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Experimental Characterisation of Ablative properties of Carbon Phenolic Composites by addition of Carbon Nano Particles

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Abstract*. A Composite Material is a macroscopic combination of two or more distinct materials, having a recognizable interface between them. Composites are used not only for their structural properties, but also for electrical, thermal, tribological, and environmental applications. Composites typically have a fiber or particle phase that is stiffer and stronger than the many types of reinforcements also often have good thermal and electrical conductivity, a coefficient of thermal expansion (CTE) that is less than the matrix, and/ or good wear resistance. The physical ablation process of composite material, is simultaneous transfer of mass, momentum, and energy. Protection of a structure in a very high temperature environment may be accomplished with ease through the use of a new class engineering materials. These thermally protective materials are known as "ablators" or "ablative materials". Ablative materials are unique in that they accommodate virtually any temperature or heat flux condition, automatically control the surface temperature, and greatly restrict any internal flow of heat. An experimental investigation was carried out by successfully manufacturing the laminated specimens of rayon precursor based carbon fabric, with phenolic resin and nano particles as additive. These laminated specimens were tested as per ASTM standards and their physical and thermal properties were evaluated.*

Key words: *Composite materials, Ablative properties, Carbon phenolic, Nano particles.*

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I. INTRODUCTION

Composites are commonly classified at two distinct levels. The first level of classification is usually made with respect to the matrix constituent. The major composite classes include organic-matrix composites (OMCs), metal-matrix composites (MMCs), and ceramic-matrix composites (CMCs). The term "organic-matrix composite" is generally assumed to include two classes of composites: polymer-matrix composites (PMCs) and carbon-matrix composites. The second level of classification refers to the reinforcement form—particulate reinforcements, whisker reinforcements, continuous fiber laminated composites, and woven composites. A reinforcement is considered to be a "particle" if all of its dimensions are roughly equal. Thus, particulate-reinforced composites include those reinforced by spheres, rods, flakes, and many other shapes of roughly equal axes. There are also materials, usually polymers, that contain particles that extend rather than reinforce the material. These are generally referred to as "filled" systems. Because filler particles are included for the purpose of cost reduction rather than reinforcement, these composites are not generally considered to be particulate composites.

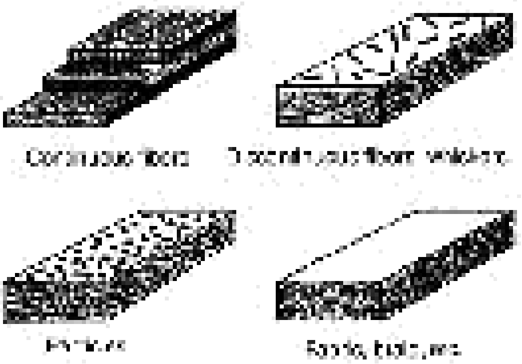

Fig 1 Different types of reinforcements

The advantages demonstrated by composites, in addition to high stiffness, high strength, and low density, include corrosion resistance, long fatigue lives, tailorable properties (including thermal expansion, critical to satellite structures), and the ability to form complex shapes

1.1 ABLATION

Protection of a structure in a very high temperature environment may be accomplished with ease through the use of a new class engineering materials. These thermally protective materials are known as “ablators” or “ablative materials”. They are applied to the exterior of a load bearing structure and there by isolate it from the hyper thermal environment [1]. The structure is thus maintained near its initial temperature, at which it exhibit optimum strength characteristics. Materials ablation in high temperature environments is a subject of great complexity, and as a consequence is not too well understood [2]. Certain chemical and physical aspects of the process have been identified, however, and they shall we given for the case of and ablating vitreous fiber reinforced plastic. Initially, heat incident to the surface absorbed and then conducted in to the materials substrate. Heat penetration proceeds at a low rate, due to the very low thermal conductivity of the ablator. The surface temperature thus rises rapidly, and thermal degradation begins in some form.

II. MATERIAL SELECTION

2.1 CARBON CLOTH (RAYON BASED)

Carbon fibers are fibers about 5–10 micro-meters in diameter and composed mostly of carbon atoms. To produce a carbon fiber, the carbon atoms are bonded together in crystals that are more or less aligned parallel to the long axis of the fiber as the crystal alignment gives the fiber high strength-to-volume ratio (making it strong for its size). Several thousand carbon fibers are bundled together to form a tow, which may be used by itself or woven into a fabric.

The properties of carbon fibers, such as high stiffness, high tensile strength, low weight, high chemical resistance, high temperature tolerance and low thermal expansion, make them very popular in aerospace, civil engineering, military, and motorsports, along with other competition sports. However, they are relatively expensive when compared with similar fibers, such as glass fibers or plastic fibers. Rayon is produced from naturally occurring cellulose polymers and has excellent characteristics. It is manufactured in three types: viscose, cup ammonium, and saponified acetate.

2.1.1 Carbon fibers from rayon:

The conversion of rayon fibers into carbon fibers is three phase process

Stabilization: Stabilization is an oxidative process that occurs through steps. In the first step, between 25-150ºC, there is physical desorption of water. The next step is a dehydration of the cellulosic unit between 150-240ºC. Finally, thermal cleavage of the cyclo-sidic linkage and scission of ether bonds and some C-C bonds via free radical reaction (240-400º C) and, thereafter, aromatization takes place.

Carbonization: Between 400 and 700ºC, the carbonaceous residue is converted into a graphite-like layer.

Graphitization: Graphitization is carried out under strain at 700-2700ºC to obtain high modulus fiber through longitudinal orientation of the planes.

2.2 PHENOLIC RESIN

Phenolics are thermosetting resins produced by the reaction of phenol with formaldehyde in the presence of a catalyst. Phenolic resins are available commercially in wide variety of types. The two main types are a single-stage resole and a two-stage novalac. The resole phenolic is the most widely used, because of its handling characteristics in the impregnated form. It cures by means of a condensation type reaction in which water is formed as a byproduct. The water is removed by vacuum or distillation and resin redissolved in alcohol for most uses. Phenolics have high heat and chemical resistance, good dielectric properties, dimensional and thermal stability, and surface hardness [3]. They yield low smoke and toxicity properties after combustion.

2.3 CARBON/PHENOLIC

The carbon cloth used to fabricate composite solid rocket motor nozzles is impregnated with the binder or matrix prior to wrap and cure. This preimpregnated material is commonly called "prepreg" in the composite industry. The diversity of the manufacturing process requires six different before final material is produced. 1) produce rayon thread; 2) weave cloth; 3) carbonize cloth; 4) produce resin; 5) produce carbon fillers; and 6) impregnate carbon cloth with resin and filler (production of prepreg).

2.4 CARBON NANO PARTICLES

The morphology of carbon nanoparticles is spherical, and they appear as a black powder. Carbon nanoparticles can be surface functionalized, with organic molecules or polymers chemically bound to the particle surface. Pure carbon has very low level of toxicity to humans. However, inhalation of coal dust or soot in large quantities can be dangerous, and can cause irritation of lung tissues and a congestive lung disease called pneumoconiosis.

III. EXPERIMENTAL PROCEDURE

An initial preparation of all the materials and tools that are going to be used is fundamental standard procedure when working with composites. This is mainly because once the resin and the hardener are mixed, the working time (prior to the resin mix gelling) is limited by the speed of the hardener chemically reacting with the epoxy producing an exothermic reaction.

3.1 Mold preparation:

Before starting with the layup process an adequate mold preparation must be done. Mainly, this preparation consists of cleaning the mold and applying a release agent in the surface of it to avoid the resin to stick.

3.2 Lay-up process: Hand lay-up is the simplest and oldest open molding method of the composite fabrication processes. It is a low volume, labor intensive method suited especially for large components, such as boat hulls. Glass or other reinforcing mat or woven fabric or roving is positioned manually in the open mold, and resin is poured, brushed, or sprayed over and into the glass plies. Entrapped air is removed manually with squeegees or rollers to complete the laminates structure. Room temperature curing polyesters and epoxies are the most commonly used matrix resins. Curing is initiated by a catalyst in the resin system, which hardens the fibre reinforced resin composite without external heat. For a high quality part surface, a pigmented gel coat is first applied to the mold surface.

3.3 Curing:

The part can be cured at elevated temperatures using an oven (usually some where around 160 degrees F) or at room temperature. Generally, the proper curing time of each type of resin-hardener, as well as the working time, is given by the supplier on the back of the containers. If the part is left on plastic sheeting be sure to use proper plastic sheet that will survive the elevated temperature. Most plastic sheet available from hardware stores (polyethylene) may melt.

IV. TESTING OF COMPOSITES

4.1. INTRODUCTION TO COMPOSITE TESTING

Before testing any composite material, it is mandatory to check whether the composite being investigated is completely cured or not. The composite curing can affect any composite adversely; hence it is mandatory to test its degree of cure before conducting any type of mechanical tests.

4.2 DIFFERENTIAL SCANNING CALORIMETER

Differential Scanning Calorimeter (DSC) measures the temperatures and heat flows associated with transitions in materials as a function of time and temperature in a controlled atmosphere. These measurements provide quantitative and qualitative information about physical and chemical changes that involve endothermic or exothermic processes, or changes in heat capacity.

4.2.1. Heat of Reaction and Degree of Cure: The heat of reaction and the degree of cure were measured using a differential scanning calorimeter. Prior to the tests, the DSC temperature (abscissa) and the DSC energy (ordinate) calibrations were checked following the procedure recommended by the manufacturer. A sample ranging in weight from 3 mg to 8 mg was encapsulated in a standard aluminium sample pan. The encapsulated sample was placed in the DSC sample holder and the rate of heat generation from the sample was measured as a function of time. An empty aluminium sample pan and cover was used as a reference. The weight of the sample was measured before and after the test. The weight losses during the tests were found to be negligible. In this experiment of dynamic scanning, the temperature was raised from room temperature to 250^{0}C at the rate of 20^{0}C/min.

Sample	Sample weight (mg)	Glass transition temperature (^{0} C)
Rayon carbon reinforced phenolic resin composite	6.6	165.95
Rayon carbon reinforced phenolic with 5% carbon nano-particles	18.8	165.34

Table 1-Glass transition temperature for different composite materials obtained experimentally.

4.3. Conclusion drawn from DSC: After adding carbon nano particles in Rayon carbon reinforced phenolic resin composite, there was almost no difference in the values of glass transition temperature obtained from DSC.

Graphs obtained from DSC

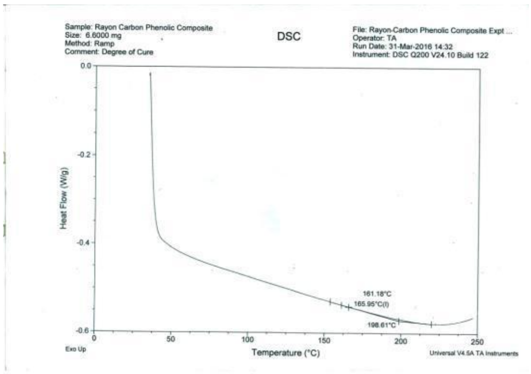

Fig 2- Degree of curing for Rayon carbon reinforced phenolic resin

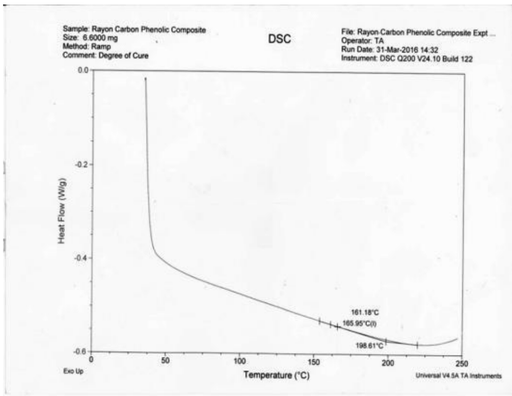

Fig 3- Degree of curing and glass transition temperature for Rayon carbon reinforced phenolic resin

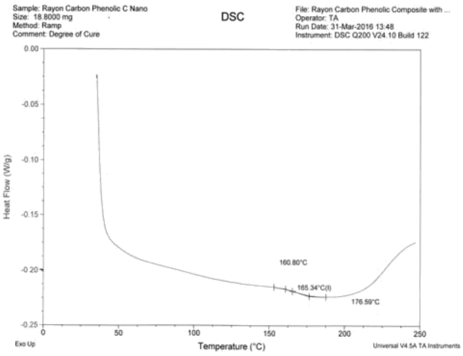

Fig 4- Degree of curing and glass transition temperature for Rayon carbon reinforced phenolic resin with 5% carbon nano particles

4.4. OXY-ACETYLENE ABLATION TESTING OF THERMAL INSULATION MATERIALS (E285-08)

This test method is intended to screen the most obvious poor materials from further consideration. Since the combustion gases more closely resemble the environment generated in rocket motors, this test method is more applicable to screening materials for nozzle and motor liners than for aerodynamic heating[4]. The environment for any specific high-temperature thermal protection problem is peculiar to that particular application. The conditions generated by oxy-acetylene heat source in this test method represent only one set of conditions; they do not simulate any specific application. Thus, the test results cannot be used to predict directly the behaviour of materials for specific environments, nor can they be used for design purposes. Hot combustion gases are directed along the normal to the specimen until burn-through is achieved. The erosion rate of the material is determined by dividing the original thickness by the time to burn through.

This test method is used to measure and describe the properties of materials, products, or assemblies in response to heat and flame under controlled laboratory conditions.

The general characteristics of the oxy-acetylene heat source are:
Heat flux = 835W/ ^{2}
Velocity = 210m/sec
Neutral flame conditions.

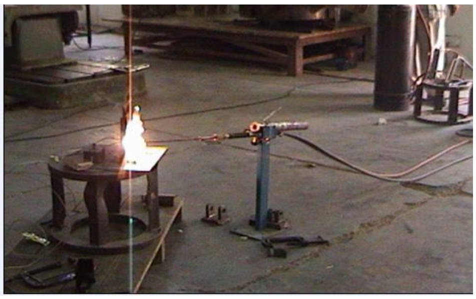

Fig 5 Oxy acetylene ablation test set-up

4.5 APPARATUS:

4.5.1 General:- The apparatus shall consist of an oxy-acetylene burner, a specimen holder and means for measuring the time to burn through and for recording the back face temperature history of the specimen.
4.5.2 Heat source:- The hot gas source shall consists of a welding torch with suitable storage for acetylene and oxygen together with suitable manifolds, flow regulators and flow and pressure indicators as shown schematically
4.5.3 Torch:- The torch shall be mounted so that the flame can be made to contact the specimen in less than half second from the time of actuation.
4.5.4 Torch tip:- The tip shall be equipped with a water jacket to minimize damage to the tip.
4.5.5 Pressure Regulators:- The regulators for the oxygen and acetylene shall be capable for supplying the flow of gases as required.

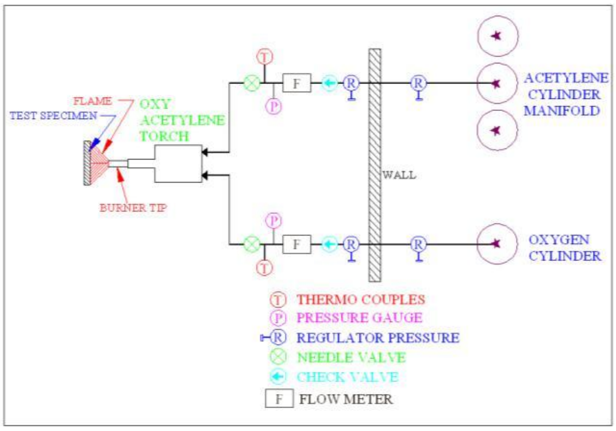

Fig 6 Schematic lay-out of oxy acetylene ablation test set-up

4.5.6 Flow meters:- The flow meters for the acetylene and oxygen shall be capable of supplying an accurate flow of gases. A variation of ±5% in gas flow rate due to instrumentation inaccuracies shall be permissible [5]. The total flow rate of un-reacted gases shall be 6.37 standard ^{3}/h (294.2K, 0.1MPa) and the volume ratio of oxygen to acetylene shall be 1.20, which corresponds to essentially a neutral (oxygen-free) atmosphere.
4.5.7 Specimen holder:-The back surface of the specimen shall be unobstructed by the holder for a distance of 25.4mm (1.00 in.) out from the centre of the specimen. Only materials with a thermal conductivity of 0.2W/m-K or less shall contact the back of the specimen. The front surface of the specimen shall be unobstructed for a distance of 48.0mm out from the centre of the specimen. The total area of contact with front and back surfaces shall not exceed 52.0 ^{2}.
4.5.8 Timer:-The DAS shall provide timing increments of 0.1-s or less, to measure the time to burn-through of the specimen.

V. EROSION RATE:

Calculate the erosion rate for each replicate by dividing the original thickness of the specimen by the time to burn-through as follows

$E = d/t$,

Where E = Erosion rate, mm/sec

d = thickness of the specimen, mm, and

t = burn-through time, sec

5.1 Average Erosion Rate:

Calculate the average erosion rate as follows,

E ave= □ E/N

E ave = average erosion rate mm/sec

□ E = Sum of the individual values of erosion rates N = number of replicates.

Fig 7 Oxy-acetylene testing

5.2. Procedure:

- Place the specimen in the holder and secure it firmly.

- Set the distance between the specimen face and torch tip to 19.0± 0.30mm and the angle between torch and specimen to 90±3°.

- Ignite the torch and adjust the gas flow rates. After flow conditions are stabilized, begin data recording and allow the torch flame to contact the specimen. Terminate the test at the instance that burn through is detected.

- Repeat the experiment for different specimens and record the time.

Fig 8, 9Specimens before & after oxy-acetylene test 5.3.

Results obtained from oxy-acetylene test:

S.No.	Specimen	Thickness	Time	Erosion rate
		(mm)	(sec)	(mm/sec)
1	CP	4.25	149.13	0.028498625
2	CP+5%N(m)	3.73	202.46	0.018423392

Table 2- Table Erosion rate for different materials

CP= Carbon fibre reinforced phenolic resin composite

CP+5%N(m) = Rayon Carbon fibre reinforced phenolic resin composite with 5% carbon nano particles (manually dispersed).
CP+5%N(u) = Rayon Carbon fibre reinforced phenolic resin composite with 5% carbon nano particles (ultrasonic mixing)

VI. RESULTS

An experimental investigation was done by successfully manufacturing the laminated specimens of rayon precursor based carbon fabric, with phenolic resin and nano particles as additive. Enhancement in the ablation properties is achieved through uniform dispersion of nanoparticles. Two Different fibre reinforced polymer matrix composite laminates were fabricated by Autoclave vacuum bagging process. Phenolic resin is used as a matrix material because of its excellent thermal properties. For high temperature applications in aerospace carbon phenolics are used as ablative materials because of their low erosion. In this study we dealt with fabrication and testing of aerospace composites carbon phenolic fibre rayon based with nano particles. Reinforcing of phenolic resin by fibers as well as nanoparticles as additive has slightly improved the mechanical properties but has resulted in massive increase in thermal and ablation properties of composites depending on kind and percentage of additives.

After adding carbon nano particles in Rayon carbon reinforced phenolic resin composite, there was almost no difference in the values of glass transition temperature obtained from DSC.

Ablative test specimens were tested at a heat flux of 835 W/cm^2 using the oxyacetylene test. The test specimens were compared on the basis of erosion rate. The distance maintained from torch tip to specimen is 19 mm. The erosion rate for control test specimens i.e carbon/phenolic was 0.028 mm/sec whereas it was 0.01 mm/sec for nanocomposite specimens i.e with rayon cabon/ phenolic with nano particles as additives containing 5 wt% nanoparticles. Based on these results, it is concluded that the increase in wt% of nanoparticles improved ablation and insulation performance of carbon phenolic composites.Hence, there was no detectable performance deterioration after adding cabon nanoparticles to the reinforced matrix.

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