Lifetime prediction for interfacial adhesion of Carbon/Cork composites with an accelerated aging test

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Abstract
In the aerospace field, Carbon/Cork composites have been used for rocket propulsion systems as a light weight structural component with a high bending stiffness and high thermal insulation properties. For the fabrication of a carbon composite with a heat insulation cork part, the bonding properties between them are very important to determine the service life of the Carbon/Cork composite structure. In this study, the changes in the interfacial adhesion and mechanical properties of Carbon/Cork composites under accelerated aging conditions were investigated. The accelerated aging experiments were performed with different temperatures and humidity conditions. The properties of the aged Carbon/Cork composites were evaluated mainly with the interfacial strength. Finally, the lifetime prediction of the Carbon/Cork composites was performed with the long-term property data under accelerated conditions.

Keywords: carbon composites, cork materials, lifetime prediction, accelerated aging, quad lap adhesion test

1. Introduction
Carbon fiber reinforced composites have been used for many applications in various fields such as aerospace, automobile, electronics, military, sporting goods, and so forth. [1-3]. Especially, carbon fiber composites with cork sandwich structures can be used in many aerospace applications because they have a high bending stiffness, are lightweight and act as thermal insulators [4-12]. In addition, because of the surface combustion property of the cork, oxygen cannot pass through the inside of the cork material when there is an oxygen combustion environment such as during the propulsion of a rocket. Although thermal decomposition of the Carbon/Cork composite occurs, cork materials protect the flame, which passes through the inner side of the carbon fiber composite, by forming a char layer on the surface.

The cork, the core material, is a lightweight material which has flexibility and thermal, sound and vibration insulation properties originating from its unique closed cell structure. A cork, which comes from an oak tree, is a unique material with a fibrous structure of suberin [4]. A cork is a natural foam material, and each cubic centimeter of a cork’s honeycomb structure contains between 30 and 40 million polyhedral cells. Additionally, a cork is an ideal material because it contains a high elastic resilience, impermeability, thermal insulating properties, and durability. Thus, it is used in many industries including the food, packaging, aerospace, automotive, and so forth. [5-12].

When a Carbon/Cork composite is used as a light weight structural component which has insulation properties, the bonding properties between the carbon fiber composite and the cork are very important to determine the service life of the structure [13]. Additionally, understanding the aging behavior of the carbon fiber com-
2.2. Adhesion test of the Carbon/Cork composites

For the adhesion test of the Carbon/Cork composites, the quad lap tensile test was performed. The tensile test was carried out using a tensile testing machine (Instron 4467) with a 30 kN load cell and a crosshead speed of 5 mm min⁻¹ following the specification of ASTM D1002. The value of the adhesion strength was determined by the average of seven specimens. The Carbon/Cork composite quad lap samples were tested, and the results are shown in Table 1.

2.3. Accelerated aging test

The Carbon/Cork composite quad laps were aged according to the determined thermal aging conditions, and then, the shear strength of the Carbon/Cork composites was evaluated by the tensile test. In this study, the end of the lifetime of the Carbon/Cork composite was set at a shear strength of 50 psi, which is the lower limit of the shear strength useful for our structural insulating application. The composite quad lap was heat treated at 100°C for 24 h to remove the post-curing effect of the adhesive which was confirmed with the pre-aging test. Otherwise, the initial part of the shear strength of the Carbon/Cork composite increases with the aging time to some extent by the post-curing effect which can mislead the aging experiment.

To remove moisture from the composite quad lap samples, they were dried at 60°C for 3 h and conditioned at room temperature for 48 h before conducting the accelerated aging test. Additionally, after the accelerated aging, all samples were con-

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Table 1. Adhesion strength of the raw Carbon/Cork composite sample before post-curing

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<thead>
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conditioned at room temperature for 48 h before the adhesion test. Table 2 shows the aging test conditions used in this study for evaluating the shear strength change of the Carbon/Cork composites. The adhesion test was conducted as mentioned above. The average values of the adhesion strength were calculated from seven samples for each condition.

2.4. Aging evaluation methodology

The Arrhenius model of thermal aging involves physical stresses to hasten product failures within a relatively short time. The Arrhenius relationship describes the effects of temperature on the lifetime as follows (1):

\[ R = A \cdot \exp\left(\frac{-\Phi}{kT}\right) \tag{1} \]

where \( R \) is the thermal lifetime; \( A \) is the non-thermal constant involving the product geometry, specimen size, test method, and other factors; \( \Phi \) is the activation energy of the materials (eV); \( k \) is the Boltzmann’s constant \((8.617 \times 10^{-5} \text{ eV})\), and \( T \) is the absolute Kelvin temperature. In generally, the thermal lifetime is also described as Eq. 2.

\[ R = A \cdot \exp\left(\frac{\Phi}{kT}\right) \tag{2} \]

Additionally, the thermal lifetime (\( R \)) is expressed as a natural logarithm function; it is shown in Eq. 3.

\[ \ln(R) = \frac{\Phi}{k} + \ln(A) \tag{3} \]

And Eq. 3 can be expressed in the form of a linear Eq. 4 with an inverse of the temperature as follows:

\[ Y = aX + b \tag{4} \]

where \( Y = \ln (R); X = 1/T; a = \Phi/k \) as the slope of the line, and \( b \) is the constant representing the Y-axis intersection of the straight line. Eq. 4 shows that the natural logarithm of the thermal life can represent a straight line inversely proportional to the absolute temperature. In Eq. 4, the values for constants \( a \) and \( b \) are obtained experimentally through a thermal aging test. In this study, the end of life of the composite quad lap was set at 50 psi, which is one fourth of its initial shear strength.

2.5. Morphology observation

Fracture surfaces of the shear tested composite quad lap samples were observed with an optical microscope and a scanning electron microscope (SEM; Hitachi S 4700, Japan).

3. Results and Discussion

3.1. Post-curing effect

In the thermosetting resin, the unreacted resin slowly cures even after the curing step. This is called the post cure; additionally, the post cure can occur in the Epoxy resin in the Carbon/Cork composite quad lap. For more precise experiments, pre-aging tests were done. The composite quad lap samples were cured at 100°C for 24 h. Fig. 2 shows the shear strength and displacement of the post cured composite quad lap. The shear strength increased, and the displacement decreased because of the post-curing phenomenon. The post cure behav-

| Table 2. Adhesion test data of the composite quad lap after accelerated aging with different temperatures |
|-----------------|-----------------|-----------------|-----------------|
|                 | Raw             | 50°C            | 70°C            | 100°C           |
| 250 h           | Shear strength (psi) | 240             | 235.58±4%       | 216.97±7%       | 201.80±3%       |
|                 | Displacement (mm) | -               | 1.21±12%        | 0.99±10%        | 0.94±10%        |
| 500 h           | Shear strength (psi) | 240             | 227.74±5%       | 215.21±3%       | 179.79±5%       |
|                 | Displacement (mm) | -               | 1.16±10%        | 1.16±8%         | 0.91±6%         |
| 1000 h          | Shear strength (psi) | 240             | 226.71±3%       | 209.61±3%       | 178.27±3%       |
|                 | Displacement (mm) | -               | 1.21±9%         | 0.99±4%         | 0.83±5%         |
| 2000 h          | Shear strength (psi) | 240             | 229.44±5%       | 201.25±3%       | 181.31±6%       |
|                 | Displacement (mm) | -               | 1.36±8%         | 1.09±6%         | 0.85±10%        |

Fig. 2. Shear properties of the Carbon/Cork composite with post-curing (100°C, 24 h).
ior of the Carbon/Cork occurred in all the composites due to the extra-curing of the adhesive, and thus, the shear strength of the Carbon/Cork composites increased to a certain extent. However, the aged samples have better mechanical properties compared to the unaged samples in the accelerated aging test, and prediction of the lifetime may be very difficult. Therefore, to prevent a rapid increase in the shear strength at the initial part of aging and to make the aging test amicable for lifetime modeling, the post-cured composite quad lap samples were used instead of the non-post-cured ones in the aging test and lifetime prediction.

3.2. Accelerated aging results

Fig. 3 shows the shear fracture behavior of the composite quad lap samples. In all the samples, regardless of the aging conditions, a similar fracture mode was observed in Fig. 3. Obviously, most of the fractures of the composite quad lap were initiated and propagated at the cork side, and finally, the cork materials broke at the end of the fracture mode. This phenomenon is due to the weak and soft nature of the cork material compared to the high modulus carbon composites.

Fig. 4 shows the microscopic images of the fracture surface of the composite quad lap with aging time. The fracture surface of the raw samples had rough shapes. Relatively smooth fracture surfaces on the cork side were observed as the aging time progressed because the cork part is soft, and the cork cell structure can easily be broken by thermal aging. The weak outer surface layer of the cork bonded with an adhesive to the carbon fiber composite was peeled off from the cork surface by the shearing force. Thus, most of the interfacial fractures of the Carbon/Cork composites came from the cohesive breakage of the cork part. Because the Carbon/Cork composites underwent thermal aging, those cohesive fractures easily occur due to the aging of the cork material. However, in the case of the long-term (over 1000 h) aged samples at 100°C, the mixed fracture mode was observed with small pieces of the aged adhesive on the fracture surface of the cork material.

The accelerated aging test results of the Carbon/Cork composites showed the typical aging process of general organic
were increased.

Fig. 7 shows the relationship between the shear load and the displacement to help understand the aging of the Carbon/Cork composites. Because of the degradation in the cork part and in the adhesive layer of the composite quad lap due to the aging temperature and time, its displacement was decreased by the stiffened and brittle fractures.

Fig. 8 shows normalized strength graphs using the initial and aged shear strengths of the Carbon/Cork composites with a linear relationship. The initial shear strength was 240 psi, which is the maximum shear strength after the post-cure test. The shear strength of all the Carbon/Cork composites tended to decrease with the aging time and aging temperature as expected. The slope of the strength line was steeper at a higher aging temperature. It shows the high aging temperature in our experimental range had a greater effect on the shear strength of the Carbon/Cork composites.

Fig. 9 shows the SEM images of the fracture surfaces of the raw and long-term aged samples of the Carbon/Cork composites (50 and 100°C) especially at the cork surface. The fracture surface of the raw Carbon/Cork composite shows a smooth and small honeycomb structure of cork (Fig. 9a). On the other hand, the fracture surfaces of the Carbon/Cork composites after the shear test showed huge breakages of the cork layer at an aging temperature of 50 and 100°C (Fig. 9b and c). In the case of the Carbon/Cork composites aged at a temperature of 100°C (Fig. 9c), some of the fractures of the adhesive coated cork layer were
with the aging time obtained by the quad lap accelerated aging test. As a result, it was found that the activation energy is 0.29 eV when the quad lap samples reach the end of their lifetime (at 50 psi). Fig. 11 shows the relationship between $\ln(k)$ and the temperature with a regression line. Fig. 12 shows the lifetime prediction result of the Carbon/Cork composite calculated from the Arrhenius plot data, which represents the lifetime at each temperature. Using the above results, the lifetime of the Carbon/Cork composite can be calculated, and for instance, when the shear strength reaches the end of the lifetime condition (50 psi) at 20°C, the lifetime of the Carbon/Cork composite is about 18.44 yr. Table 3 shows the results of the lifetime prediction calculated from different temperature conditions.

In addition, if the end of lifetime of the Carbon/Cork composite would be set at a shear strength of 18.4 psi (structural failure condition in our application system), the lifetime prediction result is shown in Fig. 13. In this case, the lifetime of the Carbon/Cork composite is 31 yr at 20°C, and Table 4 shows the results of the lifetime calculated using different temperatures.

Table 3. Predicted lifetime of the Carbon/Cork composite with different aging temperatures (50 psi limit)

<table>
<thead>
<tr>
<th>Service temperature (°C)</th>
<th>t (h)</th>
<th>t (d)</th>
<th>t (yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>161520.8</td>
<td>6730.032</td>
<td>18.43845</td>
</tr>
<tr>
<td>30</td>
<td>108333.6</td>
<td>4513.898</td>
<td>12.36685</td>
</tr>
<tr>
<td>40</td>
<td>74538.68</td>
<td>3105.778</td>
<td>8.508982</td>
</tr>
<tr>
<td>50</td>
<td>52487.39</td>
<td>2186.974</td>
<td>5.991711</td>
</tr>
<tr>
<td>60</td>
<td>37746.52</td>
<td>1572.772</td>
<td>4.308964</td>
</tr>
<tr>
<td>70</td>
<td>27672.44</td>
<td>1153.019</td>
<td>3.158955</td>
</tr>
<tr>
<td>80</td>
<td>20647.01</td>
<td>860.2921</td>
<td>2.356965</td>
</tr>
<tr>
<td>90</td>
<td>15655.77</td>
<td>652.3239</td>
<td>1.787189</td>
</tr>
<tr>
<td>100</td>
<td>12048.58</td>
<td>502.0243</td>
<td>1.375409</td>
</tr>
<tr>
<td>110</td>
<td>9400.194</td>
<td>391.6748</td>
<td>1.073082</td>
</tr>
</tbody>
</table>

Fig. 10. Arrhenius plot of the cork composite quad lap (end of lifetime at 50 psi).

Fig. 11. $\ln(k)$ versus $1/T$ graph of the Carbon/Cork composite (end of lifetime at 50 psi).

Fig. 12. Predicted lifetime of the Carbon/Cork composite with the aging temperature (end of lifetime at 50 psi).

Fig. 13. Predicted lifetime of the Carbon/Cork composite with different aging temperatures (18.4 psi limit).

observed on the surface of the cork side by the thermal degradation of the adhesive.

To establish the lifetime prediction of the Carbon/Cork composite, the end of its lifetime was determined at its shear strength of 50 psi as already mentioned above. Figs. 10-12 show the basic graphs for the lifetime prediction extracted from Eqs. 1-3. Fig. 10 shows the Arrhenius plot of the values
4. Conclusions

In this study, the aging effects on the adhesion properties between the Carbon/Cork composites were investigated. Accelerated aging tests were conducted to estimate the lifetime of the Carbon/Cork composites. The shear strengths with different aging conditions for the Carbon/Cork composites were measured by the quad lap test, and the resulting data were used for the lifetime prediction. Considering the post-cure phenomena, the initial shear strength of the Carbon/Cork composite quad lap was set to 240 psi, and its end of lifetime was set at a shear strength of 50 psi (lower limit of our structural application). In the shear strength measurements of the Carbon/Cork composites, the main cohesive fractures were found on the cork side in all samples. When applying the lifetime prediction model, most of the data in our experimental range fit well with the regression line. Based on the results of the accelerated aging test, the lifetime prediction model in this study showed that the lifetime of the Carbon/Cork composite at 20°C was 18.44 yr.

Conflict of Interest

No potential conflict of interest relevant to this article was reported.

References