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Microstructural Dependency of Diffusion in Glass Flake-Reinforced Vinyl Ester Resins

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Vinyl ester resins are utilized for long-term corrosion protection of metal, alloy, and concrete substrates against concentrated acids, alkalis, and solvents at high temperature. Glass flakes are usually added as fillers to reduce chemical diffusion within the vinyl ester matrix. A common industry practice is to use glass flakes with large aspect ratio, high volume fraction, and in parallel alignment to surface in chemical contact for barrier applications. During processing and curing of glass flake-filled vinyl ester resins, irregular microstructures such as reduced flake aspect ratio and random orientation of flakes are commonly observed. Such microstructures can affect the overall chemical diffusion, resulting to barrier properties less predictable by simple diffusion models. Therefore, in this study, a simple 2D random walk simulation procedure is used in attempt to estimate the microstructural dependency of diffusion in glass flake-reinforced vinyl ester resins.

While the random walk simulations are in good agreement with the tortuosity-based diffusion models in terms of microstructural effects, in most cases the simulation results are inconsistent with the experimental measurements of acid diffusion in glass flake-filled vinyl ester resins. A possible cause for this is the poor adherence of vinyl ester resin to glass flakes. Osmotic cracks are also formed during immersion which also influences overall diffusion through the material.

Keyword: Diffusion, Microstructure, Glass Flake, Vinyl Ester, Random Walk

INTRODUCTION

Vinyl ester resins are commonly used as barrier linings for industrial equipment handling corrosive chemicals like absorption towers, process vessels, storage tanks, and transport pipes. This thermosetting polymer has the advantage of 1) fast curing, high initial strength, and creep resistance; 2) good adhesion; 3) improved impact resistance and tolerance to cyclic temperatures, pressure fluctuations, and mechanical shock; and 4) enhanced chemical resistance to oxidation and hydrolysis. It can handle highly chlorinated and acid mixtures at elevated temperatures and is resistant to strong mineral acids, alkaline, and bleach environments (Schweitzer 2007).

To further improve the barrier properties of vinyl ester resins against corrosion, impermeable glass flakes are added as reinforcement. Suspended inside the polymer matrix, impermeable mineral flakes decrease the area available for diffusion and increase the effective path length of the diffusing chemical species (Eitzman *et al.* 1996; Moggridge *et al.* 2003; Yang *et al.* 2004).

Several physical diffusion models are proposed to predict the reduction of diffusion in flake-filled media. Lape *et al.* (2004) introduced the following realistic analytical diffusion models based on 2D flake geometries:

$$D_e/D_o = (1-\phi)/[1+(2/3)\alpha\phi]^2 \tag{1}$$

$$D_e/D_o = \frac{1-\phi}{\left[1+\left(2\phi/3a\overline{R}\right)\int_0^\infty R^2 g dR\right]^2} \tag{2}$$

where, D_e is the effective diffusivity of flake-filled medium, D_o is the diffusivity of medium without flakes, Φ is the volume fraction of flakes, α is the flake aspect ratio, a is the uniform flake thickness, g is the size distribution function in terms of R, and $\overline{R}$ is the average half flake size. In Eq. (1), the impermeable flakes, which are assumed to be rectangles of uniform size R and thickness a, are randomly placed in the medium and are oriented normal to diffusion direction (monodisperse condition). The same conditions for Eq. (1) also apply for Eq. (2), except that the flakes follow a certain size distribution g (polydisperse condition). Aside from Eqs. (1) and (2), other simpler analytical diffusion models are suggested and reviewed in literature (Chen and Papathanasiou 2007), with model estimates of diffusivity ratio (D_e/D_o) often compared with numerical simulations (Goodyer and Bunge 2009) and experimental results (Goodyer and Bunge 2007). The analytical/numerical diffusion models studied all assumed the impermeable flakes in the matrix are oriented parallel to the surface in contact with the diffusing chemical source.

Figure 1 shows a SEM image of suspended glass flakes in cured vinyl ester matrix. In contrary with the assumption used to formulate earlier analytical/diffusion models, this irregular microstructure involves glass flakes at random alignment. As such, Eq. (2) and other simpler models are somewhat limited on estimating the reduction of diffusion in flake-filled media due to random flake orientation.

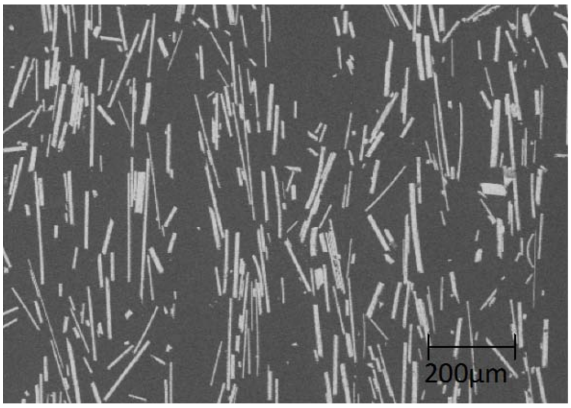

Fig. 1: Glass flakes (140 x 5 µm) in cured vinyl resin at volume fraction Φ = 0.128

In order to include microstructural information such as random flake orientation and size polydispersity on estimating diffusion in glass-flake filled vinyl ester resins, this study presents a simple 2D random walk procedure for calculating (D_e/D_o). The calculated values from simulations are then compared and discussed to the ones derived from experiments and analytical diffusion models.

SIMULATION

Microstructural Data Extraction

Flake/polymer solutions were prepared according to Table 1. Type E glass flakes and bisphenol type vinyl ester resin were used as filler and matrix, respectively. After addition of initiator and accelerator, the flake/polymer solution was stirred and degassed at room temperature before hand trowel casting. Additional thin layers were cast on a metal plate until the resulting film was 2-3 mm thick. After full curing, the film was cut into rectangular slabs (60 x 25 mm). Several samples were then taken for SEM imaging with sample micrograph shown in Figure 1.

Table 1. Sample formulations

Specimen	Flake Size [μm]	Volume fraction
A	600 x 5	0.023
B	600 x 5	0.072
C	600 x 5	0.128
D	140 x 5	0.023
E	140 x 5	0.072
F	140 x 5	0.128

The SEM cross-sectional images were used to acquire the size and angular distribution of glass flakes in the vinyl ester polymer matrix. A MATLAB script was run to assist the manual extraction of microstructural data. The script takes the SEM image file (in BMP file format) as input and loads it as a figure. Straight lines were manually drawn over each visible glass flake in the figure using the mouse and the coordinates of each drawn line were returned and saved. Figure 2 illustrates the procedure for extraction of microstructural data from sample SEM images.

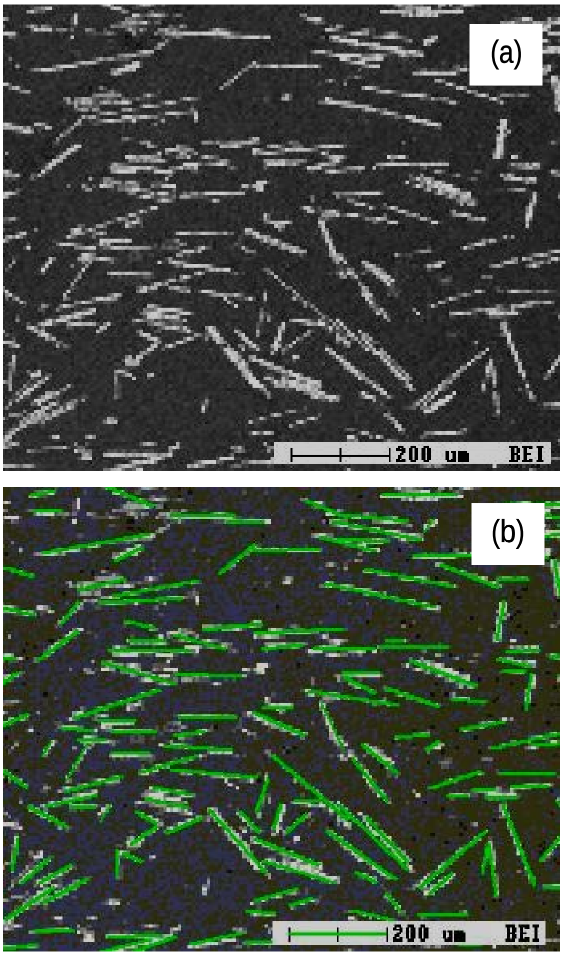

Fig. 2: SEM cross-sectional image of sample (a) was loaded as a figure in MATLAB. Lines were manually drawn over each visible flake (b) to extract microstructural information.

Figure 3 shows the aspect ratio and angular distribution histograms of glass flakes in vinyl ester resin (specimen A) analysed from the data extraction. From these results, a lognormal distribution function (with parameters $\mu(\alpha)$ and $\sigma(\alpha)$) and a Gaussian distribution function (with parameters $\mu(\theta)$ and $\sigma(\theta)$) were fitted to the extracted data. The distribution parameters are listed in Table 2. In this case, the flake aspect ratio α was defined as half the flake size R divided by its thickness a (= 5 μm). The flake angle θ is measured as the angle between the glass flake and surface in contact with diffusing environment.

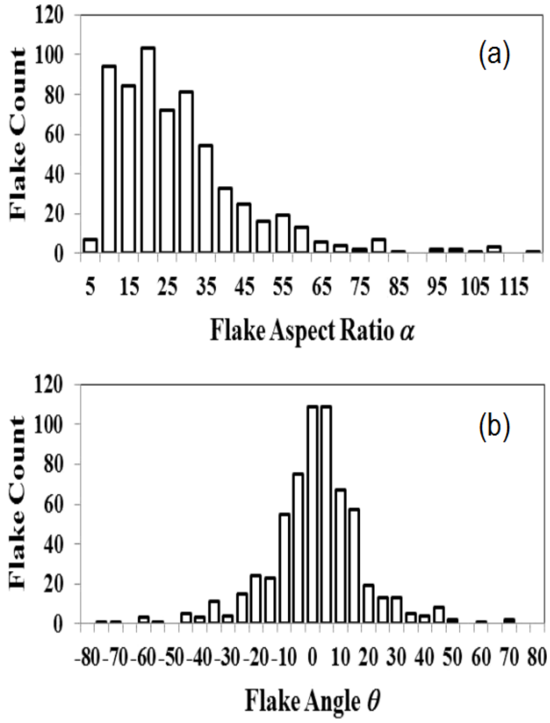

Fig. 3: Flake aspect ratio (a) and angular distribution (b) histograms of specimen A analysed after microstructural data extraction.

Generation of Simulation Medium

Figure 4 shows a computer representation of flake/polymer system which was used as a medium for 2D random walk simulation. Each flake was modelled as a randomly-placed straight line with size $2R$, thickness a and angle θ (relative to the x axis). The flake lines were produced according to the parameters specified in Table 2. A MATLAB script facilitated the generation of simulation medium using the modified random sequential addition algorithm of Widom (1966) and Chen and Papathanasiou (2007).

Table 2. Fitted distribution parameters from extracted data histograms

Specimen	Distribution parameters			
	$\mu(\alpha)$ [-]	$\sigma(\alpha)$ [-]	$\mu(\theta)$ [°]	$\sigma(\theta)$ [°]
A	25.9	17.8	-1.2	16.9
B	25.6	17.8	-4.0	16.4
C	24.6	17.4	-0.8	12.8
D	10.3	5.8	-2.2	20.0
E	10.4	5.5	-1.7	22.6
F	9.9	5.1	-2.4	22.9

2D Random Walk Simulation

This study used the simple 2D random walk procedure described in Ly and Cheng (1997), illustrated in Figure 5. At the beginning of each simulation, a particle was placed in the flake-free region along line *AB*. It was then allowed to move in any direction: up, down, left, or right with equal probability. The direction of movement was chosen based on a random number generator between 1 to 4 (for example, if the generated number was 1, then the chosen direction was up). If the position according to the randomly chosen direction was flake-free, then the particle would move to the new position; otherwise, the random number generator was called again and the process was repeated. Each call to the random number generator was counted as a time step. Periodic boundary conditions were imposed on lines *CAE* and *DBF* to make the structure repeating on the x

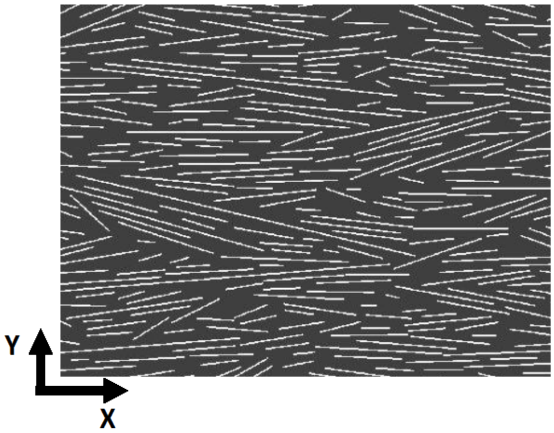

Fig. 4: Sample simulation medium for simple 2D random walk.

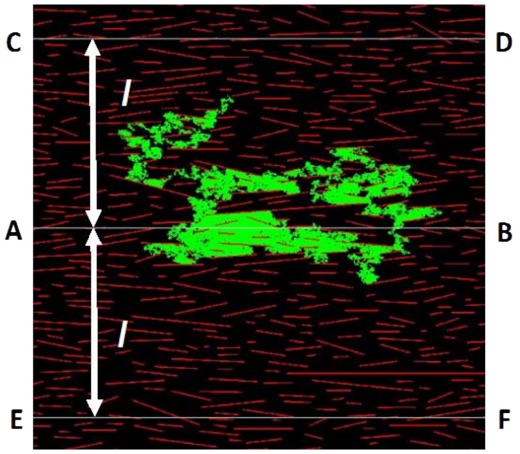

Fig. 5: The simple 2D random walk process on a flake-filled medium

direction. The total time for each particle to reach line *CD* or *EF* was recorded, and the entire process was repeated for other single particles to compute an average time <*t*>. The effective diffusivity of the simulation medium was then calculated by Eq. (3).

$$D_e = l^2 / 2 \cdot \langle t \rangle \tag{3}$$

where, *l* is the distance travelled by the particle in the *y* direction. The calculated values of D_e were normalized by dividing them with D_o, also computed from 2D random walk procedure on a simulation medium without flakes, to yield (D_e/D_o) ratios. Appropriate number of particles and optimized values of *l* were used such that the computed (D_e/D_o) results were independent to the number of particles and travelled distance *l* at minimum computation time.

EXPERIMENTAL

Specimens prepared according to Table 1 were immersed in 10 wt.% chloroacetic acid solution maintained at 80°C. Specimens were removed from immersion after a certain time, rinsed with deionized water, left in open air for an hour, and weighed. Weight uptake M_t was determined by obtaining the gain in weight relative to its initial weight before immersion. The weight uptake of polymeric materials as a function of time *t* is usually modelled as a Fickian diffusion process (Crank 1975) which, for a large plane sheet specimen of thickness 2*h*, is given by Eq. (4).

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

In here, M_∞ is the weight gain at infinite exposure time. (D_e/D_o) ratios were calculated from Eq. (4) by nonlinear fitting of weight gain data of flake-filled and pure vinyl ester resin specimens.

RESULTS AND DISCUSSION

Table 3 shows the effective diffusion coefficients D_e and equilibrium weight uptake M_∞ obtained from the test specimens by nonlinear least-squares fitting of experimental data to Eq. (4) (Pajarito *et al.* 2010). In data fitting, the objective is to minimize the sum of squared residuals at certain values of D_e and M_∞. The residual is defined as the difference between experimental value and the value provided by Eq. (4). The calculated effective diffusion coefficients D_e of test specimens are lower compared to pure vinyl ester D_o as expected. Glass flakes improve the barrier performance of vinyl ester resin in acid solutions by slowing down diffusion. It is also noticed that there is significant difference in M_∞ values for specimens at the same glass flake volume fraction (for example, specimens A and D at volume fraction of 0.023). Other specimens at different volume fractions yielded the same M_∞ values (for example, specimens B and C at volume fractions of 0.072 and 0.128).

Table 3. Effective diffusion coefficients D_e and weight uptake M_∞ of specimens

Specimen	D_e [mm^2/h]	M_∞ [g]
Vinyl Ester	3.78×10^{-2}	0.0847
A	1.14×10^{-2}	0.0652
B	7.35×10^{-3}	0.0483
C	6.99×10^{-3}	0.0496
D	1.56×10^{-2}	0.0537
E	1.83×10^{-2}	0.0573
F	1.47×10^{-2}	0.0398

Figure 6 shows the (D_e/D_o) ratios calculated from simple 2D random walk simulations compared to the immersion experiments. At low volume fraction of glass flakes, the random walk simulations overestimate the experimental effective diffusivity ratio of the material, while lower values are computed for small flakes at high volume fractions.

To verify if the results from random walk simulations were reasonable, the simulated (D_e/D_o) ratios were also compared to the predictions of Eqs. (1) and (2) as shown in Figure 7. In Eq. (1), the parameter $\mu(\alpha)$ from Table 1 was substituted to α to calculate the diffusivity ratio. Eq. (2) requires the second moment of function g to be evaluated. For a lognormal probability distribution function $g(R)$ for the size polydispersity of flakes, the second moment $\int_0^\infty R^2 g dR$ is given as (Pajarito *et al.* 2010):

$$\int_0^\infty R^2 g dR = e^{2\left(m+n^2\right)} \tag{5}$$

where the parameters m and n^2 are defined as:

$$m = \ln \mu(R) - \frac{1}{2}\ln\left(1+\frac{\sigma^2(R)}{\mu^2(R)}\right) \tag{6}$$

$$n^2 = \ln\left(1+\frac{\sigma^2(R)}{\mu^2(R)}\right) \tag{7}$$

Substitution of Eqs. (5), (6), and (7) to Eq. (2) and noting that the flake aspect ratio $\alpha = R/a$, Eq. (2) is expressed in terms of dimensionless size distribution parameters $\mu(\alpha)$ and $\sigma(\alpha)$ as:

$$\frac{D_e}{D_o} = \frac{1-\phi}{\left[1+\frac{2}{3}\frac{\phi}{\mu(\alpha)}\left\{\mu^2(\alpha)+\sigma^2(\alpha)\right\}\right]^2} \tag{8}$$

where values of the model parameters are found in Tables 1 and 2.

With inclusion of microstructural information, the results from 2D random walk simulations are in close agreement with the physical diffusion models Eqs. (1) and (8) on the following aspects:

1. the (D_e/D_o) ratio is decreased as the mean flake aspect ratio $\mu(\alpha)$ is increased;

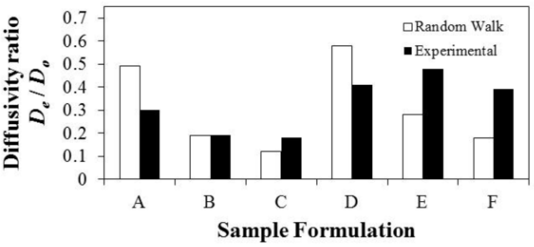

Fig. 6: Calculated diffusivity ratios (D_e/D_o) from random walk simulations compared to experimental immersion results.

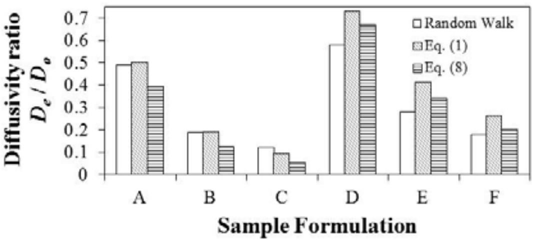

Fig. 7: Calculated diffusivity ratios (D_e/D_o) from random walk simulations compared to physical diffusion models Eqs. (1) and (8).

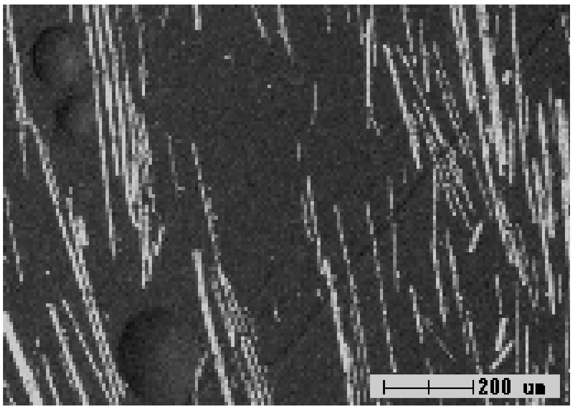

Fig. 8: Formation of penny-shaped cracks after immersion of samples in acid solution

2. the (D_e/D_o) ratio is decreased as the volume fraction of flakes is increased;
3. the (D_e/D_o) ratio is decreased when flakes are polydisperse in size, as shown when results from simulations and Eq. (8) are compared with Eq. (1); and
4. the (D_e/D_o) ratio is increased when flakes are randomly oriented, more pronounced at large aspect ratios.

These observations are based on the fact that increasing the tortuosity of material will reduce the overall diffusion. By contrast, the experimental results for acid diffusion in glass flake-reinforced vinyl ester resin are not consistent with the established tortuosity-based effects. Similar deviation of experimental results from simulations are observed in Goodyer and Bunge (2007), where estimates from their elegant finite element models are also far from the published measurements of Liu and Cussler (2006) on helium diffusion through polydimethylsiloxane membranes filled with titanium flakes. Likewise, a possible cause for deviation of experimental studies from simulations is the poor adherence of vinyl ester resin to the total surface area provided by glass flakes. During preparation of material samples, the glass flakes were used as received without silane coating. Gaps resulting from poor adherence of polymer matrix to the flakes would result to fast diffusion at the local interfaces (Goodyer and Bunge 2007).

Penny cracks are also seen after immersion during SEM imaging of sample microstructure, as shown in Figure 8. Type E glass flakes contain water soluble components which dissolve in diffused water and create osmotic pressure differences between the resulting solutions and immersion environment. Pressure pockets are then generated (Farrar and Ashbee 1978; Pajarito *et al.* 2012), which may alter the overall diffusion through the vinyl ester resin. Non-spherical, flat cavities are formed due to increased elasticity of plasticized polymer matrix.

CONCLUSIONS

In this paper, 2D random walk simulations have been compared to experimental study of acid diffusion through glass flake-reinforced vinyl ester resins for estimation of microstructural effects. The simulation results are consistent with the estimates from published tortuosity-based diffusion models. When compared against the immersion experiments, the random walk simulations generally deviate from the experimental results. One possible reason of deviation is poor adherence of vinyl ester resin to glass flakes, resulting to easier diffusion pathways at the local interfaces. Moreover, formation of osmotic cracks during immersion of samples enhances overall diffusion through the material.

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NOMENCLATURE

a	flake thickness
D_o	diffusion coefficient of chemical in the polymer matrix
D_e	diffusion coefficient of chemical in the flake-filled matrix
g	probability distribution function of flake size R
h	specimen half thickness
l	distance travelled by particle during 2D random walk simulation in the y direction
M_t	weight gain during immersion experiment at time t
M_∞	weight gain during immersion experiment at equilibrium
R	half width of flake
t	simulation time; experimental immersion time
α	flake aspect ratio = R / a
θ	orientation angle between flake and surface in contact with diffusing environment
$\mu(\alpha)$	mean flake aspect ratio
$\mu(\theta)$	mean flake orientation angle
$\sigma(\alpha)$	standard deviation in flake aspect ratio
$\sigma(\theta)$	standard deviation in flake orientation angle
ϕ	volume fraction of flakes

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