

**INVESTIGATIONS ON NaCl PARTICLE TEMPLATING METHOD
FOR THE PREPARATION OF MICROCELLULAR CARBON AND
SILICON CARBIDE FOAMS**

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by

PRAVEEN WILSON



**Department of Chemistry
INDIAN INSTITUTE OF SPACE SCIENCE AND
TECHNOLOGY**

Thiruvananthapuram – 695 547

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ABSTRACT

Carbon and silicon carbon (SiC) foams are three-dimensional porous materials comprising of uniformly dispersed pores within a solid matrix and porosity greater than 70%. Carbon foams are prepared from petroleum and coal tar pitches, synthetic polymers and natural organic molecules. They possess low density, tunable thermal and electrical and thermal conductivity, high specific surface area, chemical inertness, high permeability and electromagnetic interference (EMI) shielding. They find application in fields such as thermal insulation, thermal protection, gas and pollutant absorption, electrochemical devices, EMI shielding and catalysis. SiC foams are prepared from pre-ceramic polymers and aqueous suspensions. Properties of SiC foams include good oxidation resistance, high surface area, high permeability, high-temperature stability, excellent dielectric property, chemical inertness and high specific strength. Applications of SiC foams include catalyst support, hot-gas and molten metal filtration, membrane supports, gas-burner medium, lightweight structural parts for high-temperature applications and high-temperature EMI shielding materials. The properties of the foams depend on the porosity and pore size. Conventionally prepared foams possess large cells of size greater than 500 μm . To improve the mechanical and thermal insulation properties it is necessary to reduce the cell size. The main objective of this thesis is to produce and characterize carbon and SiC foams with microcellular (<100) microstructure through NaCl particle templating of molten sucrose resin. The porosity of the foams is tuned by varying the NaCl particle concentration.

A compression moulding process for the preparation of carbon foams with a triplex pore structure is studied. Pastes with mouldable consistency, prepared by hot-blending of sucrose-NaCl powder mixtures of NaCl to sucrose weight ratios ($W_{N/S}$) in the range of 0.7 to 1.2, are set into solid bodies due to the caramelization of molten sucrose. The caramelization in presence of NaCl results in carbon-enriched polymeric structure due to the enhanced α -elimination reactions along with the $-\text{OH}$ condensation as evidenced from the torque-time measurements, IR, TGA and elemental analysis. The pyrolysis of compression moulded bodies, followed by NaCl removal and further heat treatment produces carbon foams with a triplex pore structure. The volumetric shrinkage

during carbonization (28.5 to 24.2 vol.%), density (0.26 to 0.33 g cm^{-3}), compressive strength (2.84 to 8.37 MPa), Young's modulus (170 to 370 MPa) and thermal conductivity (0.348 to $0.257 \text{ W m}^{-1} \text{ K}^{-1}$) of the carbon foams depend on the $W_{N/S}$. The carbon foams exhibit high specific surface area of $\sim 400 \text{ m}^2 \text{ g}^{-1}$ and a combination of macropores (414 to $70 \text{ }\mu\text{m}$), microcells (2 to $12 \text{ }\mu\text{m}$) and micropore texture.

Low-density microcellular carbon foams are prepared at $W_{N/S}$ of 1.5 to 3 by using glycerol as a plasticizing additive. The glycerol required to form a mouldable paste increases from 8 to 64 g (per 100 g of sucrose) with an increase in $W_{N/S}$. The slow setting of the pastes ($5 - 13 \text{ h}$) is due to the caramelization of molten sucrose as well as the slow evaporation of glycerol. The linear and volumetric shrinkages during carbonization of sucrose polymer-NaCl-glycerol composites lie in the range of 3.64 to 7.62% and 10.02 to 20.65% , respectively. The carbon-NaCl composites have adequate compressive strength (6.9 to 17.8 MPa) and ductility for machining using conventional machine tools. Machining of the carbon-NaCl composites followed by NaCl removal is used as a strategy to produce low-density carbon foams with desired contours. The glycerol not only decreases the density of carbon foams developed from the sucrose-NaCl system but also produces a remarkable change in the foam microstructure from a combination of macropores and microcells to only microcells of sizes predominantly in the range of 3 to $6 \text{ }\mu\text{m}$. Microcellular carbon foams prepared at $W_{N/S}$ in the range of 1.5 to 3 show density, compressive strength, thermal conductivity and EMI shielding effectiveness in the ranges of 0.096 to 0.214 g cm^{-3} , 0.60 to 4.83 MPa , 0.087 to $0.235 \text{ W m}^{-1} \text{ K}^{-1}$ and 24.7 to 41.7 dB , respectively.

Thermally conducting microcellular carbon foams are prepared from sucrose with graphite as a conducting filler, NaCl particles as template and glycerol as plasticizing additive. The effect of graphite filler and NaCl template loading on density, porosity, thermal conductivity, and microstructure are carefully investigated. Microcellular conducting carbon foams (**MCCF**) exhibit high porosity (76.1 to 93.4%) and adequate compressive strength (0.225 to 14.96 MPa). The high thermal conductivity (0.282 to $5.23 \text{ W m}^{-1} \text{ K}^{-1}$), interconnected microcellular structure (cell size 2 - $12 \text{ }\mu\text{m}$) and hydrophobic nature make the foams ideal for hosting wax-based phase change materials for thermal

energy storage and management applications. Composites of conducting carbon foam and paraffin wax (**PW**) are prepared with various wax loadings (50.5 to 82.6 wt%) which exhibit thermal conductivities in the range of 0.65 to 7.72 W m⁻¹ K⁻¹. The melting and freezing characteristics and form stability of the composites are also studied. It is established that the microcellular structure is advantageous for easy wax-impregnation and retention during thermal cycling compared to macrocellular (cell size of 600 µm) foams of similar composition due to the enhanced capillary forces. Differential scanning calorimetry (DSC) study of **PW/MCCF** composites shows the highest melting enthalpy of 110.9 J g⁻¹.

Microcellular SiC foams (**MSiCFs**) are produced by the thermal setting of dispersions of silicon and NaCl powders in molten sucrose-glycerol solutions in a mould followed by carbonization, NaCl removal and reaction bonding at 1500 °C. The NaCl to sucrose weight ratio is varied from 1 to 3 to tune the porosity of the **MSiCFs**. The acidic silica layer on silicon particle surface catalyses the setting of the pastes by –OH condensation leading to setting times in the range of 1 to 3 h. The linear and volumetric shrinkages of sucrose polymer-silicon-NaCl composite bodies during carbonization at 750 °C, decrease from 4 to 1.36 % and 10.8 to 5%, respectively, when the NaCl to sucrose weight ratio increases from 1 to 3. Only a marginal linear and volumetric shrinkage of 0.2 to 2.3% and 1.17 to 7.7%, respectively, is observed during reaction bonding. The microcell size varies between 2 to 22 µm and are filled with SiC nanowires grown *in situ* by a catalyst-free vapour-solid (VS) mechanism. The **MSiCFs** with porosity in the range of 86.8 to 91.1 vol.% exhibit thermal conductivity and compressive strength in the ranges of 0.334 to 0.758 W m⁻¹ K⁻¹ and 0.97 to 2.38 MPa, respectively. The **MSiCFs** show excellent EMI shielding property in the X-band frequency region enhanced by the *in situ* grown SiC nanowires within microcells. The **MSiCFs** show highest EMI shielding effectiveness of 45.6 dB and specific shielding effectiveness of 137 dB g⁻¹ cm³.