Fabrication of Dense Carbon Fiber Reinforced SiC Composites by Controlling the Rheology of Polycarbosilane Solution†

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Dense carbon fiber reinforced silicon carbide composites were prepared by polymer impregnation and pyrolysis with rheological properties of polycarbosilane such as different molecular weight and solution concentrations. During polymer impregnation and pyrolysis process, the densification mechanism of inter-/intra-bundle pores in the carbon fiber preform was also studied by using Hg-porosimeter. Almost of the pores in the carbon preform were filled within 3rd polymer impregnation and pyrolysis cycles when 60 wt % of highly viscous polycarbosilane solution. Inter-bundle pores ranging from 20 to 400 µm were previously filled and the small pores less than 1 µm were newly formed after pyrolysis.

Keywords: Carbon fiber preform, Polymer impregnation, Polycarbosilane, Silicon carbide, Inter-/intra-bundle pores.

INTRODUCTION

Studies on the ceramic fiber matrix composites (CMCs) are actively investigated in many countries during last decades because of their excellent mechanical properties at elevated temperature and potential applications in heat exchangers, body of engine or brake discs in airplane or automotive[1-3]. Silicon carbide based ceramic fiber matrix composites can be classified according to the type of reinforcement or operation conditions such as operation temperature and life time. Carbon fiber reinforced SiC composites (C_f/SiC composites) are suitable for use in high temperature environment and relative short life time required. On the other hand, SiC fiber reinforced SiC composites can be used to long life time application such as stationary gas turbines[3].

Several fabrication processes have been developed such as forced chemical vapour infiltration (F-CVI), Reaction sintering (RS), liquid phase sintering (LPS) and polymer impregnation and pyrolysis (PIP) and their combined processes also developed recently[3-8]. One of them, PIP can make a complex and large component with high density and mechanical strength at rather easy and low cost than any other processes. C_f/SiC composites are made cyclic treatment of impregnation (I), curing (C) and pyrolysis (P) of a fiber preform. In this point of view, the strategy for filling pores in the preform is very important for reducing the number of PIP cycles.

We have investigated the effective filling method in the PIP process; (i) control of PIP cycle such as I-C-P cycle and I-C cycle, (ii) polymer rheology and solution properties. Control of PIP cycle is effective method and it is also related to polymer properties.

In this study, we have investigated the effect on the concentration of polycarbosilane solution prepared from two types of polycarbosilane (PCS) having different degree of polymerization for effective densification in the PIP process.

EXPERIMENTAL

Polycarbosilane (PCS) was synthesized from the Kumada rearrangement of polydimethylsilane (PDMS) under normal pressure in the presence of the zeolite as a catalyst[9,10]. The mixture of PDMS with 0.5-5.0 wt % of catalyst was loaded into the high pressure vessel and subsequently heated to 350 and 400 °C after purging with argon gas for the conversion of PDMS into carbosilane structure and polymerization of them. The weight average molecular weight (Mw) of PCS was controlled between 2500 and 5000 according to polymerization temperature and time. Polycarbosilane was dissolved into toluene and stirred for 3 h to obtain a homogeneous solution. Solution concentration was ranged between 20 and 80 wt %.
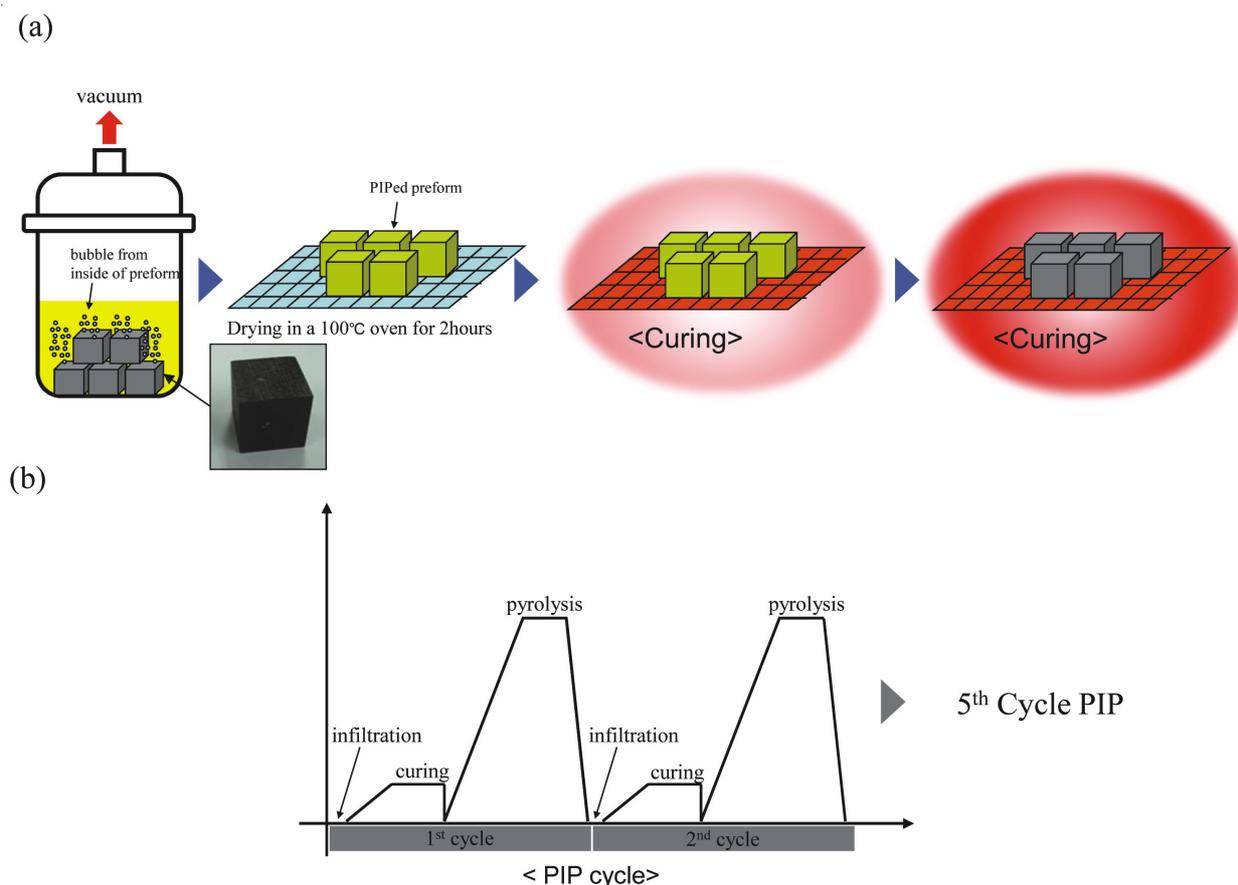

(a)

(b)

Fig. 1. Experimental processes (a) PIP cycle and (b) schedule of cyclic PIP

Polymer impregnation and pyrolysis was proceeded as following step: Carbon preform having 60 % of pores (purchased from DACC Co. Ltd.) was cut into 2 cm of cubic block and dried at 150 ℃ in the oven and it was dipped into homogeneous PCS solution. Solution was evacuated and released over again for infiltration of PCS into preform. And then, it was dried and cured at 200 ℃ for 3 h and subsequently pyrolyzed for 1 h at 1200 ℃ under Ar atmosphere in a graphite furnace. The solution condition and PIP cycle were controlled for the filling of the pores inside the preform and reducing the number of PIP cycles Fig. 1 shows the whole experimental process.

The characterization of PCS was achieved by measuring FT-IR (FT/IR-460 plus, JASCO, Japan), melting point, molecular weight distribution (GPC, Waters 2414, Ireland) and the thermal decomposition behaviour of the sample were analyzed using TGA (TGA/SDTA 851e, Mettler, USA). The microstructure and morphology were observed using FE-SEM (JSM-6700F, JEOL, Japan). The porosity and pore size distribution were investigated using mercury porosimeter (AutoPore IV 9500, Micrometritics Instrument, pressure range of 0.1-60,000 psia).

RESULTS AND DISCUSSION

Structural analysis of raw preform: Fig. 2 shows (a) the schematic model of pore structure in the carbon fiber preform through FE-SEM images and (b) the pore size distribution of the carbon fiber preform which was analyzed using mercury porosimeter. Preform was composed of 60 vol % of pores and 40 vol % of carbon fibers. In case of pore, there are two kinds of pore structures, inter-bundle pores ranging between 20 and 400 mm and intra-bundle pores ranging between 1 and 20 mm. Inter-bundle pores were 70 % in a total pore volume and intra-bundle pores were 30 %, respectively. So, successful impregnation may depend on how to fill these complex pore structures and the strategy for effective filling the inter-bundle pores were very important.

Characterization of polycarbosilane: Fig. 3 shows the results of GPC curves of (a) low M_w and (b) high M_w PCS and their FT-IR spectra (in-set of the figure). The M_w distribution of PCS was mainly detected at the elution time of 17-27 min and weigh average Mw in (a) and (b) was 2,950 and 4,870, respectively. The additional strong peak at high M_w region (at around 20 min) was caused by further polymerization. Comparison of 2100 cm^{-1} (Si-H stretching), 1400 cm^{-1} (Si-CH$_3$ deformation), 1360 cm^{-1} (C-H$_2$ stretching in Si-CH$_2$-Si), 1242 cm^{-1} (Si-CH$_3$ deformation) in FT-IR spectra also showed the increase of polymerization in the sample (b)[9-11]. Weight changes were started at 240 ℃ as shown in Fig. 4 and the ceramic yield was (a) 45 and (b) 63 % according to polymerization.

Effect of polycarbosilane solution for impregnation: It was hard to control the solution condition in case of ultra-high M_w PCS (above 10,000) and very low M_w PCS (below 2,000). Two types of PCS having different molecular weight (M_w), low M_w (2,500) and high M_w (5,000), were considered to PIP process. However, most of the inter-bundle pores were remained without filling in both PCS as shown in Fig. 5 and we tried to control the solution concentration using high M_w PCS.
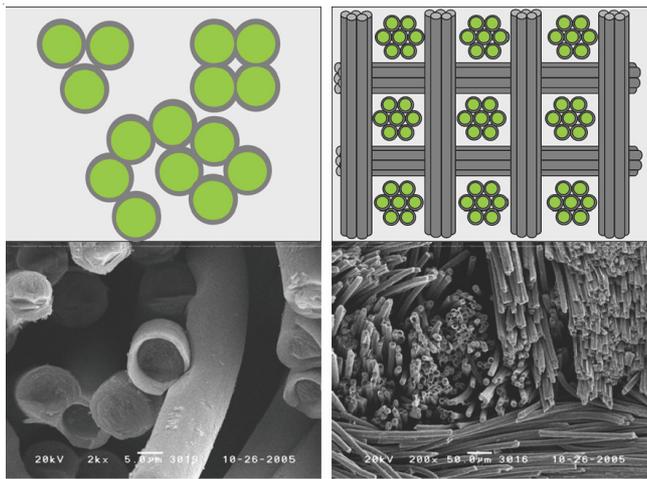
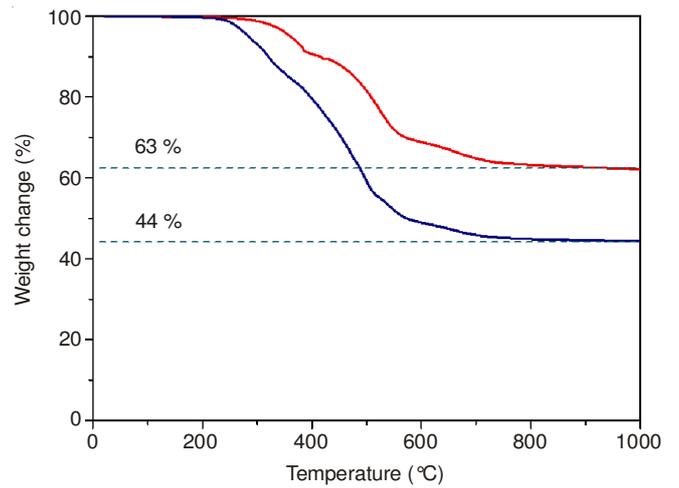(a) Schematic model with SEM images

(b) Pore size distributon

Fig. 2. Pore structure of carbon preform

Fig. 3. GPC curves of polycarbosilanes having different molecular weight and their FT-IR spectra (inset figure): (a) low M_w PCS (2,500) and (b) high M_w PCS (5,000)

Fig. 4. TGA curves of polycarbosilanes having different molecular weight): (a) low M_w PCS (2,500) and (b) high M_w PCS (5,000)
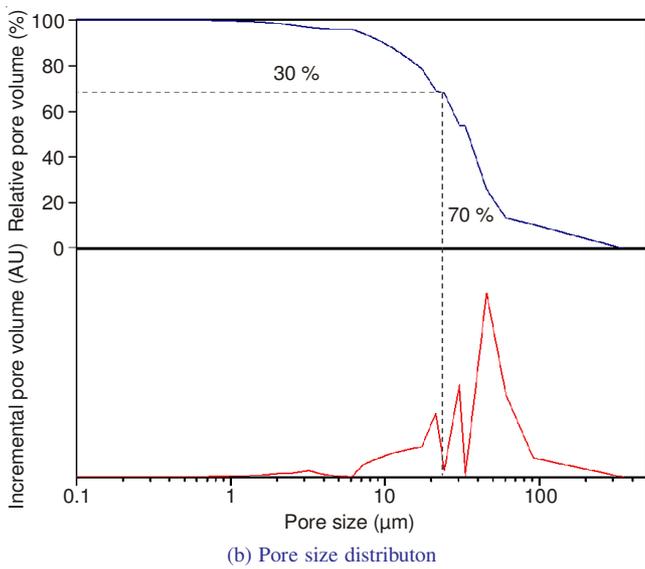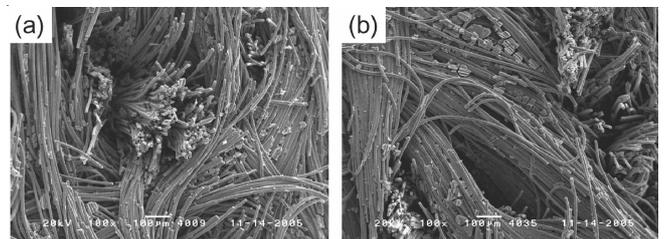

Fig. 5. SEM image of preform after 1st impregnation with different M_w of polycarbosilane

The microstructure of a cross-section of carbon fiber preform after 1st impregnation under low vacuum condition using different solution concentrations were displayed in Fig. 6.
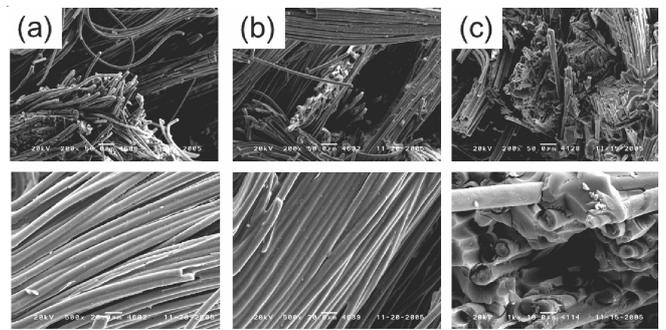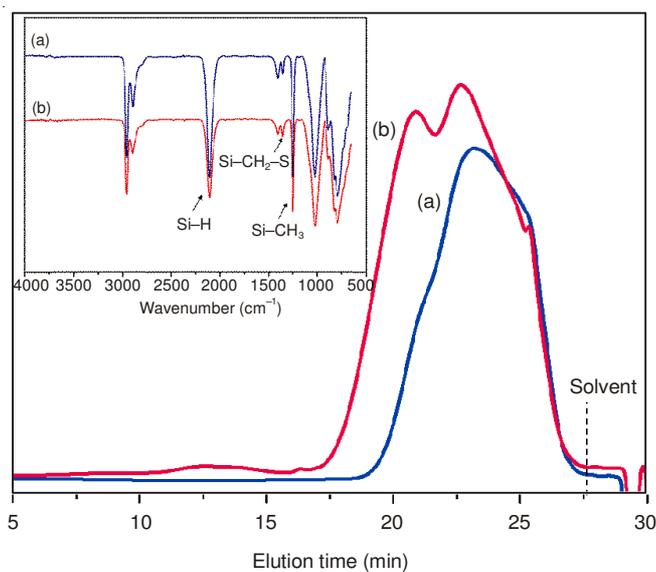

Fig. 6. FE-SEM images of carbon preform impregnated at different solution concentration of (a) 20, (b) 40 and (c) 60 wt %.

It was possible to fill inter bundle pores at 1st step impregnation by using 60 % PCS solution and there were little shrinkage after drying and curing because solvent contents were relatively low. Below 60 %, only intra-bundle pores were filled.

Fig. 7 shows the fractured cross-sectional images of C_f/SiC composites which were undergone (a) 1st, (b) 3rd and (c) 5th PIP cycles. All the samples were pyrolyzed at 1200 ℃ for 1 h in an argon atmosphere. Matrix was densely filled with silicon carbide within 3rd PIP and 15 % of pore volume was remained after pyrolysis at 1200 ℃. After 5th PIP cycles, almost open pores were considered to be filled except 10 vol % of residual pores.
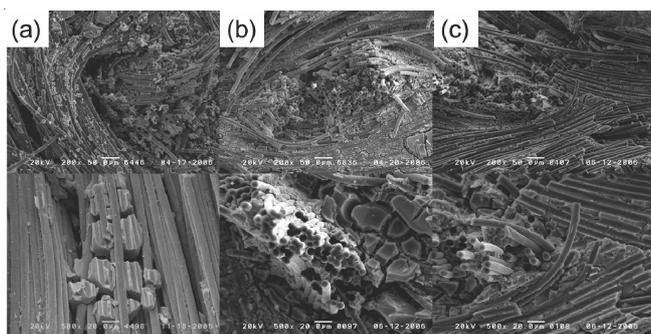
Fig. 7. SEM images of C$_f$/SiC composites prepared by (a) 1st, (b) 3rd and (c) 5th PIP

Fig. 8 shows the incremental pore volume change of PIP sample with intrusion pressure. Inter-/Intra bundle pores in raw preform were effectively reduced within 3rd PIP cycles and there was little effect for filling the pores after 4th cycle. Especially, inter-bundle pores between 20 and 200 mm was apparently removed at the 1st PIP cycle. However, small pores under 1mm were increased during PIP proceeded. It means that inter-bundle pores were previously filled and intra-bundle pores were filled with formation new pores. It may due to the shrinkage during pyrolysis of PCS matrix.
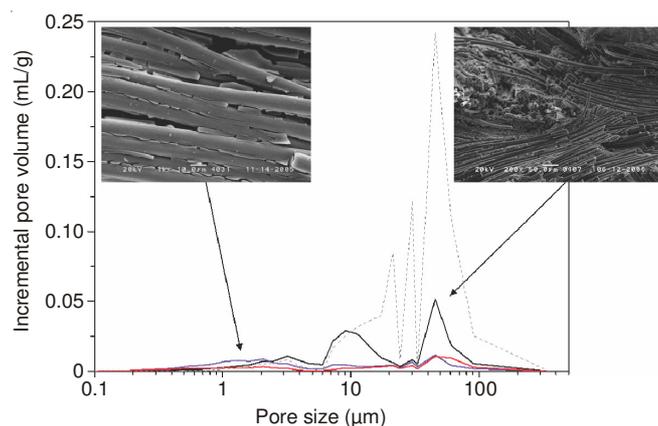

Fig. 8. Pore size distribution of carbon fiber preform with PIP cycles using incremental pore volume changes by mercury intrusion porosimetry analysis

Nametti *et al.*[5] had reported to fill 90 vol % of pores through over 10th PIP cycles at the same PIP processes and the porosity was slowly decreased. On the other hand, sample impregnated at the 60 wt % PCS solution with high M_w was effectively removed the inter-bundle pores within 3rd PIP and made it sure that improvement of initial stage filling efficiency was effective to reduce the PIP cycle times.

About 10 vol % of residual pores are expected to be filled by controlling molecular weight and solution concentration at each PIP cycles which was considered through the study of densification mechanism.

Conclusion

Three dimensional carbon fiber preform was successfully filled with silicon carbide by PIP process using high molecular weight PCS solution. Dense composite was obtained within 5th PIP cycles at the solution concentration of 60 % with low vacuum. Inter-bundle pores between 20 and 200 mm were previously filled and small pores under 1mm were newly formed during PIP proceeded. About 10 % of residual pores are expected to be filled by controlling molecular weight and solution concentration at each PIP cycles.

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