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To cite this article: M Satyanarayana Gupta and Ekta Jha 2018 IOP Conf. Ser.: Mater. Sci. Eng. 455 012041

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Review on Evaluation of properties of carbon phenolic composite structure using gas chromatography for analysis of thermal performance

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Abstract. Carbon-phenolic composites are meant for heat protection of the aerospace structures like aircraft skins, nozzles and heat shields during the aerodynamics loading conditions. Phenolic resin matrix composites are used as ablative liners to resist thermal and erosive environment. The manufacturing process of Carbon phenolic composite structure require curing. During the curing of phenolic matrix components, methylol-phenol and water are evolved as by-products due to condensation polymerization process either in the presence of heat /hardeners. In order to obtain void free component, it is required to remove the by-products by curing the component simultaneously under heat, vacuum and pressure. Therefore autoclave-curing process is the most suitable process for curing of the phenolic resin.

In this review paper, On-line cure monitoring of Carbon-Phenolic Composite Structures by Gas chromatography for wet lay ups and prepreg based components has been studied. Heat of reaction and the volume of chemical species evolved under aerodynamic heating are measured by Pyrolysis gas chromatography (Py-GC) and thermogravimetry (TG), which will be used as inputs for thermal evaluation of the structure. Properties of carbon Phenolic is estimated through this study. USIM software used to visualize properties of surrounding air and carbon phenolic structure.

1 Introduction
Aerospace structures contain multilayer structures to sustain severe aerodynamic loading and heating. Hence they will be made with carbon-epoxy internal layer (as structural layer) whereas carbon-phenolic external layer (as thermal protection layer) as multi layered component. Carbon-phenolic composites are used as thermal protection system for re-entry vehicles which observed high aerothermal loading during its travel. Carbon-phenolic composites are meant for heat protection of the aerospace structures like aircraft skins, nozzles and heat shields during the aerodynamics loading conditions.

Carbon phenolic composites are made of combining two materials one is low density, rigid, carbon fibers impregnated in the phenolic resin. Carbon phenolic act as ablative material for most of the re-entry vehicles due to its desirable properties like ablation temperature ablation is low, effective heat of
Ablation, good thermal insulation characteristics, gasification is desirable property during ablation. Blunt body get heated and large amount of gas generated increasing the thickness of the boundary layer this reduces the heat transfer. Ablation materials have high resistance to thermal and mechanical shock and easy in fabrication of large size.

During manufacture of carbon phenolic shell for RVS, process should be monitored in strict condition. Curing is required for the manufacturing of carbon phenolic composite components. During the curing phenolic is used as a matrix in the components and carbon as reinforcement fibers, methylol-phenol and water are generated as by-products due to condensation polymerization process either in the presence of heat or hardeners. This byproducts are the reason of formation of voids. This voids are dangerous during the performance of components. To obtained void free structures, it is necessary to remove this by products by curing the component simultaneously under heat, vacuum and pressure. Therefore autoclave-curing process is the most suitable process for curing of the phenolic resin.

[1, 2] Gas chromatography is used to study the decomposition of components, chemical structure, thermal properties and reason of char formation. The rate of decomposition action is the function of time and temperature. Chemical species can be identified and quantified by using gas chromatography.[4] Condensation polymerization takes place between phenol and excess formaldehyde in the presence of heat/hardener and methylol phenol and water are formed as byproducts as shown in fig. 1.

**Figure 1** Condensation reaction in phenol resin.

2. Gas Chromatography

2.1 Principle of Gas chromatography

Gas chromatography involves a mixture of gas sample being vaporized and injected onto the head of the chromatographic column. The specimen is transported through the column by the stream of inert, gaseous mobile phase. The individual gasses in the blend are isolated based on the molecular weight of the individual constituents. The constituents are detected with the suitable detectors. The area under the peak gives the corresponding concentration of the constituent. Typical gas chromatograph is shown in the Fig.2.
2.2 Gas distribution and filtering Panel

The carrier gas must be a synthetically dormant gas. Generally utilized gasses incorporate nitrogen, helium, argon, and carbon dioxide. The decision of carrier gas is frequently dependent upon the type of detector, which is utilized. The carrier gas system also contains a molecular sieve to filter water and other impurities.[3] In our present study the gases with the following purity nitrogen (IOLAR-I), hydrogen (IOLAR-II) and for air (XL grade) were used. For running of G.C nitrogen and for continuous generation of flame in Flame Ionization Detector (FID) hydrogen and air should be required. [5]To separate out the impurities from nitrogen, hydrogen and air, these gases were allowing them to travel through filters. The filters used for purification and the corresponding impurities were given in the below figure 3.

3. Result and discussion

The advancement of phenolic resin during the cure is dependent on temperature, initial resin properties, and vacuum/pressure. As curing is in progress, due to condensation polymerization, two types of by products also called as volatiles (Methylol-phenol and water) are evolved. The volatile evolution is a function of pressure/vacuum, temperature, thickness and cure duration of the composite structure.
Figure 4. FID chromatogram for M-phenol component

The chromatogram obtained from FID, analysis of methyl phenol is shown in Fig.4. The area under peak in the chromatogram gives the concentration of the constituent.

Figure 5 TCD chromatogram for water component

The chromatograph obtained from TCD, analysis of water component is shown in the Fig. 5. The area under the peak in the chromatogram gives the concentration of constituent.

Literatures shows, the parameters of the equipment are fixed to obtain the resolved M-phenol and water peaks in the chromatograms. Gas chromatograph is connected with the autoclave for online curing through a stainless steel heated line via two-way valve, suction pump and gas-sampling valve. A set of chromatograms one for M-phenol and the other for water once in every 4 minutes have been acquired and recorded. It is observed that varying the heat and pressure within the autoclave over a specific period of time to cure the composite.
Table 1 Carbon Phenolic (CP) properties

| Property     | Units  | Value  |
|--------------|--------|--------|
| Density      | Kg/m³  | 1400   |
| Specific Heat| J/kg-K | 937.8  |
| Conductivity | W/m-K  | 0.5598 |

The above analysis confirms that the criteria for on-line pressure application is

1. For large resin content, pressure application should be applied at ½ of the peak falling from its highest point with minimum void content.

2. For low void content, pressure application should be applied at 1/3 of the peak falling from its highest point with less resin content.

3. The resin content is improved to 10% by applying this technique to the laminates comparatively with the laminate cured by conventional pressure application at temperature T=80°C.

Implementation of on-line pressure application criterion on wet filament wound C-P shells of re-entry vehicle structures (RVS).

Re-entry vehicle structure (RVS) contains two shells one is the internal C-E shell for bearing mechanical loads and whereas C-P layer is wound on C-E layer for thermal loads bearing during re-entry of the missile. The outer C-P shell is fabricated by filament wound method and cured in the autoclave by following the steps of curing.

1. On the mandrel of C-E back up the carbon roving impregnated in the phenolic resin is wound on the mandrel to the required thickness.

2. Over the wet condition of the component breather layer is kept in wrap around for uniform thermal distribution and minimum bleed out during curing.

3. Entire component along with mandrel assembly was sealed in a vacuum bag and vacuum ports are connected to vacuum pump so that in the closed volume the volatiles can be easily removed during curing.

4. The entire mandrel assembly along with vacuum bag is loaded in the autoclave and cured.

C-P shell wound on C-E back up is cured in the autoclave and the m-phenol evolution curve is monitored and which is shown in the Fig.5.
USIM software is used to study the behavior of carbon phenolic composites structure with respect to re-entry surrounding air. Blunt body shape with general dimension is used to which properties of carbon phenolic given obtained from gas chromatography. The simulation is performed at an altitude of 61 km, with speed 7650 m/s, angle of attack $0^\circ$, free stream density $2.816 \times 10^{-4}$ kg/m$^3$, temperature 244.3 K are used. Effects are studied as below.

The maximum and minimum Kinematic Viscosity is $1.668 \text{ m}^2/\text{s}$ and $0.02392 \text{ m}^2/\text{s}$ respectively. Variation of kinematic viscosity along ablative surface can be observed from the Fig. 7.

| Distance (m) | 0.0  | 0.05 | 0.075 | 0.1  | 0.2  | 0.5  | 1.0  |
|-------------|------|------|-------|------|------|------|------|
| Kinematic Viscosity (Max) m$^2$/s | 0.33 | 0.33 | 0.42  | 0.42 | 0.54 | 0.22 | 0.0649 |
| Kinematic Viscosity (Min) m$^2$/s | 0.5  | 0.5  | 0.5   | 0.5  | 0.5  | 0.088| 0.056 |

Due to excessive heat generated during chemical reaction of the species effect on kinematic viscosity at different station is plotted in the table 3.
Figure 8: 1-D & 2-D Analysis of Molecular weight Average distribution from tip to aft end

In the figure 8 X-axis is the length of the blunt body and Y-axis is the Molecular weight average. Molecular weight average is found maximum at 0.0m. As the molecular weight increases the pores size increases on the surface area creating increase in ablation rate. Initially the molecular weight is less so the ablation rate is also less. The Maximum and minimum molecular weights are 28.8 kg and 17.96 kg respectively. The variation on molecular weight along the ablative surface can be observed from the graph.

Table. 3 Molecular weight Average at different stations.

| Distance (m) | 0.0  | 0.05 | 0.075 | 0.1  | 0.2  | 0.5  | 1.0  |
|--------------|------|------|-------|------|------|------|------|
| Mw(Avg)      |      |      |       |      |      |      |      |
| (Max) (kg)   | 28.8 | 28.8 | 28.8  | 28.8 | 28.8 | 28.8 | 28.53|
| Mw(Avg)      |      |      |       |      |      |      |      |
| (Min) (kg)   | 18   | 18.6 | 18.6  | 19.4 | 18.9 | 22.35| 28.82|

Above visualization shows the variation of molecular weight of the air. It is observed to be constant throughout the length of the blunt body.

Figure 9: 1-D & 2-D Analysis of Thermal Coefficient distribution from tip to aft end

In the figure 9 X-axis is the length of the blunt body and Y-axis is the Thermal Coefficient. Thermal coefficient of carbon phenolic depends on the corresponding temperature of the wall, T=300K. As the wall temperature increases the heat flux rate increases.
The maximum value of thermal coefficient obtained is 0.2522 W/mk. The minimum value obtained is 0.0211 W/mk. The variation of thermal coefficient along the surface of the blunt body can be observed from Fig. 9.

Table 4 Thermal Coefficient at different stations

| Distance (m) | 0.0  | 0.05 | 0.075 | 0.1  | 0.2  | 0.5  | 1.0  |
|--------------|------|------|-------|------|------|------|------|
| Thermal Coefficient (Max) W/mk | 0.25 | 0.24 | 0.235 | 0.235 | 0.235 | 0.177 | 24.58 x 10^{-3} |
| Thermal Coefficient (Min) W/mk  | 0.047 | 0.047 | 0.047 | 0.047 | 0.047 | 0.139 | 21.15 x 10^{-3} |

Variation of thermal coefficient at different location is plotted in the table 4. This effect the heat transfer rate through the body. It is observed that from tip to aft thermal coefficient is changing. At the nose of the blunt body aero thermal load is high this cause more heating and ablation.

Figure 10.1-D & 2-D Analysis of Specific heat at constant pressure distribution from tip to aft end

In figure 10 X-axis is the length of the blunt body and Y-axis is the Specific heat at constant pressure. Specific heat at constant pressure are obtained from simulation case with a wall temperature of 300K. Thus depicting the cold wall heat flux for that location.

Maximum and minimum Specific heat at constant pressure is 1288 x 10^3 J/kg-K and 1007 x 10^3 J/kg-K resp.

Table 5 Specific heat at constant pressure at different stations.

| Distance (m) | 0.0  | 0.05 | 0.075 | 0.1  | 0.2  | 0.5  | 1.0  |
|--------------|------|------|-------|------|------|------|------|
| CP Avg (Max) x 10^3 J/kg K | 1.28 | 1.26 | 1.245 | 1.235 | 1.255 | 1.137 | 1.00915 |
| CP Avg (Min) x 10^3 J/kg K | 1.01 | 1.01 | 1.01 | 1.01 | 1.01 | 1.076 | 1.00880 |

The specific heat at constant pressure at different location is shown in the table 5. At the tip it is observed 1.28 x 10^3 J/kg K with small variation to the aft it is observed 1.00915 x 10^3 J/kg K.

4. Conclusion
Heat of reaction and nature of Pyrolysis gases studied using gas chromatography. On-line cure monitoring of carbon-phenolic composites was done successfully by gas-chromatography technique. Studies on laminate levels confirm the on-line pressure application criteria as
1. High resin content → pressure application at ½ fall of peak

2. Low void content → pressure application at ⅓ fall of peak

The behavior study of aero thermal load on Carbon Phenolic composite structure during re-entry of blunt body is successfully done using USIM software. Study of effect of aerodynamic loads on parameters like thermal coefficient, specific heat, molecular weight, thermal diffusivity is done using USIM software. With the help of this observation ablation rate of carbon phenolic can be predicted.

References
[1] L.-H. Meng, Y.-D. Huang, G.-H. Wu 2002 Decomposition of carbon fiber/phenolic composites using supercritical water J. ResearchGate 19. 37-41.
[2] Shujuan Wang, Xiaolong Xing, Ya’nan Wang, Wen Wang, Xinli Jing 2017 Influence of poly (dihydroxybiphenyl borate) on the curing behaviour and thermal pyrolysis mechanism of phenolic resin J. Polymer Degradation and Stability 144. 378-391.
[3] Kammari Veera Brahmam, Vemana Venkateswara Rao 2014 Development of Non-contact NDE Method for Autoclave Cure Monitoring of Carbon-Phenolic Re-entry Shells of Missiles by On-line Gas Chromatography Technique J. The e-Journal of Nondestructive Testing. 20. 6.
[4] K. Veera Brahmam, V. Venkateswara Rao 2015 Gas chromatography: A new method of non-contact NDE for cure monitoring of carbon-phenolic composites for determination of the gelation region for pressure application J. Russian Journal of Nondestructive Testing 51. 379–385.
[5] K Veera Brahmam, V Venkateswara Rao 2017 Gas chromatography: A novel and new technique for on-line cure monitoring studies of carbon-phenolic composite structures J. Journal of Chromatography & Separation Techniques 8.5.