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Mechanical, thermal and ablative properties of zirconia, CNT modified carbon/phenolic composites

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ABSTRACT

Zirconium oxide (Zirconia) coating on carbon fabric (C-fabric) was developed by using zirconia sol. C-fabrics having different weight percentages (wt%) of zirconia namely 0 wt% (Blank), 3.5 wt%, 6.5 wt% and 9.5 wt% were used to make Zirconia–Carbon–Phenolic (Zr–C–Ph) composites. Similarly, 0.5 wt% multiwalled carbon nanotube (CNT) dispersed phenolic resin was used to make CNT–C–Ph composite. Thermal conductivity, ILSS and flexural strength were measured for the prepared composites. Based on the initial results, subsequently a functionally graded carbon–phenolic composite (FG-C–Ph) having CNT–C–Ph composition up to certain thickness followed by Zr–C–Ph composition for the remaining thickness was made. Thermal insulation and ablative properties for blank C–Ph, Zr–C–Ph, FG-C–Ph were studied using plasma arc jet test which was carried out at a heat flux of 4.0 MW/m^2 for 30 s. Results from the plasma arc jet test show that, the temperature drop across the Zr–C–Ph composite was found to be highest while it was least for the blank. However the ablation rate was found to be highest for the FG-C–Ph while it was least for the blank. Ablation mechanisms for all the tested composites are proposed based on the SEM and XRD studies.

1. Introduction

Rayon carbon fabric reinforced phenolic (C–Ph) composites are widely used as thermal protection systems (TPSs) for aerospace applications due to the low thermal conductivity of the rayon based carbon fabric and the high char yielding properties of the phenolic matrix [1–3]. Many research groups attempted to reduce the thermal conductivity of the C–Ph composites further, as it can offer significant weight saving for the aerospace systems. It is reported that, the spun yarn carbon fibers carbonized at low temperature can bring down the thermal conductivity of C–Ph composites significantly besides imparting better interfacial and ablative properties [4]. Silicone based anti-ablation coatings on TPS, which can form oxidation resistant silica layer during ablation and silicone polymer based ablative composites which can undergo cermetisation during ablation forming tough oxidation resistant ceramic layer were explored by different research groups [5,6]. On the other hand, addition of various nano materials like, nano silica, montmorillonite (MMT) nanoclays, polyhedral oligomeric silsesquioxane (POSS) to C–Ph composites are widely reported to reduce the thermal conductivity of the Phenolic composites besides reducing the ablation rate [7,8]. Though, zirconia (ZrO_2) is known as better thermal insulator than silica, it was not explored much, as additive to C–Ph composites to reduce thermal conductivity. Recently, Chen et al. reported that addition of zirconium diboride to C–Ph composites can significantly improve their thermal insulation properties during ablation. This is primarily due to formation of insulating zirconia layer in the C–Ph composite during oxidative decomposition of zirconium diboride [9]. Though, it is now well established that, ceramic additives can bring down the thermal conductivity of C–Ph composites, they pose new problems such as poor inter laminar shear strength (ILSS) especially at higher loadings which results in the delamination of the composites [7]. It is essential for TPS to have a good inter laminar shear strength to resist the mechanical erosion due to high velocity aerodynamic shearing exerted by the harsh environments that they are generally exposed to. On the other hand, carbon nanotubes (CNTs) and nano-fibers are reported to enhance ILSS of the C-fiber reinforced polymer matrix composites [10,11]. So far, limited studies have been reported on the effect of the ceramics and CNTs addition to C–Ph composites on their thermomechanical and ablative performance [7,12–14]. Developing zirconia coating on C-fabrics and using them as reinforcements to obtain low thermal conductive TPS is a novel concept

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which is not explored so far by any research group. This study is aimed (i) To develop zirconia coating on the C-fabric, and to study the mechanical, thermal and ablative properties of phenolic composites made out of these fabrics, and (ii) To study whether enhanced flexural strength and shear strength of C–Ph composites due to CNTs can result into reduction in ablation rate.

2. Experimental work

2.1. Zr–C–Ph composite fabrication

Zirconia sol was prepared by mixing zirconium oxy chloride, ethanol and demineralized water in the molar ratio of 0.05:8:1.1 and stirring the mixture for one hour with a magnetic stirrer at room temperature. This sol was applied on the surface of the rayon carbon fabric (C-fabric) with the help of a spray gun and allowed to dry at room temperature (approximately 96 h) till the coated fabric attained the constant weight. Expected yield of the zirconia coating from the sprayed sol was calculated by using Eq. (1).

$$ZrOCl_2 + H_2O \rightarrow ZrO_2 + 2HCl \quad (1)$$

Thus, four different compositions of zirconia coated C-fabrics (Zr–C-fabrics) having zirconia weight percentages (wt%) of 0.0 wt% (blank), 3.5 wt%, 6.5 wt% and 9.5 wt% were made by selecting the amount of the sol sprayed. Coating morphology on the Zr–C-fabrics was studied with scanning electron microscopy (ESEM-FEI Quanta 400, The Netherlands). Resol based phenolic resin was applied on the Zr–C-fabrics followed by drying at room temperature for 48 h to allow partial curing to get prepregs (Zr-C-prepregs). Zr–C-prepregs were cut into 150 mm × 150 mm pieces (approximately 60 layers) and stacked up (job) followed by curing in an autoclave. Typical cure cycle involved raising the temperature of the job up to 120 °C and then soaking the job for 120 min. 5 bar pressure was applied on the job at the time of gelling. Subsequently temperature was raised to 180 °C and maintained for four hours under the same load. Thus, four different Zr–C–Ph composites of approximate 20 mm thickness were prepared with 0.0 wt% (blank), 3.5 wt%, 6.5 wt% and 9.5 wt% Zr–C-fabrics. Representative samples were collected from the laminates to measure density and fiber volume fraction (%V_f).%V_f was measured as per ASTM D 3171.

2.2. CNT-C–Ph composite fabrication

0.5 wt% of Multiwalled carbon nanotubes (CNTs) which were amino functionalised were added to phenolic resin and ball milled for 3 h at 250 rpm to ensure better dispersion of the CNTs in the resin. This CNT-resin mixture was applied on the C-fabric and allowed to dry at room temperature for 48 h to allow partial curing to get prepregs (CNT-C-Prepreg). CNT-C-prepreg was cut into 150 mm × 150 mm pieces. These pieces were stacked up followed by curing similar to the curing process mentioned for Zr–C–Ph composites.

2.3. FG-C–Ph composite fabrication

Based on the subsequent thermal and mechanical characterization of the composites made in Sections 2.1 and 2.2, a FG-C–Ph composite was fabricated by using the combination of CNT-C-prepregs and Zr–C-prepregs made with 6.5 wt% zirconia coated C-fabric. To prepare the FG-C–Ph composite, initially nine layers of CNT-C-prepregs were stacked up, over which approximately 40 layers of Zr–C-prepregs were stacked. Curing cycle employed was similar to the curing cycle adopted for Zr–C–Ph composites. In the finished composite, approximately 3 mm from the top was having CNT–C–Ph composition while the rest 17 mm of the composite was having Zr–C–Ph composition. Samples from this composite were tested only for ablation properties.

3. Characterization

3.1. Flexural strength and ILSS

Specimens of size 5 × 10 × 100 mm and 5 × 10 × 50 mm were collected for flexural strength and ILSS tests respectively from the prepared composites. Flexural strength was measured as per ASTM D 790 while ILSS was measured as per the ASTM D 2344 using universal testing machine (United, Model STM 50 KN, USA). Minimum five number of samples were tested for each property and the average values are shown in Table 1. Tested samples were analyzed with field emission scanning electron microscope (FES-EM, Model FEI, Quanta 200, USA).

3.2. Thermal conductivity

Cylindrical specimens of diameter 25 mm and height 5 mm were machined from the prepared composites. Thermal conductivity in the through thickness direction was measured at 300 °C under steady state conditions as per ASTM E1225-99 using hot guard method. Two samples from each of the composite were tested and the average values of the thermal conductivity of the two samples is shown in Table 2.

3.3. Plasma arc jet test

Cylindrical specimens of diameter 10 mm and height 17.6 mm (±0.1 mm) were machined from the blank C–Ph, Zr–C–Ph and FG-C–Ph composites. Length of the specimens was kept perpendicular to the direction of the fabric layup. Test specimen was encircled with the guard ring which was also machined out from the same composite. Guard ring was employed to ensure unidirectional exposure of the test specimen to the plasma arc jet. 'K' type thermocouple was bonded to the rear surface (away from the surface facing the plasma arc jet) of each specimen to measure back face temperature. A schematic of the test specimen configuration is shown in Fig. 1a. Specimens were exposed to the plasma arc jet at a flame velocity of about 1 mach having a stagnant flux of 4.0 MW/m^2 for 30 s (Fig. 1b). Raise in back face temperature is continuously recorded as a function of time. Though the plasma jet was switched off after 30 s of test duration, back face temperature was recorded up to 70 s. In case of FG-C–Ph, test specimen was oriented in such a way that, CNT–C–Ph part of the composite faced the plasma jet while the back face temperature measured was for Zr–C–Ph part of the composite. Ablation rate was determined by dividing the reduction in length of the specimen with the test duration in seconds. Average back face temperature and ablation rate was determined based on the average of two samples. Obtained values are shown in the Table 3. Microstructure of the ablated surfaces was studied with FESEM. Compositional changes resulted due to ablation was studied with X-ray diffraction

Table 1
Physical and mechanical properties of the composites.

Sample description	Density (g/cc)	%V_f	[a]F.S (MPa)	ILSS (MPa)
Blank C–Ph	1.44	53	225(22)	20(1.0)
3.5 wt.%Zr–C–Ph	1.40	50	222(36)	19(2.8)
6.5 wt.% Zr–C–Ph	1.25	37	146(10)	14(2.9)
0.5 wt% CNT-C–Ph	1.42	51	262(21)	22(2.1)

[a] Flexural strength, values in the parentheses are standard deviations.