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Synthesis and Characterization of Novel Preceramic Polymer for SiC

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Abstract

Polyphenylcarbosilane as a novel preceramic polymer for SiC was synthesized from thermal rearrangement of polymethylphenylsilane around 350°C~430°C. Characterization of synthesized polyphenylcarbosilane was performed with ^{29}Si, ^{13}C, ^{1}H NMR, FT-IR, TG, XRD, and GPC analysis. From FT-IR data, the band at 1035 cm^{-1} was very strong and assigned to CH_2 bending vibration in Si-CH_2-Si group, indicating the formation of the polyphenylcarbosilane. The average of the molecular weight (M_w) of the polyphenylcarbosilane synthesized was 2,500 and easily dissolves in an organic solvent. TGA data indicates that polyphenylcarbosilane is thermally stable up to 400°C. However, the rapid weight loss occurs above 400°C due to the pyrolysis of polyphenylcarbosilane, and the diffraction peak of pyrolysis residue at 1200°C corresponds to the β-SiC ceramic. The ceramic yield calculated from TGA is approximately 65 %.

Keywords: Polyphenylcarbosilane, Preceramic polymer, Polymethylphenylsilane, β-SiC

Introduction

Recently, various types of carbide and nitride ceramics have been prepared from preceramic polymeric precursors[1-7]. The most important advantage of using polymeric precursor is the easiness of the preparation at low processing temperature. Since preceramic polymers having moderate molecular weight are easily soluble in organic solvents such as cyclohexane, THF, xylene, preceramic polymers also allow to coat on metal, ceramic or graphite surface easily using spining, dip, spray coating methods to improve their anticorrosion, antioxidation properties. After cross-linking and having thermal treatment, preceramic polymer turns into amorphous ceramic in the range of 600^{o}C~900^{o}C, and crystalline ceramic phase above 1200^{o}C. The ceramic microstructure derived and chemical composition is strongly dependent on the composition of the polymer precursors used. Polycarbosilane is the most typical polymeric precursor for SiC ceramic and has been widely used since the pioneering work done by Yajima et al. on SiC fiber [2].

In general, polycarbosilane is synthesized by thermal decomposition of polydimethylsilane under high pressure in an autoclave [1]. For the reaction, Si radical has to be formed in the initiation step of the reaction and preparation of polycarbosilane from polydimethylsilane is carried out by Kumada rearrangement [1]. Kumada rearrangement of polydimethylsilane to polycarbosilane has been mostly studied by thermal decomposition at high temperature. However, this method contains significant operational problems such as generating gaseous by-products including CH_4, Me_3SiH, SiH_4 etc. The gaseous byproducts create extremely high pressure, normally higher than 100 atmospheres inside autoclave, which renders the operation inconvenient and unsafe.

To overcome these problems of thermal decomposition process, Yajima et al. adopted catalytic process in which polycarbosilane was synthesized at normal pressure by adding small amount of polyborodimethylsiloxane to polydimethylsilane as a catalyst [2]. Kim et al. also attempted to synthesize polycarbosilane at low pressure using zeolites as a catalyst such as ZSM-5, Zeolite A, Zeolite Y[3]. Also, Hasegawa et al. developed heterogeneous catalysts for this reaction

such as $AlCl_3$, $MnCl_3$, $CrCl_3$, VCl_3, $TiCl_3$ and $GaCl_3$ etc [4]. However, the disvantage of using the catalytic method for the preparation of polycarbosilane is difficultness of catalyst sepataion, specially in case of nano catalytic powder. Also, contamination of catalyst gives deleterious effects on preceramic polymer properties.

In our study, a new method of synthesizing the preceramic polymer for SiC at low pressure is proposed by thermal rearrangement of polymethylphenylsilane. (Fig. 1) The thermal decomposition of polymethylphenylsilane above 350°C generates liquid by-products such as phenylsilane, methylphenylsilane, diphenylsilane etc. Therefore, synthesis of polyphenylcarbosilane from polymethylphenylsilane using an autoclave attached condenser generates less than 10 atmospheric pressures. Therefore polyphenylcarbosilane can be synthesized in much milder condition compared to those of polycarbosilane. The prepared polyphenylcarbosilane and by-products during the thermal conversion were characterized with ^{29}Si, ^{13}C, ^{1}H NMR, FT-IR, TG, XRD, GPC and GC analysis to understand its properties and structure.

Experimental Section

Preparation of Polymethylphenylsilane

Polymethyphenylsilane was synthesized through the reaction of methylphenyldichlorosilane with sodium metal in toluene solvent at 110°C. 40g of metallic sodium was chopped into small pieces and transferred into a 100ml toluene under inert atmosphere. At 110°C, after sodium was entirely dispersed into toluene solvent, 100g of methylphenyldichlorosilane was dropwised and refluxed for 7 h. After the reaction, the unreacted sodium metal was removed by adding methanol. To remove NaCl and lower molecular weight of polymethylphenylsilane, the solid product was washed thoroughly with deionized water and acetone. The final product of white precipitate was dried under vacuum.

Preparation and Purification of Polyphenylcarbosilane

For the preparation of polyphenylcarbosilane, 20g of polymethylphenylsilane was loaded into a 300ml autoclave reaction vessel attached condenser. After purging the sample with nitrogen gas, the temperature increased to 350 ^{o}C and kept for 6 h to occur Kumada rearrangement. Temperature was raised to 430^{o}C, and kept for another 6 h to increase the molecular weight of the polyphenylcarbosilane. During the synthesis, pressure of the autoclave does not exceed 20 atmospheres.

After the reaction, yellow viscous solid was obtained. The product was dissolved in cyclohexane and filtered to remove insoluble products, and then cyclohexane was evaporated using a rotary evaporator. Yellow brown viscous product was still obtained. Purification was done by heating under vacuum at 250^{o}C for 30 min to remove the low molecular weight products. (Fig. 2) Yellow brown solid was remained in the middle of the furnace, and clear liquid byproduct was collected at the both side of furnace.

Characterization

^{29}Si, ^{13}C, ^{1}H NMR spectra were obtained using Varian Unity Inova 200 MHz spectrometer. FT-IR spectra were obtained using a FTS-175C spectrometer in the range of 4000 to 400 cm^{-1}. Molecular weight distribution of polyphenylcarbosilane was determined by a Gel Permeation Chromatography (Agilent) with Styragel column using tetrahydrofuran as a solvent. Polystyrene standard was used for calibration. Thermal decomposition of the polyphenylcarbosilane up to 1200 ^{o}C was measured by STA-MS-Skimmer TGA (Thermal Gravimetric Analysis) instrument under nitrogen atmosphere. XRD analysis of the powder after pyrolysis was carried out using a KFX-987228-SE MAC Science make X-ray diffractometer employing a Cu target (K_{α}= 1,54 A).

In order to characterize the byproduct, the crystal precipitate out of the low molecular weight product, which is a clear solution, was coated with paratone oil and mounted on to a cryo-loop pin. The data of the small size single crystals were collected with Bruker APEX II detector with

synchrotron radiation at beamline 11.3.1 of Advanced Light Source at Lawrence Berkeley National Laboratory. All data were collected at 150(2) K by using the w scan mode and integrated by using SAINT V7.34. Absorption correction was done with SADABS. Structures were solved by a direct method and refined with SHELXS package.

Results and Discussion

West and coworkers have synthesized polymethylphenylsilane (known as polysilastyrene) from the copolymerization of dimethyldichlolosilane and phenylmethyldichlorosilane [8]. However, this polymer itself is not suitable as a SiC precursor, because it is unstable and while it decomposes at high temperature it generates gaseous by-products including CH_4, Me_3SiH, SiH_4 etc. The gaseous byproducts, especially silane gas, render the operation inconvenient and unsafe. To make SiC precursor, West et al. tried to crosslink this polymer by photolysis using ultraviolet radiation at 350nm [9], and Krishnan et al crosslinked the polymer by chemically using divinylbenzene [10]. Although ceramic yield is increased approximately 40% by crosslinking, the polymer that is finally obtained is an insoluble white powder.

Preceramic polymers soluble in organic solvent allow to coat on metal, ceramic or graphite surface. It can be easily used by a spinning, dip, spray coating methods at room temperature, and converts to amorphous ceramic by heat treatment to improve their anticorrosion, antioxidation properties. For the application of SiC coating on various substrates to improve anticorrosion, anti-oxidation properties, it is required soluble SiC precursor having high ceramic yield.

To produce soluble SiC precursor with high ceramic yield, we prepared polyphenylcarbosilane from polymethylphenylsilane by thermal rearrangement at 350^{o}C and the temperature was raised to 430^{o}C to increase molecular weight of the polyphenylcarbosilane. (fig. 1) Polymethylphenylsilane was prepared by dechlorination and polymerization of methylphenyldichlorosilane using a sodium metal.

Formation of polymethylphenylsilane was confirmed by FT-IR and ^{29}Si solid NMR. Fig. 3

(a) shows the FT-IR spectrum of prepared polymethylphenylsilane. The band at around 2950 cm^{-1} and 3066 cm^{-1} are assigned to C-H stretching vibration in methyl group and phenyl group, respectively. The adsorptions were seen at 1098 cm^{-1} and 1248 cm^{-1} represent Si-phenyl stretching in phenyl group and Si-CH_3 deformation, respectively. All other peaks are in agreement with those reported in the literature.

Fig. 4 shows ^{29}Si solid NMR of polymethylphenylsilane. Singlet peak appears at -37ppm assigned to Si-Si suggesting all the Si species are identical environment.

We tried to synthesized polyphenylcarbosilane from polymethylsilane around 350°C~430°C, since Kumada rearrangement of silane to carbosilane is known to occur around 350°C. After the reaction, yellow brown viscous product was obtained. Purification was done by heating under nitrogen atmosphere at 250°C for 30 min to remove low molecular weight product. (Fig. 2) Yellow brown solid, which is polyphenylcarbosilane, was remained in the middle of the furnace, and clear liquid, which is trimethylphenylsilane, as a byproduct was collected at the both side of furnace.

Characterization of polyphenylcarbosilane

The formation of the polyphenylcarbosilane from polymethylphenylsilane is confirmed by FT-IR spectrum. As shown in Fig. 3 (b), FT-IR spectrum of the synthesized polyphenylcarbosilane exhibits vibration bands at around 1035 cm^{-1}, which is very strong, is assigned to CH_2 bending vibration in Si-CH_2-Si group, indicating the formation of the polyphenylcarbosilane. Except Si-phenyl stretching (1098 cm^{-1}) and C-C stretching in phenyl (1486 cm^{-1}), these results are in agreement with those of polycarbosilane reported in the literature [2]. The quantitative chemical analysis data is consistent with the formulation of $SiC_{9.4}H_{11.3}$ for the polyphenylcarbosilane. Number average of molecular weight (M_w) of the polyphenylcarbosilane determined by GPC is 2,500 and is easily soluble up to 30 wt% in organic solvents such as cyclohexane, THF, xylene etc.

Fig. 5 shows the ^{29}Si MAS NMR spectrum of the as-synthesized polyphenylcarbosilane from

polymethylphenylsilane. The ^{29}Si MAS NMR spectrum as synthesized sample shows three splitted peaks at around 0, -17, -38 ppms. Generally, the peak at around 0 ppm is assigned to SiC_4. However, this peak is splitted as several peaks since neighboring SiC_xSi_{4-x} species originated from residual Si-Si bond in the structure. The peak at -17ppm is assigned to SiC_3H and also this peak is splitted as several peaks since residual $SiC_{x-1}HSi_{4-x}$ species in the structure. Fig. 5 also exhibits small peaks at around –37 ppm for residual Si-Si species.

Fig. 6 shows ^{1}H NMR spectra of the polylphenylcarbosilane. The peaks at 0.85, 1.28 and around 7.5ppm are assigned to CH_3, CH_2 and phenyl group, respectively. Figure 7 shows ^{13}C NMR spectra of the polyphenylcarbosilane. The peaks at 1.28, 29.96 and around 130ppm are assigned to CH_3, CH_2 and phenyl group, respectively. The ratio of CH_3, CH_2 and phenyl group can be calculated from the integral of the peaks from ^{1}H and ^{13}C NMR spectra data.

The TGA curve exhibits large amount of weight loss up to 700^{o}C. This means that the organic groups of the polyphenylcarbosilane are decomposed in this temperature range. (Fig. 9) The weight loss of the polyphenylcarbosilane occurs the rapid weight loss above 400^{o}C due to pyrolysis of polyphenylcarbosilane to SiC ceramic. The ceramic yield calculated from TGA is about 71 % in the air and 65% under N_2 atmosphere.

In order to examine the pyrolysis residue after heat treatment, the pyrolysis residue was crushed into a powdered form, and analyzed with XRD. Fig. 10 shows the X-ray diffraction results of the sample after heat treatment at 1200^{o}C for 1 h under N_2 atmosphere. The diffraction peak around 35^o, 60^o, and 73^o corresponded to the β-SiC. All the diffraction peaks were quite broad, which indicated that the sample was in the early stage of crystallization at the heat treatment temperatures.

Characterization of Trimethylphenylsilane

Purification was done by heating under nitrogen atmosphere at 250^{o}C for 30 min to remove low molecular weight product. (Fig. 2) Yellow brown solid which is polyphenylcarbosilane was

remained in the middle of the furnace and clear liquid was collected as a byproduct at the both side of furnace. Both crystals from the big crystals grown from the solution and tiny ones on the wall of the vial have a same crystal structure. The structure refinement was carried out in space group $P2_1/c$ with cell parameters a=18.524(6)Å, b=9.544(2) Å and c=18.346(2) Å, $\beta=107.80(1)_o$. The building unit is Si monomer with three phenyl rings and one methyl group. Its structure was reported in the literature [11].

As shown in Figure 3, FT-IR spectrum of the triphenylmethylsilane is in agreement with those of triphenylmethylsilane purchased chemical reagent. Number average of molecular weight (M_w) of the triphenylmethylsilane determined by GC is 277.

Fig. 6b shows ^1H NMR spectra of the methyltriphenylsilane. The peaks at 0.80 and around 7.5ppm are assigned to CH_3 and phenyl group, respectively. Fig. 7b shows ^{13}C NMR spectra of the methyltriphenylsilane. The peaks at -2.86 and approximately 130ppm are assigned to CH_3 and phenyl group, respectively. From the integral of the peaks from ^1H and ^{13}C NMR spectra data, the ratio of CH_3 and phenyl group can be calculated.

Conclusion

In conclusion, we report the synthesis and characterization of polyphenylcarbosilane that is a suitable precursor for SiC ceramic. Polyphenylcarbosilane can be synthesized in much milder condition compared to those of polycarbosilane due to its liquid type thermal by-products rather than volatile type. Purification was done by heating under vacuum at 250^oC for 30 min to remove the low molecular weight products. Number average of molecular weight (M_w) of the purified polyphenylcarbosilane is 2,500, and is easily soluble in organic solvents. The diffraction peak of pyrolysis residue at 1200^oC corresponds to the β-SiC ceramic. The ceramic yield calculated from TGA is about 65 %. The obtained polyphenylcarbosilane, providing a good solubility in organic solvent, is a suitable precursor for coating using a solution process.

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