Degradation and deformation of carbon phenolic ablator in elevated temperature processes

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Keywords: Composite Materials, Ablator, Pyrolysis, Degradation, Deformation

Nomenclature

\begin{itemize}
    \item \( R \) : recession
    \item \( m \) : mass of material
    \item \( q \) : heat flux
    \item \( t \) : heating time
    \item \( A \) : heating surface area
    \item \( h \) : enthalpy
    \item \( \rho \) : density
    \item \( V \) : volume
\end{itemize}

Subscripts

\begin{itemize}
    \item \( i \) : initial
    \item \( c \) : char layer
    \item \( \text{rec} \) : recession
\end{itemize}

1 Introduction

Ablation cooling is one of thermal protection methods adopted in severe heating environments such as re-entry vehicles from space. The ablator system covering space vehicles protects payloads by consumption of ablator material itself; generated gases cover the vehicle to insulate from hot environmental gases, endothermic decomposition reactions lower material temperature, and low thermal conductivity of ablation material lowers heat flow to penetrate into inside of the vehicle.

When a space capsule returns to earth, the surface of an ablator erodes by oxidation and sublimation. Retreat of surface consumption of the ablator is called recession. The recession is imperative information to design thickness of ablator. The recession \( R \) is determined by the following formula:

\[
R \equiv \frac{m}{q t A h}, \quad m = m_i - \rho V_{\text{rec}}.
\] (1)

Here, \( V_{\text{rec}} \) is the recession volume. The volumetric recession has been measured by comparing the thicknesses before and after heating using an arc wind tunnel. However, this measurement includes the thermal deformation caused by cracking of the ablator in addition to surface recession. Thus, the recession has not been estimated correctly.

When an ablator is designed, thermal analyses have been carried out to predict temperature distribution in the ablator. The analyses require the density, thermal conductivity, and heat capacity of the ablator [1]. These material properties vary widely by cracking during elevating temperature processes. Thus, these values have been used as fitting parameters in the calculation. Even if these parameters can be determined correctly, the determined values are useful only for calculations, which simulate the same material under the same heating conditions.

In order to improve the reliability to predict the recession or the thermal response, models which can estimate the thermal deformation (change of dimension) and degradation (mechanical cracking) are required. In this study, at the beginning of establishing these models, mechanisms of
deformation and degradation during heating stages were clarified.

In experiment using an arc wind tunnel, test material is heated unidirectionally and rapidly. As a result, an ablator achieves sharp temperature distribution and complex thermal stress [2]. Under such non-stationary and complicated heating conditions, we judged that it is difficult to understand basic mechanisms of thermal deformation and degradation. Therefore, mechanisms yielding deformation and degradation were discussed in this study under quasi-static heating conditions in near uniform temperature distribution.

2 Experiments

2.1 Materials
This study was performed using 2 types of Carbon Fiber Reinforced Plastic (CFRP). These materials are consisted of the same reinforcing fiber and matrix resin. The fiber was a carbon fiber, which is spun-yarned as shown in Fig 1. This fiber has low density and low thermal conductivity. The matrix was phenolic resin, which exhibits high residual carbon yield upon heating to high temperature. These properties are suitable for Thermal Protection System (TPS). Principal differences between Types 1 and 2 were porosity and pore size. As shown in Table 1, while the closed porosity of Type 1 was higher than that of Type 2, Type 2 has higher open porosity than that of Type 1. As Fig. 2 indicates, the size of pores in Type 2 is obviously larger than that of Type 1.

<table>
<thead>
<tr>
<th>Table 1. Porosity of material</th>
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<tr>
<td>Material</td>
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<tr>
<td>Type 1</td>
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<td>Type 2</td>
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Fig. 1 Spun-yarned carbon fiber bundle.

Fig. 2 Optical microscope images of Type 1 and 2 at room temperature.

2.2 Thermogravimetric Analysis / Mass Spectrometry
In order to measure mass loss during heating processes, Thermo Gravimetric Analysis (TGA: NETZSCH, STA449C) was conducted and, in order to identify gases species exhausted as a result of chemical reaction at elevated temperatures, a Mass Spectrometry (MS: NETZSCH, QMS403C)
measurements were carried out. These measurements were conducted under 1 atm of Ar atmosphere and at a heating rate of 10°C /min. The maximum temperature was set to 1000°C, because all chemical reactions at elevated temperatures almost finish until this temperature. The sample geometry for TGA was approximately 10.0×7.0×5.0 mm³.

2.3 Thermo-Mechanical Analysis
Thermal deformation was measured using Thermo-Mechanical Analyzer (TMA: SHIMADZU TM-50) under quasi-static heating fields. The measurements were conducted under 1 atm of Ar atmosphere and at three heating rates: 1.0°C/min, 10°C /min, or 50°C /min. A specimen was heated up to 900°C. As shown in Fig. 3, the deformation was measured in the thickness direction of the laminated composites. The specimen size for these tests was 5.0 × 5.0 × 7.0 mm³.

2.4 Observation by Thermo Optical Microscope
The defect development during heating process was observed with Thermo Optical Microscope (TOM). This system is combined heating furnace (MVH-5 manufactured by Japan High Tech) and optical microscopes (VHX-2000 and BH2-UMA manufactured by Keyence Japan or OLYMPUS). The geometry of the specimens was approximately 3.0 × 3.0 × 3.0 mm³. High temperature observations were made up to 900°C at a heating rate of 10°C /min and within Ar atmosphere. The observations were performed on cross-section surfaces of the laminated plates (shown in Fig. 3).

![Fig. 3 Schematic of the specimen illustrating measurement direction and an observation plane.](image)

3 Results

3.1 Thermal deformation
Figure 4 shows the thermal deformations of both the materials heated up to 900°C. From now on, we would like to discuss thermal deformation mechanisms dividing the test temperature into 3 regions. A peak due to expansion and shrinkage of the thickness occurred in Range 1 and 2 for both the materials. In contrast in Range 3, while Type 1 expanded, Type 2 shrank.

![Fig. 4 Typical thermal deformation of Types 1 and 2 under heating process up to 900°C.](image)

3.2 Thermal degradation
Figure 5 represents TOM images of damage extension during heating of Type 1 observed up to 900°C. As these photos show, visible cracks except for small interfacial debonding are not observed in Range 1 and Range 2 (up to 500°C). The cracking started actively in Range 3 as shown in the 700°C photo of Fig 5. These cracks were obviously caused by shrinkage of the matrix resin due to chemical decomposition.

The cracking process of Type 2 was different from that of Type 1. Figure 6 compares the cracking patterns of Types 1 and 2 observed at 900°C. While the cracks in Type 1 extends parallel to the fiber axis direction, the cracks in Type 2 tend to propagate perpendicular to the fiber axis direction. The difference of cracking pattern should contribute to the difference in thermal deformation after 550°C (Range 3).
Fig. 5. Typical development of damage during heating process in the Type 1 material observed on a cross-section using TOM.

Fig. 6 Comparison of damage of Type 1 and 2 observed on cross-sections using TOM.

4 Discussions

4.1 Range 1 (Type 1: RT~350°C, Type 2: RT~250°C)

4.1.1 Thermal degradation

As described above, the distinct damage was not observed in this temperature range. However, as shown in an enlarged photo of Fig. 7, the narrow gaps (debonding) appeared along interfaces between fibers and the matrix when deformation attained the peak in Range 1 (at around 300°C for Type 1). In general, the coefficient of thermal expansion of matrix is one order of magnitude higher than that of carbon fiber. Therefore, the interfacial debonding observed in Fig. 7 is characteristic phenomenon of fiber-reinforced composites when temperature is risen. The similar behavior was also observed for Type 2 in Range 1.
4.1.2 Thermal deformation

The outcome of TGA/MS for Type 1 is shown in Fig. 8. The result for Type 2 is similar to that for the Type 1. In Range 1, H$_2$O gas was emitted constantly, and the peak temperature of H$_2$O emission locates at the temperature showing the peak of thermal deformation in Fig. 4. This coincidence indicates that the emission of H$_2$O is the reason for the shrinkage after the peak in Range 1 presented in Fig. 4. This peak temperature also agrees with the temperature at which fiber/matrix debonding was observed.

Figure 9 compares the thermal deformations of Type 1 at different heating rates. As shown in this figure, the expansion in Range 1 increases concomitantly with increasing heating rate. Since the decomposition reaction does not start in this temperature range, H$_2$O trapped in the material, which is emitted by diffusion to outside of the material, should be responsible for the peaking behavior in Range 1. Roy M. S. et al. reported that H$_2$O trapped inside the material can exert significant pressure at high temperatures and accompanying deformation becomes significant when the temperature exceeds the glass transition [3]. The glass transition temperature of the present matrix is around 200°C. At this temperature, glassy resin changes to a rubber state. Therefore, the effect of H$_2$O gas pressure on deformation shows up more clearly at the temperatures higher than 200°C. The residual H$_2$O at glass transition temperature becomes higher with increasing heating rate, because H$_2$O can’t diffuse until glass transition due to the rapid heating time. This fact invokes high H$_2$O gas pressure with increasing heating rate due to the residual amount of H$_2$O gas inside material. In light of these results, the H$_2$O gas pressure inside material was reason for the significant expansion observed before the peak temperature in Range 1.

Thermal deformation of Type 2 was less than that of Type 1 as represented in Fig. 4. This difference is attributable to difference in open porosity; the open porosity of Type 2 was much more than that of Type 1 (Table 1). Therefore, in the case of Type 2, the pressure by residual H$_2$O inside material should be lowered at elevated temperatures because H$_2$O gas was easy to be emitted via open pores.
4.1.3 Relation between the deformation and degradation

As mentioned above, cracking was not observed in Range 1 except for fiber / matrix interfacial debonding. This debonding probably caused by mismatch of thermal stress between the fiber and matrix due to the difference in coefficient of thermal expansions. Thus, the H$_2$O pressure causing the deformation would not be the reason for cracking.

The emission of H$_2$O via fiber / matrix interfacial debonding was the reason for the shrinkage after the peak deformation in Range 1 by reducing H$_2$O pressure inside material.

4.2 Range 2 (Type 1: 350°C ~550°C, Type 2: 250°C ~550°C)

4.2.1 Thermal degradation

As Fig. 5 described, new crack production was not observed in this temperature range.

4.2.2 Thermal deformation

The shrinkage of each material in Range 2 was caused by the shrinkage of the matrix due to the pyrolysis reaction beginning in this temperature region as shown in Fig. 8.

4.2.3 Relation between deformation and degradation

Figure 9 indicates increase in expansion with increasing heating rate in Range 2 is similar to Range 1. The gas pressure due to the pyrolysis reaction is most likely causing the expansion in this temperature range. The pyrolysis gases causing the deformation didn’t generate the new cracking in range 2.

4.3 Range 3

4.3.1 Thermal degradation

As Fig. 5 indicates, large cracks were generated from the beginning of Range 3 due to mismatch of strains between the fiber and matrix; shrinkage of the matrix and expansion of the fiber under rising temperature. The cracks in Type 1 extended mainly along the surfaces of spun-yarned fiber bundles as described in Fig. 6. The fiber bundles were compressed to the fiber axis direction when the matrix shrinks by the pyrolysis reaction. This compressive stress makes the spun-yarned carbon fiber bundles be loosen and buckled in the pattern illustrated in Fig. 10; a fiber bundle is composed of three mini-fiber-bundles (spun-yarned bundles). Figure 11 shows degradation behavior of a material consisted of a single fiber bundle embedded in the phenolic resin matrix under heating observed using TOM. This figure clearly shows that min-fiber-bundles buckled due to the compressive stress, which begins at 700°C.

In contrast, the cracks of type 2 extended normal to fiber orientation as observed in Fig. 6. These cracks generated from the edge of large pores. As shown in Fig. 2, one of the differences in material construction between Types 1 and 2 is size of pores. The pores in Type 2 were larger than those in Type 1. A large pore becomes an origin of cracking because of stress concentration at the edge, and larger strain energy stored near an edge of a larger pore than that of a smaller pore. In the matrix to the direction of the fiber axis, tensile stress is produced due to the thermal mismatch between the fiber and matrix. Therefore, cracks in the direction normal to fiber direction should easily occur especially in the Type 2 material.
4.3.2 Thermal deformation

Figure 12 shows the deformation of Type 1 during heating (10°C/min), holding (at 550°C, 2h), and cooling (10°C/min) under 1 atm of Ar atmosphere. As Fig. 12 indicates, the expansion trend is monitored at both holding and cooling processes. This result indicates the expansion deformation is caused by the shrinkage of the matrix resin due to the pyrolysis reaction. Therefore, the compressive stress (shown in Fig. 10) caused by the shrinkage of the matrix resin due to pyrolysis reaction invokes the buckling of fiber bundles, and then broadened the cross-sections of the fiber bundles. Thus, the reason for thermal expansion of Type 1 in range 3 is the buckling of fiber bundles.

As mentioned 4.3.1, the principal cracks in Type 2 were not extended to the direction parallel to the surrounding fiber mini-bundles, but were in the direction normal to fiber. These cracks relieve the tensile stress in the matrix, and the compressive stress in the fiber bundle also relaxed. Thus, deformation of Type 2 in this temperature range followed the shrinking tendency of the matrix resin.

4.3.3 Relation between deformation and degradation

The thermal deformations in range 3 were
induced principally by thermal degradation. If the pore size of material is small, the compression stress causes the buckling of fiber bundles, which generate clacks along fiber-mini-bundle surfaces and expand the fiber bundle thickness. In contrast, when large pores are included in the matrix, the similar magnitude of shrinkage to that of the matrix resin resulted, because cracks in the direction normal to the fiber bundles release the compression stress of fiber bundles.

5 Conclusions

5.1 Range 1

In this temperature range, the expansion is caused by the pressure of H$_2$O. This pressure was released by diffusion of H$_2$O gas through the interfacial debonding caused by the difference of coefficient of thermal expansion between the fiber and matrix. This emission of H$_2$O led to the shrinkage of the materials. Thus, thermal expansion in this temperature range was affected by adsorbed H$_2$O and diffusion of H$_2$O gas.

5.2 Range 2

The pressure by pyrolysis gases is likely responsible for the thickness expansion in temperature range 2. The shrinkage follows after the expansion. This shrinkage is caused by the pyrolysis reaction of matrix resin.

5.3 Range 3

The deformation in this temperature range changed depending on a cracking process. The cracking process depended on the pore size. The shrinkage of the resin due to pyrolysis reaction produced mismatch strain between the fiber and matrix. In the case of Type 1 including small pores, this mismatch strain is released by the buckling of fiber bundles resulting in expanding the thickness. In contrast, the mismatch strain in Type 2 was released by cracking in the matrix to the direction normal to fiber axis. The cracks started at an edge of large pores where tensile stress was induced when the matrix shrunk. Consequently, the pore size determined the cracking pattern and deformation in this temperature range.

6 References

