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A study on the effect of cenosphere on thermal and ablative behavior of cenosphere loaded ceramic/phenolic composites

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ABSTRACT

Composites of ceramic woven and phenolic resin filled with cenosphere were prepared and their thermal properties and ablative properties were studied by Thermogravimetric Analysis (TGA) and oxyacetylene ablation test. Classical thermal stability parameters, based on initial decomposition temperature and mass loss at various temperatures were calculated before and after subtraction of cenosphere concentration from the TGA curves. Ablation behavior of the filled composites were investigated based on the linear ablation rate, mass ablation rate and back face temperature profiles. Without cenosphere mass subtraction, the thermal stability of the filled composites seems to be improved and reduction of mass loss was achieved with addition of cenosphere. Ablation results showed that the addition of cenosphere content exhibits the favorable ablation resistance. In comparison to neat ceramic/phenolic composites, the introduction of micro sized cenosphere particles embedded in the phenolic matrix significantly improved the ablative properties in terms of mass ablation rate and linear ablation rate.

1. Introduction

Composite based ablative material plays an important role in the aerospace industry. Mainly ablative materials are used in Thermal Protection System (TPS) which protects the aircrafts and space probes during hypersonic flight through a planetary atmosphere. Ablative materials provide thermal insulation by ablation process. Ablation process is a thermochemomechanical phenomenon which provides thermal insulation through the degradation of the outer surface of the material and the formation of a refractory char on the material surface, thereby ablative materials hindering the transfer of heat into the interior of the material or structure. Reinforced polymeric materials are used to produce wide range of heat shield currently used in the aerospace industry. Among the various types of polymer materials, phenolic based ablative materials are widely used in heat shields, because of its good thermal resistance, high thermal stability, good oxidation and chemical resistance.

Srikanth et al. [1] manufactured the high ablation resistance carbon phenolic composites using nanosilica as a filler material. Nanosilica filled carbon phenolic composite exhibited higher ablation resistance when compare to the unfilled composite. Addition of silica not only enhanced the mechanical properties but also considerably restricted the thermal degradation of phenolic resin [2]. Natali et al. [3] revealed the fact that the introduction of nanosized silica particles on the glass/phenolic composites, significantly improved the ablative properties in terms of mass loss and erosion rate.

Zuo-Jia et al. [4] developed carbon nanotubes (CNT) filled phenolic composites which showed improved ablation resistance at high temperatures, and the uniformity of the CNT dispersion played an important role in the ablation resistance of the composite. Pulci et al. [5] used phenolic resin with carbon based graphitic felt and graphitic foam to manufacture ablative material for re-entry space vehicles. Toshio et al. developed silicon carbide (SiC) fiber reinforced carbon composite which showed reduction in mass loss rate in plasma arc jet testing. Also SiC/C composites exhibited excellent oxidation resistance [6]. Wang et al. found that reduction in both mass ablative rate and linear ablative rate of SiC reinforced ceramic composites when compared to the carbon reinforced composites [7]. Xiao et al. showed reduction in ablative rate of SiC–ZrC coated Carbon/Carbon (C/C) composites when compared to uncoated C/C composites [8].

Maurizio Natali et al. [9] showed improvement in thermal stability of the phenolic composite by adding carbon black and multiwall carbon nanotubes as filler. Patton et al. [10] used phenolic resin with vapor grown carbon fiber as reinforcement to develop a

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composite for rocket motor nozzle application which showed improvement in the mechanical and the thermal properties. Fly ash cenosphere was used as reinforcing filler along with polyethylene resin to develop light weight composites in numerous studies [11–13]. The characterization of cenosphere filled polyethylene composite revealed that the addition of cenosphere improved the mechanical properties and the thermal stability of the composites and also showed reduction in shrinkage.

The aim of this study is to quantify the effect of the different concentration of the filler contents on the thermal stability and the ablation properties of filled phenolic composites. Methods for investigating the thermal stability of cenosphere filled composites by TGA include initial decomposition temperature (IDT) and mass loss at different degradation stages. The IDT determined the temperature at which a determined amount of mass loss, normally 5%, is initially observed [14]. Ablation behavior was characterized by linear ablation rate, mass ablation rate and back face temperature [9,15–17].

2. Experimental

2.1. Materials and its characteristics – an overview

In this current study phenolic resin was selected as matrix material because of its unique thermal stability and good chemical resistance. Phenolic resin was prepared by mixing appropriate ratio of phenol and formaldehyde in suitable alkaline medium. Phenolic resin starts to harden when exposed to heat. Phenolic resin used in this study which was supplied by Linear Polymer Pvt., Ltd., Chennai. Reinforcement used in this study was ceramic woven fiber which was supplied by Dail Electricals Pvt., Ltd., Mumbai. The material properties of ceramic fiber, Phenolic resin and cenosphere are listed in Table 1.

Cenosphere was used as filler in present study which was supplied by Cenosphere India Pvt., Ltd., Kolkata. Generally cenosphere is found in fly ash, an industrial by-product of the coal combustion in thermal power plant. Cenosphere is perfectly spherical in shape. Because of unique properties of cenosphere such as thermal stability, oxidization and chemical resistance, it is used as filler or functional expander in the manufacturing of paint, resin, plastic, light weight cement, composites etc. The spherical shape of cenosphere not only increases the flow ability, but also provides most uniform distribution as filler material in composite application. The characteristics of cenosphere are listed in Table 2.

2.2. Specimen preparation

Composite samples were prepared with filler loadings of 5, 10, 15 and 20% by weight of cenosphere. Weight percentage of fillers varied from 5 to 20% in the phenolic resin in order to quantify the effect of fillers on ablative and thermal stability of the filled ceramic/phenolic composites. The necessary amount of phenolic resin and filler particles were mixed for 30 min and stirred for 10 min in an Ultrasons J.P. Selecta ultrasonic bath to disperse the agglomerates. Then the composite specimens were prepared using this modified phenolic resin as matrix and woven ceramic fiber as reinforcement. This procedure was repeated for second filler. Prepared composite specimens consist of 7 layers of bi-directional woven ceramic fiber. The specimens were cured at 140 °C for one hour in hot air woven at very slow rate of heating (2 °C per minute) and then done post cure at 180 °C for 2 h.

Table 1
Properties of Ceramic Woven Fiber, Phenolic resin and Cenosphere.

Reinforcement: ceramic woven fiber	Matrix: phenolic resin	Filler: cenosphere
Density: 2.7 g/cc GSM: 200 gsm Constituents: alumina (<99%) Thickness: 0.6 mm Color: white	Density: 1.2 g/cc Constituents: phenol and Formaldehyde Curing temperature: 160 °C Color: dark red	Density: 0.85 g/cc Constituents: silica and alumina, Particle size: 60 μm (avg) Color: light gray

Table 2
Chemical constituent and sleeve analysis of cenosphere.

Chemical composition	Percentage	Particle size	Percentage
SiO2	52–62	250–200	4
Al203	30–36	200–150	4
K20	1.2–3.2	150–100	10
Fe203	1.0–3.0	100–75	12
TiO2	0.8–1.3	75–50	40
MgO	1.0–2.5	>50	30

3. Characterization and testing

Thermogravimetric Analysis (TGA) and ablative test were conducted to evaluate the effect of cenosphere on the thermal ablative behavior of ceramic/phenolic composite. Thermogravimetric Analysis was performed by a NETZSCH STA 409 PC/PG thermal system. The analysis was performed at a heating rate of 10 °C/min under nitrogen atmosphere with temperature ranges of about room temperature to 1400 °C. This analysis was performed to evaluate the weight loss of the composite under various temperatures.

Ablation test was carried out with an oxyacetylene flame system to simulate the severe hyperthermal environment [9,15,16]. The ablation test was carried out to evaluate mass ablative rate and liner ablative rate according to ASTM E285-80 [18]. The standard describes the testing of flat cenosphere filled ceramic/phenolic composite panels in an environment of a steady flow of hot gas provided by an oxyacetylene burner. The ablation test bed consists of gas vessels, torch, pressure gauge, K-type thermocouples and a specimen holder. In this test bed, test specimen is placed perpendicular to flame. The distance between the specimen and torch nozzle is kept constant at 20 mm [15]. The front and back surface temperature of the cenosphere filled ceramic/phenolic composites is measured by the two K-type thermocouple which are fitted on the front and back surface of the composite specimens. In this current study, the ablative time is fixed at 120s. The linear ablation rate and mass ablation rate are calculated using the following formulas [17],

$$\text{Linear ablation rate (ARL)} = (d_1 - d_2)/t$$

$$\text{Mass ablation rate (ARM)} = (m_1 - m_2)/t$$

where ARL is Linear ablation rate (mm/s), ARM is Mass ablation rate (g/s), d_1 and d_2 are thickness of specimens before and after ablation test (mm), m_1 and m_2 are mass of specimen measured before and after ablation test and t is ablation time (s).

4. Results and discussions

4.1. Thermal behavior

Experimentally generated TGA curve of the specimens containing various percentage of cenosphere are displayed in Fig. 1. The