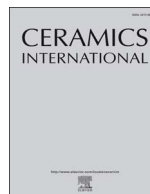




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Enhancing the yield of polycarbosilane synthesis via recycling of liquid by-product at atmospheric pressure

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ABSTRACT

Polycarbosilane (PCS) is a typical ceramic precursor for the fabrication of SiC fibers and SiC matrix composites. However, it is still costly and not widely employed in industry, mainly due to its low yield by typical chemosynthesis methods.

In this work, we reported for the first time a novel method to significantly increase the PCS yield from 51.3% to 62.8% by recycling the liquid by-products (LBP), which was mainly made up of low-molecular-weight PCS, as revealed by FT-IR, GPC, and NMR analysis. The results showed that recycling LBP did not alter the chemical structure of the PCS products, making it very promising for mass production and application of PCS at the industrial scale.

1. Introduction

Silicon carbide (SiC) fibers and SiC matrix composites are currently employed widely in various industries, such as aerospace engines, nuclear power, etc., due to their high resistances to oxidation and corrosion, high specific strength/modulus, low density, etc. [1–6]. They are generally fabricated via the high-temperature pyrolysis of polycarbosilane (PCS), a typical precursor of SiC having molecular weight of 1800–2100 g/mol and softening point of ~210 °C [7,8]. However, the chemosynthesis of PCS is still limited by its low yield, making it very costly to be widely applied in industry. In addition, large quantities of by-products from typical chemosynthesis methods are also harmful to the environment. Therefore, there is an urgent need to increase the yield of PCS and to reduce the discharging of its by-products.

At present, the main method to synthesize PCS at the industrial scale is the thermal rearrangement of polydimethylsilane (PDMS), which can be carried out under either high pressure [9–11] or atmospheric pressure [12] conditions. Fig. 1 shows the synthetic procedures using this method. For high pressure method, the reactor is required to withstand high temperature (470 °C) and high pressure (> 10 MPa) at the same time, which is very demanding on production facilities [9,10]. The atmospheric-pressure method is less demanding on equipment and is thus more promising for mass production. This method includes two steps [13]: the first step is the pyrolysis of PDMS at 400 °C, which produces liquid polysilane (LPS) with a yield of 80%, and the second step is the

thermal rearrangement of LPS and polycondensation, which finally produce PCS with a yield of 50%. However, the overall synthetic yield of PCS from this two-step process is still very low, ~40%, which is mainly due to the formation of gaseous by-product (GBP) and solid by-product (SBP) during the first step and the GBP and liquid by-product (LBP) during the second step.

One possible method to enhance the PCS yield is to reduce the yields of by-products. Rescuing GBP requires the employment of sealed reactors to liquefy the gaseous molecules at high pressure. Thus, high-pressure equipment is needed, which places stringent demands on production facilities [13]. Therefore, one may consider reducing the yields of SBP and LBP in order to increase the yield of PCS instead.

Based on the characterization of LBP structures, it was found that LBP could be recycled to improve the PCS yield. In addition, this method fits very well with current PCS production methods, as it does not necessitate any modification of current PCS production facilities, nor does it affect subsequent processes in the preparation of SiC fibers or substrates. Hence, this method has immense potential for application in industrial PCS synthesis.

2. Materials and methods

2.1. Raw materials and reagents

PDMS (purity > 98%) was fabricated at Shenzhen Gujia Chemicals

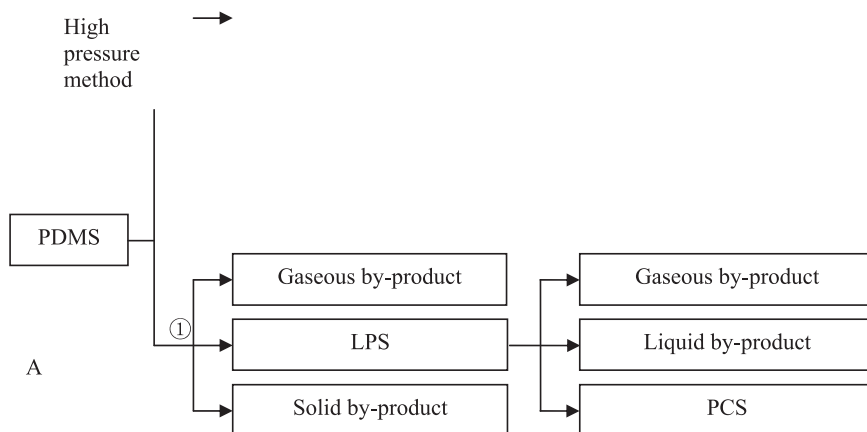
Abbreviations: PCS, polycarbosilane; PDMS, polydimethylsilane; LPS, liquid polysilane; GBP, gaseous by-product; SBP, solid by-product; LBP, liquid by-product; GPC, gel permeation chromatograph; THF, tetrahydrofuran; NMR, nuclear magnetic resonance; FT-IR, Fourier-transform infrared spectroscopy; TG, thermogravimetric

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Co., Ltd, and xylene (purity > 99%) at Tianjin Hengxing Chemical Reagent Co., Ltd.

2.2. PCS synthesis

PDMS was placed in a three-neck flask fitted with a condenser and receiving trap, for pyrolysis at 400 °C in a protective N₂ atmosphere. LPS was obtained after the resulting solution was cooled and filtered.

360 g of LPS was placed in a three-neck flask fitted with a quartz reactor tube, a condenser, and a receiving trap. The LPS was then heated to 450 °C in a protective N₂ atmosphere. This temperature was maintained for 10 h, and the solution was then cooled to room temperature to obtain P-PCS (pre-PCS). The P-PCS was dissolved in xylene, filtered, and vacuum-distilled at 300 °C for 10 min. Finally, the reactor was cooled to room temperature to obtain PCS-1 and distilled LBP. The yields of PCS-1 was calculated by dividing their qualities to the quality of LPS.

The distilled LBP was mixed with another 360 g of LPS and then used as raw materials for repeating the synthesis of PCS; this finally yields PCS-x and LBP-x (x = 2, 3 ... n, with n - 1 being the number of recycling rounds). The yields of PCS-x and LBP-x were calculated by dividing their qualities to the quality of LPS, and the additional ratio of LBP was also determined by this rule (Fig. 2).

2.3. Analysis and characterization

The softening points of the samples were measured using a Shanghai Precision Scientific Instrument WRS-2A microprocessor melting point apparatus, with a heating rate of 2 °C/min. The molecular weight and distribution of molecular weights of the samples were measured using a Wyatt Technology DAWN HELEOS-II high-performance gel permeation chromatograph (GPC), with an s-Styragel column, and tetrahydrofuran (THF) as the solvent and eluent. The rate of elution was 1 mL/minute. A Bruker AV 400 nuclear magnetic resonance (NMR) spectrometer was used to perform ¹H NMR and ²⁹Si NMR measurements, with deuterated chloroform (CDCl₃) as the NMR solvent. Fourier-transform infrared spectroscopy (FT-IR) was also performed, for which the samples were

pressed into KBr pellets and analyzed using a Thermo Nicolet Avatar 360 FT-IR spectrometer, with a scan range of 400–4000 cm⁻¹ and resolution of 4 cm⁻¹.

3. Results and discussion

3.1. Characterization of LBP structure

The GPC analyses of P-PCS, PCS-1, and LBP are shown in Fig. 3. The curves indicate that the distillation of P-PCS results in its separation into PCS-1 and LBP. The GPC curves of P-PCS and PCS-1 presents a “double-peak” distribution, overlapping with that of LBP presenting a “single-peak” distribution. The molecular weights of P-PCS and PCS-1 are higher than that of LBP (Table 1). However, the parts where their molecular weights overlap imply that P-PCS and PCS-1 contain components with molecular weights similar to LBP.

The FT-IR analyses of P-PCS, PCS-1, and LBP are shown in Fig. 4. The most important characteristic peaks in the FT-IR spectra are as follows: C-H vibration peaks at 2950 and 2900 cm⁻¹, Si-H vibration peaks at 2100 cm⁻¹, C-H in Si-CH₃ deformation vibrations peaks at 1400 cm⁻¹, CH₂ in Si-CH₂-Si out-of-plane rocking vibrations peaks at 1350 cm⁻¹, CH₃ in Si-CH₃ deformation vibrations peaks at 1250 cm⁻¹, Si-C-Si in Si-CH₂-Si stretching vibrations peaks at 1020 cm⁻¹, Si-C stretching vibrations at 820 cm⁻¹. This figure shows that there are no significant differences between the characteristic IR absorption peaks of each sample, thus indicating that LBP has a Si-C backbone and Si-H active groups similar to those of P-PCS and PCS-1, going a step further, LBP is the low-molecular-weight PCS components (M_L).

The intensity ratio between the characteristic absorption peaks of Si-H and Si-CH₃ in the FT-IR spectra, I_{Si-H}/I_{Si-CH₃}, was used to characterize the Si-H content of PCS, while the intensity ratio between the characteristic absorption peaks of Si-CH₂-Si and Si-CH₃, I_{Si-CH₂-Si}/I_{Si-CH₃}, was used to characterize the Si-CH₂-Si content of PCS. LBP shows the lowest Si-CH₂-Si content and highest Si-H content, compared with P-PCS and PCS-1 (Table 1).

A high M_L content will affect softening point and ceramic yield of PCS. Therefore, it is necessary to remove some of the M_L component

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