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Effect of rapid interfacial moisture penetration on moisture distribution within adhesive layers

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ABSTRACT

In this study, we numerically calculated the moisture distribution through the thickness of the adhesive layer in an adhesive joint and considered rapid interfacial moisture diffusion. Additionally, the effects of the diffusion coefficient and layer thickness were investigated. An accurate understanding of moisture diffusion in adhesive joints is essential for enhancing their long-term performance and reliability, particularly in applications demanding high environmental durability. However, the moisture behavior near interfaces, which causes faster moisture penetration into the adhesive layer than into the bulk is still not clearly understood. In this study, a model was developed using the finite difference method, considering both bulk and interfacial diffusion properties. The diffusion coefficient near the interface was back-calculated using the experimentally measured moisture distribution in the adhesive layer, which revealed that the moisture distribution in the thickness direction was almost uniform for thin adhesive layers, and parabolic distribution became more pronounced as the adhesive layer became thicker.

1. Introduction

It is crucial to reduce the weight of transportation equipment for energy conservation and environmental protection. Adhesive bonding is the key to achieving a lightweight design by effectively joining dissimilar materials. However, moisture diffusion damages adhesive joints [1–3]. Therefore, it is important to understand the moisture diffusion behavior to improve joint performance.

Moisture permeates more rapidly near the interface owing to capillary diffusion caused by the difference in surface/interface energies [4]. A region called the interphase also affects moisture diffusion. Owing to the gradient in the cross-link density at the interface between the epoxy and adherend, the material properties of the epoxy near the interface and in the center of the adhesive layer are different. The near-interface region forms an interphase [5]. The change in the elastic behavior of polymers [4] and the deterioration of fracture surfaces [6] indirectly suggest rapid interfacial diffusion, which is considered to lead to a parabolic moisture distribution through the thickness, as shown in Fig. 1a [4,5].

In previous studies [7–9], we developed a method to directly

visualize the in-plane moisture distribution in adhesive layers using near-infrared (NIR) spectroscopy and back-calculated the diffusion coefficient. The experimentally-obtained diffusion coefficients were $5.09 \times 10^{-4} \text{ mm}^2/\text{h}$ for the bulk and $7.89 \times 10^{-4} \text{ mm}^2/\text{h}$ for a 0.3 mm thick adhesive layer [9]. Hence, faster moisture diffusion through the adhesive layer was observed. Additionally, thinner adhesive layers exhibited faster moisture penetration [8]. However, the NIR spectrum only captures the average moisture content in the thickness direction. Therefore, the moisture distribution through the thickness remains unknown. Investigating this would enable more accurate predictive models, considerably improving the reliability and design of adhesive joints in humid and aqueous environments. In this study, the moisture distribution along the thickness direction was numerically investigated by assuming a fast diffusion layer at the interphase, as shown in Fig. 1b.

2. Numerical method

2.1. Two-dimensional diffusion model

The two-dimensional moisture distribution can be expressed using

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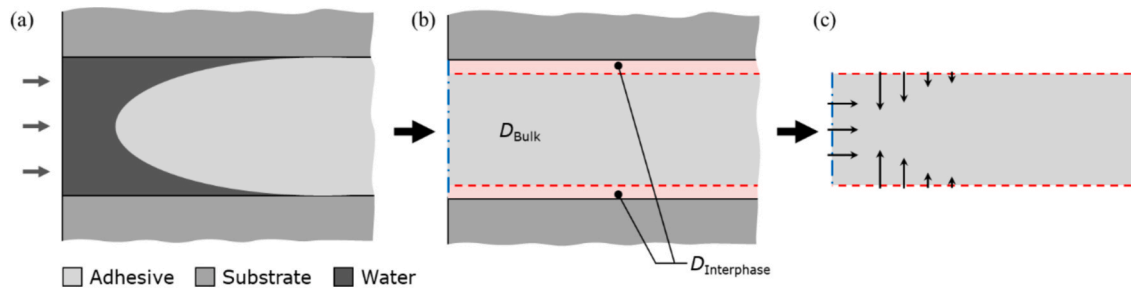


Fig. 1. Schematic illustration of (a) moisture distribution in the thickness direction, (b) different diffusion coefficients for the bulk and interphase, and (c) moisture penetration in the adhesive layer.

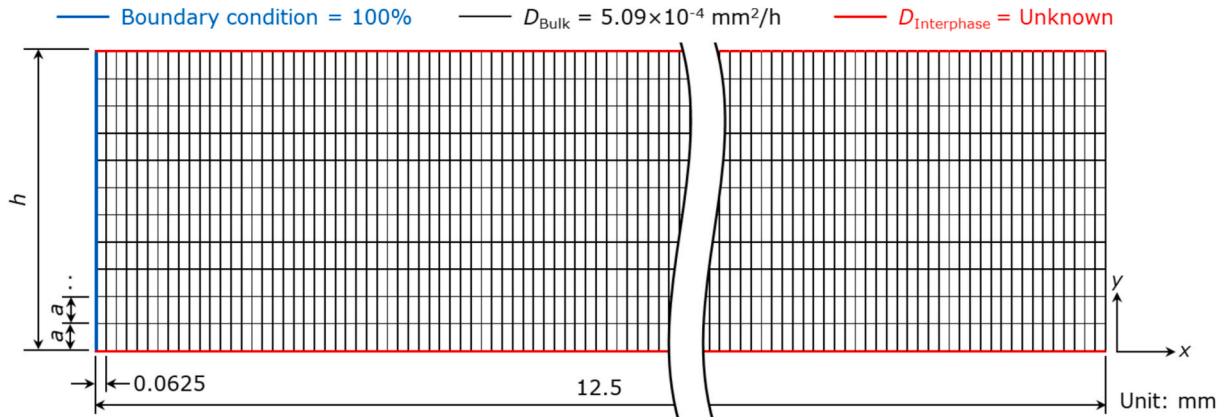


Fig. 2. Details of the mesh used in the two-dimensional model.

Fick's second law of diffusion [10].

$$\frac{\partial C}{\partial t} = D \left\{ \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} \right\}, \quad (1)$$

where, C is the concentration, t is the exposure time, and D is the diffusion coefficient. The main adhesive and interphase layers were

assigned different diffusion coefficients D_{Bulk} and $D_{Interphase}$, respectively, and two-dimensional diffusion was considered in the main adhesive layer as shown in Fig. 1c.

The boundary condition at the edge (blue dashed-dotted line in Fig. 1c) was set as 100%, representing a fully saturated environment. This aligns with the experimental conditions of the specimens immersed

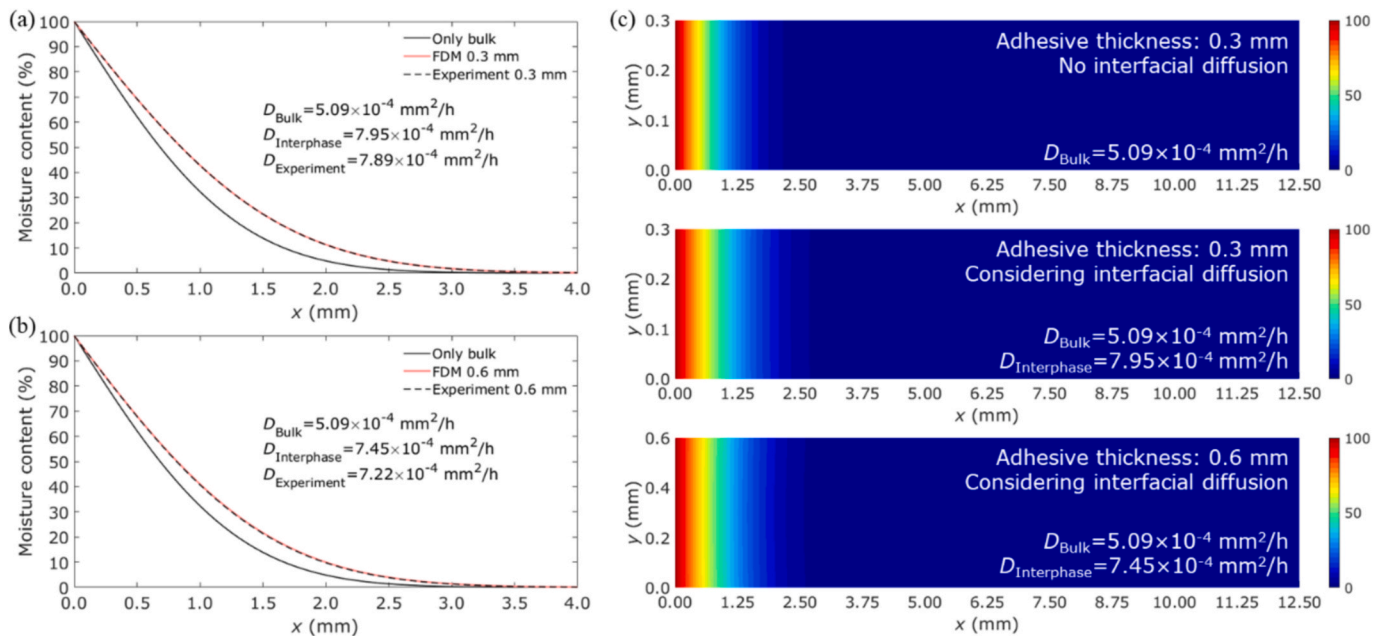
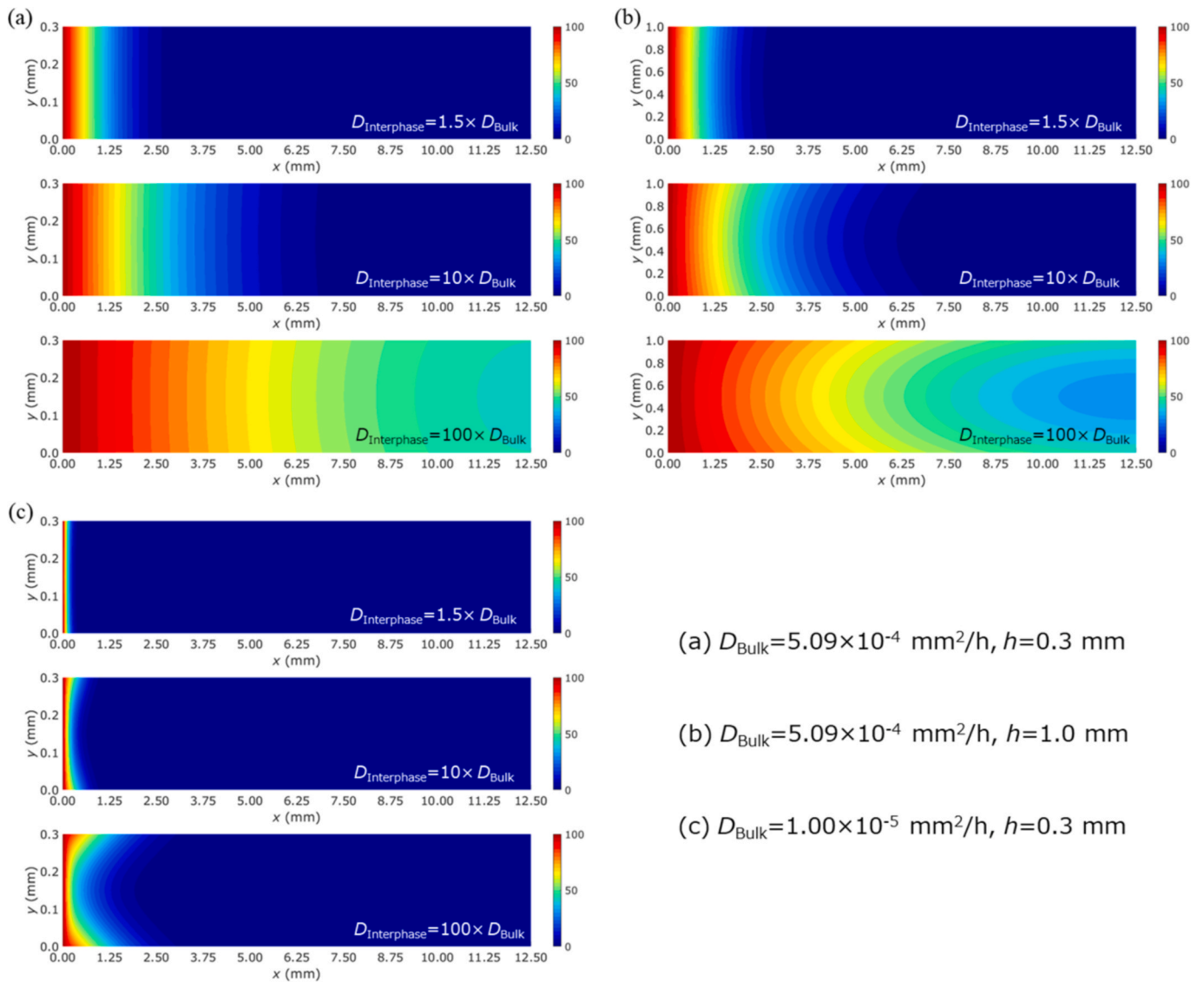


Fig. 3. One-dimensional distribution at 6 weeks exposure with a mesh size of 10 μm and an adhesive thickness of (a) 0.3 mm and (b) 0.6 mm, and (c) their two-dimensional distributions.



(a) $D_{Bulk}=5.09 \times 10^{-4} \text{ mm}^2/\text{h}$, $h=0.3 \text{ mm}$

(b) $D_{Bulk}=5.09 \times 10^{-4} \text{ mm}^2/\text{h}$, $h=1.0 \text{ mm}$

(c) $D_{Bulk}=1.00 \times 10^{-5} \text{ mm}^2/\text{h}$, $h=0.3 \text{ mm}$

Fig. 4. Moisture distribution at 6 weeks exposure with varying $D_{Interphase}$ with (a) 0.3 mm and (b) 1 mm adhesive layer for the experimentally obtained D_{Bulk} , and (c) 0.3 mm adhesive layer for a smaller D_{Bulk} .

in purified water [9]. In contrast, at the boundary of the interphase layer (red dashed lines in Fig. 1c), the moisture content changed over time. To express this situation, $D_{Interphase}$ was adopted for the diffusion coefficient of the outermost meshes in the x-direction and D_{Bulk} was adopted for the remaining meshes as shown in Fig. 2. These assumptions ignore the effects of the interphase thickness and chemical interactions, which may require further discussion. However, diffusion in the main adhesive layer can be adequately discussed if a sufficient amount of water is supplied to the interphase to diffuse into the adhesive layer.

2.2. Finite difference method

Using the finite difference method (FDM), Eq. (1) can be transformed into:

$$C(x, y, t + \Delta t) = C(x, y, t) + D\Delta t \times \left\{ \frac{C(x + \Delta x, y, t) - 2C(x, y, t) + C(x - \Delta x, y, t)}{(\Delta x)^2} + \frac{C(x, y + \Delta y, t) - 2C(x, y, t) + C(x, y - \Delta y, t)}{(\Delta y)^2} \right\}. \quad (2)$$

In addition, for the convergence of the computation, the Courant-Friedrichs-Lewy condition was used to determine the time step as [11]:

$$\Delta t \leq \frac{1}{2D} \frac{(\Delta x \Delta y)^2}{(\Delta x)^2 + (\Delta y)^2}. \quad (3)$$

A half-model was adopted considering the analysis time. The FDM was performed by defining each mesh using Eq. (2), and solving it using MATLAB. At the interphase boundary, the diffusion coefficients differed in the x and y-directions. Therefore,

$$C(x, y, t + \Delta t) = C(x, y, t) + D_{\text{Interphase}} \Delta t \left\{ \frac{C(x + \Delta x, y, t) - 2C(x, y, t) + C(x - \Delta x, y, t)}{(\Delta x)^2} \right\} + D_{\text{Bulk}} \Delta t \left\{ \frac{C(x, y + \Delta y, t) - 2C(x, y, t) + C(x, y - \Delta y, t)}{(\Delta y)^2} \right\} \quad (4)$$

In the remaining region, the diffusion coefficient is the same in both the x and y -directions, i.e., D_{Bulk} . The adhesive layer thickness h was set as 0.3 and 0.6 mm corresponding to the experimental conditions. The mesh size in the y -direction a was set to 10–50 μm at 10 μm intervals to investigate the size effect, while in the x -direction it was fixed at 62.5 μm . The diffusion coefficient of the adhesive D_{Bulk} was determined using a gravimetric method [9].

First, $D_{\text{Interphase}}$ was set to a certain value, and the two-dimensional moisture distribution in the adhesive layer was calculated using FDM. Next, the moisture distribution was averaged through the thickness to allow comparison with the experimental results. The coefficient of determination R^2 was obtained by comparing the numerical and experimental one-dimensional distribution curves. Finally, the $D_{\text{Interphase}}$ was optimized to maximize R^2 .

3. Results and discussion

3.1. Moisture distribution in comparison with experimental results

For an adhesive thickness of 0.3 mm, $D_{\text{Interphase}}$ is obtained as $7.95 \times 10^{-4} \text{ mm}^2/\text{h}$ for a mesh size 10–30 μm , and $7.96 \times 10^{-4} \text{ mm}^2/\text{h}$ for 50 μm . For an adhesive thickness of 0.6 mm, it is $7.45 \times 10^{-4} \text{ mm}^2/\text{h}$ for 10 and 20 μm , and $7.44 \times 10^{-4} \text{ mm}^2/\text{h}$ for 30–50 μm . Therefore, the diffusion coefficient does not change significantly with the mesh size.

The numerically obtained one-dimensional moisture distribution considering fast interphase layer moisture penetration agrees well with experimental results, as shown in Fig. 3a and b. However, the penetration decreases when it is not considered. This demonstrates that moisture diffusion in the main adhesive layer is accelerated by that in the interphase layer. Conversely, the two-dimensional distribution is not as expected in Fig. 1a. The calculated two-dimensional moisture distributions are shown in Fig. 3c. Diffusion in the main adhesive layer is accelerated by fast diffusion in the interphase layer. However, the distribution through the thickness is approximately linear, particularly with a thinner adhesive layer because a shorter time is required for the moisture to reach the center of the adhesive layer.

3.2. Parametric study

Indirect observations suggest that the diffusion coefficient increases by almost an order of magnitude [4]. The values of D_{Bulk} , $D_{\text{Interphase}}$, and the adhesive thickness were varied to investigate the changes in the two-dimensional moisture distribution. First, when only $D_{\text{Interphase}}$ was varied, the overall moisture content increased with increasing $D_{\text{Interphase}}$, but there was little distribution through the thickness (Fig. 4a). Next, the thickness of the adhesive layer was increased to 1.0 mm and $D_{\text{Interphase}}$ was varied (Fig. 4b). Compared to the results for 0.3 mm thickness, it took longer for moisture to reach the middle of the adhesive layer, resulting in a more parabolic distribution. This effect became more pronounced as $D_{\text{Interphase}}$ increased. Conversely, the moisture penetration near the interface was almost the same, regardless of the adhesive layer thickness. Thus, for a thicker adhesive layer, the average diffusion distance is lower. This tendency agrees well with the experimental

results reported by Han et al. [8]. Finally, when D_{Bulk} was reduced (Fig. 4c), the distribution became parabolic, even for the thin adhesive layers often used in epoxy adhesive joints.

4. Conclusion

The moisture distribution was investigated by focusing on the differences between bulk diffusion and interfacial diffusion in thin and thick adhesive layers. A finite difference method was applied to develop a numerical calculation model for the two-dimensional moisture distribution in the adhesive layer, and the diffusion coefficient of the interphase layer was calculated by fitting it to the experimental results. It was revealed that (a) fast interfacial diffusion promotes moisture distribution throughout the adhesive layer, (b) moisture distribution in the thickness direction is negligibly small for a thin adhesive layer, and (c) thicker adhesive layers produce a more parabolic distribution, but the overall moisture penetration is reduced.

CRedit authorship contribution statement

Jin-Woo Han: Writing – original draft, Visualization, Validation, Software, Methodology, Investigation, Formal analysis, Data curation. **Yu Sekiguchi:** Writing – review & editing, Validation, Supervision, Project administration, Data curation, Conceptualization. **Kazumasa Shimamoto:** Writing – review & editing, Validation, Methodology. **Haruhisa Akiyama:** Writing – review & editing, Validation, Methodology, Conceptualization. **Chiaki Sato:** Supervision, Project administration, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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