



Fabrication of Polyvinylsilazane and SiC/Si₃N₄ Ceramic Microspheres

HONGLI LIU*, WEI KANG, JING LI and CAILOU ZHOU

School of Materials Science and Engineering, Tianjin Chengjian University, Tianjin 300384, P.R. China

*Corresponding author: Tel: +86 22 23085109; E-mail: liuhonglitianjin@163.com

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The polyvinylsilazane microspheres were synthesized using polyvinylsilazane as precursor by emulsification technology. The effect of operating conditions on the morphology and size of the polyvinylsilazane microspheres were investigated by SEM. The polyvinylsilazane microspheres were then converted to SiC/Si₃N₄ ceramic microspheres through pyrolysis at 800-1400 °C under nitrogen atmosphere. The resultant ceramic microspheres kept their dense spherical shape with about 14 % linear shrinkage. The morphology and pyrolysis process were characterized by FTIR, TGA, SEM, TEM and XRD. This technique can be further extended to other preceramic polymers and can be used to prepare single/multi-material ceramic microspheres.

Keywords: Polyvinylsilazane, Emulsification, Microspheres, Ceramization.

INTRODUCTION

Silicon-based non-oxide ceramic microspheres have recently gained increasing concerns due to their superior thermal and mechanical properties¹ over oxide-based materials. Silicon-based non-oxide materials with controlled morphologies from nanometer to micro- size make them ideal candidates for catalytic substrates² and for light weight fillers in thermal insulation³.

One of the commonly used techniques for fabricating ceramic microspheres is sol-gel processing⁴. However, the sol-gel processing is mainly used for making oxide ceramics and cannot be easily applied for fabricating non-oxide ceramics. Thus, it is necessary to further investigate how to synthesize this kind of materials more easily and feasibly. Polymer-derived ceramics (PDCs) have become one of the most promising technologies for the advanced ceramics and it is beneficial to synthesize materials with inconvenient complex shapes. The technical route of polymer-derived ceramics is that the components with complex structures and shapes can be first fabricated in organic forms using well-documented technologies developed for plastic materials and then converted to ceramics by pyrolysis. Recently, the polymer-derived ceramics method has been successfully used for fabricating film, composites, fibers and nano-particles⁵⁻⁸. As precursor polymers revealed high solubility in various solvents, it can be conveniently combined with emulsion processing. Researchers have made study on this novel technology, especially on controlled fabrication of ceramic spheres⁹⁻¹². However, to the best of our

knowledge, there have been not many researches on thermal cross-linking process in aqueous emulsion, so it is crucial to make further investigation in this field.

In this paper, polyvinylsilazane (PVSZ) microspheres were prepared based on thermal cross-linking procedure combined with precursor polymers emulsification. Further pyrolysis of the polyvinylsilazane microspheres produced ceramic microspheres. The size and morphology of polyvinylsilazane microspheres could be adjusted through varying experimental conditions, which promises a potential route to fabricate the morphology controlled SiC/Si₃N₄ ceramic microspheres.

EXPERIMENTAL

Polyvinylsilazane with the molar mass of 2500-3000 g/mol was adopted as precursor polymer. Acetonitrile (analytically grade) and doubly deionized water were used as solvent. Octylphenol polyoxyethylene ether (OP-10; chemically grade) was chosen as surfactant. All chemicals were used without any further purification.

The polyvinylsilazane microspheres were synthesized *via* an oil-in-water-type (O/W) emulsification technique. Typically, O/W ratio was 1:15 and water phase consisted of deionized water and acetonitrile while oil phase was polyvinylsilazane precursor. The emulsion was prepared at room temperature by ultrasonating and poured into an autoclave Teflon liner, sealed, heated to 180-250 °C and kept 2-8 h in an oven. The microspheres were centrifuged and dried at 80 °C. The polyvinylsilazane microspheres were subsequently pyrolyzed under

nitrogen atmosphere by heating to 800, 1200 and 1400 °C, respectively, with heating rate of 3 °C/min, holding time of 1 h and cooling rate to room temperature of 5 °C/min as typical pyrolysis programme. The ceramic microspheres were obtained. And the process of preparing polyvinylsilazane microspheres and ceramic microspheres were summarized in Fig. 1.

Characterization: Fourier transform infrared (FTIR) spectroscopy was performed with Nicolet 380 FT-IR Spectrometer in the wave number range of 4000-400 cm⁻¹, which was used to analyze molecular structure. The morphology and size of microspheres were characterized using scanning electron microscope (SEM, Hitachi S-4300 and S-4800 at 15 kV) and transmission electron microscope (TEM, JEOL 1011 at 100 kV). X-ray diffraction (XRD) data were collected with CuK α radiation to determine phase composition. The pyrolysis performance of polyvinylsilazane was analyzed by thermogravimetric analysis (TGA), which was conducted with TG/DTA 6300 at a heating rate of 10 °C/min, from 25 to 1400 °C under nitrogen atmosphere.

RESULTS AND DISCUSSION

Polyvinylsilazane microspheres were synthesized *via* an oil-in-water-type (O/W) emulsification process followed by curing process. Fig. 2 showed SEM micrographs of the polyvinylsilazane microspheres obtained from different water phase, doubly deionized water and aqueous acetonitrile (mass ratio 1:1), respectively. Single water phase induced to numbers of nano-particles impurities (Fig. 2a). When the water was replaced partially by acetonitrile (Fig. 2b), monodispersed microspheres with smooth surface were full of the SEM vision. It indicated that the dispersing ability of the aqueous acetonitrile was better than that of single water phase. Besides, aqueous acetonitrile provided better emulsion stability and uniformity, which prevented non-emulsificated precursor growing into impurity particles.

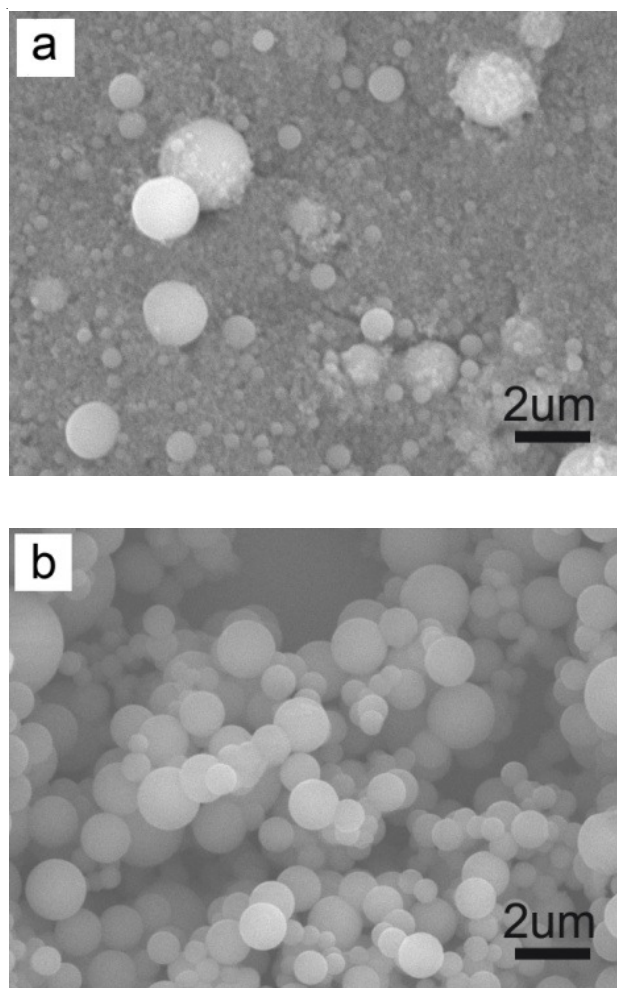


Fig. 2. SEM images of polyvinylsilazane microspheres obtained by different water phase, (a) doubly deionized water, (b) aqueous acetonitrile

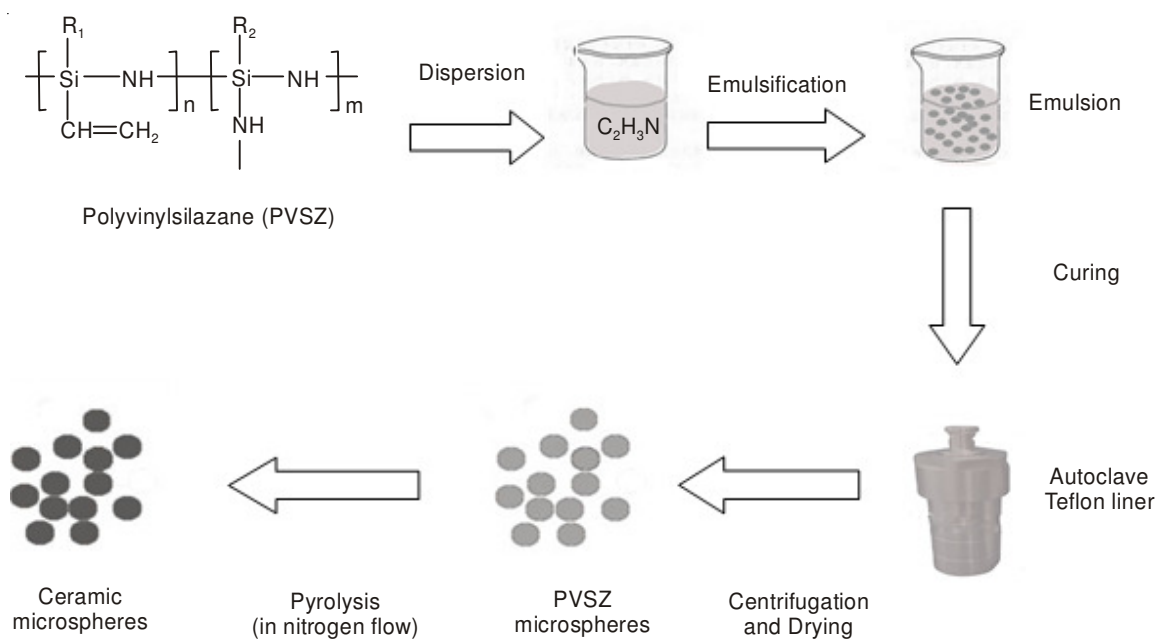
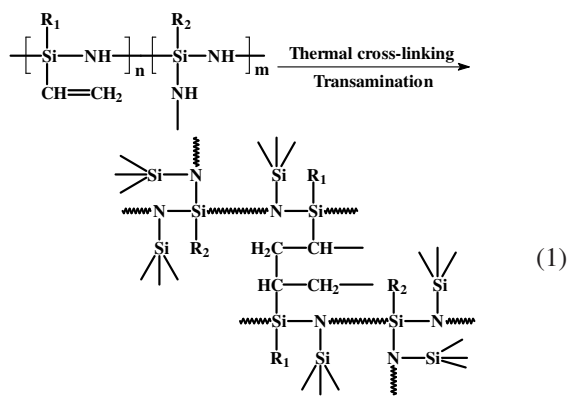


Fig. 1. Flowchart of the synthesis process of the microspheres

The effect of temperature on morphology of polyvinylsilazane microspheres was observed by SEM (Fig. 3). SEM observation (Fig. 3a) revealed that the polyvinylsilazane microspheres possessed regular spherical morphology with average size of 0.7 μm . Increasing heating temperature to 220 $^{\circ}\text{C}$, the microspheres distributed between 0.8-2.0 μm . With reaction temperature up to 250 $^{\circ}\text{C}$, the maximum size of microspheres was 2.6 μm . With increasing temperature from 180 to 250 $^{\circ}\text{C}$, the emulsion stability became poorer and substance exchange became more vigorous as well. It resulted in the fact that emulsion droplets were prone to integrating with each other. Higher temperature, however, led to inhomogeneous distribution and generating small amount of microspheres with 2-3 μm . It could be concluded that appropriate curing temperature was in the interest of microspheres uniformity.

Polyvinylsilazane precursor and polyvinylsilazane microspheres (curing at 180 $^{\circ}\text{C}$) were characterized with FTIR, respectively (Fig. 4). The IR spectra of polyvinylsilazane precursor showed typical absorption bands assigned to N-H (3400, 1170 cm^{-1}) and vinyl (-CH=CH₂) related to C-H vibration (3047 cm^{-1}) and C=C stretching (1406 cm^{-1}). The intensity of vinyl absorption in polyvinylsilazane microspheres apparently decreased than that of polyvinylsilazane precursor, indicating that the mechanism of curing was thermal cross-linking. The intensity of N-H (3400, 1170 cm^{-1}) obviously decreased, while a new shoulder peak corresponding to Si₃-N (947 cm^{-1}) was detected, due to transamination reaction. The reactions of thermal cross-linking and transamination were showed in eqn. 1:



To analyze the influence factors of curing process, products obtained at 180 $^{\circ}\text{C}$ with different curing times were

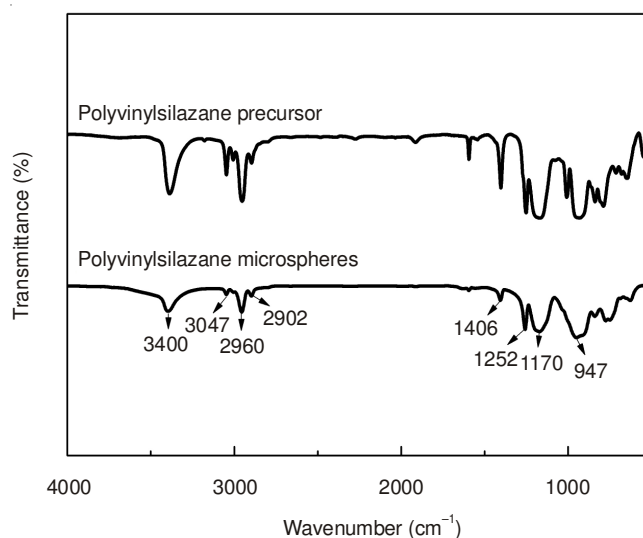


Fig. 4. FTIR spectra of polyvinylsilazane precursor and polyvinylsilazane microspheres

characterized by SEM. Fig. 5 showed the formation process of polyvinylsilazane microspheres from microgels to monodisperse microspheres. It can be seen that the loosely packed microgels formed after reacted for 2 h (Fig. 5a). With the increase of curing time to 4 h, the microgels then aggregate to form colloidal particle networks and some spherical particles exhibited slightly bridge-connected by residual micro-gels (Fig. 5b). Further increasing the reaction time to 8 h or more, the microspheres formed perfect spherical shape with smooth surface (Fig. 5c). The size distribution was around 0.6-1.2 μm . It was indicated that the curing process of the polyvinylsilazane precursor finished kinetically after 8 h.

Ceramic conversion of polyvinylsilazane microspheres:

The polyvinylsilazane microspheres were further pyrolyzed under nitrogen atmosphere and then ceramic microspheres were obtained. Fig. 6 showed the TGA curve of polyvinylsilazane. The weight loss increased with the rising temperature and the overall ceramic yield of polyvinylsilazane was 75.8 %. The pyrolysis procedure showed three decomposition steps: (1) 180-250 $^{\circ}\text{C}$, the curves showed a weight-loss stage, indicating that the thermal cross-linking reaction proceeded within this temperature range. (2) 250-800 $^{\circ}\text{C}$, significant weight-loss was detected, as the pyrolysis of polyvinylsilazane started and the microspheres transferred from organics to inorganics. (3) Above 800 $^{\circ}\text{C}$, polyvinylsilazane did not show any

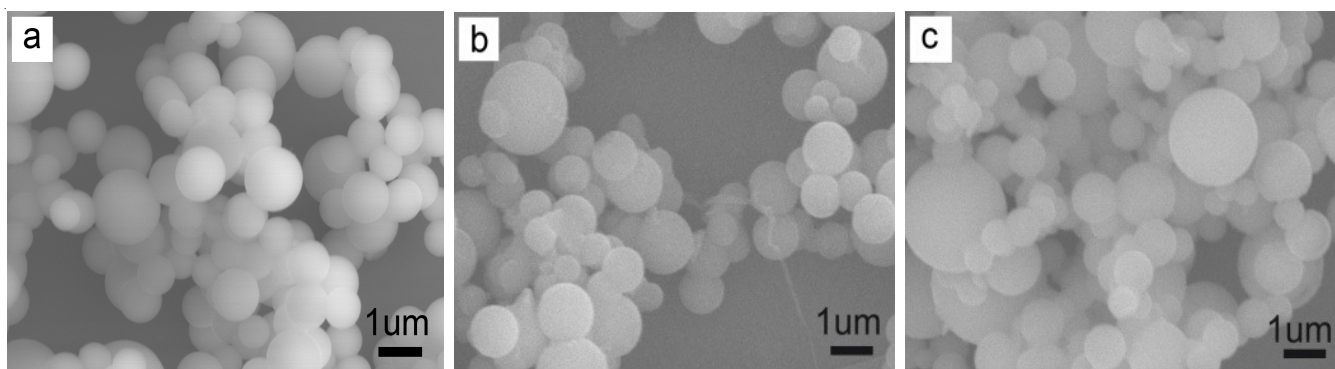


Fig. 3. SEM images of polyvinylsilazane microspheres prepared by different curing temperatures, (a) 180, (b) 220 and (c) 250 $^{\circ}\text{C}$

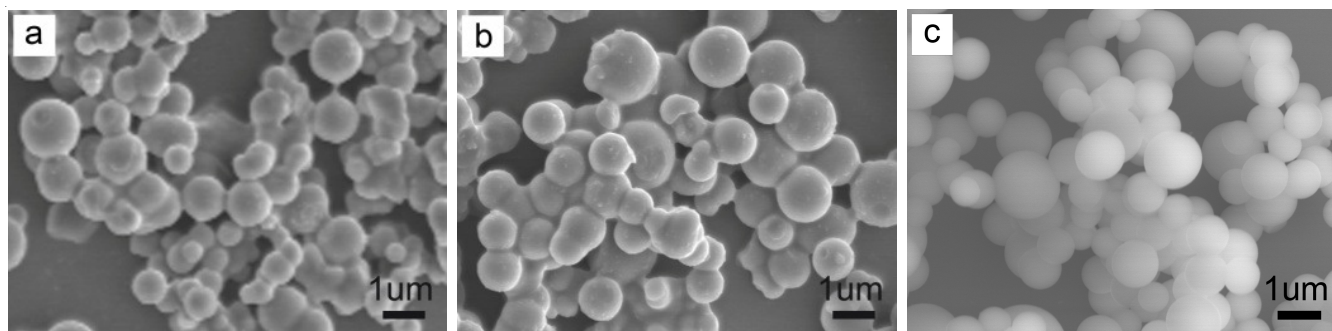


Fig. 5. SEM images of polyvinylsilazane microspheres obtained at 180 °C with different curing times (a) 2 h, (b) 4 h and (c) 8 h

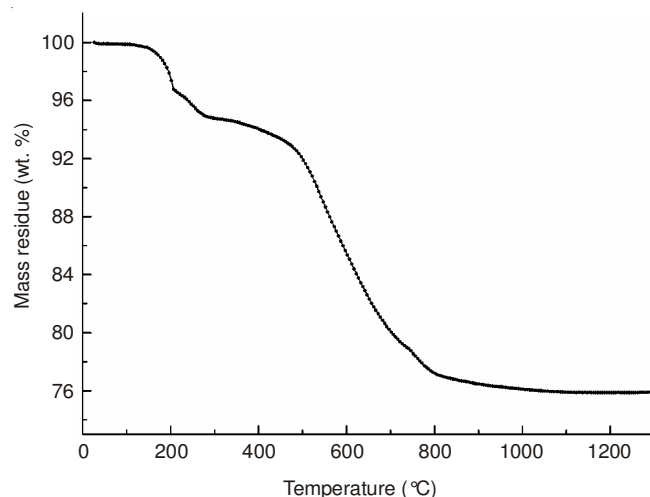


Fig. 6. TGA curve of polyvinylsilazane

significant weight loss and it can be predicted that the ceramization was mostly finished and the ceramic microspheres were obtained above 800 °C.

The morphology of the ceramic microspheres was shown in the Fig. 7. From the SEM photographs (Fig. 7a, b), the spheres shape still kept after pyrolysis and the size shifted to smaller compared with that of the corresponding polyvinylsilazane microspheres. The size was in the range of 0.4-0.7 μm with an average size of 0.6 μm, representing about 14 % linear shrinkage. Pyrolysis at 1400 °C (Fig. 7c), the microspheres exhibited roughness surface with numbers of fine grains. The TEM image (Fig. 7c, inset) showed that the SiC/Si₃N₄ ceramic microspheres kept the dense spherical structure after pyrolysis at 1400 °C.

The evolution of the crystalline phase was studied by XRD (Fig. 8). For the samples pyrolyzed at 800 and 1200 °C in nitrogen, the XRD patterns showed board diffraction peak, indicating that the pyrolysis products were in amorphous state and highly disordered. Rising the pyrolysis temperature to 1400 °C, the XRD patterns of the pyrolysis products showed diffraction peaks belong to β-SiC and α-Si₃N₄. Thus it can be seen that the pyrolysis products transferred from amorphous to crystalline within the range of 800-1400 °C.

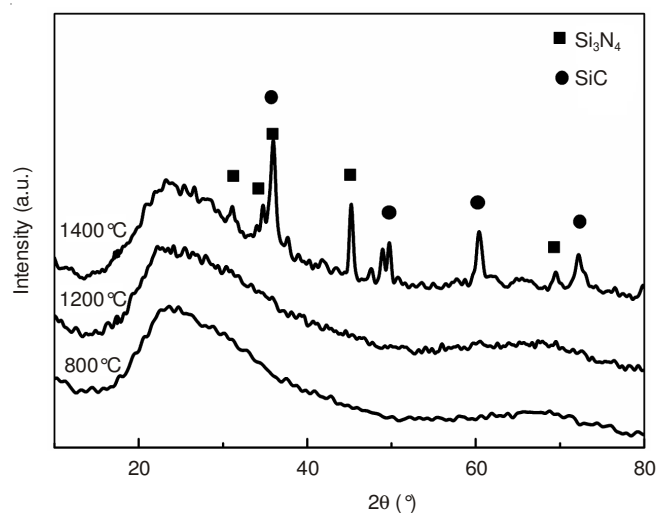


Fig. 8. XRD patterns of the microspheres pyrolyzed at 800, 1200 °C and 1400 °C

Conclusion

The fabrication of polyvinylsilazane microspheres using emulsification technique with polyvinylsilazane as precursor

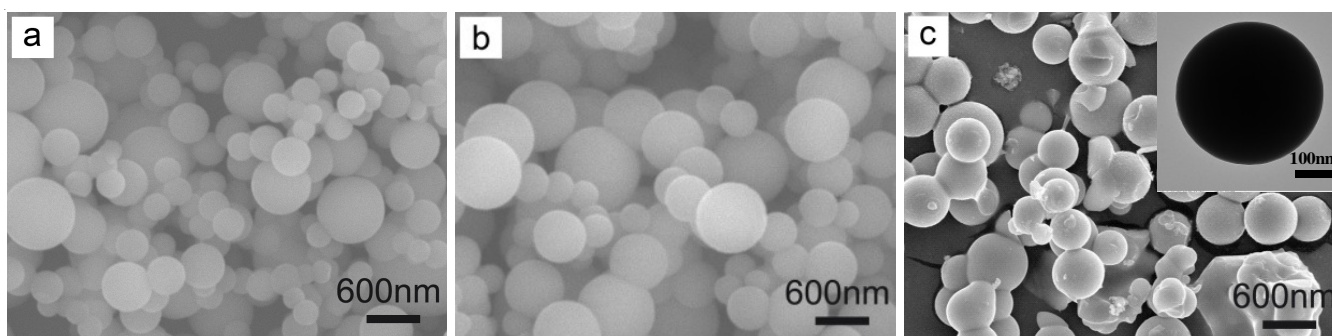


Fig. 7. SEM and TEM micrographs of ceramic microspheres pyrolyzed at (a) 800, (b) 1200 and (c) 1400 °C

was described. The size and morphology of polyvinylsilazane microspheres were adjusted by varying curing conditions. Optimizing selection of operating condition was proceeded with aqueous acetonitrile, curing at 180 °C for 8 h. Pyrolysis products transformed from amorphous to crystalline with the increase of pyrolysis temperature, within the scope of 800-1400 °C. SiC/Si₃N₄ ceramic microspheres were obtained by pyrolysis of the polyvinylsilazane microspheres at 1400 °C, which still held the dense spherical structure with smooth surface.

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