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Feature article

A heat-resistant preceramic polymer with broad working temperature range for silicon carbide joining

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ABSTRACT

A room temperature curable heat-resistant adhesive with broad working temperature range was prepared through organic and inorganic modification. The preceramic polymethylsiloxane showed low bonding strength for silicon carbide from 400 °C to 600 °C because of the decomposition of polymer network. So the modification with epoxy resin was used to generate strong blending and copolymerization network which decomposed at higher temperature over 500 °C. The ceramization of active fillers and preceramic polymer compensated the bonding strength with rising temperature, thus eliminating the weak stage from 400 °C to 600 °C. The modification with fillers greatly improved its bonding strength at high temperature over 1000 °C. Consequently, the modified adhesive exhibited outstanding bonding strength tested at room temperature between 9.29 ± 0.56 MPa and 37.28 ± 1.33 MPa after heat-treatment from 25 °C to 1500 °C and the bonding strength directly tested at the temperature from 25 °C to 800 °C over 8.21 ± 0.40 MPa. The adhesive shows the potential to extend the application for engineering ceramic joining.

1. Introduction

Engineering ceramics such as silicon carbide (SiC), silicon nitride, alumina, mullite and carbon/carbon composite exhibit high strength, high thermal and chemical stability, low density and thermal expansion coefficient [1–4]. Ceramic components have been widely applied to thermal protection system in aerospace, energy and industrial manufacturing fields as well as brake system and engines system [4]. Unfortunately, ceramics are so hard and brittle that make it difficult and expensive to fabricate complex components with ceramics. What's more, it's likely to introduce potential defect into ceramics through considerable machining. However, ceramic joining provides a feasible way to fabricate complex components.

Some methods of ceramic joining such as diffusing bonding, green-state joining, glass or glass ceramic joining, active metal brazing and plastic deformation joining have been proposed so far [4–7]. But most of them need high temperature heat-treatment, leading to internal stress concentration because of thermal mismatch among different materials. Adhesive bonding is a viable and potential way with several advantages: (1) Adhesive bonding process is simple and can avoid high temperature heat-treatment; (2) Adhesive bonding can disperse stress uniformly in the bonding zone, preventing stress concentration; (3) Adhesive bonding can generate chemical gradient layer in the bonding zone that alleviates stress concentration [8].

Until now, adhesive joining has been used for assembling thermal protection system, sealing, structural bonding and repairing [9–11]. Organic-inorganic composite adhesives composed of polymer and inorganic fillers have been demonstrated to be promising heat-resistant adhesives for engineering ceramic joining over 1000 °C [12–18]. Wang et al. [19] used the adhesive with modified dichlorosilane as matrix to bond SiC specimens. After heating at 1200 °C, its shear strength was over 50 MPa. Koyam et al. [20] joined carbon/carbon composites using adhesives with modified phenolic resin as matrix. The bonding strength of the joints was up to 10 MPa although the joints were heat treated at 2000 °C. Our group's previous work prepared adhesives with polymethylsiloxane as matrix and Si, Al, B_4C as fillers. Engineering ceramic SiC, mullite and C/C composites joints were bonded with the adhesives. The adhesives kept outstanding bonding strength at 1100 °C and 1300 °C [16,18]. In addition, the adhesives' bonding toughness could be improved with SiC whiskers [21].

Composite adhesives exhibit outstanding bonding properties at high temperature over 1000 °C. However, composite adhesives show low bonding strength tested at room temperature for SiC within a particular heat-treatment temperature range due to the decomposition of the polymer network when there aren't enough strengthening mechanisms. J. Zhang [22] and X. Wang [23] obtained adhesives whose bonding

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strength after heat-treatment at 600 °C were 2.01 MPa and 4.80 MPa respectively. In this paper, we also found low bonding strength of our adhesives after heat-treatment from 400 °C, 500 °C and 600 °C respectively by our own, and this temperature range is named as "weak stage" which is fatal for safe bonding within a broad temperature range. Up till now, lots of researches have concentrated on improving bonding strength at high temperature instead of alleviating "weak stage" to ensure the safety within the working temperature range. Post-heating over the polymer decomposition temperature can be used to alleviate the "weak stage" [24], but high temperature heat-treatment inhibits application of composite adhesives.

For that reason, a room temperature curable adhesive with broad working temperature range was prepared. Polymethylsiloxane was selected as the matrix of the adhesive. The "weak stage" was eliminated through blending and copolymerization of epoxy resin and polymethylsiloxane which improved the decomposition temperature of the polymer network over 500 °C. The ceramization of active fillers and preceramic polymer compensated the bonding strength with rising temperature. Coupled with the modification with inorganic fillers which contributed to the high bonding strength over 1000 °C, the modified adhesive kept acceptable bonding strength tested at room temperature for silicon carbide (SiC) between 9.29 ± 0.56 MPa and 37.28 ± 1.33 MPa after heat-treatment from 25 °C to 1500 °C. Meanwhile, its bonding strength directly tested from 25 °C to 800 °C without heat-treatment kept over 8.21 ± 0.40 MPa. By the way, the modified adhesive added with curing agent could be cured at room temperature. This adhesive shows the potential to extend the application of heat-resistant adhesives.

2. Experimental procedure

2.1. Adhesive preparation and joining process

Solid polymethylsiloxane was selected as the matrix of the adhesive, and the solid epoxy resin was chosen to blend and copolymerize with polymethylsiloxane. Meanwhile, Si, mullite, Al, B_4C, low melting point $SnO{\cdot}SiO_2{\cdot}P_2O_5$ glass (SSP) powder were selected as inorganic fillers. First, solid polymethylsiloxane powder was dissolved in isopropanol with magnetic stirring and constant heating at 50 °C for 0.5 h. Then the solid epoxy resin powder and silicone resin coupling agent γ-(2, 3-epoxypropoxy) propytrimethoxysilane (KH560) were dissolved in the obtained solution with magnetic stirring for 0.5 h. Next the mixed solution was heated at 80 °C and magnetically stirred in condensing reflux device for 2 h. After the obtained adhesive cooled down, it was spooned into a container, and the inorganic fillers were added into the container with constantly stirring. Then the low molecular polyamide 650 (PA650) as curing agent were added into the container, the obtained adhesive was magnetically stirred for 0.5 h.

To find out the mechanical properties of the unmodified preceramic polymethylsiloxane, the unmodified adhesive was prepared (the weight ratio of polymethylsiloxane, Si, Al, B_4C and SSP is 10:2:2:1:3.5). First, solid polymethylsiloxane powder was dissolved in isopropanol with magnetic stirring and constant heating at 50 °C for 0.5 h. Then it was spooned into a container. After that, the inorganic fillers were added into the container with constantly stirring for 0.5 h to get the unmodified adhesive.

To optimize the addition of epoxy resin, the weight proportions of epoxy to polymethylsiloxane was separated into 5 wt.%, 10 wt.%, 15 wt.%, 20 wt.%, 25 wt.% and 30 wt.%. To improve adhesive's bonding strength at high temperature, different proportions of inorganic fillers (the weight ratio of fillers: polymethylsiloxane = 1:1) listed in Table 1 were studied. To optimize its curing conditions, different contents of curing agent PA650 (the weight ratio of PA560: polymethylsiloxane = 4 wt.%, 8 wt.%, 12 wt.% and 16 wt.% respectively) were discussed. Since the main costs of the adhesive come from raw material, it should be pointed out that the cost of the raw material of the adhesive with optimal bonding properties is 200 ¥/kg (29.98$/kg).

Table 1
Samples with different composition of fillers.

Number	Si (Wt.%)	SSP glass (Wt.%)	Al (Wt.%)	B_4C (Wt.%)
A_0	80	20	0	0
A_{30}	50	20	30	0
A_{35}	45	20	35	0
A_{40}	40	20	40	0
$A_{35}B_5$	45	15	35	5
$A_{35}B_8$	45	12	35	8
$A_{35}B_{10}$	45	10	35	10

After the preparation of the adhesive, SiC specimens were overlapped and bonded together in close thickness of 80 μm according to the configuration shown in Fig. 1(A), (D) and (E) The bonding substrate materials of SiC are the same as our group's previous research [16]. Then the obtained joints bonded by modified adhesive were cured at room temperature under the pressure of 0.5 MPa, while the unmodified adhesive were cured at 200 °C for 2 h. After curing process, some of these joints were heat-treated at 200 °C, 300 °C, 500 °C, 700 °C, 900 °C, 1100 °C, 1300 °C and 1500 °C in air for 1 h.

2.2. Mechanical testing and characterization

The silicon carbide joints heat-treated at 200 °C, 300 °C, 500 °C, 700 °C, 900 °C, 1100 °C, 1300 °C and 1500 °C were tested at room temperature with the Electronic Universal Testing Machine (UTM4204; Shenzhen, China) at a cross-head speed of 0.2 mm/min seen in Fig. 1(A), while the silicon carbide joints without heat-treatment were directly tested at 25 °C, 100 °C, 150 °C, 200 °C, 250 °C, 300 °C, 400 °C, 500 °C, 600 °C, 700 °C, 800 °C after maintaining at these high temperatures for 0.5 h seen in Fig. 1(B) and (C).

The chemical bonding was tested with Infrared Radiation (IR; WQF-510, Mitech Instrument, Beijing, China). Besides, D/Max-2500 X-ray diffraction (XRD) was employed to analyze the phase transformation of the adhesives heat-treated at different temperatures. The structural morphology of both the cross-section and the fracture surface of the joints was analyzed by scanning electron microscopy (Tungsten Filament SEM). In addition, the curing process was recorded with optical photos and its mechanism was studied.

3. Results and discussions

3.1. Modification of preceramic polymer

The previous research of our group have developed a heat-resistant preceramic polymethylsiloxane with excellent mechanical properties for a variety of engineering ceramic joining. However, decomposition of polymer network caused the low bonding strength of the adhesive for SiC at 500 °C [16]. In this paper, this preceramic polymethylsiloxane was called unmodified adhesive whose sheer strength after heat-treatment from 300 °C to 700 °C with an interval of 100 °C were tested at room temperature and shown in Table 2. As is seen in Table 2, the adhesive showed low bonding strength for SiC after heat-treatment from 400 °C to 600 °C whose lowest bonding strength was 5.04 ± 0.64 MPa. Similarly, J. Zhang [22] and X. Wang [23] obtained adhesives whose bonding strength after heat-treatment at 600 °C were 2.01 MPa and 4.80 MPa respectively. Consequently, the "weak stage" which threatened safe bonding needed to be eliminated. Meanwhile, polymethylsiloxane had to be cured with heat-treatment at about 200 °C and the bonding strength of the adhesive at high temperature remained to be improved. As a result, the modification of the adhesive was utilized.