ABLATION PERFORMANCES OF CARBON COMPOSITE BASED ON DIFFERENT RESINS UNDER SEVERE AERO-THERMAL FLUX

E. ARNAUD[1,2], D. HALM[1], D. BERTHEAU[1] and J. BEAUDET[2]

[1] P' Institute, DPMM, ISAE ENSMA, 86360 Chasseneuil du Poitou, FRANCE
Email: emeline.arnaud@ensma.fr
[2] NAVAL GROUP Research, Rue de l'Halbrane, 44300 Bouguenais, FRANCE

Keywords: Thermal Protection Systems, Ablation, Carbon Composites

Abstract
Carbon reinforced composites are widely used as thermal protection systems for space and defense applications. Phenolic resin is the most commonly used matrix because of its high degradation temperature and its massive carbon content. However, phenolic resin has numerous drawbacks such as a complex industrial processing, its cost and its toxicity. The development of an alternative thermal protection system based on another type of matrix would be a significant progress. Therefore, different alternative composites have been tested. In this paper the ablative behavior of a carbon reinforced phenolic composite, considered as the reference, is compared with that of a carbon/epoxide composite, of a carbon/flame retardant epoxide composite and of a carbon/silicone composite. The materials have been tested on two different benches: on the first one, the aggression is mostly thermal; on the second one, the samples are exposed to a severe aero-thermal flux. It reveals that phenolic matrix has a good resistance to a severe aero-thermal load but the flame retardant epoxide and silicone composites could be as efficient as phenolic in less severe conditions.

1. Introduction

Composites based on phenolic matrix are widely used in thermal protection systems for defense and aerospatial applications and have been deeply studied in the literature. Numerous researches have been carried out on phenolic composite for thermal protection systems. The materials used for the reinforcement are various as well as the architecture of the reinforcement. Concerning the materials, carbon is one of the most commonly used [1-6] but to handle oxidation concerns above 500°C, silica, basalt [7] or glass [8] fibers are used as well. Regarding the architecture, the possibilities are several from the unidirectional fiber to 3D fabric [5] through the nano reinforcements [1-3,8], powders, short fibers [2,4] or felts [6]. As a general remark, examples are easy to find concerning the impact of the reinforcement (content, type, and architecture) on the ablative performances of composite. However, studies comparing composite materials having the same type of reinforcement and different matrix are rarer. The high degradation temperature of phenolic matrix and its massive carbon content are good reasons to select it. But its cost, its toxicity and the complexity of industrial processing leads to look for alternative matrix. In this study, the ablative properties of phenolic/carbon composites were compared with epoxy, flame retardant epoxy and silicone. The aim, here, is to know if it could be possible to replace phenolic matrix by another one, and if so, to what extent. In order to respond to this question, the materials have been tested on a thermo-gravimetric analyzer (TGA) and then their ablative behaviors have been characterized under oxygen-acetylene torch and on a larger scale bench, equipped with a jet nozzle.

2. Tested materials and methods

2.1. Materials

Table 1 gives the names and compositions of the six tested materials composed of four different matrices and two different carbon reinforcements. All the materials have the same reinforcement ratio.

Table 1. Denomination and composition of the different tested materials.

Matrix \ Reinforcement	Phenolic	Epoxy	Flame retardant epoxy	Silicone rubber
Carbon powder	-	B - CP	C - CP	D - CP
Short carbon fiber	A - SCF	B -SCF	C - SCF	-

Due to mixing and curing problems, phenolic composite reinforced with carbon powder and silicone rubber reinforced with short carbon fibers have not been tested. The flame retardant epoxy used in C-CP and C-SCF is based on the same matrix as the epoxy (B-CP and C-SCF) with addition of flame retardant particles

2.2. Thermo-Gravimetric Analysis (TGA)

The chemical degradation of the composites has been evaluated by thermo-gravimetric analysis. The sample's initial weights were between 15 and 25 mg. The heating rate has been set as 5°C/min from 30°C to 900°C for all the experiments. The tests have been carried out under air atmosphere.

2.3 Ablation behaviour under thermal flux

The ablation behaviour under a thermal flux has been assessed with an oxygen-acetylene torch. The flux, here, is considered to be essentially thermal. The characterization of the ablative and thermal properties with an oxy-acetylene torch is a usual test [1,4-5,9] and the experimental setup is described in the ASTM E-285 Standard [10]. The settings chosen for the experiments are given in Table 2.

Table 2. Setting of the oxygen-acetylene torch

Estimated temperature	Torch diameter	Pressure (bar)		Flow rate (Ln/h)	
(°C)	(mm)	O_2	C_2H_2	O_2	C_2H_2
3000	1.1	2	0.3	120	100

The gas stoichiometry has been chosen to enhance the flame temperature, around 3000°C according to the Air Liquide Documentation [11]. The samples have been exposed at a distance of 15 mm from the torch. The samples are few centimeters large. The mass loss rates have been evaluated by weighting the samples before and after the tests.

2.4 Ablation behaviour under severe aero thermal flux

The ablative behaviour under severe aero thermal flux has been tested on the MARTEL bench. This unique facility in Europe takes place in CEAT, P' Institute, France. As shown in Figure 1., the MARTEL bench is equipped with a jet underexpanded nozzle. The pressure is 30 bar and the temperature 1900°C at stagnation point. The combustion is made with a mix of air and hydrogen. The speed is equal to Mach 3 at the exit of the nozzle. Large samples (few tens of centimeters) and structures can be tested.

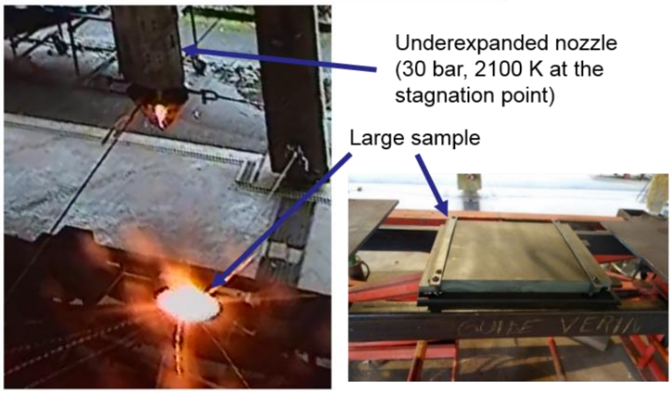

Figure 1. MARTEL facility.

The test sequence is the following one. The jet nozzle is ignited, the sample is protected by heat-resistant steel plates until the jet is stabilized. Then, the steel plates are opened thanks to hydraulic cylinders. The sample is exposed for a chosen time. And finally, the steel plates are closed and the jet shut down. As for the oxy-acetylenic bench, the mass loss has been measured. In addition, a laser-profilometer has been used to measure the ablation profile in general and the ablation depth in particular. The exposure times cannot be automatically controlled on this bench. They have been measured, thanks to the videos of the experiments. Differences of few seconds of exposure have been observed. Consequently, the mass loss rate and ablation rate have been calculated by dividing the mass loss and the ablation depth by the exposure time, in order to interpret consistently the results.

3. Results and discussions

3.1. TGA

Figure 2 presents the results of the thermogravimetric analysis. The relative mass loss and the relative mass loss rate are plotted in the first and the second graph respectively.

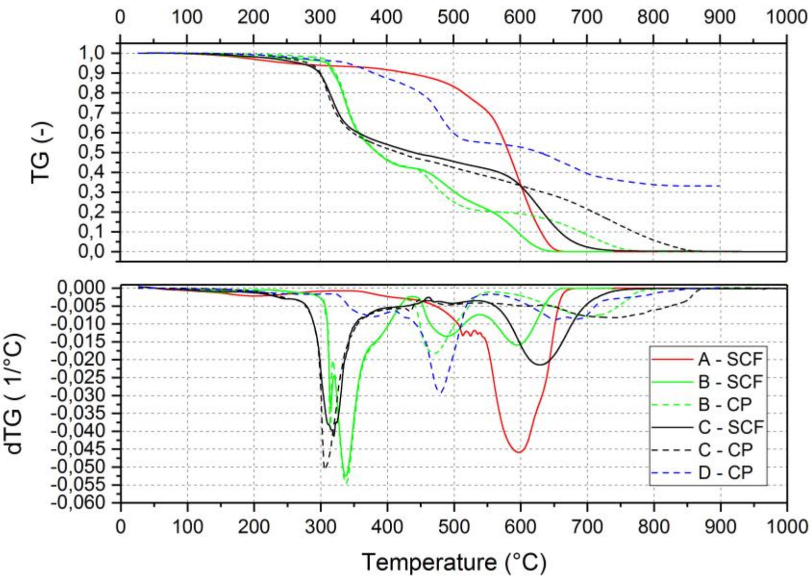

Figure 2. TGA results, 5°C/min heating rate from 30°c to 900°C

Concerning the matrix:

- for the epoxy matrix, B –SCF and B-CP composite, the maximum of the degradation occurs around 300°C
- the flame retardant additives in the epoxy (composites C –SCF and C-CP) rise by 50°C the degradation temperature in comparison with the epoxy without additive.
- silica presents in the silicone rubber is still present at 900°C (about 35% of the initial mass), silicone rubber is the only one tested material for which the degradation is not total. The principal degradation peak occurs at 475°C
- phenolic matrix has the higher degradation temperature, small degradation peaks appear at 250°c and 450°C but the major degradation starts around 550°C.

TGA shows as well, an impact of the reinforcement. Indeed, composites reinforced with carbon powder seems to last longer. The degradation of the reinforcement occurs around 625°C for the carbon fiber and around 700°C for the carbon powder.

3.2. Ablation behaviour under thermal flux

Figure 3 presents the mass loss observed after exposure under the bench equipped with an oxy-acetylenic torch.

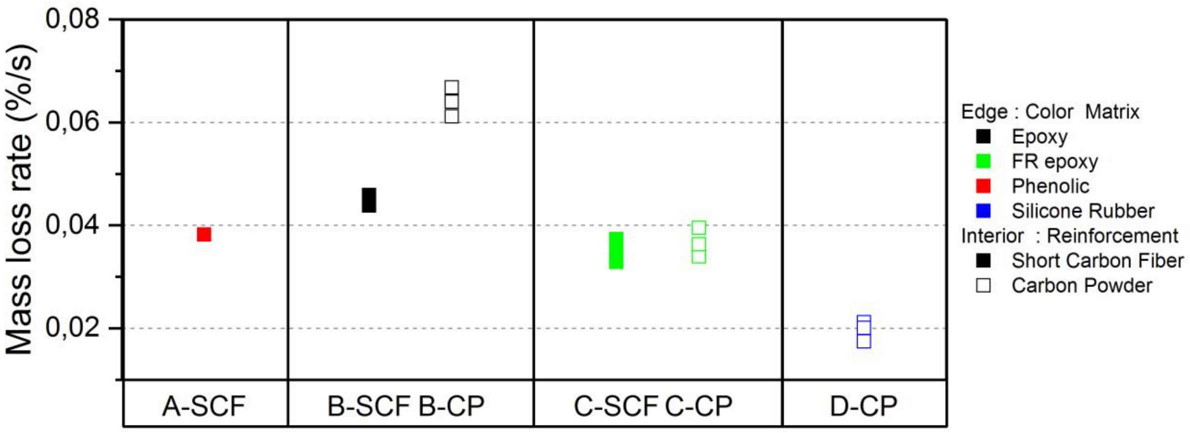

Figure 3. Mass loss (%) after a 90s-exposure under an oxygen-acetylene torch

The mass losses of materials A-SCF, B-SCF and C-SCF are comparable. However, the material D-CP performances are twice better. Except for the silicone rubber composite, D-CP, the carbon powder reinforcement degrades the performances of the composite. It is particularly true for the composite based on epoxy.

Looking at the results obtained under the oxy-acetylenic torch, materials B-SCF, C-SCF and D-CP could be good candidates to replace phenolic matrix.

3.3. Ablation behaviour under severe aero thermal flux

Figure 4 presents the mass loss rate and ablation rate obtained after exposure under MARTEL test bench. The mass loss rate is in percent of the initial mass and the ablation rate in percent of the initial thickness.

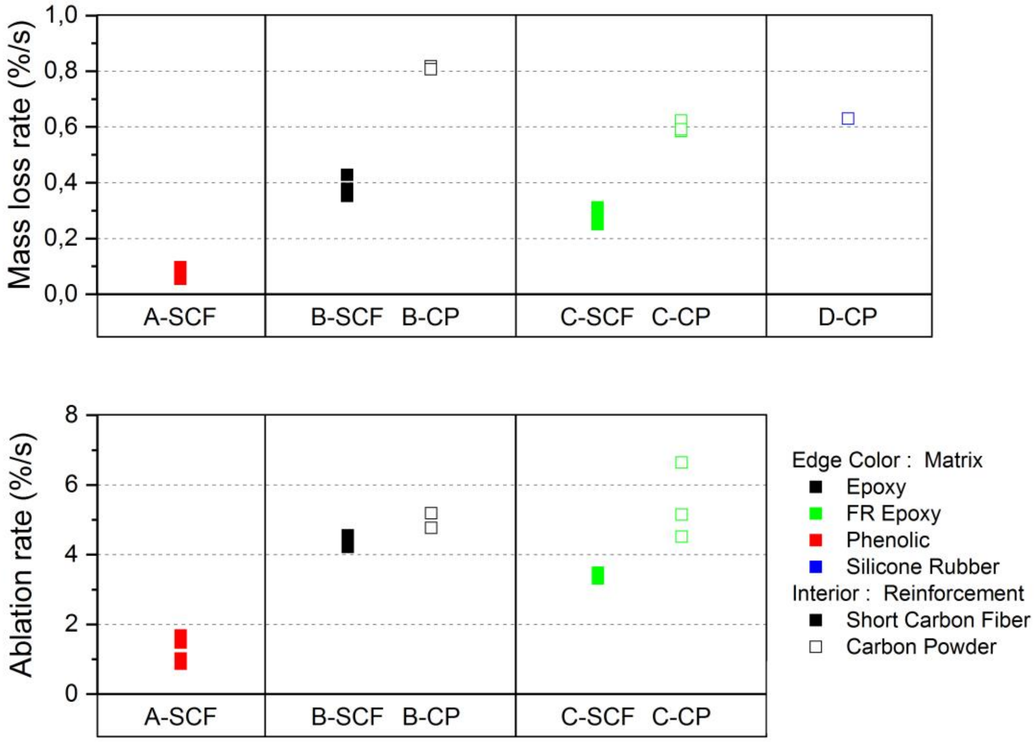

Figure 4. Mass loss rate and ablation rate after exposure on MARTEL test bench.

Firstly, as under the oxy-acetylenic torch, Figure 4 highlights the impact of the reinforcement-size. The composites reinforced with carbon powder are less efficient. The cohesion of the char is primordial under an aerothermal flux and it seems that the carbon fibers bring cohesion and adhesion between the char and the virgin material.

Secondly, the A-SCF composite is clearly more competitive. The mass loss rate and the ablation rate of A-SCF are the lowest of the tested materials. The omnipresence of phenolic composites in thermal protection systems is well understandable, when looking at the performances of the material A-SCF under the MARTEL test bench. The addition of the flame retardant charges in C-SCF and C-CP improves the ablation behaviour in comparison with B-SCF and B-CP.

Thirdly, large cracks appeared in the silicone rubber samples. The mass loss was evaluated for the only sample stayed in one part during the test. But the ablation profile was impossible to analyze. It seems that the material is subject to mechanical damages in addition of the thermal degradation. The mechanical damages are probably due to a low stiffness, which leads to high deformations and rupture.

3.4. Discussions

The link between the three experimental setups is not trivial. The results are not consistent, the performance of a material is not the same on the three benches. It shows the difficulty to assess the ablative behaviour of the material with a reduced number of experimental setup. Each of the three experimental setups brings a different type of information.

Concerning the type of reinforcement, on TGA, the carbon powder tends to increase the degradation temperature. The contrary is observed under the oxy-acetylenic torch and under MARTEL bench. The carbon powder reinforcement deteriorates the ablative performances of the phenolic carbon reinforcement composite, but it is not revealed by TGA. The improvement of the degradation temperature provided by the carbon powder is not enough to balance the lack of cohesion due to the small size of the reinforcement.

Regarding the matrix type, the comparison of the results under the oxy-acetylenic torch with the results obtained on MARTEL bench highlights the importance of the aerodynamical loading. Ablation performances are often evaluated with an oxy-acetylenic torch. But, the use of a larger scale bench as MARTEL bench reveals that the ablation behaviour of a carbon composite under a severe flux cannot be extrapolated from experiments made on an oxy-acetylenic bench. In this study, short carbon fiber composite show equivalent performances under the oxy-acetylenic bench. But the phenolic based composite turns to be much more efficient under an aerothermal flux than the other tested materials. The char of epoxy and flame retardant epoxy are probably cohesive enough to withstand the thermal flux of an oxy-acetylenic torch but too weak for an aerothermal aggression. Under MARTEL test bench, the erosion is enhanced and the strength of the char become primordial.

5. Conclusions

The mass loss rate of several carbon-reinforced composite exposed to three different thermal solicitations has been measured. Experiments at different scales in terms of samples size but as well in terms of severity of the loading have been done.

For critical structures withstanding severe aero-thermal fluxes, no alternative material seems to show performances as efficient as those of the phenolic matrix. However, in the case of only-thermal solicitation, the phenolic matrix could be replaced by an epoxy or a silicone rubber.

Investigations to understand the variations of performance observed on the oxy-acetylenic bench and on MARTEL bench needs to be carried out. Post- mortem observations are in process, in order to propose degradation scenarios for the both benches.

References

[1] Naderi, S. Mazinani, S. J. Ahmadi, M. Sohrabian et R. Arasteh. Modified Thermo-physical properties of phenolic resin/carbon fiber composite with nano zirconium dioxide. *Journal of Thermal Analysis and Calorimetry*, vol. 117, pp. 393-401, 2014.

[2] Park, Joung-Man, Kwon, Dong-Jun, Wang, Zuo-Jia, Roh, Jeong-U, Lee, Woo-Il, Park, Jong-Kyoo, & Lawrence DeVries, K. Effects of carbon nanotubes and carbon fiber reinforcements on thermal conductivity and ablation properties of carbon/phenolic composites. *Composites Part B : Engineering*, vol 67, pp 22-29, 2014.

[3] Wang, Zuo-Jia, Kwon, Dong-Jun, Gu, Ga-Young, Lee, Woo-Il, Park, Jong-Kyoo, Lawrence DeVries, K., & Park, Joung-Man. Ablative and mechanical evaluation of CNT/phenolic composites by thermal and microstructural analyses. *Composites Part B : Engineering*, vol. 60, 597-602, 2014

[4] Y. Chen, P. Chen, C. Hong, B. Zhang et D. Hui. Improved ablation resistance of carbon-phenolic composites by introducing zirconium diboride particles. *Composites : Part B*, vol. 47, pp. 320-325, 2013.

[5] C. Hong, J. Han, X. Zhang, H. David, W. Li, Y. Chen et S. Du. Novel phenolic impregnated 3D fine-woven pierced carbon fabric composites, microstructure and ablation behavior. *Composites: Part B*, vol. 43, pp. 2389-2394, 2012.

[6] Covington, M. A., Heinemann, J. M., Goldstein, H. E., Chen, Y.-K., Terrazas-Salinas, I., Balboni, J. A., Olejniczak, J., & Martinez, E. R.. Performance of a Low Density Ablative Heat Shield Material. *Journal of Spacecraft and Rockets*, 45(4), 854-864, 2008.

[7] Li, Weidong, Cao, Hailin, Chen, Guodong, & Shi, Pengfei. Preparation and Characterization of BFReinforced Phenolic Resin-based Composites. *Journal of Advanced Materials*, 42(3), 67-73, 2010.

[8] Natali, Maurizio, Monti, Marco, Kenny, José Maria, & Torre, Luigi. A nanostructured ablative bulk molding compound : Development and characterization. *Composites Part A : Applied Science and Manufacturing*, 42(9), 1197-1204, 2011

[9] X.-T. Shen, K. Li, H. Li, Q.-G. Fu, S.-P. Li et F. Deng. The effect of zirconium carbide on ablation of carbon/carbon composites under an oxyacetylene flame. *Corrosion Science*, vol. 53, pp. 105-112, 2011.

[10] ASTM E-285. Standard Test Method for Oxyacetylene Ablation Testing of Thermal Insulation Materials, 2002.

[11] Air Liquide Welding, "Cemont Catalogue Général Soudage", AirLiquide, 2015.