

# Fabrication of Multi-Scale Microstructured SiCNO Films via Block Copolymer Microphase-Separation Approaches

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**Abstract:** We report a simple, versatile approach for forming microstructured SiCNO films from polyvinylsilazane (PVSZ) swelled F127 micelles. Different sizes of particles can be formed by altering the weight percent of F127 in xylene/ethanol (1:1 v/v) solution. In addition the lamellar, foam, microsphere and worm-like microstructures can be formed in the SiCNO films by altering the PVSZ to F127 weight ratios. We find that the change of these structures have an impact on the water-repellent properties of the SiCNO films.

**Keywords:** Polyvinylsilazane; Block Copolymers; Microstructure

## 1 Introduction

Mesoporous inorganic materials consisting of a polymer matrix with embedded functional modifiers, have potential use in chemical, optical and microelectronic technology<sup>[1,2]</sup>. The self-assembly of block copolymer (BCP) are good candidates for the synthesis of ordered mesoporous inorganic materials with different nanostructures<sup>[3,4]</sup>, which can readily self-assemble to form a rich variety of structures such as spherical micelles, cylinders, gyroids, lamellas and fiber-like under certain conditions<sup>[5,6]</sup>. Moreover, the structure can be tuned by changing the molecular weights, pH, solvents and temperature<sup>[7,8]</sup>.

Polymer-derived-ceramics (PDCs) are a new class of materials produced from the decomposition of organic polymer precursors<sup>[9,10]</sup>. Compared to traditional ceramic materials, PDCs have some unique properties including good fluidity<sup>[11]</sup>, high thermal stability<sup>[12]</sup>, and excellent electrical property<sup>[13]</sup>. Recently, efforts have been made in the synthesis of mesostructured ceramic materials by using the co-assembly of amphiphilic block copolymers and preceramic polymers<sup>[14-16]</sup>. However, there are fewer studies in multi-length scale ceramic materials, which have potential for the design of fuel cell membranes, hydrogen-storage adsorbents and electrode materials.

Herein, we describe a simple, straightforward process for fabricating micro- and nanostructured SiCNO films by using polyvinylsilazane (PVSZ) swelled-F127 micelles as a precursor and dicumyl peroxide (DCP) as a radical initiator through multistep thermal treatments. We find that different sizes of particles can be formed

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by altering the weight percent of F127 in xylene/ethanol (1:1 v/v) solution. In addition, the lamellar, foam, microsphere and worm-like structures can be formed in the SiCNO films by changing the PVSZ to F127 weight ratios in xylene/ethanol solution. Moreover, we study the effect of the micro- and nano-structures on the water-repellent properties of SiCNO films.

## **2 Experimental procedure**

### **2.1 Materials**

PVSZ was synthesized following the procedure reported by Reutenauer et al<sup>[17]</sup>. The molecular weight of PVSZ with  $M_w=500$  g/mol was determined with the gel permeation chromatography (GPC). Pluronic F127 (H-(OC<sub>2</sub>H<sub>4</sub>)<sub>100</sub>(OC<sub>3</sub>H<sub>6</sub>)<sub>70</sub>(OC<sub>2</sub>H<sub>4</sub>)<sub>100</sub>-OH,  $M_w=12600$  g/mol, Sigma-Aldrich) block copolymer was used as a directing agent. The micelle formation and phase diagram of F127 in solution have been reported in the literature<sup>[18,19]</sup>. DCP (Sigma-Aldrich) was used as a radical initiator. Xylene and ethanol purchased from Aldrich were used as solvents. These chemicals were used as-received without further purification.

### **2.2 Synthesis**

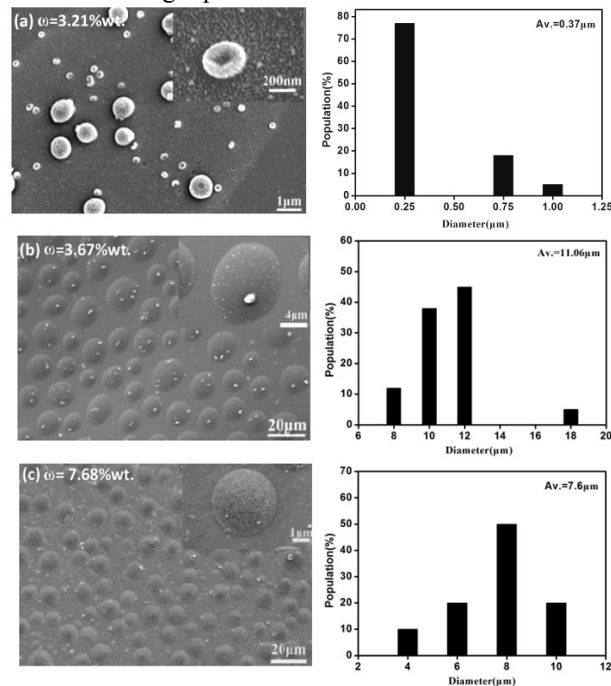
A typical synthesis process is as follows: the PVSZ was mixed with the DCP radical initiator (4 wt.% with respect to the mass of PVSZ added) and the different weight percent of F127 in xylene/ethanol (1:1 v/v) solution. The mixed solution was subsequently poured into a Teflon dish and slowly evaporated under vacuum conditions at different evaporation temperatures for 48 hours. Then, the temperature was increased to 140 °C for 1 hour to crosslink the PVSZ and peeled off from the Teflon dish. Finally, the F127/PVSZ films were transferred into a furnace under nitrogen for the thermal treatment at 800 °C for 6 hours (heating rate=0.2 °C/min) to form ceramic films.

### **2.3 Characterization**

The structure of the resultant ceramic films were characterized with scanning electron microscope (SEM, SU-70, Hitachi High-Tech, Tokyo, Japan), differential scanning calorimeter (DSC, DSC204C, Netzsch, Selb, Germany). The elemental analysis was performed by an electron probe microanalyzer (EPMA, JEOL-8100, Tokyo, Japan). The elemental proportion was calculated with the Oxford Instruments INCA software package (INCA Energy 200, Oxford Instruments, Buckinghamshire, U.K). A contact angle analyzer (JC2000A, Shanghai Advanced Photoelectric Technology, Shanghai, China) was employed to measure the contact angle of water.

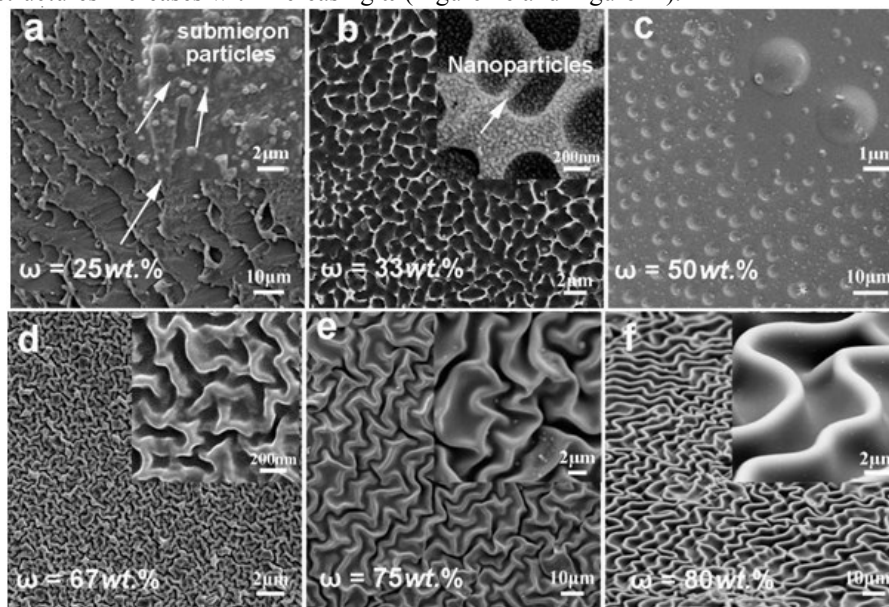
### 3 Results and discussion

Fig 1 shows the SEM images of the microstructured SiCNO films formed at different weight percent of F127 but same PVSZ/F127 weight ratios(2:1) in xylene/ethanol (1:1 v/v) solution. When the weight percent of F127 is 3.21wt%, the formation of microspheres is observed in microstructured SiCNO films with an average diameter of 0.37  $\mu\text{m}$ , but there is a pit at the surface of microsphere [Fig.1(a)]. If the weight percent of F127 increases to 3.67wt%, the formation of oval microspheres with an average diameter of 11.06  $\mu\text{m}$  is observed and there are small particles with different sizes on the surface of microspheres [Fig.1(b)]. When the weight percent of F127 is 7.68wt%, we observe the oval microsphere turn into regular microsphere with an average diameter of 7.6  $\mu\text{m}$  and the small particles are distributed relatively equally on the surface of microspheres [Fig.1(c)]. To sum up, the microspheres can be formed by altering the weight percent of F127 from 3.21% to 7.68%, but the scale of the microspheres is changed by altering the weight percent of F127. The formation of multi-scale microstructures of SiCNO films in Fig.1 may be explained based on the microstructure evolution of F127/PVSZ film. The F127 micelles were swelled better with increasing the weight percent of F127, so the scale of the microsphere will increase with increase the weight percent of F127. But the solution system has a critical micell concentration, the scale of the microsphere will decrease with increase the weight percent of F127 above the critical value.



**Fig. 1.** SEM images of microstructured SiCNO films together with the size distribution of microspheres formed at different weight percent of F127. The enlarged SEM images were inset.

To further understand the change about the scale of the structure, we alter the PVSZ/F127 weight ratios in xylene/ethanol (1:1 v/v) solution. Figure 2 shows the SEM images of SiCNO films from different PVSZ/F127 weight ratios ( $\omega$  is the proportion of F127 in wt. %), which are formed at 60 °C for 48 hours, followed by the crosslinking at 140 °C and the pyrolysis at 800 °C for 6 hours. When the  $\omega$  is 25%, the formation of lamellar structures is observed in SiCNO films (Figure 2a) and the average spacing of the lamellar structures is about 10  $\mu\text{m}$ . If the  $\omega$  increases to 33%, we observe the formation of nanoscale foam structures (Figure 2b) in SiCNO films. Microspheres are observed in SiCNO films when the  $\omega$  increases to 50% (Figure 2c). Nanoscale worm-like structures are formed in SiCNO films with the  $\omega$  increases to 67% (Figure 2d). The worm-like structures gradually develop into microscale lamellar structures with the further increase of the  $\omega$ . The average spacing of the lamellar structures increases with increasing  $\omega$  (Figure 2e and Figure 2f).



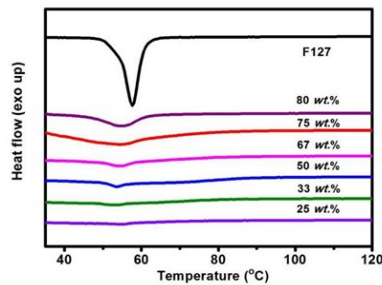
**Fig. 2.** Low-resolution SEM images of SiCNO films from the different weight ratios of PVSZ and F127. Corresponding high-resolution SEM images were inset in Figure 2.

Table 1 shows the elemental proportion of the microstructured SiCNO films from the different PVSZ/F127 weight ratios formed at 60 °C for 48 hours, followed by the crosslinking at 140 °C and the pyrolysis at 800 °C. The obvious differences are the appearance of a nitrogen and oxygen content of the SiCNO films. When the proportion of F127 is 25 wt. %, the microstructured SiCNO films contain 14.23 wt.% N, 13.16 wt.% O, 27.48 wt.% C and 45.13 wt.% Si. The nitrogen content decreases and the oxygen content increases with the increasing the proportion of F127. This is in agreement with the suggested mechanism of the Si–N bond to the Si–O bond conversion through the polymerization reaction between the PEO segment and the PVSZ swelled in F127 micelles<sup>[14-16]</sup>.

**Table 1.** Elemental characteristics of SiCNO films from the different weight ratios of PVSZ and F127

the proportion of F127 in wt. %	Elemental ratios (wt. %)			
	Si	C	N	O
25%	45.13	27.48	14.23	13.16
33%	47.74	27.16	9.27	15.83
50%	49.58	28.74	3.36	18.32
67%	49.52	29.04	1.83	19.61
75%	49.34	30.13	0.42	20.11
80%	49.08	29.61	-	21.31

Figure 3 shows the DSC curves of F127 and PVSZ/F127 films with different weight ratios. The F127 exhibits a melting peak at 58 °C, which is higher than that PVSZ/F127 films with different weight ratios. Moreover, the melting peak of F127/PVSZ films decreases with decreasing the proportion of the F127, suggesting the crystallization of the PEO phase of F127 is suppressed by the selective swelling of the PVSZ in the block PEO shell of F127 micelles, and the crystallization phenomenon will completely disappear when the weight ratio of the F127 is lower than 25%.

**Fig. 3.** DSC curves of F127 and PVSZ/F127 films with different weight

In order to investigate the hydrophobicity of SiCNO films, we measured the water contact angle of the SiCNO films with different microstructures. Figure 4 shows the contact angle of water droplets on the SiCNO films with different microstructures. As can be seen in Figure 4, the evolution process of lamellar, foam, microsphere and “worm-like” structure in the SiCNO films can be achieved by controlling the proportion of F127 in wt.%. We find that the SiCNO films with nanoscale foam- and worm-like structures have higher water contact angles, compared to the SiCNO films with microscale lamellar and sphere structures (Figure 2). The hydrophobicity behavior of SiCNO films with different microstructures can be explained with Wenzel

model, which shows that the contact angle of water droplets on a substrate with its surface roughness.

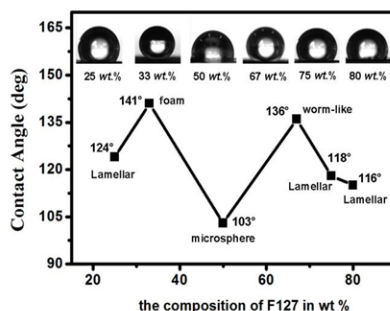


Fig. 4. The contact angle of water droplets on the SiCNO films with different structures, which were formed at the different proportions of F127 (wt. %).

## 4 Conclusions

In summary, we report a facile route to synthesize different sizes of particles by altering the weight percent of F127 in xylene/ethanol (1:1 v/v) solution. In addition, we synthesize multi-length scale structured SiCNO ceramic films by PVSZ swelled F127 micelles as a precursor through multi-step thermal treatments. The lamellar, foam, sphere and worm-like structures can be formed in SiCNO films by changing the PVSZ to F127 weight ratios. Meanwhile, we find that the SiCNO films with nanoscale foam- and worm-like structures have more hydrophobic than the SiCNO films with microscale lamellar and sphere structures.

## Acknowledgement

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