Supplementary Materials

Improved Thermal Stabilities, Ablation and Mechanical Properties for Carbon Fibers/Phenolic Resins Laminated Composites Modified by Silicon-containing Polyborazine

Hui Zhao,[1,2] Lixin Chen,[1,2]* Jin Yun,[1,2] Lin Tang,[1,2] Ziyou Wen,[1,2] Xiao Zhang,[1,2] Junwei Gu[1,2,3]*

[1] Research & Development Institute of Northwestern Polytechnical University in Shenzhen, Guandong, 518057, P.R. China.

[2] MOE Key Laboratory of Material Physics and Chemistry under Extraordinary Conditions, Shaanxi Key Laboratory of Macromolecular Science and Technology, Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi' an, Shaanxi, 710072, P.R. China.

[3] Institute of Intelligence Material and Structure, Institute of Unmanned Systems, Northwestern Polytechnical University, Xi' an, Shaanxi, 710072, P.R. China.

*Corresponding authors: E-mail: lixin@nwpu.edu.cn (L. Chen); gjw@nwpu.edu.cn & nwpugjw@163.com (J. Gu).

2.2 Synthesis of SPBZ

Synthetic process of SPBZ (Structural formula in **Figure S1**) was performed under argon atmosphere in 250 mL Schlenk-type glassware equipped with a Teflon magneton. Hexamethyldisilazane (0.1 mol) was then dropwise added into the above glassware containing the borontrichloride (0.05 mol) mixed with 50 mL *n*-hexane with stirring at -40~-50^{o}C, then the reaction temperature was slowly cooled to room temperature, followed by stirred under reflux for 2h. The colorless liquid was finally obtained by filtration and vacuum distillation at 50^{o}C.

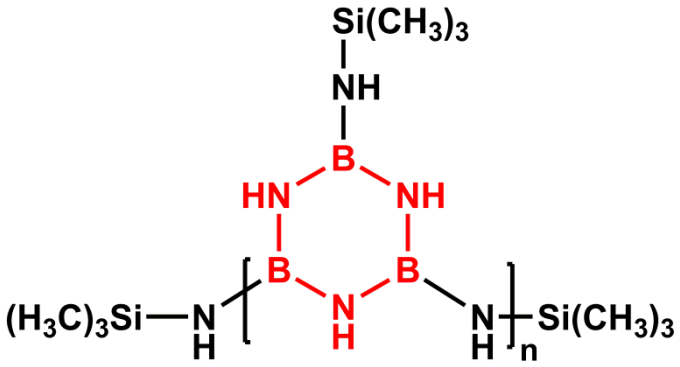

Figure S1 The structure diagram of SPBZ

Note: SPBZ represents silicon-containing polyborazine.

2.4 Characterization

Fourier transform infrared spectroscopy (FTIR) spectra of the samples were performed on Bruker Tensor 27 equipment (Bruker Co., Germany). 1H, 13C, 11B nuclear magnetic resonance (NMR) spectra of the samples were obtained by Bruker Avance 600 MHz nuclear magnetic resonance spectrometer (Bruker Co., Switzerland), and dimethylsulfoxid-d6 as solvent. Thermogravimetry-mass spectrum analysis (TG-MS) of the samples was performed on a simultaneous thermoanalyzer STA 449 F3 coupled with a quadrupole mass spectrometer QMS 403 C Aëolos (Netzsch Group, Germany) in

argon (gas flow, 50 mL/min). Thermal gravimetric (TG) analyses of the samples were performed with a heating rate of 10oC/min (argon atmosphere), over the whole range of temperature (25～1200oC) by Q600SDT (TA Instruments, USA); X-ray photoelectron spectroscopy (XPS) of the samples was conducted on a K-Alpha spectrometer (Axis Ultra, Kratos Analytical Ltd., U.K.). Raman spectra of the samples were recorded from 600 cm-1 to 2000 cm-1 on a confocal Raman Microprobe (HORIBA Jobin Yvon, France) using the 514.5 nm excitation line of an Argon-ion laser. Scanning electron microscope (SEM) morphologies of the samples were observed by a VEGA3 XMH instrument (Tescan Co., Czech Republic) and digital microscope (DM) morphologies of the samples were performed on a VCR-800 (Hirox Co., Ltd. Japan). The interlaminar shear strength (ILSS) of the samples was measured by SANS CMT 5105 electron universal testing machine according to ASTM D2344-2006. The ablation test of the samples was conducted by placing the samples in the flame of an acetylene-oxygen torch according to standard GJB 323A-1996.

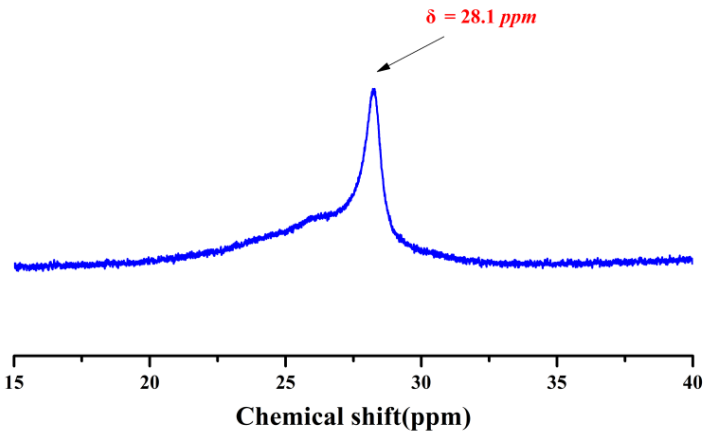

Figure S2 The ^{11}B NMR spectrum of SPBZ

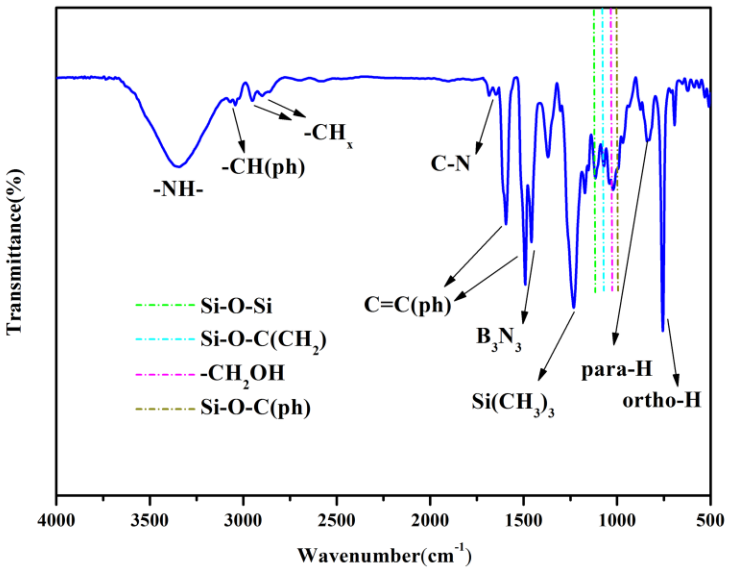

Figure S3 FTIR spectrum of $SPBZ_{15}$-PR

Note: $SPBZ_{15}$-PR represents phenolic resin modified by silicon-containing polyborazine.

Table S1 Characteristic thermal data of the cured PR and SPBZ-PR.

Content of SPBZ/%	T_5/°C	T_{10}/°C	T_{max}/°C	C_{800}/%	C_{1000}/%	C_{1200}/%	Weight loss between 400°C and 800°C/%
0	379.6	460.5	531.5	61.4	60.8	60.4	32.9
5	414.5	485.9	536.3	68.9	67.9	67.1	26.8
8.8	411.4	491.6	550.1	70.5	69.8	68.8	25.0
10	408.5	493.8	557.6	70.5	69.8	68.5	24.9
15	406.8	496.7	570.4	72.5	71.2	70.3	22.6
20	414.6	493.6	539.6	69.7	69.0	68.4	26.1

Table S2 Composition of the cured $SPBZ_{15}$-PR and its carbonization products.

T/°C	Element component/%					Chemical structure of Si/%	
	C	B	N	O	Si	Si-O-C	Si-O-Si
Untreated	79.18	0.89	1.33	16.94	1.66	88.22	11.78
400	81.31	0.45	1.19	15.40	1.64	69.75	30.25
600	85.37	1.30	1.33	10.54	1.46	37.77	62.23
800	86.64	0.72	0.83	9.83	1.98	35.93	64.07
1000	86.88	0.68	1.20	9.06	2.18	34.60	65.40
1200	87.12	1.12	1.37	8.69	1.70	32.24	67.76