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Fabrication and characterization of PIP based C/SiC composites having improved mechanical properties using high modulus M40J carbon fiber as reinforcement

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ABSTRACT

PIP based C/SiC composites are fabricated using high modulus M40J carbon fiber. High ceramic yield polycarbosilane (PCS) was also synthesized in the laboratory and the same was used to infiltrate the fibrous preforms. The infiltrated preforms were pyrolyzed at three different temperatures viz. 1400, 1500 and 1600 °C and termed as set-1, set-2 and set-3. Flexural strength was determined using 3-point bend fixture and the data obtained are analyzed using Weibull distribution. Average flexural strengths were found to be 691 ± 23 MPa, 654.6 ± 24 MPa, and 504 ± 31 MPa for the sets 1, 2 and 3 respectively and the corresponding Weibull moduli were found to be 27.9, 25.5 and 15.6. The composites pyrolyzed at 1400 and 1500 °C, have been found to exhibit extensive fiber pull-out and thus demonstrated pseudo-ductile fracture behavior. A relatively brittle fracture was observed for the composites pyrolyzed at 1600 °C. Area under the flexural stress and displacement curve is found to be in the ratio 1.0:0.92:0.8 for the for the sets 1, 2 and 3 respectively. The effect of the pyrolysis temperature on the mechanical properties is discussed in the light of the microstructure of the composites.

1. Introduction

Carbon fiber reinforced silicon carbide (C/SiC) composites have been widely accepted as prospective materials for high temperature applications [1–3]. They are fabricated mainly using: (i) Chemical Vapor Deposition and Chemical Vapor Impregnation (CVD/CVI), (ii) Polymer Impregnation and Pyrolysis (PIP) and (iii) Liquid Silicon Infiltration (LSI) processes [1]. PIP process is preferred over CVD/CVI and LSI processes when large size product needs to be fabricated [1]. Effect of heat treatment on mechanical properties of T300 carbon fiber based C/SiC composites has been reported [4,5]. Apart from the heat treatment, the properties depend on multiple factors like type of interface, fiber type, precursor type and processing methodology [5–8]. Fiber/matrix interface plays an important role for drawing the desired mechanical properties of the SiC matrix based composites [9,10]. In the presence of a weak interface or interphase, the cracks propagate through the dense matrix and get deflected around the fiber surface [9,10]. In the weak matrix composites, the crack propagates through the porous matrix and does not form a notch on the fiber surface [6]. Therefore, crack would propagate through the weak matrix of the PIP based C/SiC composite. C/SiC composite rocket nozzles are fabricated using filament winding technique [1,11]. For the filament wound C/SiC composites, the fabrication process needs to be optimized without employing fiber/matrix interface; hence, the weak matrix composites would suffice for many applications.

Strength of the reinforcing fibers is critical as the load transfers to the fibers in the wake of the matrix crack. Weak fibers lead to catastrophic failure, whereas strong fibers can accommodate the stresses within the composite structure [12]. The amount of fiber pull-out (which contributes to the toughening of the composite) is strongly influenced by the mean strength and the variability in the strength of the reinforcing fibers [13]. The ultimate load-bearing capacity of the composite is determined by the fiber strength [12]. Tensile strength and modulus of the M40J carbon fiber are higher than the T300 carbon fiber. Further, the M40J fiber fabricated at higher temperature in comparison of the commonly used T300 carbon fiber. Higher temperature alters the surface groups on the fiber which would control the fiber/matrix bonding. LSI based C/C-SiC composites fabricated using high modulus pitch based carbon fibers have resulted improved flexural [14]. Therefore, an improved set of C/SiC composite properties are expected with M40J carbon fiber due to their higher modulus, higher process temperature than the commonly used T300 fibers. In the present study, it is aimed to fabricate M40J fiber based C/SiC composites using PIP process. The composites would be evaluated

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for flexural properties. The optimal and most appropriate fabrication conditions are identified and the results are discussed in detail.

2. Experimental

2.1. Precursor synthesis

Polycarbosilane (PCS) was synthesized following the thermal backbone re-arrangement reaction of polydimethylsilane at 250–400 °C in nitrogen atmosphere. Details of the PCS synthesis process is reported elsewhere [15]. The PCS fraction having softening point in the range of 220–250 °C was used for fabricating the composites. Functional groups of the PCS were analyzed using Fourier Transform Infrared Spectroscopy (FTIR), molecular weight was determined using Gel Permeation Chromatography, while the ceramic yield was determined using Thermal Gravimetric Analysis (TGA). Detailed characteristics of the PCS are available elsewhere [15].

2.2. Composite fabrication

M40J grade carbon fibers were used as the reinforcement. Average strength of a single fiber is reported to be ≈4.4 GPa while modulus up to ≈377 GPa. Multiple tows (6k carbon fibers) were wound on the slotted specially machined stainless steel fixture to obtain multiple numbers of Uni-Directional (UD) fibrous preforms. Dimensions of the preforms were: thickness =0.9–1.7 mm, width ≈10 mm and length 250 mm. Fiber volume fraction (V_f) in the preforms was controlled between 52% and 55% by varying the number of tows and spacers. Resin solution was prepared by mixing PCS and Di-Vinyl-Benzene (DVB) in the ratio of 5:1 (wt./wt. basis). The resin solution was further diluted by adding petroleum ether (50:50, vol/vol). Few drops of the Speier's catalyst were also added in the solution. The preform along with the fixture was impregnated with resin solution using vacuum infiltration technique. The fixture was taken out from the resin solution and placed between the two large sized metallic flat plates. The plates with the infiltrated preforms were heated up to 300–320 °C in 150 min. Simultaneously, (1 MPa) pressure was applied on the plates using a hydraulic press. Thus, UD carbon fiber reinforced PCS composite strips (45 numbers) were obtained. The strips were grouped into three sets (15 numbers in each set). The strips were pyrolyzed under vacuum at pre-decided temperatures (set-1 at 1400 °C, set-2 at 1500 °C and set-3 at 1600 °C) for two hours. Heating was carried out at the rate of 30 °C/h. All the three sets of the composite strips were processed separately for all the subsequent steps. The pyrolyzed C/SiC composite strips were infiltrated again with the specific resin solution using the vacuum infiltration technique followed by pressurizing the infiltration system up to 10 atm with argon gas. The composite strips were taken out from the infiltrated system and heated up to 300 °C under N_2 atmosphere and then pyrolyzed at the designated temperature. Infiltration and pyrolysis cycles were repeated six times to obtain dense (density 1.82–1.9 g/cm^3) C/SiC composite strips.

2.3. Characterization and testing

Flexural strength of the composite strips (corresponding to the set-1, set-2 and set-3) was determined using 3-point bend fixture over a span length of 70 mm. The testing was carried out at Universal testing machine (Instron, model 5967) at a crosshead speed of 0.5 mm/min. The calculations were carried out as per ASTMC-1341. A minimum number of 10 samples were tested from the each set. Microstructure of the tested samples was studied using Scanning Electron Microscope, Make: JEOL, JSM 6010LA. XRD analysis was carried out using XPERT-PRO equipment. Field Emission Scanning Electron Microscope, Make: JSM/FESEM −7100F, JEOL was used to study the fiber matrix interaction at higher magnification.

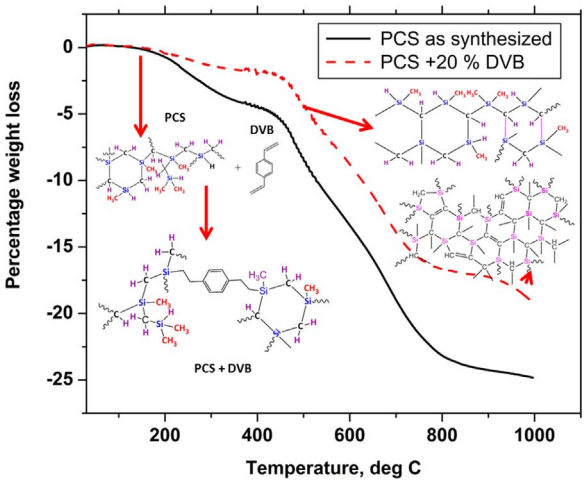

Fig. 1. TGA of the PCS and PCS+20%DVB resin.

3. Results and discussion

3.1. PCS analysis

Density of the PCS pieces was found to be about 1.0 g/cm^3. FTIR spectra of the as synthesized PCS were found to be similar to the ones reported elsewhere [16,17]. Details of the FTIR analysis are available elsewhere [15]. The number average molecular weight of the PCS was found to be 1250. Ratio of the weight average to number average molecular weight (Mw/Mn) was found to be about 5.0. TGA of the as synthesized PCS and PCS+20%DVB was carried out up to 1000 °C, under N_2 atmosphere. Ceramic yield of the as synthesized PCS was found to about 79% while of PCS+20%DVB, it was about 82% (Fig. 1). The ceramic yield of PCS+20%DVB was found to be only 72.0% and 68.4% at 1400 °C and 1600 °C. It is evident that, the PCS loses about 5% of its mass up to 400 °C. In this temperature range, H_2 goes out due to Si-H bond cleavage [18]. Also, the smaller chain length PCS fraction might have got evaporated as such without undergoing decomposition. Beyond 450 °C, rate of decomposition is higher due to Si-CH_3 bond cleavage and decomposition of the side chains of the PCS [17]. Decomposition of the side chains leads to the evolution of hydrocarbons (gases) like CH_4, C_2H_6 etc. [18]. The decomposition continues up to 800 °C and about 20% weight reduction takes place. Beyond 800 °C, crystallization starts where amorphous natured SiC converts in to β-SiC [18].

PCS+20% DVB exhibited higher ceramic yield compared to the PCS. Up to 450 °C, weight loss is only about 2%. Higher ceramic yield of PCS+20%DVB is interpreted due to two reasons. (i) The smaller chain length (lower molecular weight) PCS fraction might also got reacted with DVB and participated in the decomposition along with the larger chains of the PCS; (ii) Most of the Si-H bonds present in PCS might have reacted with DVB. Therefore, with fewer unreacted Si-H bond could not produce H_2 gas in this temperature range. Si-CH_3 bond does not take part in the reaction with DVB which is considered responsible for the evaluation of CH_4 and C_2H_6 gases. Therefore, between 450 and 800 °C, PCS and PCS+20%DVB, have similar decomposition rate. Similar observations are reported elsewhere [18]. For the sake of the readers, a simplified scheme of decomposition of PCS+20%DVB is presented along with TGA (Fig. 1).

3.2. Densification of the C/SiC composite

Crystalline matrix is desirable for better mechanical properties [4,5]. A fully crystalline SiC matrix is expected by pyrolyzing the PIP based composites at 1400 °C. Beyond 1400 °C, a small amount of CO(gas) evolves due to the decomposition of Si-O-Si or Si-O-C