Numerical Simulation of Failure of Composite Coatings due to Thermal and Hygroscopic Stresses

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Abstract: Due to the higher thermal and moisture expansions of epoxy coatings than the rigid substrate, these coatings suffer from high thermal and hygroscopic stresses, leading to coating/substrate interfacial crack growth. Herein, a parametric study was conducted systematically on epoxy coatings incorporated with fillers, in order to understand their effects on coating/substrate interface delamination caused by thermal and hygroscopic stresses. A finite element model (FEM) was developed to determine an indicator $J$-integral value ($J_i$), in comparison with a critical $J_C$ value to interpret the obtained interface delamination experimental results. FE simulations showed that interfacial pre-cracks located at coating edges were more serious than those at the centre. Once delamination was triggered by thermal shock or moisture absorption, it propagated rapidly along the coating/substrate interface. However, by adding suitable micro-/nano-fillers to the coating the thermal and hygroscopic stresses give lower $J_i$ values, so that delamination crack growth can be effectively controlled. The simulation results demonstrate that the incorporation of fillers with lower Young’s modulus, lower thermal expansion and moisture absorption coefficients, smaller size for soft fillers, larger size for rigid fillers, and suitable aspect ratios for rod-shape fillers to the coatings, are more effective against interface delamination. Hence, useful guidelines for improving the design of epoxy composite coatings against delamination growth can be obtained for different engineering applications.

Keywords: epoxy composite coating; crack propagation; $J$-integral; thermal stress; hygroscopic stress

1. Introduction

Epoxy resins have been widely used as protective coatings in many engineering applications, where they are applied on the surfaces of various structures, such as any metal components of electrical cables, pipelines, aircrafts and submarines, preventing them from corroding and/or rusting in harsh environments. However, the epoxy coating may expand or contract, depending on the environmental temperature and humidity changes. The mismatch in the thermal or moisture expansion between the epoxy coating and its substrate induces high thermal or hygroscopic stress, which may lead to growth of the interfacial pre-cracks/defects [1,2]. Hence, it is essential to design an effective coating against interface delamination due to thermal and/or hygroscopic stresses.

Various fillers have been widely used to modify epoxy matrices, and the effect has been thoroughly analysed. For example, in our recent studies, the benefit of nano-silica particles in epoxy
on adhesive strength was retained even after hygrothermal exposures [3]. The relationships between 
the mechanical properties of composites and the parameters of added round fillers were studied in [4]. 
The improvement of the interlaminar toughness of the composites depended upon the fibre orientation 
angle [5]. Flow-induced fibres slowed down the speed of moisture diffusion in polyamide 6,6 [6]. 
Several experimental studies also examined the effects of fillers on polymer coating performance 
subjected to a thermal or a hygroscopic stress. Thus, in [7], thermal shock failure was controlled when 
glass beads were added in an epoxy coating; and in [8,9], graphene oxide (GO) was incorporated into polyurethane and epoxy coatings to improve their corrosion resistance. Moreover, in [10], the effects of 
geometry and material properties of the fillers on the crack pattern in the coating were also examined. 
However, not all material parameters were investigated in these previous investigations [7–10]. 
Attempts have also been made to study the coating failure behaviour when subjected to a thermal 
or a hygroscopic stress by finite element analysis (FEA). Haider et al. [11] showed that the highest 
thermal stresses occurred at the coating/substrate interface, and coating interface delamination was 
observed in experiments. Song et al. [12] established an analytical model to explain the thermal 
stress evolution in the coating during fabrication upon cooling. Wong et al. [13,14] performed 
systematic experimental and numerical studies on the interface delamination under thermal and 
ygroscopic stresses in epoxy-based electronic packages. Batard et al. [15] analysed the water vapour 
and gas permeation through an aluminium/polymer multilayer coating by simulation and experiments. 
These studies showed that FEA is efficient to help understand in-depth the mechanical performance of 
epoxy coatings under thermal and/or hygroscopic stresses. Nonetheless, the effects of fillers on the 
coating/substrate interface failure behaviour have not been fully analysed. 

Herein, the effects of epoxy composite coatings on interface delamination owing to thermal and 
ygroscopic stresses are systematically analysed by FE simulations (Sections 2–4), and compared with 
experimental results (Section 5). The parameters examined are pre-crack location and length, coating 
thickness, temperature change, also the coefficients of thermal/moisture expansion (CTE/CME), size, 
aspect ratio, and Young’s modulus \(E\) of (rigid/soft) fillers. Coating/substrate interface crack growth is 
assessed by a \(J\)-integral value \(J_i\) at the crack tip, based on linear elastic fracture mechanics. Interface 
delamination is avoided by reducing the \(J_i\) value caused by thermal and hygroscopic stresses below 
the critical value \(J_C\), by optimal design of fillers incorporated in the epoxy coating.

2. Finite Element Analysis Consideration

2.1. Finite Element Model

A plane strain two-dimensional (2D) finite element (FE) model according to [16] was established 
to simulate interfacial crack growth between epoxy coating and substrate under thermal or hygroscopic 
stress (see Figure 1), using a commercial FE package ABAQUS, based on linear elastic fracture 
mechanics [17]. The coating was perfectly bonded to the substrate, except the edge and central 
pre-cracks at the coating/substrate interface (highlighted in red colour). The interface between coating 
and substrate was flat, and the virtual crack extension direction was assumed along the interface (see 
blue arrows). The thickness of the substrate was sufficiently large to simulate as semi-infinite. Fixed 
condition was implemented to the left lower corner of the model (at point A), and the bottom of the 
substrate (along line AB) was constrained in the through-thickness direction, i.e., \(U_2 = 0\). The other 
edges were not constrained to allow free expansion or contraction of the coating caused by thermal or 
ygroscopic stress. The geometrical parameters varied depend on the simulation cases listed in Table 1 
and their relevant Section numbers are given in Column 1 of the table.
The coating and substrate materials were assumed to follow linear thermo-elastic or hygro-elastic behaviour. The thermal and moisture expansions of the substrate were neglected, since the coefficients of thermal or moisture expansion of the substrates (that is, glass and stainless steel), were at least one-order lower in magnitude than those of the epoxy coating. After mesh sensitivity analysis, high-precision eight-node bi-quadratic quadrilateral and six-node quadratic triangle plane strain elements were selected for the FE model. Fine meshes were introduced near the crack tip (see inset in Figure 1). Following the stress simulations, the stress intensity factors $K_I$, $K_{II}$, and $J$-integral value ($J_I$) of the corresponding FE models with an interfacial crack can be obtained [18]. The simulation methods and material properties considered in both thermal and hygroscopic stresses are introduced in Section 2.2 and 2.3, respectively, below.

### Table 1. Parameters of the geometries of pre-crack/coating and boundary conditions.

<table>
<thead>
<tr>
<th>Section Number</th>
<th>Variable</th>
<th>Initial Crack Location</th>
<th>Initial Crack Length (mm)</th>
<th>Coating Length (mm)</th>
<th>Coating Thickness (mm)</th>
<th>Exposure Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>Temperature change</td>
<td>Edge</td>
<td>3.0</td>
<td>25</td>
<td>0.5</td>
<td>± 0~250 °C</td>
</tr>
<tr>
<td></td>
<td>Crack location/length</td>
<td>Edge/central</td>
<td>0.05~2.0</td>
<td>25</td>
<td>0.2</td>
<td>± 200 °C</td>
</tr>
<tr>
<td></td>
<td>Coating thickness Fillers</td>
<td>Edge</td>
<td>3.0</td>
<td>25</td>
<td>0.4~2.0</td>
<td>± 100 °C</td>
</tr>
<tr>
<td>3.2</td>
<td>Moisture diffusion</td>
<td>Edge</td>
<td>2.0</td>
<td>25</td>
<td>0.9, 1.15, 2.0</td>
<td>100% RH, 0~400 h</td>
</tr>
<tr>
<td>4.1</td>
<td>Fillers</td>
<td>Edge</td>
<td>2.0</td>
<td>25</td>
<td>2.0</td>
<td>100% RH, 0~400 h</td>
</tr>
</tbody>
</table>

1 In this work, we will use the term “thermal shock” for cold shock $\Delta T < 0$ and heat shock $\Delta T > 0$.

### 2.2. Thermal Stress

Temperature changes were applied to the FE model to induce thermal stresses in epoxy coatings. Neat epoxy and filler modified epoxy coatings were prepared by bonding the polymer onto a glass substrate. The material properties of this epoxy matrix and these fillers are defined separately for the composites. $E$ and $CTE$ of epoxy were taken from previous studies [4,19,20]. It was assumed that round or rod-shape fillers with different $E$ and $CTE$ were distributed uniformly within the epoxy as shown in Figure 2. The crack tip was under the nearest filler. The diameter (Ød) of the round particles varied from 7 to 80 μm; and the aspect ratio (A) of rod-shape fillers was in the range 1~50. Table 2 lists the material properties of coating, substrate and fillers for thermal stress simulations.
Coatings 2019, 9, x FOR PEER REVIEW 4 of 16

Figure 2. Model of epoxy composite coatings on glass substrate with an interfacial pre-crack. The epoxy matrix is modified with (a) round and (b) rod-shape fillers.

Table 2. Material properties of epoxy, fillers and substrate for thermal stress simulation.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E$ (GPa)</th>
<th>$v$</th>
<th>CTE ($\times 10^{-6}$K$^{-1}$)</th>
<th>Fillers</th>
<th>Shape</th>
<th>Vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glass substrate</td>
<td>60</td>
<td>0.30</td>
<td>0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Epoxy matrix</td>
<td>2.86</td>
<td>0.35</td>
<td>64.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fillers Rigid</td>
<td>10, 70</td>
<td>0.17</td>
<td>0.75, 10</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fillers Soft</td>
<td>70</td>
<td>0.17</td>
<td>10</td>
<td></td>
<td>Rod-shape: A = 1−50</td>
<td>26</td>
</tr>
<tr>
<td>Fillers Round</td>
<td>0.06, 0.6</td>
<td>0.49</td>
<td>100, 200</td>
<td></td>
<td>Round: Ød = 7−80 μm</td>
<td>26</td>
</tr>
</tbody>
</table>

1 Ød: The diameter of the round fillers; A: The aspect ratio of the rod-shape fillers.

2.3. Hygroscopic Stress

Polymers swell upon the absorption of moisture. The coefficient of moisture expansion (CME) describes the change in strain $\varepsilon$ with moisture concentration $C$, i.e., $\varepsilon = CME \times C$. Due to a CME mismatch between coating and substrate, a hygroscopic stress is introduced. With appropriate thermal-moisture analogies, moisture diffusion and hygroscopic stress can be modelled through the thermal conduction and thermal stress functions in ABAQUS [14]. The local wetness concentration, $w$, is a continuous value across the filler/epoxy interface, calculated by $w = C/C_{Sat}$, where $C_{Sat}$ is the maximum moisture concentration that can be absorbed by the material. The lower limit $w = 0$ represents a dry condition, and the upper limit $w = 1$, is for the full saturation of moisture. Some studies also considered the effect of vapour pressure within the plastic IC packages [13,21], but this is not considered here.

It should be noted that, in experiments (Section 5), the samples were cooled slowly in the oven to relieve any possible residual stresses. Thus, the thermal residual stress was not included in Section 4. The accelerated moisture absorption speed and increasing moisture saturation content in epoxy due to high temperature were, however, considered. The values of $C_{Sat}$ and the diffusion coefficient $D$ of neat epoxy were obtained by experiments under 60 °C (see Appendix A). The CME value of neat epoxy was taken from [14,22]. $D$, $C_{Sat}$ and CME values for the substrate were assigned zero values. Round or rod-shape fillers were used to fill the epoxy coating. The material properties of the epoxy matrix and the fillers are defined in Table 3.

Table 3. Material properties of epoxy, fillers and substrate for hygroscopic stress simulation.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$E$ (GPa)</th>
<th>$v$</th>
<th>CME (mm²/mg)</th>
<th>$C_{Sat}$ (g/mm³)</th>
<th>$D$ (mm²/s)</th>
<th>Fillers</th>
<th>Shape</th>
<th>Vol.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel substrate</td>
<td>200</td>
<td>0.30</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Ød</td>
<td>237.9 μm</td>
<td>40</td>
</tr>
<tr>
<td>Epoxy matrix</td>
<td>2.86</td>
<td>0.35</td>
<td>$CM_{epoxy} = 0.222$</td>
<td>$C_{Sat,epoxy} = 1.84 \times 10^{-5}$</td>
<td>$D_{epoxy} = 5.12 \times 10^{-6}$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fillers Rigid</td>
<td>70</td>
<td>0.17</td>
<td>0.5 $CM_{m}$</td>
<td>0.5 $C_{Sat,m}$</td>
<td>0.5 $D_{m}$</td>
<td>Rod-shape: A = 3.4/11/22</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Fillers Soft</td>
<td>0.6</td>
<td>0.49</td>
<td>2 $CM_{m}$</td>
<td>2 $C_{Sat,m}$</td>
<td>2 $D_{m}$</td>
<td>Ød</td>
<td>237.9 μm</td>
<td>40</td>
</tr>
</tbody>
</table>

1 Ød: Represents the diameter of the round fillers; A: Is the aspect ratio of the rod-shape fillers.

Figure 3 schematically shows the boundary conditions used in the FE model for moisture absorption. The blue arrows represent the moisture diffusion paths. Prior to FE simulation of moisture absorption, the wetness of the coating was set at $w = 0$, and the wetness of the pre-crack and the environment was set at $w = 1$. After the epoxy coating/steel substrate sample was placed in the humid
environment, the coating material wetness \((w \neq 0)\) varied with exposure time \((t)\) and the wetness contour \([w = w(t)]\) was recorded.

![Figure 3. Schematic of boundary conditions for moisture absorption.](image)

**2.4. Crack Growth**

The critical \(J_C\) value was used as the fracture criterion for interfacial crack growth. When \(J_i \geq J_C\), the crack propagated. From the fracture test result (see Appendix B), \(J_C\) was assumed equal to the epoxy adhesive fracture energy, hence, \(J_C = G_{IC} = 55 \text{J}\cdot\text{m}^{-2}\). Here, we assumed that the \(J_C\) value was independent of temperature and wetness \([23,24]\). Even if \(J_c\) may be affected by these variables, the FE methods of analysis for \(J_i\), subjected to thermal shock and moisture absorption induced stresses are still valid; and the interface failure criterion, \(J_i \geq J_C\), remains applicable.

The flowchart of the crack propagation simulation under hygroscopic stress is shown in Figure 4 with the following steps: (1) The epoxy coating/substrate sample with initial crack length \(a\) and initial wetness \(w = 0\) is exposed to 100% RH \((w = 1)\) at 60 °C for several hours \(t\). The wetness contour of the epoxy coating is recorded, and the interfacial \(J_i\) is calculated. (2) Then, the \(J_i\) value is compared with the \(J_C\) value. If \(J_i < J_C\), the crack will not extend; the exposure time \(\Delta t\) is increased. Conversely, if \(J_i \geq J_C\), the crack grows for a certain length. Here, we assume \(\Delta a = 2 \text{mm}\), and the boundary condition is changed; i.e., the wetness \(w\) of the interfacial new crack area becomes 100% \((w = 1)\). (3) Before step 2, check that the epoxy coating is not fully debonded (i.e., \(a < 25 \text{mm}\)), or not fully saturated \((w < 1)\). Otherwise, the FE simulation finishes.

![Figure 4. Flowchart of FE simulation of coating/substrate interfacial crack growth.](image)
3. Parametric Design for Coatings against Interface Delamination due to Thermal Shock

3.1. Pure Epoxy Coatings

In this section, the parametric design of pure epoxy coating under thermal shock is discussed. Figure 5a,b show $K$ and $J_i$ values after rapid cooling and heating, respectively. When $\Delta T < 0$, the coating (in the debonded length) shrinks and forms an angle with the substrate (see, for example, the deformed shape at $\Delta T = -250$ °C in Figure 5c); the interface crack tip residual stresses $S_{12}$ and $S_{22}$ are responsible for the shearing $K_{II}$ and opening $K_I$ stress intensity factors (Figure 5a). By contrast, when $\Delta T > 0$, the coating (over the debonded length) stretches along the substrate (see the deformed shape and interface crack tip residual stresses at $\Delta T = 250$ °C in Figure 5c), the high $S_{12}$ but low $S_{22}$ give corresponding high shearing $K_{II}$ and low opening $K_I$ stress intensity factors (Figure 5b). Clearly, for thermal shocks with $\Delta T < 0$, both $K_I$ and $K_{II}$ increase linearly, and $J_i$ increases quadratically, with temperature. For $\Delta T > 0$, this conclusion still holds except that, in practice, $K_I$ can be neglected, so that $J_i$ is determined by the shearing $K_{II}$.

![Figure 5](image:https://example.com/figure5.png)

**Figure 5.** Effect of temperature changes on interfacial $K$ and $J_i$ values when the pure epoxy coating system is subjected to (a) $\Delta T < 0$ and (b) $\Delta T > 0$. (c) Residual stresses near the crack tip after rapid cooling or rapid heating. The displacements are magnified 5 times in the deformed model.

In practice, defects/pre-cracks may exist at any of the locations of the coating/substrate interface. Here, we examined $J_i$ of interfacial edge and central cracks, with a crack length ranging from 0.05–2 mm (see Figure 1). The simulation results are shown in Figure 6. For central cracks, the maximum $J_i$ is calculated as $1.4 \times 10^{-3}$ J m$^{-2}$ at a length of 2 mm, a few orders of magnitude lower than $J_C$ (55 J m$^{-2}$). Hence, we can conclude that the thermal stress is unlikely to cause crack growth in the centre, and thus central cracks will not be further considered in this study. By contrast, $J_i$ for pre-cracks at the edges increases quickly with increasing crack length until ~0.5 mm. After that, $J_i$ reaches a plateau value. That is, if the length of the edge crack reaches a critical value, and the plateau $J_i$ is higher than a critical $J_C$, the crack will spread quickly through the whole coating/substrate interface.
Figure 7 shows the interfacial $J_i$ value plotted against coating thickness ($h$) due to thermal shock. The two curves overlap each other, following a linear relationship: $J_i = 480 \times h$, which means that $J_i$ increases with coating thickness, consistent with a previous study [7]. This finding shows that a thinner epoxy coating has a higher fracture resistance to interfacial crack growth.

**Figure 6.** $J_i$ of edge crack and central cracks after rapid heating and cooling of the pure epoxy coating system.

3.2. Epoxy Composite Coatings

Here we investigate the interfacial crack growth in epoxy composite coatings with round and rod-shape particles on a glass substrate. The effect of the round particles (see Figure 2a) on $J_i$ is shown in Figure 8. The diameter of the round particles is 7~80 $\mu$m. $E = 70$ GPa represents rigid fillers, and $E = 60$ and 600 MPa represent soft fillers. Several observations can be made. (a) Unlike the results obtained for pure epoxy coating, $J_i$ values of epoxy composite coatings subjected to positive and negative thermal shocks of the same $\Delta T$ are different, indicating that the fillers have a noticeable effect on the stress field at the crack tip region. (b) $J_i$ curves have larger slopes for smaller filler sizes, suggesting that nano-size fillers exhibit a more important size effect than micro-size fillers. (c) For rigid filler (dark and red lines) modified epoxies, $J_i$ values for thermal shocks through heating are lower than those through cooling. By contrast, soft fillers (blue and pink lines) impart epoxies of higher $J_i$ for thermal shocks through heating than cooling. (d) For soft fillers, $J_i$ increases with increasing filler size, whereas for rigid fillers, $J_i$ decreases with increasing filler size.
The influence of the horizontally-distributed fillers (Figure 2b) on the relative interface sliding distance (rapid heating) and opening angle (rapid cooling) are larger increasing aspect ratio $A$ until ~10.

For thermal shocks through heating than cooling. (d) For soft fillers, the round fillers, the filler aspect ratio varies from 1 to 50, but the cross-sectional area remains constant ($\approx$). The relative opening displacement/angle as alternative fracture toughness measurements [25,26].

Figure 8. Effect of the diameter of round fillers on interfacial $J_i$ values due to thermal shock. (a) $\Delta T > 0$; and (b) $\Delta T < 0$.

The stress fields near the crack tips of pure epoxy ($E = 2.86$ GPa, $CTE = 64.5 \times 10^{-6}$ K$^{-1}$), rigid ($E = 70$ GPa, $CTE = 0.75 \times 10^{-6}$ K$^{-1}$) and soft ($E = 0.6$ GPa, $CTE = 100 \times 10^{-6}$ K$^{-1}$) round fillers (radius = 21.6 $\mu$m) modified epoxy coatings are shown in Figure 9. When the coatings are rapidly heated, since there is a very weak opening, the normal stresses in the Y-direction ($S_{22}$) are not listed. The relative interface sliding distance (rapid heating) and opening angle (rapid cooling) are larger for soft than rigid fillers and pure epoxy. These results agree well with the CTOD/CTOA (crack tip opening displacement/angle) as alternative fracture toughness measurements [25,26].

<table>
<thead>
<tr>
<th></th>
<th>Pure epoxy</th>
<th>$+$ Rigid fillers</th>
<th>$+$ Soft fillers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heating up $S_{22}$</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
</tr>
<tr>
<td>Cooling down $S_{22}$</td>
<td><img src="image4.png" alt="Image" /></td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 9. Stress distribution around the crack tip. (The fillers are hidden for simplicity, and the displacements are magnified five times in the deformed model).

The effects of rod-shape fillers on $J_i$ of modified epoxy composites are also examined. The aligned filler aspect ratio varies from 1 to 50, but the cross-sectional area remains constant ($\approx 1466$ $\mu$m$^2$). The influence of the horizontally-distributed fillers (Figure 2b) on $J_i$ is given in Figure 10. Compared to the round fillers, the $J_i$ of the composite coatings with rod-shape fillers is lower, and decreases with an increasing aspect ratio $A$ until ~10.
The crack extends from an initial length of 2 to 4 mm, and the minimum wetness does not increase linearly with exposure time, even at the initial diffusion rate in the epoxy coating, which show an evidently decreasing rate with increasing thickness. However, the rate of wetness increases with exposure time, and the middle point of the coating/substrate interface has a minimum wetness value of the whole coating. The minimum wetness values in Figure 11a are 0.2%, 5% and 44%, respectively. The minimum wetness value as a function of diffusion time can be calculated and plotted in Figure 11c. Obviously, the plateau $J_i$ values increase with increasing coating thickness. However, the rate of $J_i$ increase with exposure time $t$, prior to the $J_i$ plateaus, is higher for thinner epoxy coatings.

According to the method described in Section 2.4, crack growth was simulated. Figure 12a shows $J_i$ (see blue curve) and crack length (see black curve) plotted against exposure time. In the initial stage, $J_i$ increases with increasing exposure time in the humid environment. After 75 h, $J_i$ reaches $J_C$, $55 \, \text{J m}^{-2}$. The crack extends from an initial length of 2 to 4 mm, and $J_i$ has a significant decrease. With longer exposure times, $J_i$ increases until the crack grows again (from 4 to 6 mm @90 h). After 100 h, the coating is nearly moisture saturated, and $J_i$ approaches $J_C$, thus the crack quickly extends through the whole interface. In Figure 12b, the wetness contours and deformation for 90, 91 and 100 h exposures are displayed, showing that the coatings have experienced obvious deformations compared with their original shapes (see dashed lines).

Figure 10. Effect of rod-shape fillers on interfacial $J_i$ values subjected to thermal shock.

4. Parametric Design for Coatings against Interface Cracking due to Moisture Absorption

Since hygroscopic stress is analogous to thermal stress ($\Delta T > 0$) in the model, some conclusions can be deduced from the above discussions on thermal stresses. However, before moisture saturation in the coating, there exists a wetness gradient in the coating that is different from the uniform temperature field studied in Section 3. Therefore, the effects of exposure time and coating thickness on pure epoxy coating will be first discussed in Section 4.1. The fillers also affect moisture diffusion and the stress field. Thus, the filler design on moisture diffusion and crack growth will be next examined in Section 4.2.

4.1. Pure Epoxy Coatings

Three pure epoxy coating samples with thickness, i.e., 0.9 and 1.15 and 2.0 mm, were exposed in a humid condition (100% RH, 60 °C), and the wetness contours were recorded. For example, after the 2.0 mm thick coating samples were exposed for 5, 20 and 75 h, the wetness contours are shown in Figure 11a. Clearly, wetness increases with exposure time, and the middle point of the coating/substrate interface has a minimum wetness value of the whole coating. The minimum wetness values in Figure 11a are 0.2%, 5% and 44%, respectively. The minimum wetness value as a function of the exposure time is shown in Figure 11b for the three samples. The curves reflect the moisture diffusion rate in the epoxy coating, which show an evidently decreasing rate with increasing thickness. The minimum wetness does not increase linearly with exposure time, even at the initial diffusion stage (see inset in Figure 11b), showing generally decreasing slopes with increasing wetness and exposure time.

By assuming non-propagating cracks, interfacial $J_i$ values as a function of diffusion time can be calculated and plotted in Figure 11c. Obviously, the plateau $J_i$ values increase with increasing coating thickness. However, the rate of $J_i$ increase with exposure time $t$, prior to the $J_i$ plateaus, is higher for thinner epoxy coatings.

According to the method described in Section 2.4, crack growth was simulated. Figure 12a shows $J_i$ (see blue curve) and crack length (see black curve) plotted against exposure time. In the initial stage, $J_i$ increases with increasing exposure time in the humid environment. After 75 h, $J_i$ reaches $J_C$, $55 \, \text{J m}^{-2}$. The crack extends from an initial length of 2 to 4 mm, and $J_i$ has a significant decrease. With longer exposure times, $J_i$ increases until the crack grows again (from 4 to 6 mm @90 h). After 100 h, the coating is nearly moisture saturated, and $J_i$ approaches $J_C$, thus the crack quickly extends through the whole interface. In Figure 12b, the wetness contours and deformation for 90, 91 and 100 h exposures are displayed, showing that the coatings have experienced obvious deformations compared with their original shapes (see dashed lines).
Coatings 2019, 9, x FOR PEER REVIEW 10 of 16

4.1. Pure Epoxy Coatings
Three pure epoxy coating samples with different coating thickness were studied: 0.9 mm, 1.15 mm, and 2.0 mm. The wetness contours and deformation for 90, 91, and 100 h exposures were recorded. For example, after the first 90 h of exposure, the wetness contours show significant increases compared to the initial state. The wetness values in Figure 11a are 0.2%, 5% and 44%, respectively. The minimum wetness value as a function of exposure time can be calculated and plotted in Figure 11c. Obviously, the plateau thickness. However, the rate of moisture diffusion in the epoxy coating, which show an evidently decreasing rate with increasing thickness. The minimum wetness does not increase linearly with exposure time, even at the initial stage (see inset in Figure 13a). With round soft/rigid fillers, the slopes of the curves at the initial stage (see inset in Figure 13a), are only increased 13% and decreased 26% by soft and rigid fillers, respectively, compared to pure epoxy samples. However, rod-shaped fillers have the same area, but different aspect ratio A. That is, for a rod-shape filler (A > 1), its area of width × length is equal to the area of (39% and 41%, respectively. It is noted, with long exposure times, that the coating will finally saturate

Figure 11. (a) Transient moisture wetness distribution in a 2 mm thick coating. (b) Relationship between minimum wetness value and exposure time in epoxy layer with different coating thickness. (c) Interfacial $J_i$ values as a function of exposure time for non-propagating cracks.

Figure 12. (a) $J_i$ and crack length plotted against a humid environment exposure time. (b) Wetness contour and deformation of 2 mm thick coating layer while exposing for 90, 91 and 100 h. The displacement was magnified 20 times in the deformed model shape. (c) The effect of coating thickness on interfacial crack growth.
Moreover, crack growth in the coating samples with different thickness were studied (Figure 12c). For thick coatings (1.15 and 2.0 mm), the crack growth rates increase with exposure time. For the thin coating (0.9 mm), the plateau \( J_i \) (see Figure 11c) is less than \( J_C \), so there is no crack growth (see the blue line).

4.2. Epoxy Composite Coatings

As reported, fillers can be added to epoxy coating to reduce the moisture diffusion [27] and degradation of mechanical properties after hygrothermal treatment [3]. Here we use different fillers to embed within the coatings. Round soft/rigid fillers and horizontally dispersed rod-shape rigid fillers that have the same area, but different aspect ratio \( A \). That is, for a rod-shape filler \((A > 1)\), its area of width \( \times \) length is equal to the area of \( \pi \times (\text{radius})^2 \) for a round filler \((A = 1)\).

The effect of fillers on moisture diffusion in epoxy coatings is shown in Figure 13a. With round fillers, the slopes of the curves at the initial stage (see inset in Figure 13a), are only increased 13% and decreased 26% by soft and rigid fillers, respectively, compared to pure epoxy samples. However, rod-shape rigid fillers with an aspect ratio \( A = 3.4, 11 \) and 22 reduce the moisture diffusion rate by 35%, 39% and 41%, respectively. It is noted, with long exposure times, that the coating will finally saturate \((w = 100\%)\), but this only with a different moisture concentration, which depends on the different \( C_{Sat} \) value of the matrix and fillers.

![Figure 13. Effect of fillers on (a) moisture diffusion and (b) \( J_i \) values.](image)

To prevent delamination due to moisture content, the plateau \( J_i \) values (such as in Figure 11c) should be smaller than the critical \( J_C \). By assuming at any moisture absorption stage, \( J_i < J_C \), we can, in theory, plot \( J_i \) values vs exposure time for composite coatings with different kinds of fillers (see Figure 13b). The rate of increase of \( J_i \) with exposure time depends on the \( D, C_{Sat} \) and \( CME \) values of the epoxy and filler. Although the round soft fillers only increase the moisture absorption rate by 13%, the initial slope (see inset in Figure 13b) and plateau of the \( J_i \) curve (red chains) are twice higher than those of pure epoxy. By contrast, round rigid fillers reduce the slope and plateau of the \( J_i \) curve (blue chains) by 30% and 12%, respectively. Increasing the aspect ratio of the rigid filler to 3.4 (green \( J_i \) curve) decreases the slope and plateau values by 64% and 40%, compared to pure epoxy. Note for this case, \( J_i < J_C \) (= 55 J m\(^{-2}\)), which effectively means no interfacial crack growth can happen. Further increasing the aspect ratio (=11, 22) of the rigid fillers does not bring much more reduction on the \( J_i \) plateau value.
5. Materials and Experimental Work

5.1. Materials

Epoxy coatings were prepared by curing bisphenol A diglycidyl ether resin (also called DGEBA, Huntsman Chemical Company of Australia Pty Ltd (HCCA), Brimbank, Melbourne, Victoria, Australia) with a cycloaliphatic secondary amine curing agent piperidine (Sigma-Aldrich, Sydney, New South Wales, Australia). The epoxy resin had an epoxide equivalent weight of 185 g/equiv. 40 wt.% 20 nm nano-silica particles in DGEBA resin (Nanopox F400, Evonik Hanse GmbH, Geesthacht, Schleswig Holstein, Germany) and 25 wt.% 100 nm nano-rubber particles in DGEBA resin as master batches (Kaneka Corporation, Osaka, Japan) were used as rigid and soft fillers incorporated in the epoxy coating samples. Pure epoxy or filler-modified resin was degassed first in a vacuum, and then a curing agent piperidine was added into the resin with a weight ratio of 100:5. The resin/curing agent mixture was subsequently cured in an oven at 120 °C for 16 h. Modifications on silica and rubber surfaces enabled cross-linking with epoxy during curing, and prevented agglomeration in the epoxy matrix. The fabrication process for silica/epoxy and rubber/epoxy composite coatings was the same as that described in [4,19].

5.2. Coating Delamination due to Thermal Shock

For thermal shock experiments, a pure epoxy resin and piperidine mixture was carefully applied onto the surface (76 × 26 mm²) of a 1.5 mm thick glass substrate to prepare the epoxy coating samples. After the coating/glass substrate samples were heated for 16 h in a 120 °C oven, it was quickly transferred to a 20 °C chamber, introducing a thermal shock of −100 °C. Edge cracks were found to grow rapidly along the coating/substrate interface. Figure 14 shows a side-view of a failed sample with a crack stopping half-way along the length. The deboned epoxy coating shrinks, displaying an angle with the glass substrate. Thus, the phenomenon observed in our experiments offers strong support to these simulation results in Section 3.1.

![Side-view of a delaminated coating/substrate sample due to a thermal shock of −100 °C.](image)

5.3. Coating Delamination due to Moisture Absorption

Pure epoxy with different thickness (0.5, 0.9 and 1.15 mm) was applied on clean steel substrates as coatings. These epoxy/steel samples were then cured at 120 °C for 16 h and slowly cooled down to 60 °C. To accelerate moisture absorption, these samples were put into a high temperature humid environment (100% RH and 60 °C). After several hours, interfacial cracks emerged from the edges in some samples. The inset in Figure 15 shows the top-view of a sample with interfacial cracks which grew around the coating due to moisture absorption. The grey areas are uncoated steel substrate, and the blue dashed line represents the crack front. Due to the irregular shape of the coating, only the average width of the regions outlined by the blue arrows is considered as the crack length. For samples with 0.5 and 0.9 mm thick coatings, no cracks can be detected in the experiments (red and blue curves). However, the crack grows easily with exposure time in the sample with 1.15 mm thick coating (see black curve). These experimental observations are in complete consistency with the simulation results given in Section 3.1 and Section 4.1. Hence, thick coatings yield lower moisture diffusion rates, but sufficiently thin coatings stop interface cracking during moisture absorption.
Experiments on epoxy composite coatings filled with nano-silica and nano-rubber particles were conducted here. After the coating/steel substrate samples were exposed in a humid environment (100% RH, 60 °C) for 38, 24 and 13 h, interfacial cracks initiated in 0.8, 1.3 and 1.9 mm thick epoxy/nano-rubber coating samples, respectively. However, no interfacial delamination was found in epoxy/nano-silica coating samples, regardless of the coating thickness (0.5 to 2 mm), after they were exposed to the same wet environment for 110 h. These results confirm the effectiveness of incorporating rigid fillers in epoxy coatings against interface crack growth in Section 4.2.

6. Conclusions

In this study, the factors affecting epoxy and epoxy composite coatings interfacial failure caused by thermal and hygroscopic stresses were systematically investigated by finite element analysis. $J$-integral value ($J_i$) at the coating/substrate interfacial crack tip was obtained to evaluate the propensity for interfacial cracking. Experimental results confirmed the numerical simulation model. The major findings are:

(a) To prevent the coating from interfacial cracking by moisture absorption or thermal shock (rapid heating/cooling), thinner coatings are preferred;
(b) Small soft fillers or large rigid fillers near the crack tip regions are more effective in preventing the coating from interface crack growth. In addition, nano-size fillers have a more prominent size effect than micro-size fillers on the $J_i$ value;
(c) Compared to round fillers (aspect ratio = 1), rod-shape rigid fillers with large aspect ratio (aspect ratio > 1) decrease the $J_i$ values of the modified coatings more significantly. However, $J_i$ does not change much when the filler aspect ratio is larger than 10;
(d) For pure epoxy coatings, the $J_i$ value only depends on the absolute value of the temperature change, $\Delta T$. However, due to the effects of fillers and the stress field at crack tip, the $J_i$ values of the composite coatings are different during the heating and cooling processes, even though the absolute $\Delta T$ changes are the same.

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**Appendix A. Calculations of Moisture Diffusion Coefficient and Maximum Moisture Concentration**

Moisture absorption tests were conducted on pure epoxy bulk samples to obtain the relevant parameters for moisture absorption. Bulk cuboid samples were prepared by casting the epoxy resin and curing agent piperidine in a rubber mould, and cured. The cured epoxy was slowly cooled down in an oven to 60 °C to remove any residual stresses. Then, the epoxy samples were exposed in a humid environment (100% RH, 60 °C) for moisture absorption until saturation. Sample weight changes against exposure time were recorded in the Table A1 below. The volume of a cuboid pure epoxy sample was 1998 mm³. The thickness of the sample, \( h = 2.84 \) mm, was one order smaller than the length and width, thus the moisture mainly diffused through the thickness across the upper and bottom surfaces. Diffusion coefficients \( D \) of pure epoxy were obtained by curve fitting the moisture weight gain data in the initial stages of moisture absorption (\( C/C_{Sat} < 50\% \)) by Fick’s Law; thus,

\[
D = \frac{\pi h^2}{16} \left( \frac{C_{Sat}}{\sqrt{At}} \right)^2 = 5.12 \times 10^{-6}\ mm^2/s.
\]

The maximum moisture concentration was determined from the weight change recorded at \( t = 384\ h \), \( C_{Sat} = 18 \times 10^{-6}\ g/mm^3\).

<table>
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**Appendix B. Determination of Critical \( J \)-Integral Value**

The critical \( J \)-integral value, \( J_C \), used as a criterion for coating/substrate interface delamination was determined by a double-cantilever-beam test as mode I adhesive fracture energy. Epoxy resin and piperidine were mixed and applied between two stainless steel plates (150 × 20 × 1.6 mm³) as a 0.28 mm thick adhesive (see Figure A1a), being controlled by short copper wires [3]. A 0.2 mm polyimide film was inserted between the steel plates to introduce an initial crack. After being cured, the specimens were cooled down slowly in the oven to relieve any residual stresses, then tested in an Instron 5567 machine, based on the standard ISO-25217 [28]. A load-displacement curve was recorded during the test (see Figure A1b). Brittle fracture was observed, and the mode I adhesive fracture energy was calculated by the equation:

\[
G_{IC} = \frac{3P\delta}{2ab},
\]

where \( P \) is the maximum force in the load-displacement curve, \( \delta \) is the displacement, \( a \) represents the crack length, and \( b \) the sample width. An average \( G_{IC} \) value 55 J·m⁻² was determined from three samples. The fracture surfaces were clean, without any cracks (Figure A1c). Additionally, the bulk epoxy fracture energy (270 J·m⁻²) [4,20] is much larger than 55 J·m⁻². Here, any crack growth was between epoxy and steel substrate. The critical \( J_C \) value was assumed equal to the \( G_{IC} = 55\ J\cdot m^{-2} \).
References


