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Synthesis of polyphenylcarbosilane via thermal rearrangement of polymethylphenylsilane in supercritical cyclohexane

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Abstract : A new process for the synthesis of polyphenylcarbosilane (PPCS) via thermal rearrangement of polymethylphenylsilane (PMPS) in supercritical cyclohexane was proposed and investigated at reaction temperatures of 380-420℃, reaction times of 1-2 h, and a pressure of 15 MPa. The structure, molecular weight, and molecular weight distribution of the product were characterized by FT-IR, Si-NMR, and GPC. The ceramic yield was also measured by TGA analysis. High-quality PPCS with high molecular weight and ceramic yield can be synthesized via a supercritical process. Furthermore, this process, when compared to the conventional method, tends to moderate the reaction conditions such as reaction temperature and time. It is concluded that thermal rearrangement in supercritical fluid is an efficient and viable process in terms of the resulting yield, efficiency, and reaction time compared with those of the conventional PCS production process.

Keywords : polyphenylcarbosilane; polymethylphenylsilane; SiC; supercritical cyclohexane; thermal rearrangement

1. Introduction

Silicon carbide (SiC) is an extreme material that exhibits high thermal and chemical stability, high strength, hardness, and thermal conductivity. Because of these attributes, it is widely used in the space shuttle, aircraft, and nuclear industries,[1] including applications requiring clean environmental materials, such as for radiation gas burners[2] and high-power electrical cables.[3]

Pure silicon carbide can be made by chemical vapor deposition (CVD), in which carrier gases such as argon or hydrogen pass though the reaction tube, and reaction gases decompose on the substrate to produce SiC.[4] It can also be prepared by thermal decomposition of the polymer, polymethylsilane, in an inert atmosphere at relatively low temperatures. Compared to CVD, the pyrolysis method is advantageous because the polymer can be formed into various shapes prior to thermalization into the ceramic.[5-6] Since Yajima offered a new method to synthesize the polymeric precursor of SiC using Kumada rearrangement,[7] the

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synthesis of SiC precursor from polysilane has been gaining greater attention, and a number of studies have been conducted to synthesize polycarbosilane (PCS) as the polymeric precursor of SiC. For instance, Lu et al.[8] synthesized the PCS from liquid polysilane and $B(OBu)_3$ according to different weight ratio at temperatures of 370-400℃ for 1 h. It was found from their results that the increase in molecular weight of PCS is accelerated in the presence of $B(OBu)_3$, and the synthesis of PCS can be performed at lower temperature, that is, $B(OBu)_3$ plays a catalytic role in the synthesis of PCS. Shin et al.[9] synthesized PCS from polydimethylsilane (PDMS) using Kumada rearrangement in the presence of zeolite (ZSM-5) catalyst. They have proposed the two-step thermal rearrangement of PDMS to improve the spinnability of PCS, and the best result was obtained at a temperature of 350-400℃ and reaction time of 30 h. Thermal decomposition of PDMS for PCS as a precursor of SiC fiber was performed by Cheng et al.[10] It was found that PCS synthesized under high pressure had bette rproperties such as ceramic yield, reaction activity, and molecular weight compared to PCS produced at normal pressure. Huh et al.[11] used a nanoporous anodized aluminum oxide (AAO) catalyst to develop the simple synthetic route of PCS. Their results showed that AAO catalysts can be reused and do not require a filtering process, which can simplify the complex synthetic processes of PCS and save time and cost.

These conventional thermal rearrangement processes, however, generally have disadvantages including non-uniform heat transfer, low yields of desired products, excessive char and gas formation, longer reaction time, and difficulty of separating the catalyst from the product.

There has been several studies on polymer degradation for chemical recycling using supercritical fluids which demonstrate that degradation in supercritical fluids is more efficient than conventional pyrolysis.[12-14] Similarly, thermal rearrangement of polysilane in supercritical fluids can enhance mass and heat transfer rate to result in high product yield and a relatively shorter reaction process without using any catalysts.

In this work, a new process for the synthesis of polymeric SiC precursor via thermal rearrangement of polymethylphenylsilane (PMPS) in supercritical fluid was proposed and investigated. The structure, molecular weight, and molecular weight distribution of the product were characterized by FT-IR, Si- NMR, and GPC. The ceramic yield was also measured by TGA analysis.

In general, organic solvents such as cyclohexane, tetrahydrofuran, and xylene were used to dissolve the preceramic polymers of moderate molecular weight for easy coating on metal, ceramic, or graphite surfaces using spinning, dip-coating, and spray-coating methods.[15] In the present study, we chose cyclohexane as a supercritical fluid because achieving a supercritical state with cyclohexane is relatively easy due to its low critical point, and PCS can be easily obtained since cyclohexane can dissolve the product after reaction. Furthermore, due to its low boiling point, cyclohexane can be easily distilled and recycled at the end of the reaction.

2. Experimental

The experimental apparatus designed for the Kumada rearrangement of PMPS in supercritical cyclohexane is shown in Figure 1. The reactor, manufactured by Parr Instrument Co., was made of 316 grade stainless steel with the volume of 25ml. The temperature and pressure of the reactor were measured by a K-type thermocouple and pressure gauge, respectively. The reaction temperature was controlled using a PID controller, and reaction pressure was controlled through variation of cyclohexane volume fed into the reactor. A magnetic bar was used to stir the reactant on the hotplate using a magnetic stirrer.

Fig. 1. Experimental apparatus designed for the preparation of PPCS in supercritical cyclohexane.

PMPS used in this study was supplied from ToBeM Tech, Korea. Cyclohexane (Samchun Chemical Co., Ltd.) was used as a supercritical fluid. The critical temperature and pressure of cyclohexane are 280.6℃ and 4.08 MPa, respectively.

PMPS and cyclohexane were loaded into the reactor, and then the reactor was degassed and refilled with argon to achieve an inert state. The reaction was started by heating the vessel in an electronic furnace at a heating rate of 15℃/min and an agitation speed of 1000 rpm. The reaction temperature and pressure were monitored in real time during the period of heating. Reaction time was defined as zero when the reaction temperature reached a prescribed value. When the reaction conditions reached the pre-set values, the reactor was immersed into a cold water bath and cooled rapidly to terminate the reaction. The product solution was removed from the reactor and filtered to remove the insoluble product. Then, cyclohexane was recovered by evaporation. The filter paper with the remaining solid residue was dried overnight in a drying oven at 90℃. The product yield was calculated by weighing the remaining substances.

A FT-IR spectrometer (Avator 360E.S.P) was used to obtain the IR spectra of PPCS over the range of 400-4000 cm^{-1}. The pellet, which was mixed as a solid state sample with KBr, was used to obtain IR spectra. ^{29}Si-NMR (Varian UNITY/INOVA200) was employed to characterize the structure of PPCS, and the CP/MAS technique was used to obtain better signal-to-noise ratios. The molecular weight distributions of PPCS were estimated by gel permeation chromatography (GPC, Agilent 1100 series) with tetrahydrofuran eluant at a flow rate of 1.0 ml/min. Narrow-molecular-polystyrene standards (PDI≤1.05, Shoko, Japan) were used for calibration. Thermogravimetric analysis (TGA, Sinco, TA1000) was employed to determine the ceramic yield of PPCS. For this measurement, the samples were heated at 10℃/min from 25 to 800℃ in a N_2 atmosphere.

3. Results and discussion

Polymethylphenylsilane (PMPS) was recently used to synthesize the polyphenylcarbosilane (PPCS) as a novel pre-ceramic polymer for SiC, which is more suitable for coating due to its high solubility in organic solvents. Lee et al.[15] produced PPCS without catalyst using a two- step thermal rearrangement at reaction temperatures of 350-430℃ for 12 h. In this two-step reaction, PMPS was converted to PPCS by thermal rearrangement at 350℃ for 6 h, and then the temperature was increased to 420℃ and maintained for 6 h to increase the molecular weight of PPCS. The average molecular weight (M_w) and ceramic yield were 2500 and 60%, respectively. However, using this method, large quantities of unpolymerized monomer byproducts such as triphenylmethylsilane, diphenylmethylsilane and diphenyldimethylsilane were also produced, which led to lower the PPCS yield.[15]

In the present study, the synthesis of PPCS by thermal rearrangement of PMPS in supercritical cyclohexane was performed at various reaction conditions to verify the efficiency and viability of the supercritical process, and the results were compared with those from the preceding conventional method.[15] The experimental conditions are listed in Table 1, and the reaction pressure was fixed at approximately 15 MPa. For the application of coating on various substrates via a solution coating process, PPCS should be soluble in organic solvents. Therefore, the product yield was defined as the weight ratio of product dissolved in cyclohexane to the reactant. High yields greater than 98% were obtained at all tested reaction conditions.

Table 1. Experimental conditions of the thermal rearrangement of PMPS in supercritical cyclohexane.

Polymer	Experimental conditions
PPCS-A	380° C, 1 h
PPCS-B	380° C, 2 h
PPCS-D	400° C, 1 h
PPCS-E	400° C, 2 h
PPCS-G	420° C, 1 h
PPCS-H	420° C, 2 h

According to the reaction mechanism for producing PCS by Kumada rearrangement,[7,16,17] the Si-Si bond in polysilane is initially cleaved by thermal treatment, and a silicon free radical is formed. Subsequently, the rearrangement including insertion of a methyl group between the silicon free radicals occurs to generate the Si-CH_2-Si and Si-H groups. Generally, a high molecular weight and broad molecular weight distribution of PCS can be obtained as the rearrangement proceeds. Hence, the molecular weight (M_w) and its distributions of PPCS were measured by GPC, and the results are shown in Figure 2. From the figure, PPCS samples had a wide range of molecular weight as 2,000~3,500 and its polydispersity depended on the reaction conditions. It was obvious that higher PPCS molecular weights were obtained without unpolymerized monomer byproducts through the supercritical process in a very short time (below 2 h) compared to that in preceding conventional rearrangement.

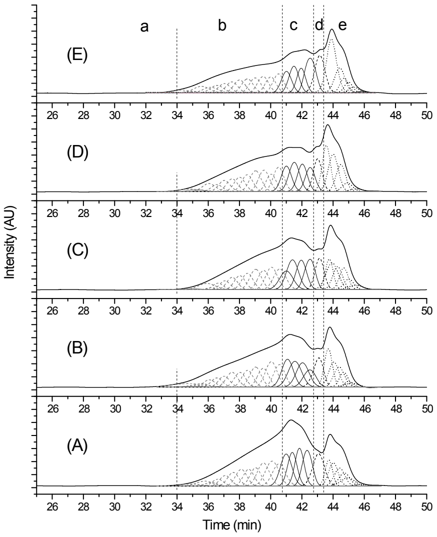

Fig. 2. Molecular weight and molecular weight distributions of PPCS produced at various reaction conditions: (A) PPCS-A, (B) PPCS-B, (C) PPCS-D, (D) PPCS-E, and (E) PPCS-G at a reaction pressure of 15 MPa.

The distribution of molecular weight can be divided as 5 parts in GPC analysis. The area a and b are the higher molecular weight zone, and the area d and e are the lower molecular weight zone. The area c is the intermediate molecular weight zone. The area of intermediate zone (area c) depended on the synthesis temperature and the time. When the synthesis temperature was increased, the intermediate zone was relatively decreased with increasing the area of the higher molecular weight zone (in area b). And, it was also comparably decreased with the rearrangement of the molecular weight distribution with increasing the intensity and area in higher molecular weight zone, when the synthetic time is longer in each condition with synthesis temperature in 350° C and 400° C respectively ; comparing PPCS-A with PPCS-B, and PPCS-D with PPCS-G (Figure 2 (A) with (B), and (C) with (E)).

The formation of PPCS was confirmed by FT-IR as shown in Figure 3. As can be seen in Figure 3, the peaks at 1035 cm^{-1} and 2100 cm^{-1} corresponding to CH_2 bonding in Si-CH_2-Si and Si-H were detected in all PPCS samples, indicating that PPCS with a Si-C backbone was produced by thermal rearrangement of PMPS in supercritical cyclohexane.

Fig. 3. FT-IR spectroscopy of PMPS and PPCS produced in supercritical cyclohexane under various conditions: (A) PPCS-B, (B) PPCS-E, and (C) PPCS-H at a reaction pressure of 15 MPa.

Figure 4 shows the Si-NMR spectrum of PPCS synthesized in supercritical cyclohexane. The peaks at -32 ppm represent Si-Si bonds, and peaks at 0 ppm and -21 ppm are attributed to $\mathit{Si}\mathrm{C}_4$andH$\mathit{Si}\mathrm{C}_3$,respectively.[18,19]

The $\mathit{Si}\mathrm{C}_4$ and H$\mathit{Si}\mathrm{C}_3$ peaks with broad signal through 10 ~ -20 ppm indicate that the formation of -Si-C- networks. Moreover, the Si-Si bond at -32 ppm was newly appeared, comparing to the Si-Si bond in PMPS which was detectable at -41 ppm. The new Si-Si bond caused by the new bond formation through dehydrogenation between Si-H bonds in PPCS.[21] When the temperature is growing the H$\mathit{Si}\mathrm{C}_3$ peaks were significantly decreased (Figure 4 (B), (C)) with decreasing the area of intermediate zone in GPC results (Figure 2 (D)). It means that the polymerization of PPCS can be derived not only by Kumada rearrangement but also by dehydrogenation in supercritical fluid like as conventional method.[21] Complex or high branched structure was formed effectively at over 400℃.

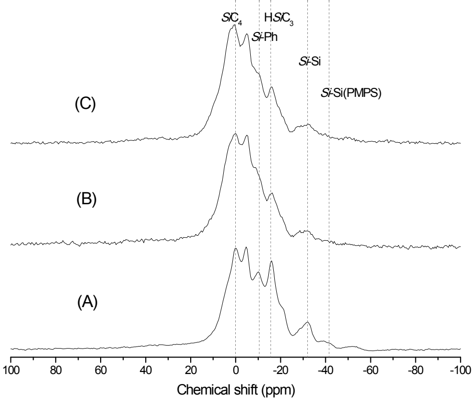

Fig. 4. ^{29}Si-NMR spectrum of PPCS produced via conventional thermal rearrangement [15] and those produced by supercritical cyclohexane process under various conditions: (A) PPCS-B, (B) PPCS-E, and (C) PPCS-H at a reaction pressure of 15 MPa.

At 380℃ condition, there was a weak peak at -41 ppm showing that the PMPS as starting material was still remained (Figure 4 (A)). But it was disappeared with higher synthesis temperature. It means that the thermal condition of 380℃ was not enough to convert to PPCS from PMPS, even through the GPC analysis and the FT-IR spectra couldn't show the critical difference between the differences of synthesis temperature.

The ceramic yield from a polymer after coating and heat treatment is one of the most important pre-ceramic polymer properties. Figure 5 shows the ceramic yields obtained from TGA curves. Weight loss of PPCS began to occur around 200℃ and continued until 600° C under a nitrogen atmosphere, indicating that the PPCS was decomposed into SiC ceramic. The ceramic yield of PPCS-B was 58%, and the PPCS-E and -H were 70%. There are several factors to ceramic yield. To obtain higher ceramic yield, PPCS must be higher polymerized or hyper-branched structure with higher boiling point. The decrement at 200 ~ 300° C was caused by the low molecular weight PPCS which was indicated at area d and e in GPC analysis, because it has lower boiling point and easily evaporated or decomposed at lower temperature. But, the final ceramic yield through 400 ~ 600℃ must be dependent on its structure. In case of PPCS-B, it contains much intermediated polymerized PPCS with lower branched structure, and it showed that lower ceramic yield as compared with PPCS-E and -H.

Fig. 5. TGA curves of PPCS produced in supercritical cyclohexane under various conditions: (A) PPCS-B, (B) PPCS-E, and (C) PPCS-H at a reaction pressure of 15 MPa.

From these results, highly cross-linked PPCS without byproducts with high molecular weight and ceramic yield was obtained at a relatively mild temperature and at lower pressure in a very short time compared to those in the preceding conventional method. The optimum reaction conditions for the synthesis of PPCS by thermal rearrangement of PMPS in supercritical cyclohexane were 400℃, a reaction time of 2 h, and a pressure of 15 MPa. Supercritical cyclohexane was proven to be a promising reaction medium for the PPCS production from PMPS.

4. Conclusions

The synthesis of PPCS by thermal rearrangement of PMPS in supercritical cyclohexane was performed at reaction temperatures of 380-420℃, reaction times of 1-2 h, and a pressure of 15 MPa to determine if the supercritical process is efficient and viable, and the results were compared with those from the preceding conventional method. The structure, molecular weight, and molecular weight distribution of the product were characterized by FT-IR, Si- NMR, and GPC. The ceramic yield was also measured by TGA analysis. High-quality PPCS with a high molecular weight and ceramic yield can be synthesized via the supercritical process. Furthermore, this process, when compared to the conventional method, tends to moderate the reaction conditions such as reaction temperature and time. It is concluded that thermal rearrangement in supercritical fluid is an efficient and viable process in terms of the yield, efficiency, and reaction time compared to the conventional PCS production process.

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