

Contents lists available at www.sciencedirect.com

Journal of the European Ceramic Society

journal homepage: www.elsevier.com/locate/jeurceramsoc

Accelerating the crosslinking process of hyperbranched polycarbosilane by UV irradiation

Xiqiang Zhong^{a,b}, Xueliang Pei^{a,c,*}, Yulong Miao^a, Liu He^{a,c,*}, Qing Huang^{c,**}^a National Engineering Laboratory of Carbon Fiber Preparation Technology, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, PR China^b College of Material Science and Chemical Engineering, Ningbo University, Ningbo 315211, PR China^c Engineering Laboratory of Specialty Fibers and Nuclear Energy Materials, Ningbo Institute of Materials Engineering and Technology, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, PR China

ARTICLE INFO

Article history:

Received 24 December 2016

Received in revised form 25 March 2017

Accepted 27 March 2017

Available online xxx

Keywords:

Liquid hyperbranched polycarbosilane

UV irradiation

Divinyldimethylsilane

Ceramic yield

SiC ceramic

ABSTRACT

A liquid hyperbranched polycarbosilane (LHBPCS) with stoichiometric C/Si ratio but without unsaturated groups was synthesized. Different from traditional thermal crosslinking, ultraviolet (UV) irradiation crosslinking was taken. The molecular weight, the consumption of –Si–H group and ceramic yield of LHBPCS showed an increase trend with increasing the UV irradiation time. After 30 min of UV irradiation, 71.8 wt% ceramic yield was obtained. In addition, extra divinyl dimethylsilane was added into LHBPCS. Under UV irradiation, both the –Si–H group and vinyl group of divinyl dimethylsilane were consumed. But the reaction extend of vinyl group was much faster than that of –Si–H group. Compared with pure LHBPCS, the mixture of LHBPCS and 5 wt% divinyl dimethylsilane gave a higher ceramic yield of 79 wt% after 30 min of UV irradiation. By heating the crosslinked LHBPCS to 1000 °C, a near stoichiometric SiC ceramic was got. It exhibited excellent thermal stability at 1400 °C in air.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

Silicon carbon ceramic, which has excellent tensile strength, high modulus, low density, high thermal stability and high oxidation resistance, is one of the best candidates for ceramic-matrix-composites (CMC) [1–6]. As a key ceramic matrix precursor material in the polymer infiltration and pyrolysis (PIP) process, polycarbosilane (PCS) has gained comprehensive attention for over 40 years [7–13]. However, this solid polymer precursor still has some shortcomings in the PIP process: (1) its low ceramic yield; (2) a large amount of solvent is needed to solve it. As a result, more number of PIP cycles and complicated operation are required. So, extensive efforts have been devoted to the exploration of proper SiC ceramic precursors. Several researchers [14–16] deduced that a good ceramic precursor should be liquid or very fusible, and should possess proper molecular-weight, latent reactivity and high ceramic yield. Among various SiC ceramic precursors, liquid hyperbranched polycarbosilane (LHBPCS) [17–20], which has low

viscosity, high reactive functional groups, high ceramic yield and the ratio of Si to C approaching SiC stoichiometry etc, is regarded as the most excellent one.

LHBPCS was originally synthesized by Greber and Degler [21] through Grignard coupling of chloroalkyl chlorosilane, followed by reduction of the residual chlorine group. Whitmarsh and Interante [22] prepared the LHBPCS with the approximate formula $[\text{SiH}_{1.85}\text{Et}_{0.15}\text{CH}_2]_n$ by Grignard coupling of chloromethyltrichlorosilane ($\text{Cl}_3\text{SiCH}_2\text{Cl}$). But its ceramic yield was only 35%. And then, in an analogous route, a LHBPCS with an overall composite $[\text{SiH}_2\text{CH}_2]_n$ and a ceramic yield of 55% was prepared [23].

In order to increase the ceramic yield, unsaturated functional groups [24–26], such as vinyl and allyl, which could obviously promote crosslinking reaction, were introduced into precursor. It was because that hydrosilylation reaction between unsaturated groups and active –Si–H group occurred during the cross-linking process, which significantly improved molecular weight and reduced the vaporization of precursor fragments [24–26]. For example, by coupling of allyl chloride or acetylene magnesium bromide into the carbosilane backbone, LHBPCS with approximate formulas $[\text{SiH}_{1.2}(\text{CH}_3)_{0.71}(\text{CH}_2\text{C}=\text{CH}_2)_{0.09}\text{CH}_2]_n$ and $[\text{SiH}_{1.35}(\text{CH}_3)_{0.37}(\text{C}=\text{CH})_{0.28}\text{CH}_2]_n$ were synthesized respectively [26,27]. These precursors had ceramic yields of over 70% after high-temperature pyrolysis. Starfire Systems Inc., a leader in the field of Polymer-to-Ceramic™ technology, also fabricated

* Corresponding authors at: National Engineering Laboratory of Carbon Fiber Preparation Technology, Ningbo Institute of Material Technology and Engineering, Chinese Academy of Sciences, Ningbo, Zhejiang 315201, PR China.

** Corresponding author.

E-mail addresses: peixueliang@nimte.ac.cn (X. Pei), heliu@nimte.ac.cn (L. He), huangqing@nimte.ac.cn (Q. Huang).

<http://dx.doi.org/10.1016/j.jeurceramsoc.2017.03.063>

0955-2219/© 2017 Elsevier Ltd. All rights reserved.

a commercial LHBPCS named SMP-10 [7,28], which was partially allyl-substituted and widely studied as a SiC ceramic precursor. After crosslinking, the precursor produced a SiC ceramic with a high ceramic yield of over 72% and high performance as matrix of CMCs.

Although LHBPCSs with unsaturated functional groups show good performance and high ceramic yield, traditional thermal-crosslinking process needs long crosslinking time and high energy consumption [29–31]. Furthermore, even after long-time thermal treatment, the reaction extent of hydrosilation reaction between unsaturated functional groups and $-\text{Si}-\text{H}$ group is very low [32]. Moreover, the unsaturated groups, which were devoted to the ceramic yield, can increase the free carbon residual in the resulting SiC ceramic and affect the performance of SiC ceramic [24,30,33]. In order to reduce the problems, the amount of unsaturated substituents should be optimally balanced between ceramic yield and residual free carbon content [33].

Different from traditional thermal cross-linking, Zhou et al. cross-linked a LHBPCS with divinylbenzene in the presence of cyclohexanone peroxide-cobaltous naphthenate (CHP-CN) initiator system at room temperature for 12 h [25]. For the cross-linking mechanism, the radical copolymerization of LHBPCS and divinylbenzene was involved via the vinyl polymerization initiated by CHP-CN initiator system. For LHBPCS containing 10 wt% divinylbenzene, its ceramic yield increased from 45 wt% to 70.1 wt% after the cross-linking treatment. Nevertheless, initiator and divinylbenzene also had negative effect on the resulting SiC ceramic. Therefore, it is necessary to seek more efficient crosslinking methods to improve crosslinking reaction and ceramic yield.

Ultraviolet (UV) curing technology, which converts reactive liquid polymers into solids through photo-polymerization or crosslinking reaction, has spread rapidly throughout many industrial sectors, like protective coatings, wire insulation, adhesives and electronic packaging [34–36]. Compared with traditional thermal or catalyst treatment, this technology has lots of advantages, such as ultra-fast curing, ambient temperature operation and environment protection [37,38].

In this study, LHBPCS with the ratio of Si to C equaling SiC stoichiometry but without unsaturated functional groups was prepared. Different from traditional thermal or catalytic crosslinking for LHBPCS, UV-crosslinking technology was used. Additionally, in order to improve crosslinking degree and ceramic yield, additional divinyl dimethylsilane $[(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2]$ monomer, which has the capability of crosslinking with LHBPCS under UV irradiation, was mixed with the LHBPCS and cured by UV irradiation. Influence factors on the ceramic yield and SiC ceramic properties, including UV irradiation time, crosslinking monomer ratio and sintering temperature, were studied.

2. Experimental

2.1. Materials

Chloromethyltrichlorosilane ($\text{Cl}_3\text{SiCH}_2\text{Cl}$) (industry grade, more than 97% purity) was purchased from Shanghai Ruishuo Chemical, China. Divinyl dimethylsilane $[(\text{CH}_3)_2\text{Si}(\text{CH}=\text{CH}_2)_2]$ (analytical grade) was purchased from Gelest, Inc, US. Lithium aluminum hydride (LiAlH_4), n-hexane, magnesium and anhydrous sodium sulfate were bought from Aladdin Chemistry Co. Ltd, Shanghai. Other chemical reagents were obtained from Sinopharm Chemical Reagent Co, China.

2.2. Synthesis of LHBPCS without unsaturated functional groups

Anhydrous THF (600 ml) and 40.00 g magnesium powder (1.67 mol) were added into a 2 L four-neck flask equipped with a

reflux condenser, a mechanical stirrer, a constant pressure dropping funnel (nitrogen inlet) and a thermometer. At first, several grains of iodine and $\text{Cl}_3\text{SiCH}_2\text{Cl}$ (20 mL) were added into the flask and heated at 40°C to initiate the Grignard reaction. Then, the remaining $\text{Cl}_3\text{SiCH}_2\text{Cl}$ (180 mL) was dropped into the flask over a period of 2 h. After dropping, the reaction mixture was heated at 60°C for 12 h. The resulting dark brown slurry was reduced by LiAlH_4 (1.04 mol, 60% excess) dissolved in THF (400 mL) at 60°C for 12 h. At last, the slurry was hydrolyzed by a mixture of HCl aqueous solution (185 g, 3.0 mol/L) and n-hexane (1 L) in an ice-salt bath. The organic phase was separated, washed with HCl aqueous solution (100 g, 1.0 mol/L) and dried over anhydrous sodium sulfate. After removing the solvent by distillation, a yellow LHBPCS with yield of 62.5% and viscosity of 0.046 Pa s at 25°C was obtained.

2.3. UV curing and pyrolysis of LHBPCS without unsaturated functional groups

The pure LHBPCS or the mixture of LHBPCS with extra divinyl dimethylsilane was crosslinked by a UV lamp (UVITRON INTERNATIONAL-IntelliRay 600, irradiation wavelength-365 nm, light intensity-100%) at room temperature with a distance of 10 cm from lamp to specimen. The irradiation time was 0, 1, 2, 3, 5, 15, 20, 25 and 30 min, respectively.

Then, the UV-cured samples were placed in alumina boats and pyrolyzed in an electrical resistance tubular furnace. The furnace was firstly vacuumed with a pump to eliminate air, and then filled with high-purity argon. The temperature increased from ambient temperature to 1000°C with a heating rate of $10^\circ\text{C}/\text{min}$ and pyrolyzed at this temperature for 2 h.

2.4. Characterization

Gel permeation chromatography (GPC): the average molecular weight and polydispersity index (PDI) of LHBPCS were determined by TOSOH HLC-8320 GPC using THF as the eluent. The samples were dissolved in THF at a concentration of 1 mg mL^{-1} .

Nuclear magnetic resonance (NMR): the NMR spectra were recorded on a Bruker 400 MHz AVANCE III NMR spectrometer using deuterated chloroform (CDCl_3) as the solvent. All chemical shifts were referenced to tetraethylsilane.

Fourier transform infrared spectroscopy (FTIR) spectra: FTIR spectra were recorded on a Thermos Nicolet Nexus 470 FTIR spectrometer using a KBr pellet which was prepared by compressing a finely ground mixture of about 2 mg of sample and 100 mg of KBr powder, and a total of 32 scans were acquired with a spectral resolution 4 cm^{-1} .

Thermogravimetric (TG): TGA was carried out using a NETZSCH STA 449 thermal analyzer. Typically about 5 mg of sample was heated from room temperature to 1000°C at $10^\circ\text{C}/\text{min}$ in a stream of pure nitrogen atmosphere.

Elements analysis: the carbon element content was measured by an infrared absorption carbon/sulfur analyzer CS844 (LECO, America) and an oxygen/nitrogen determinator EMGA-620W (HORIBA, Japan) was used for measuring the oxygen element content.

X-ray diffraction (XRD) analysis: the XRD analysis was performed on a Bruker D8 Advance diffracts meter using nickel filtered copper K α radiation. The samples were scanned over the 2θ range from 10° to 90° .

Scanning electron microscope (SEM): the morphology of SiC ceramic was characterized by a Hitachi S-4800 field emission scanning electron microscope. The samples were sputter-coated with gold before imaging.

Download English Version:

<https://daneshyari.com/en/article/5440267>

Download Persian Version:

<https://daneshyari.com/article/5440267>

[Daneshyari.com](https://daneshyari.com)