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# Microstructural interpretation of the ablative properties of phenolic–quartz hybrid fabric reinforced phenolic resin composites

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ABSTRACT

The thermal decomposition behavior of phenolic fiber and phenolic resin (PR) matrix was investigated by using a thermo gravimetric analyzer in nitrogen. The ablative properties of the composite specimens were quantitatively evaluated by performing oxyacetylene flame test and exhaust plume ablative test with a small liquid motor. The ablative properties of phenolic–quartz hybrid fabric reinforced phenolic resin (P–Q/PR) composites were compared with those of phenolic fabric and quartz fabric reinforced (P/PR and Q/PR) composites. The patterns and microstructures of the ablated composite specimens were also studied, and the advantages of the hybrid reinforced composites under ablation conditions were interpreted. The phenolic fiber decomposed similarly to the manner in which the PR did. The mixture rule can be used to predict the mass loss rate of the P–Q/PR composites during the oxyacetylene flame test. After the oxyacetylene flame test, there was no crack or delamination can be observed in P–Q/PR composite specimens and the carbonaceous residue blocks which were produced by the phenolic fiber and the PR were attached well to the quartz fibers. The resistance to heat-flow erosion of the P–Q/PR composites had significantly improved and the mass loss of the P–Q/PR composites (24.6%) was much lower than those of the Q/PR composites (56.4%) and the P/PR composites (86.3%) in the exhaust plume ablative test with a small liquid motor. A vis-à-vis char layer of the P–Q/PR composites formed during this ablation.


## 1. Introduction

Thermal protection systems (TPS) effectively shield inner structures from severe heating environments in working conditions. For example, continuous carbon fiber reinforced ultra-high temperature ceramic matrix composites, such as C/C and C/SiC composites, are usually used for hypersonic vehicles [1,2], while fiber reinforced polymer (FRP) composites are usually used for re-entry vehicles, probes and ballistic missiles (high heating rates, short duration). FRP composites, which are typical ablative TPS, protect inner structures from high temperature by being consumed. Phenolic resins are the most widely used matrices for ablative composite materials. The matrices pyrolyze into gaseous products above 300 °C, leaving the carbonaceous residue as char. The gases function by convection and transpiration cooling. The char layer is a good insulator and radiator, the recession of which is accompanied by many endothermic reactions and changes [1–15]. The fiber reinforcements also react at high temperature to protect the inner structure from heat. Glass fibers and quartz fibers melt at 1600–1800 °C and carbon fibers sublime at approximately 3000 °C. Phenolic fibers, invented by Economy and Clark in 1968 [4], pyrolyze to form fibrous carbonaceous residues in high temperature environments and are also used as reinforcements for ablation owing to their low density and thermal conductivity [5,6].

An ablator forms a char layer, a pyrolytic layer and an original layer under ablative conditions. The char layer plays a significant role in ablation by absorbing the generated heat and protecting the inner materials. Some weak parts of the char may be mechanically removed by heat flow with high pressure and velocity, which can lead to additional mass loss [7–9]. Meanwhile the weak interfaces between the char layer and the underlying materials or between the pyrolytic layer and the original layer also induce large mass losses. Recently, the ablative properties of composites have been improved to decrease mass loss. For example, advanced ablative materials based on innovative polymer matrix composites, such as new types of silicone polymer composites [10], have been developed. Moreover, nano-additive modified composites, such as montmorillonite or kaolinite layered silicate modified ablative materials [11,12], and active carbon fiber or other carbon nanoparticle modified composites [13–15], have also been prepared. The ablative properties have been improved due to stronger char layers formed. A previous study showed that the mechanical stability of composites was increased with an integrated char structure

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formed in ablation conditions, thus decreasing the mass loss. Horrocks et al. [16] found that organic flame retardant cellulose fiber–intumescent combinations formed a char-bonded structure from the fibers that were embedded and bonded to an expanded intumescent char above 300 °C. However, in their study, the phenolic fiber did not produce a char-bonded structure because it did not react with the intumescent. Nevertheless, the phenolic fiber reinforced phenolic resin matrix composite laminates yielded integrated chars among different layers, but these brittle chars were prone to peeling off from the underlying materials [17]. The deficiencies may be remedied by hybridization with inorganic fibrous components.

Phenolic-silica or phenolic–quartz hybrid fabric reinforced polymer matrix composite materials showed better heat-obstructive effects and thermal insulation performance than those of silica or quartz composites in low heat flux [18]. Therefore, the aim of this study was to prepare phenolic–quartz hybrid fabric reinforced phenolic resin matrix composites and to study the ablative properties of these composites under high temperature conditions with aerodynamic shear. Moreover, the microstructure of the char layer of the composite specimens after the ablative tests was discussed.

## 2. Experimental details

### 2.1. Materials and processing

Phenolic resin (PR), which was supplied by Institute of Chemistry, the Chinese Academy of Science, was cured according to the program of 80 °C (7 h) + 90 °C (1 h) + 110 °C (1 h) + 130 °C (1 h) + 150 °C (2 h). The curing degree of the PR is approximately 96% and the density of the PR is approximately 1.25 g $cm^{-3}$ [19]. Phenolic fiber (trade name: Kynol®) was manufactured by Gun-Ei Chemical Industry Co., Ltd. (Japan). The density of the fiber is 1.27 g $cm^{-3}$. The phenolic fabrics, the quartz fabrics and the phenolic–quartz hybrid fabrics were supplied by Yixing KINO Weaving Co., Ltd. (China). The mass ratio of phenolic fiber to quartz fiber in the hybrid fabric is 1:1. The densities by area of the three types of fabrics are the same (175 g $cm^{-2}$).

Compression molding was used to prepare the composite specimens. The fabrics were dried at 100 °C for 2 h and then placed in a mold. Each layer was left for a few minutes after brushing the resin thereon. Trapped air was gently squeezed out using an erasing knife. The composites were cured under heating and pressure. The program for curing the composites was the same as that of the PR. In order to eliminate gas production, the pressure was held at 1 MPa for 1 h at the temperature of 90 °C and at 3 MPa for 1 h at the temperature of 130 °C. The phenolic–quartz hybrid, the phenolic and the quartz fabrics reinforced phenolic resin composites were abbreviated as P–Q/PR, P/PR and Q/PR, respectively. The density of the P–Q/PR, P/PR and Q/PR are approximately 1.34, 1.22 and 1.58 g $cm^{-3}$, respectively. The mass fraction of the quartz fiber ($W_Q$) of the P–Q/PR and Q/PR composites are approximately 22.9% and 54.2%, respectively.

### 2.2. Measurements

#### 2.2.1. Thermo-gravimetric analysis

The thermal decomposition behavior of the phenolic fibers, Kynol, and the cured phenolic resin, PR, was investigated by thermo gravimetric analysis (TGA) using a TGA/DSC 1-1100SF instrument (Mettler). The tests were run from 25 °C to 1000 °C at a heating rate of 10 °C $min^{-1}$ in a nitrogen atmosphere. Each specimen weighed approximately 20 mg.

#### 2.2.2. Oxyacetylene flame test

The oxyacetylene flame test is widely used to evaluate the surface erosion of composite specimens in a high-temperature environment [2,20]. This ablative resistance test was carried out in a flowing oxyacetylene torch environment with a heat flux of approximately 4187 kW $m^{-2}$ and a flame temperature of approximately 3100 °C, during which the specimen was vertically exposed to the flame. The distance between the nozzle tip and the surface of the specimen was 10 mm. The test lasted for 20 s. The specimen was cylinder with 30 mm in diameter and 10 mm in height, and five samples were measured for this ablation test. The mass loss rates ($R_m$) of the specimens as a function of surface erosion were compared, which can be calculated based on the following equation:

$$R_m = (m_1 - m_2)/t \quad (1)$$

where $m_1$ and $m_2$ are the masses of the specimens before and after the oxyacetylene test, respectively, and $t$ is the testing time.

The mixture rule for the mass loss rate of the composite can be expressed as Eq. (2). It is supposed that the PR matrix and phenolic fiber had the same mass loss rate, which is same as that of the P/PR composite. So the mass loss rate of the P–Q/PR composite can be expressed as Eq. (3).

$$R_{m,c} = \sum W_i \cdot R_{m,i} \quad (2)$$

$$R_{m,h} = R_{m,P/PR} \cdot (W_r + W_p) + R_{m,Q} \cdot W_Q \quad (3)$$

where $W$ is the mass fraction and the subscripts of $c$, $h$, $P/PR$, $P$ and $Q$ denote the composite, hybrid fabric reinforced composite, phenolic fabric reinforced composite, phenolic fabric and quartz fabric, respectively. Because the mass ratio of the phenolic fiber to quartz fiber is 1:1 of the hybrid fabric in this paper, $W_p$ is equal to $W_Q$ and $W_r$ is equal to $1 - 2W_Q$.

#### 2.2.3. Exhaust plume ablative test with a small liquid motor

An exhaust plume ablative test with a small liquid motor (EPSLM) is also widely used to measure the ablative properties of composite specimens [21]. As shown in Fig. 1(a), the specimen was placed behind the nozzle. A state flame produced by the small liquid motor produced flow on the surface of the specimen. Heat flux and pressure were determined by changing the angle between the specimen and the level as well as the distance between the nozzle tip and the specimen. This test can simulate aerodynamic force accompanied by aerodynamic heating effects, which is superior to the oxyacetylene flame test in its closer resemblance of the actual environment. As shown in Fig. 1(b), the specimen is 200 mm in length, 140 mm in width and 3 mm in thickness. The heat fluxes were approximately 3940, 6705, 6400 and 5800 KW $m^{-2}$ at the four measurement points (1, 2, 3 and 4) on the specimen, respectively. The pressures at the four points were 0.09, 0.163, 0.161 and 0.108 MPa, respectively. The test lasted for 8 s.

#### 2.2.4. Scanning electron microscopy

An FEI Quanta 200 scanning electron microscopy (SEM) was used to observe the surface of the specimens after the ablative tests. Energy dispersive spectroscopy (EDS) was used to analyze the elements present on the surface.

## 3. Results and discussion

### 3.1. Results by TGA

Fig. 2 shows the TGA and derivative thermo gravimetric (DTG) curves of the PR and Kynol phenolic fibers. Clearly, the PR and the phenolic fibers underwent similar degradation processes due