MECHANICAL AND ABRASIVE CONSIDERATION OF ADDITIVES EFFECTS ON THE CARBON FABRIC/PHENOLIC COMPOSITES

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Abstract- Carbon/phenolic composites are used in the nozzle parts of solid rocket motors due to their heat-resisting, ablation, and high strength characteristics, which are required to endure the high temperature and pressure of combustion gas passing through the nozzle. One of the most important factors on erosion rate is the void content of the ablative composites. Facilities should be designed to simplify the exhaust of volatile components, in order to reducing the void content in the manufactured samples. Accordingly, to reduce the void percentage of carbon/phenolic composites in this study, samples are manufactured by the vacuum bag molding technique, and they are cured in autoclave. In order to comparison of the effect of manufacturing process on the ablation characteristic of carbon/phenolic composites, another batch of samples has been produced by the acid curing method. According to ASTM E 285-80, they are exposed to a plasma torch flame. The results show that the void percentage of samples which are manufactured by the autoclave process is 60% lower than the acid-cured samples, and this leads to reduce the linear erosion rate of these composites.

Keywords- carbon/phenolic composites, ablation, autoclave, acid curing, plasma torch

I. INTRODUCTION

It During atmospheric re-entry, ballistic or space vehicle is subjected to severe aerodynamic heating and its successful return through the Earth’s atmosphere depends largely on the provision that is made for reducing aerodynamic heat transfer to its structure. For this purpose ablative heat shield is normally used which undergoes physical, chemical, and mostly endothermal transformations. These transformations produce new liquid or gas phases which are subsequently injected into the environment [1]. Ablation is an effective and reliable method largely used in aerospace structures to protect the pay load from the damaging effects of external high temperatures. In the ablation process, the high-heat fluxes are dissipated by the material through a series of endothermic processes. That finally led to the loss and the consumption of the material itself. The working process of an ablative heat shield as shown in fig. 1 can be briefly summarized as follows; the convective heat that reaches to the vehicle surface is balanced by surface radiation, phase transitions, and chemical reactions. Moreover, part of the incoming convective heat flux is blocked by the out coming flow of hot gases that result from the degradative processes. The ablative material keeps the surface temperature within a certain range and as a consequence an increase of the heat flux will not cause a consistent temperature raise, but will cause an increase of the surface recession rate [1].

Among the common plastics, the phenolic resins give the highest yield of carbon during pyrolysis, and they have been widely used as surface charring ablative materials. Since the char is relatively weak, and is removed mechanically by high shear forces associated with re-entry, fibers of carbon, silicon dioxide, refractory oxides, mineral asbestos, or even glass have been added to assist the char retention [2].

For solid rocket motor applications, the key requirements of carbon fiber composite are not only of low thermal conductivity to minimize the thickness of paralyzed carbon layer but also of high interfacial strength to reduce possible catastrophic erosion by abnormal ablation behaviour Therefore, development of PAN-based carbon fiber composites having comparable thermal conductivity and interfacial strength with rayon-based carbon fiber composites has been in great demand [3]. Additional processes could be done on the constructive materials of these composites or additive material can be used in order to improve the thermal resistance, ablative, interlaminar characteristics and thermal conductivity reduction of these composites [4, 5].

The interlaminar shear strength was studied to evaluate the effect of PVB and PTSA on the attachment strength of reinforcement to matrix and finally it’s relation with the ablation characteristics of the composites. In order to explore the interlaminar shear strength of the composites, short-beam shear test was conducted. Also thermal conductivity was...
measured in transverse directions. To explore the ablative characteristic of the composites in terms of insulation index and erosion rate an arc plasma torch with heat flux of 15 Mw/m² at approximately 2700°C was used.

II. EXPERIMENTAL DETAILS

A. Starting Materials
High-strength PAN-based carbon fabric with (0-90) plain texture (TC33 3K, Taiyifil Co., Taiwan) was used as a reinforcement for carbon/phenolic in this study. The physical properties of the carbon fabric are summarized in Table1. Also Resole-type phenolic resin (IL800, Resitan Co.) was used as the matrix precursor of the composites (Table2). Polyvinyl Butyral resin (PVB) (B30H, Catrin Co.) and p-toluene Sulfonic acid (PTSA) purchased from 895Aldrich Chemical Co. were used as an additives to matrix phase.

<table>
<thead>
<tr>
<th>Fiber texture (g/m²)</th>
<th>Thickness (mm)</th>
<th>Fiber density (g/cm³)</th>
<th>Tensile Strength (MPa)</th>
<th>Tensile Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plain (0-90)</td>
<td>200</td>
<td>0.3</td>
<td>1.80</td>
<td>3790</td>
</tr>
</tbody>
</table>

Table 1 The physical properties of PAN-based carbon fabric (TC33-3K).

B. Preparation of Samples
Four groups of carbon/phenolic composites manufactured in this study are defined as follow:

a) C/P = Resole matrix composite reinforced with carbon fabric (50-50 wt %)
b) C/P/PVB = Resole matrix composite reinforced with carbon fabric with 20 wt% polyvinyl Butyral resin
c) C/P/PTS = Resole matrix composite reinforced with carbon fabric with 4-6 wt% p-toluene Sulfonic acid.
d) C/P/PVB/PTSA = Resole matrix composite reinforced with carbon fabric with 20 wt% polyvinyl Butyral resin and 4-6 wt% p-toluene Sulfonic acid.

Carbon/phenolic composites were fabricated in an autoclave by a conventional vacuum bag molding method. At the beginning Carbon fabric was cut to desired dimensions (10x10 cm²) and they were saturated with Resole and then the prepared batch was pre-cured in an oven. Prepreg layers were hand laid up in a metallic mold. In the manufacturing of samples with 4-6 wt% PTSA, because of the presence of water absorption agent (PTSA), the process of the prepregs manufacturing in oven was eliminated.

C. Thermal Analysis
Thermal Gravimetric Analysis (TGA) is done on Resole in atmosphere from ambient temperature to 700°C with 10°C/min heating rate, to determine the mass reduction of Resole in different temperatures in order to finding the Resole curing cycle, by Ushimatso 50 apparatus.

D. Composite Curing
After layer saturation and hand lay-up into the mold the samples are cured in autoclave at 160°C final temperature with 8.1°C/min heat rate and 100 psi pressure. Samples will stay 1 hour at final cure temperature (160°C) and then it will cool down slowly to ambient temperature.

E. Ablation Test
According to ASTM E 285-80 [7], a plasma torch test was performed to investigate the ablation property for carbon/phenolic and other three different types of composites. This test method covers the screening of ablative materials to determine the relative thermal insulation effectiveness when tested as a flat panel also the surface erosion when is tested as a cylindrical element in an environment of a steady flow of hot gas provided by in an environment of a steady flow of hot gas provided by a burner. Fig. 2 shows the oxyacetylene flame test apparatus.

During the ablation test, each specimen of a plate form with 100 mm×100 mm size was exposed to the flame composed of argon. A Chromel-Alumel thermocouple was firmly attached with phenolic resin at the centre of back faces of a specimen in order to
record the temperature variations as a function of time during the ablation test. The distance and the angle between the front surface of the specimen and the nozzle tip of a plasma gun were 40 mm and 90˚, respectively. The flame was of high velocity and pressure at about 2700°C and 15MW/m2 heat flux. The specimen was placed vertically to the flame direction in air by the designed fixture. The burn-through time was measured. The erosion rate was calculated by dividing the specimen thickness or the weight change before and after the test into a burn-through time for each specimen. The average value was taken from the result after repeating the test with several specimens. The erosion rate according to equation 1 was calculated by dividing the specimen thickness before and after the test by a burn through time for each specimen. Where \( E = \frac{d}{b} \) (m/s), \( d = \) thickness of panel (m), and \( b = \) burn-through time (s).

\[ E = \frac{d}{b} \quad (1) \]

The insulation index was obtained from the time reaching the temperature change of 80, 180, and 380°C (from ambient) of the back-face of the specimen divided by the specimen thickness specimen, as follows:

\[ I_T = \frac{t_T}{d} \quad (2) \]

Where \( I_T = \) insulation index at temperature \( T \) (s/m), \( t_T = \) time for back-face temperature changes of 80, 180, and 380°C (s), and \( d = \) thickness of specimen (m). This sample during the plasma flame test is shown in Fig.

\[ F_{bs} = 0.75 \times \frac{P_m}{b \times h} \quad (3) \]

Where; \( F_{bs} = \) short-beam strength (MPa), \( P_m = \) maximum load observed during the test (N), \( b = \) measured specimen width (mm), and \( h = \) measured specimen thickness, (mm).

**III. RESULTS AND DISCUSSION**

**A. Physical and Thermophysical Characteristics**

Physical properties of manufactured composite samples are shown in table 3. As you see, samples cured with Paratoluene sulphonic acid have more void content percent than other samples. This amount for C/P/PVB/PTSA samples is 59.6 % more than C/P composites. Furthermore among C/P composites, those which are manufactured with autoclave technique have more density and void content percent. The cause of void content exist in the structure of composites cured with Paratoluene sulphonic acid is high level of PH in resin and acid mixture that leads to capture of freed water-Formaldehyde vapor in composite, which this vapor itself is a result of exothermic reaction between acid catalyst and methyl-ether meanwhile curing process [9].

We can conclude from the diagram shown in figure 5, that void content is in direct relation with linear erosion rate. The cause of higher erosion rate in C/P samples, despite the fact that their void content is lower, is their strong layers connection and in addition of high thermal conductivity that is more improved in PVB containing samples. In addition, adding PTSA that has not a good effect on linear erosion rate because of its remarkable increasing of void content, decreases the weight erosion rate.
Table 3 Physical properties of manufactured composite samples

<table>
<thead>
<tr>
<th>Characteristics</th>
<th>C/P</th>
<th>C/P/PVB</th>
<th>C/P/PTSA</th>
<th>C/P/PVB/PTSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry weight, g</td>
<td>106.5</td>
<td>115.47</td>
<td>88.67</td>
<td>93.42</td>
</tr>
<tr>
<td>Thickness, mm</td>
<td>8.05</td>
<td>9.03</td>
<td>7.70</td>
<td>8.24</td>
</tr>
<tr>
<td>Bulk density, g/cm³</td>
<td>1.43</td>
<td>1.30</td>
<td>1.11</td>
<td>1.15</td>
</tr>
<tr>
<td>Apparent porosity, %</td>
<td>3.74</td>
<td>5.02</td>
<td>9.10</td>
<td>9.26</td>
</tr>
<tr>
<td>Thermal conductivity, W/mK</td>
<td>0.593</td>
<td>0.1792</td>
<td>0.2281</td>
<td>0.2540</td>
</tr>
</tbody>
</table>

B. Ablation Test Results

Table 4 shows the results of thermal ablation test with plasma torch and oxy-acetylene torch on these four types of composite samples. This table shows the amount of thermal and erosion rate in composite samples with two factors of linear erosion rate (mm/s) and weight erosion rate (gr/s). Linear erosion rate that is obtained by division of sample thickness into passed time till seeing red hale in the back of sample, is the most important factor in study of function manner in ablative heat sinks.

Table 4 Comparison between two effective factors in erosion resistant of composites

<table>
<thead>
<tr>
<th>Composite Type</th>
<th>C/P</th>
<th>C/P/PVB</th>
<th>C/P/PTSA</th>
<th>C/P/PVB/PTSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Erosion Rate in Plasma Torch (mm/s)</td>
<td>0.101</td>
<td>0.0866</td>
<td>0.1108</td>
<td>0.1048</td>
</tr>
<tr>
<td>Erosion Rate in Oxyacetylene Torch (mm/s)</td>
<td>0.119</td>
<td>0.0936</td>
<td>0.1251</td>
<td>0.1122</td>
</tr>
</tbody>
</table>

According to table 4 we can conclude that linear and weight erosion rate in resol base composites reinforced with carbon fabric in plasma torch test are respectively 15% and 20% and in oxyacetylene torch test are respectively 16% and 62% lower than that in one-way fiber reinforced composites. From this fact, we conclude that decrease in carbon/phenolic composites mechanical strength, has a remarkable effect on ablation resistance in this type of composites. Table 5 compares the amount of increase and decrease in factors related to tested composites with both torches by percent.

Table 5 Comparison between increase and decrease of the main factors in ablation test of composite samples with plasma and oxyacetylene torch

<table>
<thead>
<tr>
<th>Sample</th>
<th>Linear Rate Increase From Plasma Torch (mm/s)</th>
<th>Weight Rate Increase From Plasma Torch (gr/s)</th>
<th>Linear Rate Increase From Oxyacetylene Torch (mm/s)</th>
<th>Weight Rate Increase From Oxyacetylene Torch (gr/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C/P</td>
<td>15%</td>
<td>11%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C/P/PVB</td>
<td>7%</td>
<td>0%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C/P/PTSA</td>
<td>11%</td>
<td>52%</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C/P/PVB/PTSA</td>
<td>7%</td>
<td>57%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

According to table 5, we conclude that linear erosion rate for C/P composites under oxyacetylene torch, is 15% more than similar value in plasma test torch. This increase in erosion rate in oxyacetylene torch despite higher thermal flux in plasma torch is result of two things:
1. Increased chemical degradation as a result of the oxygen oxidation agent meanwhile thermal ablation process
2. 33% higher front distance of nozzle from samples’ surface in plasma torch test (30mm) than oxy-acetylene torch test.

CONCLUSION

Three types of carbon/phenolic (CP) composites with PVB and PTSA were fabricated, and their mechanical, thermal and ablative properties were measured. Short-beam shear test indicate that the interlaminar shear Strength of the C/P/PVB composite is 17% greater than that of the other samples. Observations show that presents of 20% PVB has an important effect on proper adhesion between carbon fibers and Resole matrix of C/P composites and achieving to improved interlaminar characteristics.

The ablation test results reveal that composites with 20% polyvinyl Butyral resin (C/P/PVB) have the highest ablation resistance and the erosion rate (mm/s) of these specimens are 20% lower than the other specimens. Additionally the high insulation index of the C/P/PVB samples indicates that these composites are the best ablative materials in the present study. But results show that the mass reduction percentage of C/P/PTSA/PVB samples is around 28% lower than C/P/PVB samples. According to Table 3 addition of PVB to C/P composites caused 70% improvement in the thermal conductivity of C/P/PVB composites.

About samples with 4-7 wt% PTSA, against our expectation, these samples because of porose structure, hadn’t appropriate ablative performance.
REFERENCES

The IEEE citation format is used. Books and book chapters should be referenced as [1] and [2] respectively. Patents are referenced based on [3] and a thesis can be referenced as [4]. Finally, conference presentations/papers and journal papers need to be reference based on [5] and [6] respectively.

With the increasing availability of useful information that can be found on the internet, website references must also be reported based on [7]. Meanwhile, due to the dynamic nature of web pages and the fact that in most cases the information is not peer-reviewed, the use of published resources are very much preferred and advised over online references.

The reference section at the end of the paper should be edited based on the following:


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Mechanical and Abrasive Consideration of Additives Effects on the Carbon Fabric/Phenolic Composites

52