calculated from the late-time approximation of eq. (3) with $n = 0$, which results in

$$Q_t = 1 - (8/\pi^2) \times \exp(-D\pi^2 t/L^2) \quad (4)$$

Sorption results in E/G (45°)

At short times, Q_t varies linearly with $t^{1/2}$ up to a value of $Q_t = 0.45$ (Fig. 1), indicating Fickian diffu-

sion behavior,²⁰ but at longer times, the maximum uptake exhibits a protracted non-Fickian asymptotic approach toward equilibrium. Fickian diffusion is characterized by the rate of diffusion being much less than that of the polymer segmental relaxation because of mechanical, structural, and other such modes of penetrant-polymer system interaction. Non-Fickian type diffusion is the result of diffusion faster than the segmental relaxation process and is hence termed relaxation-controlled diffusion. In this case, the fiber/resin interface also plays a role as far as diffusion is concerned. This kind of diffusion kinetics is often described by the Berens and Hopfenberg model, which is otherwise called dual-mode sorption.²¹ According to this model, the rapid Fickian diffusion process dominates the sorption during the initial stages of a penetrant-free polymer sample, whereas incremental sorption shows larger relative contributions from the slow relaxation process. The relaxation process appears to be related to a slow redistribution of the available free volume through relatively large-scale segmental motions in the relaxing polymer. An analysis of experimental sorption data through this model yields kinetic and equilibrium parameters describing the individual contributions from the Fickian controlled diffusion and relaxation-controlled diffusion process. This model has been shown to provide a meaningful analysis of several non-Fickian anomalies, including a very slow approach to the apparent equilibrium.²¹ From a careful examination of the weight uptake plot in Figure 1, we have found that the diffusion in this case is non-Fickian. Hence, we have used the dual-mode sorption model to analyze the two-stage sorption kinetics in E/G (45°).²² The mathematical representation of this model, which explicitly separates contributions from Fickian diffusion and relaxation-controlled diffusion, is given by

$$Q_t = (1 - \alpha_r) \left\{ 1 - \sum 8/\pi^2 (2n + 1)^2 \times \exp[-D(2n + 1)^2 \pi^2 t / L^2] \right\} + \{1 - \alpha_r \exp[-t/\tau_r]\} \quad (5)$$

where $(1 - \alpha_r)$ and α_r are the fractions of mass uptake in the overall sorption contributed by Fickian and relaxation parts, respectively, and τ_r is the first-order time constant associated with the long time drift in mass uptake. The long time drift in sorption kinetics is usually ascribed to mass uptake controlled by the viscoelastic relaxation of the polymer chains to accommodate a penetrant.²¹ Another aspect of this model is that it represents diffusion and relaxation as parallel processes, and the faster process controls the initial mass uptake. Because the rate of sorption in the initial stage is usually controlled by Fickian diffusion, the initial portion may be used to

estimate the Fickian diffusion coefficient (D), even though the overall sorption does not follow the Fickian model.²³ As such, D for E/G (45°) is estimated from the linear portion of the sorption curve (Fig. 1) with eq. (1). To separate the pure Fickian contribution in the sorption curve, the experimental data were fitted to this model²⁴ with the first part of eq. (5). That is

$$Q_t / (1 - \alpha_r) = 1 - \sum 8/\pi^2 (2n + 1)^2 \times \exp[-D(2n + 1)^2 \pi^2 t / L^2] \quad (6)$$

The solid curve in Figure 1 represents this fit. From the second part of eq. (5), the polymer relaxation-controlled mass uptake is described as a single exponential:

$$\ln(1 - M_t/M_\infty) = \ln \alpha_r (t/\tau_r) \quad (7)$$

A graph of $\ln(1 - M_t/M_\infty)$ versus sorption time t was drawn for E/G (45°) data, and the inverse of the slope of this graph provides the first-order relaxation time constant τ_r (11.12 days), which characterizes the non-Fickian drift in mass uptake toward equilibrium after the initial diffusion controlled by a Fickian process. Furthermore, the intercept of this plot yields the α_r value. The parameters so obtained are tabulated in Table I. The dashed curve in Figure 1 represents the fit to the experimental data with the calculated values of τ_r and α_r . The α_r value indicates what percentage of sorption corresponds to non-Fickian diffusion.

Sorption measurements in E/G (0°)

The sorption curve is linear during the early stages of sorption and reaches equilibrium in the later stages of sorption; that is, the Q_t ratio varies linearly with $t^{1/2}$ up to $Q_t = 0.98$ and levels off thereafter, and this is characteristic of Fickian diffusion.²⁰ The D values for E/G (0°) are estimated from the linear portion of the sorption curve (Fig. 2) with eq. (1).

Now it becomes evident from separated Fickian diffusion and relaxation-controlled diffusion curves that the change in the fiber orientation from 0 to 45° changes the mode of diffusion from Fickian to non-Fickian. An earlier report on epoxy-based resins²⁵ simply reports that water diffuses as dispersed molecular species (water) rather than aggregated clusters.

Positron lifetime results

All the measured positron lifetime spectra were resolved into three lifetime components, τ_1 , τ_2 , and τ_3 , with intensities I_1 , I_2 , and I_3 , respectively. The

TABLE I
Parameters Derived from the Sorption Data

Sample	Sorption mode	Fickian (%)	Non-Fickian (%)	Maximum uptake (%)	$D (\times 10^{-13} \text{ m}^2/\text{s})$	τ_r (days)	$1 - \alpha_r$	α_r
E/G (0°)	Fickian	100	0	1.57	6.09	0.00	1	0
E/G (45°)	Non-Fickian	45	55	2.77	11.01	11.12	0.45	0.55

attribution of these lifetime components is as follows. The shortest lifetime component, τ_1 , with intensity I_1 is attributed to *p*-Ps and free positron annihilations. The intermediate lifetime component, τ_2 , with intensity I_2 is attributed to the annihilation of positrons trapped at the defects present in the crystalline regions or at the crystalline–amorphous interface regions of the medium. The longest-lived component, τ_3 , with intensity I_3 , is due to pick-off annihilation of *o*-Ps in the free-volume sites present mainly in the amorphous regions of the resin matrix.²⁶ A simple empirical relation developed by Nakanishi et al.²⁷ relates the *o*-Ps lifetime (τ_3) to the free-volume hole size, which is based on the models of Tao and later Eldrup et al.²⁸ In this model, the Ps atom was assumed to be localized in a spherical potential well with an infinite potential barrier of radius R_0 with an electron layer in the region of $R < r < R_0$, where R is the radius of the free-volume hole or cavity. According to this, the relation between τ_3 and R is given by

$$(\tau_3)^{-1} = 2 \left[1 - \frac{R}{R_0} + \frac{1}{2\pi} \sin\left(\frac{2\pi R}{R_0}\right) \right] \text{ns}^{-1} \quad (8)$$

where $R_0 = R + \delta R$ and δR is a fitting parameter. By fitting eq. (8) with τ_3 values for known hole sizes in molecular materials such as zeolites, we determined a value of $\delta R = 0.166$ nm. We also found that the

same value of $\delta R = 0.166$ nm holds well. This relation is used to calculate the average free-volume radius. If free-volume cavities are assumed to be spherical, their average free-volume size (V_f) is evaluated as follows:

$$V_f = (4/3)\pi R^3 \quad (9)$$

In composite materials, the resin matrix surrounds the reinforced fibers, or in other words, the fibers are embedded in the resin. Therefore, positrons seem to be preferably localized and annihilate in the free-volume cavities of the resin and at the interface of the glass fiber and the resin.¹ It is difficult to determine whether *o*-Ps is annihilating from the interface or from the free-volume cavities of the resin from the average value of the lifetime. If the swelling of the matrix occurs because of increased uptake of water in the composite, certainly it points to the fact that a fraction of *o*-Ps annihilates from the voids at the interface. τ_3 and hence V_f as a function of $t^{1/2}$ are plotted and shown in Figures 3(a) and 4(a) for E/G (0°) and E/G (45°), respectively, whereas the *o*-Ps intensity (I_3) as a function of $t^{1/2}$ is shown in Figures 3(b) and 4(b), respectively. From these figures, it is evident that the sorption kinetics in epoxy/glass composites is certainly influenced by the orientation of glass fibers in the resin matrix, particularly at the interface.

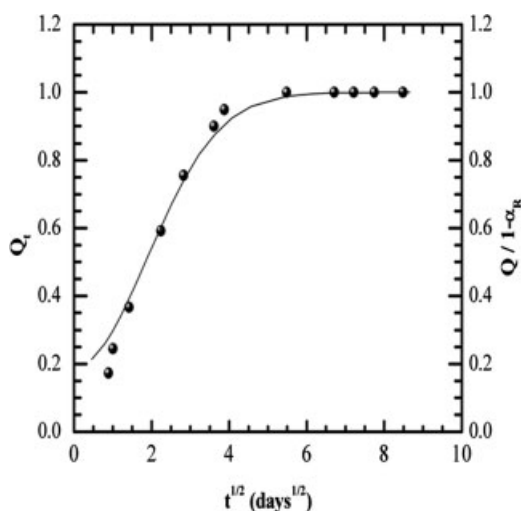


Figure 2 Variation of Q_t and $Q_t/(1 - \alpha_r)$ as a function of $t^{1/2}$ in E/G (0°).

Positron results in E/G (45°)

In Figure 3(a), we can see a reasonable increase in τ_3 and V_f (up to 16 days) that may be attributed to swelling of the composite, which is commonly observed in many polymer systems that swell in liquid media.²⁹ Seawater diffusion through the free-volume cavities and fiber/epoxy interface may induce local molecular rearrangement, possibly through conformational changes. It is known that a polymeric chain of a given configuration shows any number of conformational changes depending on external forces, such as thermal energy and solvent interactions.¹⁶ The phenomenon of swelling depends on the forces of interaction between the solvent molecules (seawater) and the epoxy chain segments. The two fundamental approaches proposed for the interaction of water molecules with thermoset polymers are binding to polar groups

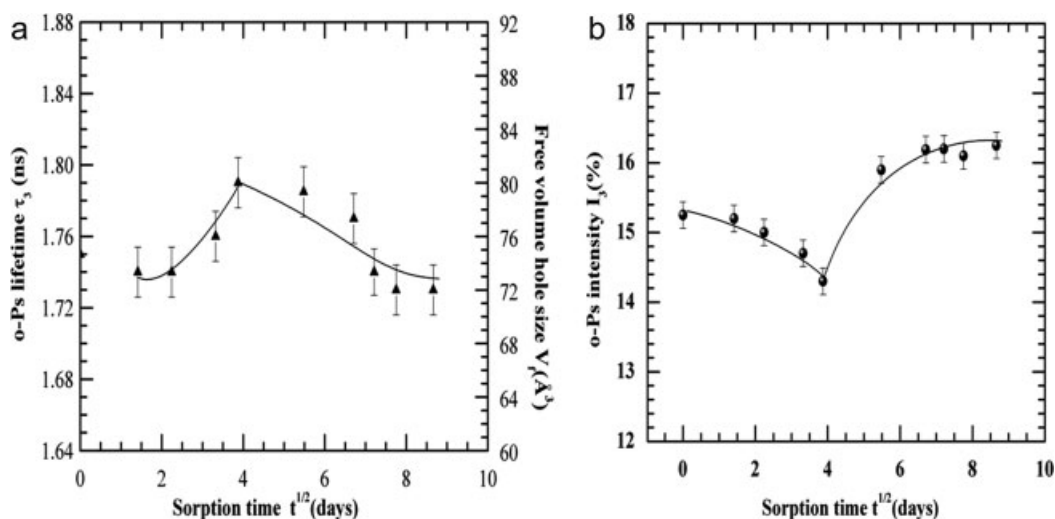


Figure 3 (a) Variation of τ_3 and V_f as a function of $t^{1/2}$ in E/G (45°) and (b) variation of I_3 as a function of $t^{1/2}$ in E/G (45°).

and hydrogen bonding and clustering. Various researchers have suggested that water molecules can exist in one of two states (bound or free state). In the free state, water molecules fill the free volume present in the dry state of the system, and they are relatively mobile within the free-volume hole. If seawater fills existing free-volume cavities, it will not cause swelling to occur; that is, this involves no interaction between the seawater and the resin matrix. In the bound state, water filters through the fiber/matrix interface, leading to hydrogen bonding, and becomes immobilized, and this causes swelling.^{30–32} Beyond 16 days, τ_3 decreases and reaches a constant value, and this suggests that on further sorption, bond formation may cease as the fiber matrix interface is in a wet environment.³³ Furthermore, this interfacial bond-

ing between the adhesive and the filler (seawater) may act as a nucleus for the formation of hydrogen-bonded clusters. These clusters, formed in the voids at the interface, reduce V_f . The formation of these clusters blocks or impedes further diffusion of water molecules, thus leading to saturation at most of the polar sites; hence, τ_3 reaches a constant value.³⁴ Initially, I_3 decreases [Fig. 3(b)] up to $t = 16$ days, and this can be viewed as free-volume holes being filled by seawater. Beyond this, I_3 increases, and the change is about 2.2%. This may be attributed to the fact that seawater contains few bigger ions (especially Cl^- of an ionic radius of 1.81 \AA) that can form crosslinks or bridges between molecular chains, resulting in an increase in the crosslink density of the network.³⁵ It is known that the free-volume hole number increases with an increase in the crosslink density at the inter-

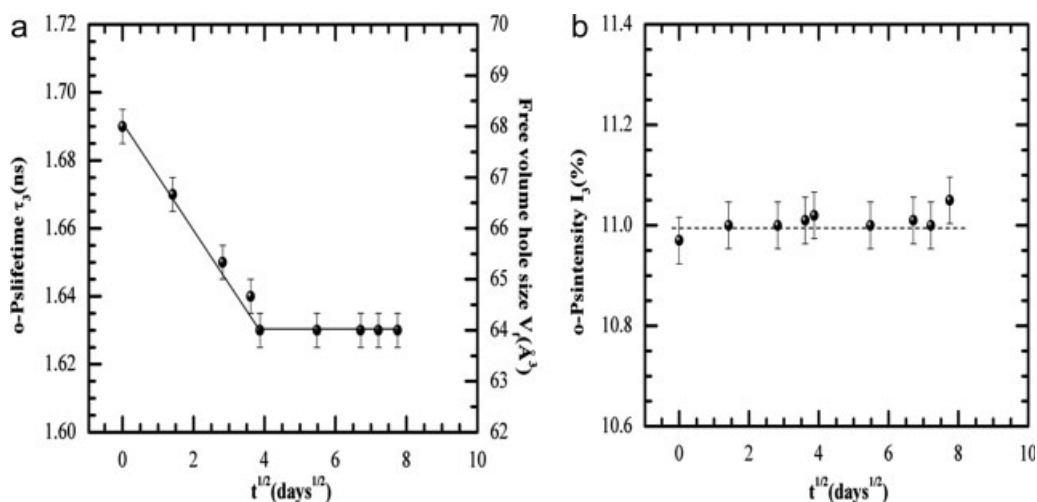


Figure 4 (a) Variation of τ_3 and V_f as a function of $t^{1/2}$ in E/G (0°) and (b) variation of I_3 as a function of $t^{1/2}$ in E/G (0°).

face as well. Thereafter, I_3 reaches a constant value on attaining equilibrium.

Positron results in E/G (0°)

In this composite, the decrease in V_f and τ_3 [Fig. 4(a)] is initially linear up to $t = 16$ days. This indicates no swelling behavior, although seawater enters the matrix through free-volume cavities and the interface regions. This might be due to the hindrance put up by 0° orientations of the fibers. This also indicates that no additional free volume is evolving. Beyond 16 days of sorption, τ_3 and V_f remain constant, and this suggests that the filling of free-volume holes is almost complete. With decreasing V_f , I_3 remains constant [Fig. 4(b)]. This suggests that the number density of free-volume cavities is not affected by seawater filling the holes, and it appears that the diffusion of seawater from the resin side to the interface is restricted.

Matrix–fiber interaction

It is interesting to note that there exists stronger bonding between the matrix and fiber in composites when the fiber loading is greater than 40%. When the fiber loading is lower, the packing of the fibers will not be efficient in the composite. This leads to the matrix-rich regions and therefore easier failure of bonding at their interface.³⁶ In these samples, the fiber loading is 60 wt %, and the chemical nature of the matrices is similar. The different behavior observed for E/G (45°) and E/G (0°) reflects the influence of orientation of the fibers in the matrix, which results in a different interface profile. To understand the effect of fiber orientation on the swelling behavior of the matrix and the extent of interaction between the matrix and fiber in a seawater environment at the interface, the theoretical approach developed by Kraus³⁷ is used. According to this, if one assumes that the swelling is completely restricted at the surface and that the resin matrix at some distance away from the surface is swollen isotropically and in a manner characteristic of an unloaded resin, then Kraus arrives at eq. (10) using purely geometrical arguments:

$$V_{ro}/V_{rf} = 1 - m(f/1 - f) \quad (10)$$

The ratio V_{ro}/V_{rf} represents the degree of restriction to swelling of the matrix in the presence of the fibers. V_{ro} is the volume fraction of the solvent-swollen epoxy matrix, V_{rf} is the volume fraction of the matrix in the solvent-swollen filled composite sample, f is the weight fraction of the fibers, and m is the polymer–fiber interaction parameter at the interface. This theory suggests that the restriction to swelling depends only on the establishment of a firm bond

between the resin and the fiber but does not depend critically on the number of such bonds. We use the relations developed by Ellis and Welding³⁸ to evaluate V_{rf} and V_{ro} in eq. (10):

$$V_{rf} = (d - fW_{Iw})\rho_c^{-1}/(d - fW_{IW})\rho_c^{-1} + A_{sc}\rho_s^{-1} \quad (11)$$

$$V_{ro} = d\rho_p^{-1}/d\rho_p^{-1} + A_s\rho_s^{-1} \quad (12)$$

where d is the weight of the dry composite, W_{Iw} is the dry weight of the epoxy matrix, ρ_c is the density of the composite, ρ_p is the density of the epoxy matrix, ρ_s is the density of the solvent (seawater), A_{sc} is the amount of the solvent absorbed by the composite sample, and A_s is the amount of the solvent absorbed by the epoxy matrix. From eqs. (11) and (12), V_{ro} and V_{rf} have been calculated for different sorption times for E/G (45°) and E/G (0°). The inverse of the slope of the plot shown in Figure 5 gives V_{ro}/V_{rf} values of 0.743 and 1.169 for E/G (45°) and E/G (0°), respectively. This indicates that the degree of restriction to the swelling in the matrix is more in E/G (0°), for which the ratio is 1.169, than in E/G (45°), for which the ratio is 0.743. Making use of this ratio and eq. (10), we have further evaluated polymer–fiber interaction parameter m and found it to be 1.477 for E/G (45°) and -0.672 for E/G (0°). From the values of m , we understand that the interaction between the resin and fiber at the interface seems to be more in the E/G (0°) composite because there is a greater probability that the surface of the fiber in contact with the resin is large through Si–OH and similar bonds of other oxides of the E glass, and this seems to decrease for the 45° orientation composite. Therefore, one may conclude that resin–fiber bonds affect the swelling behavior, which depends on the orientation of the reinforced fiber.

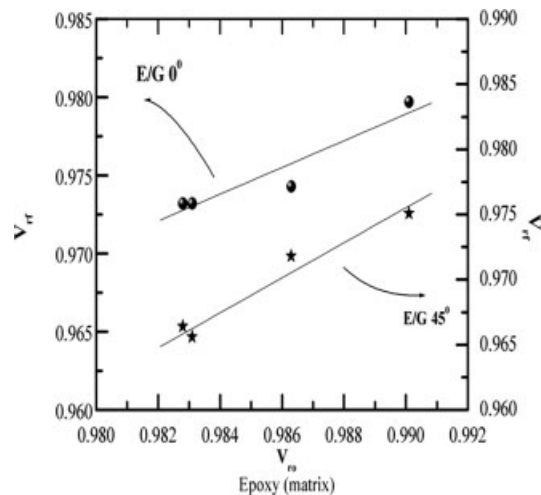


Figure 5 Variation of V_{rf} of E/G (0°) and E/G (45°) with V_{ro} .

Therefore, the molecular chain movement is restricted strongly by the 0° oriented fibers, and this results in no structural relaxation and hence no swelling in the seawater environment. On the other hand, the 45° fiber oriented composite comes with fewer bonds at the interface of the fiber and resin, which result in additional voids, and accommodates more water. This is also reflected in the maximum water uptake in the E/G (45°) sample (see Table I). The reduced diffusion rate in E/G (0°) can be attributed to the improved interfacial adhesion and reduced interfacial voids, which lower the amount of water entering from the matrix side.³⁹ This is what is expected for a good marine structure.

CONCLUSIONS

From the seawater diffusion kinetics studied in E/G (0°) and E/G (45°) fiber oriented composites, we have observed that as the orientation of glass fibers changes from 0 to 45°, the mode of diffusion changes from Fickian to non-Fickian. The reason for this is swelling of the composite in the 45° case due to poor bonding at the interface, which allows more water to diffuse from the matrix side to the interface. The swelling results in relaxation, and the separated Fickian and relaxation contributions to diffusion from the dual-mode sorption model suggest that the 45° orientation produces an increased diffusion rate, which is supported by the increased average free-volume size measured for the aforementioned reason. The fiber–resin interface interaction parameter further supports the idea that adhesion at the interface through bonding is more in the 0° fiber oriented sample than in the 45° oriented composite. We have found that the sorption results are in good agreement with the free-volume data.

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