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Nano silica modified carbon–phenolic composites for enhanced ablation resistance

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High ablation resistant carbon–phenolic (C–Ph) composites were fabricated by the addition of nano silica powder and tested under plasma arc jet at a flux of 2.5 MW m^{-2}. Nano silica C–Ph composites exhibited much higher ablation resistance compared to conventional C–Ph composites under similar conditions. Microstructure and X-ray diffraction studies reveal that nano silica reacts with char at high-temperature, forming ablation resistant silicon carbide phase. The mechanism of in situ siliconization and the thermophysical properties of the C–Ph composites are discussed.

Keywords: Nano silica; Fiber reinforced composites; Erosion; Thermal conductivity

Ablation is an endothermic and erosive process which involves complex physical and chemical reactions. Phenolic resin reinforced with rayon-based carbon-fabric has been a popular ablative material for rocket nozzles. Phenolic resin is the preferred matrix material due to its ability to form char efficiently during endothermic pyrolysis [1,2]. Rayon-based carbon-fabric is preferred as reinforcement due to its ability to resist high-temperature erosive aerodynamic shear forces because of its high thermal stability, low thermal conductivity and higher interlaminar shear strength (ILSS) in the composite form [3]. However, there is always an urge to improve the ablation resistance of carbon–phenolic (C–Ph) composites further to realize relatively thinner ablative composite structures to reduce the overall weight of aerospace systems. A number of recent investigations have used carbon nano fibers, nano clay additives in phenolic resin [4,5], silicone resin-based anti-ablation coatings [2], or changes in the weave patterns of carbon-fabric [6] to improve ablation resistance. The effect of various matrices and their microstructures on ablation properties has also been reported [7]. Published data in this area is limited as many patents [8–11] have been filed due to the significance of immediate applications. However, most of the patents reported complex composite processes leading to complex infrastructure requirements.

In this work efforts were made to develop simpler methods to improve the ablation resistance of C–Ph composites.

The aims of this paper are: (1) to study the effect of nano silica addition on the ablation resistance, ILSS and thermal conductivity of C–Ph composites; (2) to study the microstructure of the ablated specimens to understand the mechanisms operating during ablation.

Rayon-based carbon-fabric supplied by M/s AMPL, Coimbatore, was used as the reinforcing material; resol-based phenolic resin supplied by M/s ABR Organics, Hyderabad, was used to realize the matrix. Nano silica powder having an average size of 40–50 nm supplied by M/s Chemapal Industries, Mumbai, was used as ablation-resistant filler.

Nano silica powder was added to the phenolic resin and stirred. Four different mixtures were prepared by adding 0.0 (blank), 0.5, 2.0 and 4.0 wt.% of nano silica powder in the phenolic resin. Viscosity of the mixture was controlled in the range of 250–300 cp (measured by a Brook–Field viscometer at 20 rpm, 30 °C) by adding ethanol. Each of the above compositions were applied to carbon-fabric with a brush and allowed to dry at room temperature to form prepegs. These were cut

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into 150 mm × 150 mm pieces, stacked up and cured in an autoclave at 120 °C for 2 h, followed by 4 h curing at 180 °C and 5 bar pressure. Thus four different composite laminates (blank, 0.5, 2.0 and 4.0 wt.% nano silica C–Ph) were realized. Representative samples were collected from the composite laminates to measure the fiber volume fraction (ASTM D 3191-09) and density.

Six specimens of size 5 × 10 × 60 mm were prepared from each laminate. ILSS was measured as per ASTM D 2344 at room temperature using UTM (United, Model STM 50 KN, USA).

Specimens of 25 mm diameter × 5 mm were machined out from each laminate. Thermal conductivity in the through-thickness direction was measured at 300 °C under steady-state conditions as per ASTM E–1225-99 with in-house-developed equipment.

Three samples from each of the laminate were machined to a size of 10 mm diameter × 20 mm. The length of the sample was perpendicular to the direction of the fabric layup. Samples were encircled with the guard rings which were made up of the same compositions as that of the test specimens. The guard rings ensured unidirectional exposure of the test specimens to the plasma arc jet. Specimens were exposed to a plasma arc jet at a flame velocity of about 1 mach and a stagnant flux of 2.5 MW m^{-2} for 20 s (Fig. 1). Ablation rate was determined by dividing the weight loss during the test by the arcing time in seconds. Average rate was determined after repeating the test for three specimens from each laminate. Microstructure and compositional changes resulted due to ablation were studied using environmental scanning electron microscopy (ESEM, FEI Quanta 400, The Netherlands) and X-ray diffraction (XRD, Philips PWD, Model 1830, The Netherlands).

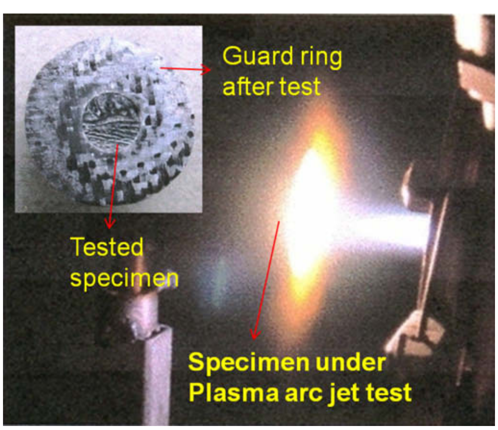

Figure 1. Composite specimen testing under plasma arc jet.

Microstructure studies of the representative prepeg samples reveal that nano silica loaded resin forms a thin and uniform layer on the fabric surface. Nano silica, due its higher surface area, could cover the entire surface of the carbon fibers even at the 0.5 wt.% loading in the phenolic resin. As the loading of nano silica increased, the compressibility of the prepegs during curing reduced. This resulted in the reduced volume fraction of the reinforcement (V_f) in the finished composites (Table 1). ILSS is found to increase with percentage nano silica addition up to 2.0 wt.%, beyond which it decreased (Table 1). This shows that nano silica layer on the carbon-fabric resisted the slippage of different layers against applied shear forces. However, at 4.0 wt.% loading of nano silica, reduction in the ILSS of C–Ph composites can be attributed to the poor adhesion between the fabric layers as higher amounts of nano silica would have prevented formation of the continuous matrix network while the gaseous by-products escaped during curing. Enhanced ILSS makes the composites more resistant to the high aerodynamic shear forces and is expected to result in enhanced ablation resistance.

Plasma arc jet test results are summarized in Table 1. Similar to the ILSS values, ablation resistance also increased with nano silica addition up to 2.0 wt.%, beyond which it was substantially lower, indicating the significance of retaining the minimum ILSS for C–Ph composite while altering them with ceramic fillers.

Nano silica addition brought down the thermal conductivity of the C–Ph composites significantly as shown in Table 1. Thermal conductivity of composites depends on the lattice vibrations and the microstructure (micro cracks, grain boundaries, porosity, etc.). Nano silica loading has increased the number of grain boundaries, resulting in lower thermal conductivity. Similar observations for the C–SiC composites have been reported elsewhere [12]. Reduced thermal conductivity also assists in increasing the ablation resistance as the heat front advancement will be slowed down there by allowing the phenolic resin to hold the fabric layers together for longer durations.

During ablation, elimination of groups along polymer chains predominates over chain cleavage, leading to char formation. As the formation of char from phenolic resin is an endothermic process, heat dissipation during the ablation depends on the efficiency of char formation. Moreover, char that has formed on the surface during ablation dissipates a large fraction of incident heat through surface radiant emission. Complete charring of the resin, holding the char for maximum duration, gives better heat dissipation during ablation.

Table 1. Measured properties of NS C–Ph.

Sl no.	Sample description	Density (g cm^{-3})	V_f	Thermal conductivity (W m^{-1} K^{-1})	ILSS (MPa)	Ablation rate (g s^{-1})
1	C–Ph (blank)	1.42	51	0.59	16	0.22
2	0.5 wt.% NS C–Ph	1.41	51	0.48	21	0.20
3	2.0 wt.% NS C–Ph	1.38	48	0.40	22	0.18
4	4.0 wt.% NS C–Ph	1.27	40	0.37	14	0.28

NS: nano silica.