

Huixing Zhang, Clara Lana Fidelis, Ana Luiza Teixeira Serva, Michaela Wilhelm,
Kurosch Rezwan



Water-based freeze casting: Adjusting hydrophobic polymethylsiloxane for obtaining
hierarchically ordered porous SiOC

Journal Article as: peer-reviewed accepted version (Postprint)

DOI of this document* (secondary publication): 10.26092/elib/2498

Publication date of this document: 22/09/2023

* for better findability or for reliable citation

Recommended Citation (primary publication/Version of Record) incl. DOI:

Zhang, H, Fidelis, CL, Serva, ALT, Wilhelm, M, Rezwan, K. Water-based freeze casting: Adjusting hydrophobic polymethylsiloxane for obtaining hierarchically ordered porous SiOC. J Am Ceram Soc. 2017; 100: 1907-1918. <https://doi.org/10.1111/jace.14782>

Please note that the version of this document may differ from the final published version (Version of Record/primary publication) in terms of copy-editing, pagination, publication date and DOI. Please cite the version that you actually used. Before citing, you are also advised to check the publisher's website for any subsequent corrections or retractions (see also <https://retractionwatch.com/>).

"This is the peer reviewed version of the following article: [Zhang, H, Fidelis, CL, Serva, ALT, Wilhelm, M, Rezwan, K. Water-based freeze casting: Adjusting hydrophobic polymethylsiloxane for obtaining hierarchically ordered porous SiOC. J Am Ceram Soc. 2017; 100: 1907-1918. <https://doi.org/10.1111/jace.14782>], which has been published in final form at [<https://doi.org/10.1111/jace.14782>]. This article may be used for non-commercial purposes in accordance with Wiley Terms and Conditions for Use of Self-Archived Versions. This article may not be enhanced, enriched or otherwise transformed into a derivative work, without express permission from Wiley or by statutory rights under applicable legislation. Copyright notices must not be removed, obscured or modified. The article must be linked to Wiley's version of record on Wiley Online Library and any embedding, framing or otherwise making available the article or pages thereof by third parties from platforms, services and websites other than Wiley Online Library must be prohibited."

This document is made available with all rights reserved.

Take down policy

If you believe that this document or any material on this site infringes copyright, please contact publizieren@suub.uni-bremen.de with full details and we will remove access to the material.

Water-based freeze casting: Adjusting hydrophobic polymethylsiloxane for obtaining hierarchically ordered porous SiOC

Huixing Zhang | Clara Lana Fidelis | Ana Luiza Teixeira Serva | Michaela Wilhelm | Kurosch Rezwan

Advanced Ceramics, University of Bremen,
Bremen, Germany

Correspondence

Michaela Wilhelm, University of Bremen,
Advanced Ceramics, Bremen, Germany.
Email: mwilhelm@uni-bremen.de

Funding information

Deutsche Forschungsgemeinschaft, Grant/
Award Number: GRK 1860; German
Research Foundation (DFG).

Abstract

The hydrophobic properties of methyl poly siloxane (MK) were pushed into the “hydrophilic” range by cross-linking it with (3-aminopropyl)triethoxysilane (APTES) and subsequent pyrolysis to enable water-based freeze casting. Filler properties are investigated by varying the ratios of MK to APTES (1:1, 1:2, 1:3, 1:4, 1:5), and pyrolysis temperatures (400°C, 500°C, 600°C) for the purpose of determining an optimal set of characteristics for freeze casting. Additionally, filler selection for this purpose is facilitated by analysis of zeta potential values and vapor adsorption. It was found that water-based freeze casting with hybrid fillers, followed by a pyrolysis step (600°C-700°C), leads to a SiOC ceramic monolith with a lamellar pore morphology and a hierarchically ordered micro/meso/macropore structure. Samples pyrolyzed at 1000°C contain mesopores, having a SSA as high as 51.6 m²/g. The hierarchically porous structure is very promising for applications involving gas or liquid transportation.

KEYWORDS

freeze casting, micro/meso/macropore, polymer derived ceramics, silicon oxycarbide, surface characteristics

1 | INTRODUCTION

Applications like catalysis, gas adsorption, water filtration, molten metal filtration, bone tissue engineering, and energy storage/conversion involving the gas or liquid transportation processes normally require that the material has a high permeability to avoid mass transportation problems. These problems can be mitigated by introducing macroporosity into the materials' structure.¹⁻⁷ Depending on the specific applications, hierarchical porous structures (meso/micropore) and/or a high specific surface area may be required. There are several techniques for fabricating macroporous monoliths, such as sacrificial templating, direct foaming,

replica method, and additive manufacturing⁸⁻¹¹; each of these techniques have various benefits and drawbacks. These methods have often been combined with other techniques to produce macroporous monolith of hierarchical structures.^{12,13}

Freeze casting techniques (a special sacrificial templating method) create porosity by freezing a stable suspension at low temperatures during which the freezing solvent pushes the suspended ceramic particles away from the frozen front.¹⁴ This near-net shape and powerful technique has been widely used to produce bulky macroporous monoliths having different pore shapes by using water, camphene, or tert-butyl alcohol or mixtures as the sublimate medium.¹⁴⁻¹⁸ Additionally, additives can influence the final pore morphology of the monolith.¹⁹

Presented in HTCMC9-GFMAT2016, 27th June-1st July in Toronto, Canada.

Polymer-derived ceramics (normally SiC, SiCN, SiOC, etc.) are prepared by pyrolyzing pre-ceramic polymers at relatively low pyrolysis temperatures: 1000°C to 1400°C.²⁰ When pre-polymers are pyrolyzed at even lower temperatures (500°C-700°C), microporosity, and occasionally mesoporosity, can be obtained.²¹ Sacrificial templating, direction foaming, and additive manufacturing methods have been applied to shape porous polymer-derived ceramics (foams, membranes, components with hierarchical porosity). Meso/macroporous SiOC monoliths were obtained by embedding periodic mesoporous organosilica particles into foamed siloxane preceramic polymer.²² Micro/macropore SiOC monoliths have been prepared by adding polymer-derived fillers and controllable pyrolysis by direct foaming and sacrificial templating.²³⁻²⁵

Inorganic powders, mainly (Al₂O₃, ZrO₂, SiC, Si₃N₄ etc.), have been mixed with water, camphene, or tert-butyl alcohol to form stable suspensions for freeze casting to produce macroporous monoliths.^{15,16,26-28} Organic precursors, such as polycarbosilane were mixed with camphene to get a homogenous polymer solution; the pores formed by thermally induced phase separation during freezing.²⁹ Poly(methyl-silsesquioxane) has also been used with tert-butyl alcohol, camphene, and cyclohexane to get SiOC porous material; precise control of cross-linking is required to prevent early gelation or poor mechanical integrity.³⁰ Polymer-derived ceramics have the advantages of adjusting pore sizes at different scales and altering surface characteristics via processing parameters, while freeze casting can be used to adjust the pore structure and permeability of the macroporous monolith. The combination of polymethylsiloxane with water-based freeze casting renders open the possibility of producing a hierarchically ordered porous monolith, however, few studies have been done, due to the strong hydrophobicity of most preceramic polymers.

Methyl phenyl polysiloxane (H44) has been “hydrophilicized” by thermal decomposition in an inert gas atmosphere, and has been successfully applied in water-based freeze casting in our group, resulting in hierarchically ordered micro/meso/macroporous SiOC monoliths.³¹ However, in case of methyl polysiloxane (MK), the hydrophilicization by thermal decomposition will not be practical due to high decomposition temperature of methyl groups, therefore, other methods are required for modifying surface characteristics (hydrophilicity/hydrophobicity). For example, hydrophilic sodium silicate-based gels have been composited with silylating agents to produce hydrophobic aerogels.³² The wettability of polydimethylsiloxane has been improved by plasma treatment, producing a thin, brittle, oxidized surface layer.³³ And, a thin film composite polyamide nanofiltration membrane has been chemically modified by graft polymerization and functional group substitution to increase the negative charge and hydrophilicity

of the raw membrane.³⁴ In this work, we develop a way to modify the surface characteristics of methyl polysiloxane to use it as a filler for water-based freeze casting by cross-linking it with (3-aminopropyl)triethoxysilane (APTES) and subsequent pyrolysis. The optimization of hydrophilicity was achieved by varying the ratios of polymethylsiloxane to APTES and pyrolysis temperatures. The obtained hybrid material was mixed with silica sol (which served as both a binder and water phase) during freeze casting. After pyrolysis, hierarchically ordered micro/meso/macropore SiOC ceramic monoliths with lamellar macropores were obtained. This work not only render applying hydrophobic polysiloxane to water-based freeze casting for producing hierarchically ordered porous monoliths by combining freeze casting with preceramic precursors, but also offers multiple possibilities in terms of surface characteristics, and microstructures on different scales.

2 | EXPERIMENTAL PROCEDURE

2.1 | Materials

A silicone resin poly(methyl-silsesquioxane) was acquired from Silres[®] MK, Wacker Chemie AG, Germany. Silica sol (30 wt% SiO₂ nanoparticles, 8 nm, BegoSol[®] K) was acquired from Bremer Goldschlägerei Wilh. Herbst GmbH & Co. KG., Bremen, Germany. Polyacrylic acid (PAA, Syntran 8140) was purchased from Interpolymer GmbH, Hasloch, Germany. (3-aminopropyl)triethoxysilane (APTES) was purchased from abcr GmbH, Germany.

2.2 | Processing

The silica sol acts as a binder and water source during the freezing process. There are some criteria for choosing the precursors applicable for water (silica sol)-based freeze casting. The particles need to be hydrophilic to mix with water, and negatively charged, due to the negatively charged silica particles, and have a zeta potential (Zeta potential <−30 mV) high enough to form a stable suspension.³⁵ The hydrophobic MK is altered to hydrophilic material via cross-linking with APTES and a following pyrolysis process. These hydrophilic materials prepared with varied MK: APTES ratios and pyrolysis temperatures were screened for fillers usable for freeze casting.

2.2.1 | Preparation of fillers

A quantity of 70.3 g (1 mol) of MK was dissolved in 70 mL ethanol. APTES was added into the above solution. The molar ratios of MK:APTES were varied (1:1; 2:1; 3:1; 5:1). Water was used to catalyze the cross-linking, added dropwise to the solution. The mixture obtained was stirred

until the solidification was complete. The amount of water added was calculated based on the active groups of MK and APTES.³⁶ The solid was then transferred to the cross-linking oven using a multi-stage heat treatment in air at 80°C, 140°C, and 200°C (all dwell times 2 hour), with a heating rate of 60°C h⁻¹ in between dwell times. The pre-cross-linked polysiloxane pieces were then pyrolyzed at various temperatures (400°C, 500°C, or 600°C) under a nitrogen atmosphere. The heating rate was set to 120°C h⁻¹ up to 100°C below the target temperature and then 30°C h⁻¹ to the final temperature, with a dwell time of 4 hour. The powders were then transferred to a planetary ball milling machine (PM 400; Retsch, Hann, Germany) and ground at 350 r min⁻¹ for 6 hour to produce fine powders. These hybrid fillers are used for the following freeze casting process.

2.2.2 | Preparation of porous monolith

A total of 30 wt% precursor powders were added to 70 wt% silica sol under stirring. The pH was adjusted to 6-7 using PAA to ensure the complete condensation reaction of silica sol. Compared to water, the negatively charged MK-APTES-derived fillers had higher stability in anionic colloidal silica, due to stronger interparticle repulsion. The pH value of the slurry also influences the zeta potential of particles, and thus the suspension stability. A slurry pH value of 6 to 7 was experimentally determined to produce the mechanically strongest monoliths after freezing. The cross-linking (condensation) rate between silica particles is greatly influenced by the pH of the slurry; this effect allows silica to act as a binder during the preparation process. A pH value below 6 led to suspensions having very low stability, while pH values of 8 to 11 lead to insufficient condensation. The obtained slurry was then placed under vacuum at 300 mbar for 5 minute to remove bubbles created during stirring. Then, it was poured into a 120 mm (adjustable to account for slurry amount) × 70 mm × 25 mm mold, made of 2 aluminum plates (high heat conduction), and a polyvinyl chloride (PVC) U-shaped plate (relatively insulating). Then, the mold was quickly transferred to a freezer (-150°C) for 2 hour to produce a completely frozen body. The samples were then transferred to a freeze dryer for 5 days at -30°C for sublimation. Finally, the samples were pyrolyzed at different pyrolysis temperatures (600°C, 700°C, 1000°C) under a nitrogen atmosphere. A scheme of the preparation process is shown in Figure 1. The fillers followed the nomenclature “xMK-yAPTES-xxx” and the post-pyrolysis freeze cast samples followed the nomenclature “xMK-yAPTES-xxx-yyy”; the molar ratio of MK:APTES is x/y, the first value xxx is the pyrolysis temperature of the filler material (200°C means the

samples were only cross-linked with the heating program: 80°C, 140°C, and 200°C), and the second value yyy describes the pyrolysis temperature of the monolith.

2.3 | Characterizations

Thermogravimetric analysis (TGA; STA503, Bähr-Thermoanalyse GmbH, Hüllhorst, Germany) was performed at a temperature range of 20–1000°C under flowing nitrogen (2 L h⁻¹) with a heating rate of 10°C min⁻¹. Zeta potentials of the hybrid fillers were measured (Dispersion Technology Zeta & Size 1200; Dispersion Technology Inc., Bedford, NY, USA) to evaluate the surface charges of particles and the stability of the suspension. Specific surface areas and pore size distributions were determined by nitrogen adsorption and desorption isotherms (Belsorp-Mini, Bel Japan, Inc., Toyonaka, Osaka, Japan). The monolith materials were ground and sieved with a 300 µm mesh sieve in order to minimize nitrogen diffusion effects during the measurements, and were degassed at 120°C for 3 hour before the analysis. Water vapor and *n*-heptane adsorption measurements were carried out by placing vessels with ~0.5 g of sample powder (particle sizes ≤300 µm) inside of closed Erlenmeyer flasks filled with the solvents at equilibrium with their vapor phase at room temperature. Samples were weighed at the start and end of a 24 hour measurement period in order to determine the vapor uptake of the material. The uptake was then recalculated into g/m² using the specific surface area of the materials (measured by nitrogen adsorption). The particle size and pore morphology of samples was analyzed via scanning electron

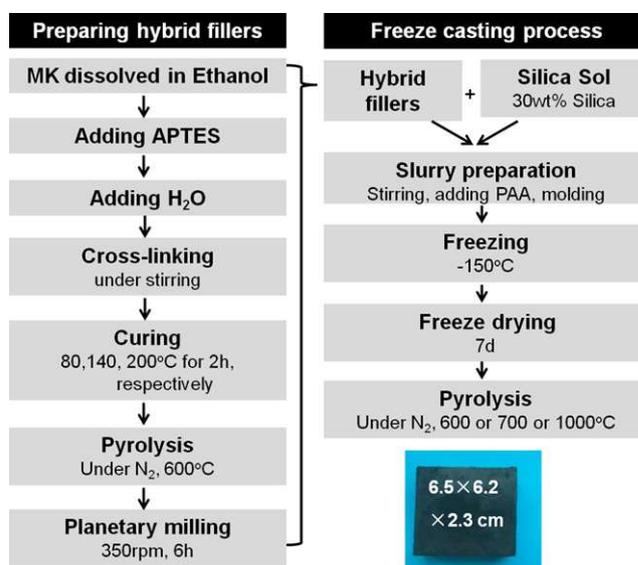


FIGURE 1 Process scheme, parameter variations of synthesized samples, and sample monolith pyrolyzed at 1000°C [Color figure can be viewed at wileyonlinelibrary.com]

microscopy (SEM, Camscan Series2, Obducat CamScan Ltd., Dortmund, Germany). Samples were sputtered with gold (K550, Emitech, Judges Scientific plc., London, UK) before measurements. Mercury intrusion porosimetry (Pascal 140/440, POROTEC GmbH, Frankfurt am Main, Germany) was used to determine the macroporosities.

3 | RESULTS

3.1 | Fillers

3.1.1 | Thermal decomposition of fillers

The cross-linked APTES, MK, and cross-linked xMK-yAPTES-xxx samples were investigated by TGA, as shown in Figure 2, to determine the pyrolysis temperature to produce the fillers. The cross-linked MK shows less than 3% decomposition before 700°C, due to the high thermal stability of methyl groups in the resin.³⁶ Decomposition of amino groups in the cross-linked APTES begins around 400°C; the majority of the decomposition happens before 600°C.

Mass loss of cross-linked xMK-yAPTES-200 shows thermal decomposition behaviors similar to “pure” APTES. The decomposition starts at 400°C, and proceeds to 900°C. Pyrolysis temperatures of 400°C, 500°C and 600°C were chosen for pyrolyzing xMK-yAPTES-200, after the observation that 600°C was high enough to decompose the -NH₂ group while preserving a certain number of -CH₃ groups, which can help bonds formation between the pre-pyrolyzed granulates. The thermal decomposition of resultant hybrid filler xMK-yAPTES-600 was also investigated. It was shown that the decomposition of xMK-yAPTES-600 was negligible even up to 1000°C, which highly reduces the gas produced during pyrolysis.

3.1.2 | Specific surface areas of fillers

The specific surface areas (SSA) of the hybrid fillers were investigated in order to determine the influence of their SSA on the final monoliths. The specific surface areas (SSA) of the hybrid fillers in Table 1 show that both the pyrolysis temperature and MK:APTES molar ratios have an influence on the SSA. The SSA of the fillers ranged from 164 to 321 m²/g. This high specific surface area is due to micropores produced during pyrolysis, which can be inferred from the nitrogen adsorption isotherms. For the pure (unmixed) precursors, a SSA of 350 m²/g was observed for APTES, while MK showed a SSA of 280 m²/g after cross-linking and pyrolysis at 600°C.^{37,38} However, the SSAs of xMK-yAPTES-600 filler prepared with different MK:APTES ratios (from 5:1 to 1:1) decreased with the increasing APTES content. Interestingly, SSA at the ratio

1:2 is 281 m²/g also among the highest values. That means a linear relation between the SSA and the MK:APTES ratio was not observed. A possible explanation is that the SSA are not only influenced by the MK:APTES ratio, but also by the cross-linking behavior, which was also influenced by other factors, the stirring rate or the ambient temperature, or even different batches of MK from the same supplier, etc. Both APTES and MK needed to be hydrolyzed to cross-link. 1 mol MK has only 4% of active groups that can be cross-linked, while 1 mol of APTES can be easily hydrolyzed and has 3 mol hydroxyl groups after hydrolysis that can cross-link fully. The cross-linking between hydrolyzed APTES molecules is much faster than with hydrolyzed MK, which can be influenced by the stirring rate or the ambient temperature, etc. accordingly resulting in different networks and SSA. Pyrolysis of different cross-linked products at different temperatures resulted in different SSA. The SSA of single material cross-linked

TABLE 1 Prepared material, MK:APTES molar compositions, pyrolysis parameters and resultant specific surface area

Sample	MK: APTES molar ratio	Pyrolysis temperature (°C)	Specific surface area (m ² /g)
5MK-1APTES-600	5:1	600	283
3MK-1APTES-600	3:1	600	227
2MK-1APTES-600	2:1	600	224
1MK-1APTES-600	1:1	600	164
1MK-1APTES-500	1:1	500	321
1MK-1APTES-400	1:1	400	124
1MK-2APTES-600	1:2	600	281

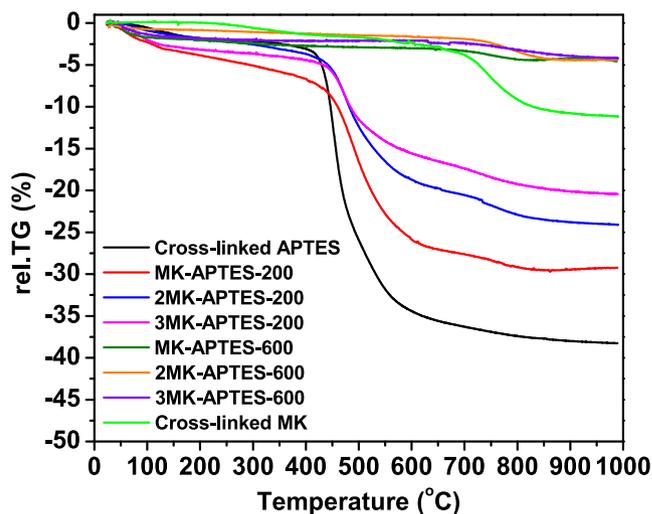


FIGURE 2 TGA of cross-linked xMK-yAPTES-xxx and cross-linked APTES and cross-linked MK [Color figure can be viewed at wileyonlinelibrary.com]

APTES and MK at pyrolysis temperature of 500°C are 440 m²/g and smaller than 25 m²/g, respectively.^{37,38} Higher SSA were achieved at 500°C for APTES and at 600°C for MK, which explains the relation of SSA with pyrolysis temperature. The SSA of 1MK-1APTES-xxx at 400°C, 500°C, and 600°C are 124, 321, and 164 m²/g, respectively. At 500°C, the molar ratio MK: APTES = 1 produced the highest SSA among all the fillers.

3.1.3 | Surface characteristics of fillers

The applicability of preceramic polymers for water-based freeze casting will be greatly influenced by hydrophobicity. Thus, the influence of the pyrolysis temperature and the MK:APTES molar ratios on the surface characteristics were investigated. Hydrophilicity and hydrophobicity of the pyrolyzed samples are determined using water and *n*-heptane vapor adsorption at 22°C (Figure 3). The vapor adsorption (mmol/m²), recalculated based on the SSA values, were influenced by the specific surface area. However, the hydrophilicity was reflected by the ratio of water/heptane adsorption, instead of the absolute value of the water or vapor adsorption. All the samples except 1MK-APTES-400 have a much higher water vapor adsorption than *n*-heptane adsorption, displaying hydrophilic surface characteristics, which might be applicable for freeze casting. However, only 1MK-1APTES-600 in Figure 3A shows anomalously high hydrophilicity. The pyrolysis temperature was fixed to 600°C, at which most of the -NH₂ groups are decomposed.

Hydrophilicity varies with the molar ratio of MK: APTES. The highest hydrophilicity was obtained with the sample 1MK-1APTES-600. Higher MK content normally produces a filler having more hydrophobic groups, resulting in a less hydrophilic material. Higher APTES content results in higher hydrophilicity, due to the hydrophilic SiO₂, formed by decomposition of APTES. 1MK-2APTES-600 (MK:APTES=2) shows lower adsorption than 1MK-1APTES-600 (MK:APTES=1). This can be explained by the difference of SSA. 1MK-1APTES-600 has a SSA of 164 m²/g, and 1MK-2APTES-600 has a SSA of 281 m²/g. Therefore, the vapor adsorption of 1MK-1APTES-600 is lower than 1MK-2APTES-600. The ratios of water/heptane adsorption are 1.2, 1.5, 1.6, 2.5, and 2.4, respectively, when the MK:APTES ratios were changing from 5:1, 3:1, 2:1, 1:1, 1:2. This showed the increase of the hydrophilicity with increasing APTES contents (The ratios of water/heptane 1MK-1APTES-600 and 1MK-2APTES-600 are 2.5 and 2.4, respectively, which means that the hydrophilicity is very similar). The surface characteristics of the fillers produce predictable surface characteristics in the final porous monolith.

The zeta potentials of the xMK-yAPTES-xxx fillers were measured by dispersing the precursor particles into

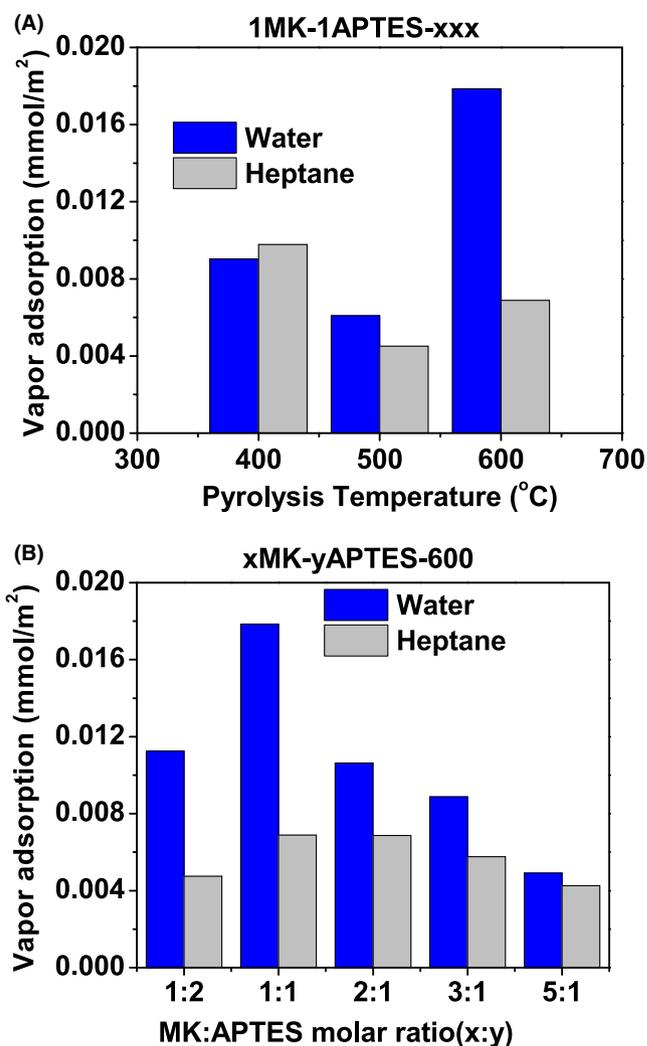


FIGURE 3 Water and *n*-heptane vapor adsorption at 22°C for precursors pyrolyzed (A) at varied temperature and (B) with varied MK to APTES amount pyrolyzed at 600°C. The sorption data were recalculated using the specific BET surface area from N₂ adsorption [Color figure can be viewed at wileyonlinelibrary.com]

water to form a suspension. Normally, an absolute value of zeta potential greater than 30 mV is considered to be stable suspension.³⁵ As seen from Figure 4, the particles are mostly negatively charged. At the pH value higher than 6, it was observed that, the absolute values of zeta potential of 1MK-1APTES600, is higher than 30 mV, which can form stable suspension. During freeze casting, the pH is adjusted to 6-7 to improve the condensation of silica sol.

Due to inadequate hydrophilicity, the other fillers can only be partially wet by water, forming an unstable suspension, which would not be useful in water-based freeze casting.

At almost the whole pH range, 1MK-1APTES-400 fillers are positively charged, still having considerable numbers of surficial -NH₂ groups due to incomplete thermal decomposition. Fillers with more organic groups (higher MK:APTES ratios) also produced unstable suspensions. Except for forming a stable suspension, the filler should

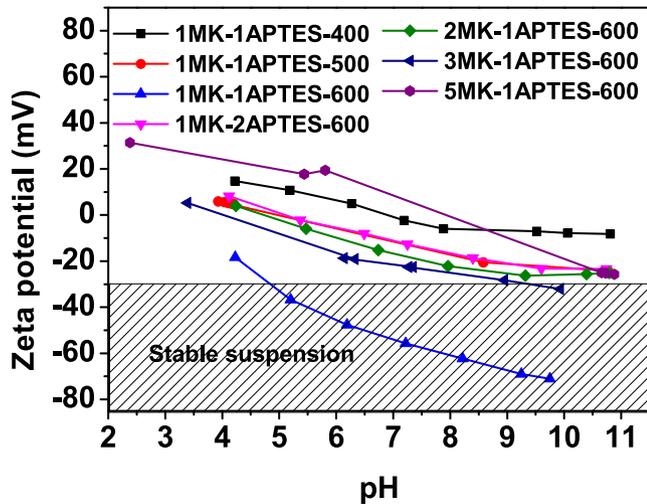


FIGURE 4 Zeta potential of the hybrid fillers with different compositions at various temperatures in de-ionized water [Color figure can be viewed at wileyonlinelibrary.com]

have as much as possible organic groups to form more bonds during pyrolysis. After accounting for surface charge, hydrophilicity, of fillers and mechanical strength of final monolith, 1MK-1APTES-600 was determined to be the optimal precursor for freeze casting.

3.2 | Monoliths prepared by freeze casting

SEM images of pyrolyzed monoliths and fillers are shown in Figure 5A. Figure 5A,B are two cross--sections perpendicular to each other, showing the most unidirectional pore structure. The ice front propagation will follow the

temperature gradient, which was controlled by the configuration of the mold in this work. The ice will grow simultaneously from both metal plates to the center and joined in the middle of the sample, and the structure was seen with double-size freezing as well.³⁹ Figure 5A shows that the pores are composed of parallel lamellae up to several mm long. Figure 5B shows typical pore sizes in the range of 20-50 μm . Shrinkage in pore direction after the second pyrolysis is calculated to be around 8%, and the direction perpendicular to it is less than 7%. Since the macropores were created before the final pyrolysis at 1000°C, gases, by-products of the MK decomposition, can escape easily from the porous structure. Moreover, the macropores acted as a buffer for the thermal shrinkage, which assisted in the production of crack free monoliths.

Figure 5C shows the hierarchically ordered pore structure of the monoliths, and how the packing of the particles results in a secondary pore size distribution. It has been reported that the sintering necks of SiOC had formed at pyrolysis temperatures around 1400°C.⁴⁰ Due to lower pyrolysis temperatures and the low organic content of the fillers, pre-pyrolyzed granulates are not completely jointed together. The same hierarchical structure has also been observed for freeze-cast monoliths using methyl-phenyl polysiloxane.³¹ Figure 5D shows that the particles were mostly below 1 μm , and aggregated, however, unable to be sieved due to the high surface charges and surface area. Therefore, the particle size distribution may be inhomogeneous due to limitations of the planetary ball-milling process.

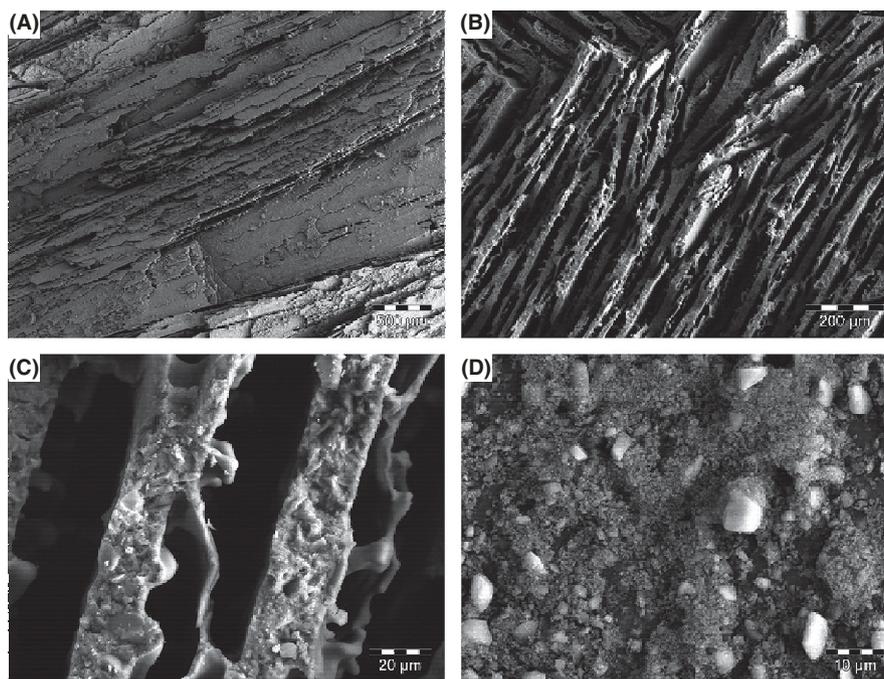


FIGURE 5 SEM images of monoliths pyrolyzed at 1000 °C. (A) Cross-section parallel to the lamellar pores, (B-C) cross-sections perpendicular to the lamellar pores, (D) SEM image of hybrid filler after planetary milling at 350 r min^{-1} for 6 h

The Hg intrusion porosimetry of the monolith 1MK-APTES-600-1000 shown in Figure 6 indicates an open porosity around 55%, a pore size range around 20-50 μm , in agreement with the pores' sizes observed with SEM. A secondary pore size distribution was also observed in the Hg intrusion porosimetry; however, it was of very low relative volume. Thus, nitrogen adsorption and desorption were needed for further information about secondary porosity.

The nitrogen adsorption and desorption isotherms for samples pyrolyzed at various temperatures are shown in Figure 7. Filler MK-APTES-600 has IUPAC type I isotherms, indicating large numbers of micropores (Figure 7A). Monoliths prepared with this filler contain micropores and mesopores after a second pyrolysis at 600°C or 700°C. At pyrolysis temperatures around 1000°C, the micropores structures collapsed; however, mesoporosity is still observed—inferred from the type IV isotherms of MK-APTES-600-1000, with a SSA as high as 51.6 m^2/g .

The mesoporosity was further analyzed using the BJH model; as shown in Figure 7B, the mesopore diameter is around 4–10 nm. Pyrolysis temperatures between 600°C and 700°C result in similar mesopore distributions, indicating few mesopores collapse; however, pyrolysis at 1000°C resulted in a reduction in the number of mesopores. The specific surface area of samples prepared with xMK-yAPTES-600 and pyrolyzed at various temperatures were investigated (Figure 7C) and the results show 2MK-1APTES-600 has highest SSA, and the influence of MK: APTES ratio on SSA was much less comparing to the pyrolysis temperature.

Compared to the 1MK-APTES-600 filler, water adsorption of the pyrolyzed monoliths was greatly improved, indicating increased hydrophilicity, shown in Figure 8. This

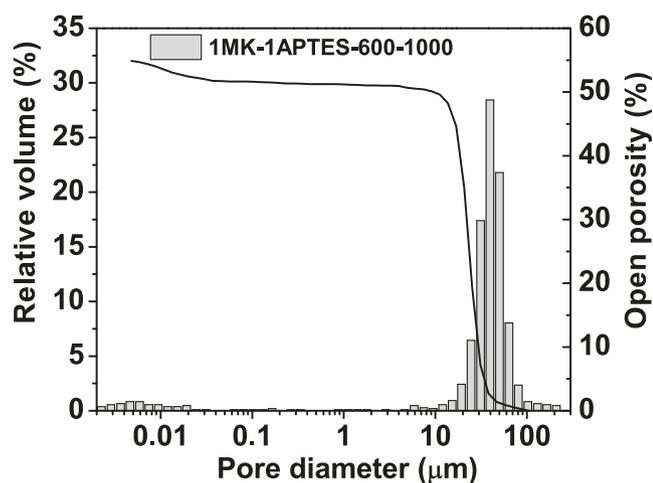


FIGURE 6 Pore size distribution vs relative pore volume and open porosity curves obtained from Hg-porosimetry of pyrolyzed samples

improvement is likely due to the significant incorporation of hydrophilic silica (by silica sol) and further decomposition of the organic groups during the second pyrolysis. The higher pyrolysis temperatures lead to higher hydrophilicity, due to the higher degree of decomposition of the fillers.

4 | DISCUSSION

4.1 | Modification of surface characteristics of fillers

In this work, silica sol went through freeze gelation by condensation during the freezing process. The reason of using silica sol as water source is to improve the mechanical properties of the green body as well as the pyrolyzed monolith, eg, combination of freeze casting Al_2O_3 with freeze gelation of the acrylamide has been used to improve the mechanical properties.¹⁶ Due to the negative charge of the silica particles, only other negative and hydrophilic particles should be additionally used in the freezing process.

Thermal decomposition of the phenyl groups in methylphenyl polysiloxane produced an easily wet hydrophilic, at the same time, negatively charged surface. Thermal decomposition is an easy way to alter the surface characteristics of methyl phenyl polysiloxane; however, it does not work for the methyl polysiloxane (MK). The release of methane takes place at pyrolysis temperatures around 700°C-800°C³⁶; a hydrophobic surface is still preserved at a pyrolysis temperature of 600°C. Thus, other methods are required to alter the surface characteristics of the methyl polysiloxane, eg compositing or cross-linking with hydrophilic components.

Compositing polysiloxane with SiO_2 particles (1 μm) was investigated (results not presented here), however, inadequate hydrophilicity was observed, limiting its application in our water-based freeze casting. Cross-linking MK with tetraethyl orthosilicate (TEOS, molar ratios MK: TEOS=1:1) also produces a hydrophobic surface after pyrolysis (see Figure S1), thus cannot be used in water-based freeze casting. There has been significant work done using 3-(triethoxysilyl)propylsuccinic anhydride (TESPSA) to alter the surface of the silica,⁴¹ which results in materials with carboxyl groups. Thus, it is possible that fillers prepared by MK cross-linking with TESPSA (negatively charged in the basic pH range) could coexist with silica sol, at a pH around 10. Therefore, cross-linking of MK with TESPSA was also carried out; however, the resultant material is a solid elastomer, very elastic, and unable to be ball milled to produce powders. This might be due to the structure of the TESPSA, which might have steric hindrance during cross-linking, resulting in less bonds formation. For example, one evidence of the steric hindrance was found to be between the anhydride groups and approaching TESPSA

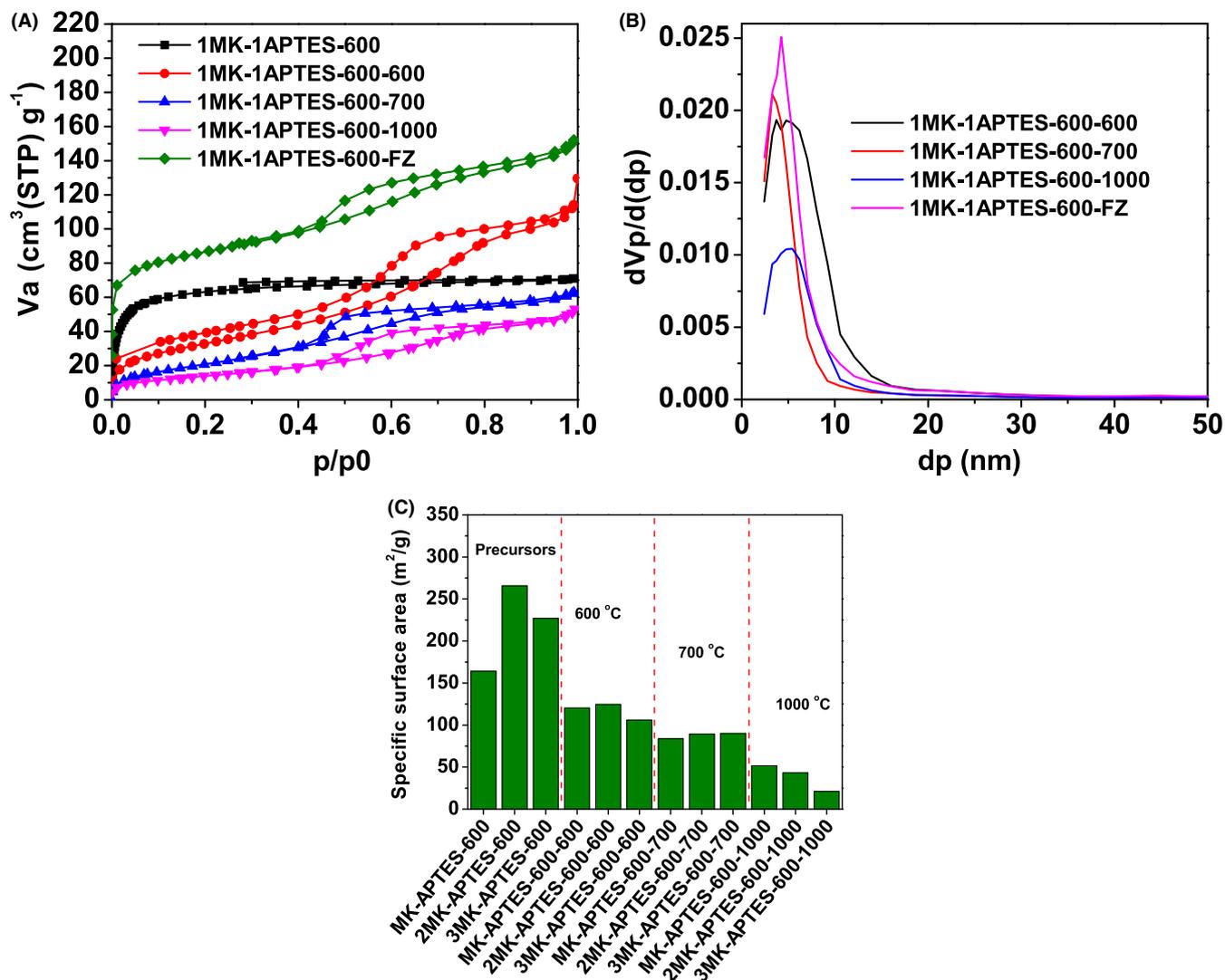


FIGURE 7 (A) The nitrogen adsorption and desorption isotherms, (B) the BJH analysis of samples pyrolyzed at various temperatures or only freeze-cast, (C) SSAs of all precursors and samples pyrolyzed at various temperatures [Color figure can be viewed at wileyonlinelibrary.com]

species during immobilizing TESPSA on the surface of nanoparticles.⁴²

As shown in Figure 9, the surface modification of MK from hydrophobic to hydrophilic was achieved by compositing it with APTES, however, at pH range 6-7, amino groups on the surface of the cross-linking product should attract protons. This results in a positive charge on cross-linking product particles, making it incompatible with negative silica particles, thus resulting in an unstable suspension. Therefore, a following pyrolysis step is necessary to decompose the amino group in the cross-linked materials to get negatively charged and water-insoluble fillers. As seen from the TGA in Figure 2, APTES in 1MK-1APTES-200 underwent significant decomposition at 600°C, producing hydrophilic SiO_2 nano-domains and the resultant MK-APTES-600 displayed considerable hydrophilicity. Another advantage of cross-linking MK with APTES is that APTES has a potential use

for helping with dispersion of metal ions to produce catalytic centers in the matrix.²⁵

4.2 | The hierarchical porous structure

The pore structure of freeze-cast samples is characterized by nitrogen adsorption and Hg intrusion porosimetry, and micro-, meso- as well as macropores were observed. The macropores are created during the freeze casting process, and the mesopores are produced were formed after freeze casting and the following pyrolysis. Introducing solid filler particles into the matrix should hinder the elimination of porosity and shrinkage during pyrolysis, due to its negligible volume change.⁴⁴ As shown in Figure 7A, nitrogen adsorption and desorption confirmed that 1MK-1APTES-600 fillers had only micropores while 1MK-1APTES-600-FZ (only freeze cast, without pyrolysis) had micropores as

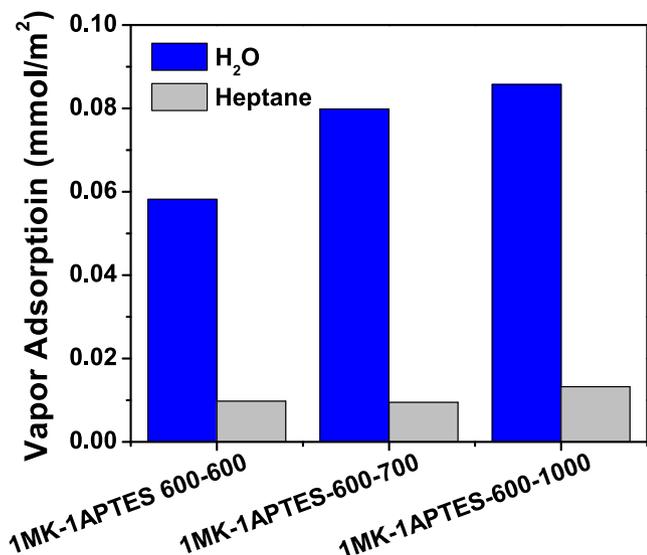


FIGURE 8 Water and *n*-heptane vapor adsorption at 25°C for monoliths pyrolyzed at various temperatures, compared with those for 1MK-1APTES-600 fillers. The sorption data were recalculated using the specific BET surface area from N₂ adsorption [Color figure can be viewed at wileyonlinelibrary.com]

well as mesopores, and the mesopores survived the following pyrolysis. During the freeze casting, the packed granulates consist of silica nanoparticles (8 nm, silica sol) and sub-micrometer hybrid filler (xMK-yAPTES-600 filler). The pressure generated by repulsion from ice and silica condensation between the particles formed the mesopores. There has been some work using binders with

nanoparticles to get mesoporous or close to mesopore range materials. Brandes et al⁴⁵ have used 200 nm alumina and alginate as binder to get mono-sized 71 nm pores after sintering and Besser⁴⁶ and Bartels et al⁴⁷ have used 30 and 90 nm yttria-stabilized zirconia with PVA as binder to produce 30 nm mesopores and 5-200 nm meso/macropores, respectively. This process is very similar to our silica condensation to get mesopores. The mesopores were highly influenced by the initial particle size. The filler sizes are mostly smaller than 1 μm, and have a relatively broad particle size distribution. This broad particle size distribution and the silica nanoparticles (8 nm) made the packing much denser, resulted in mesopores. During the pyrolysis, the bonds formation of fillers and the sintering of silica particles did not affect the mesopore size obviously as shown in Figure 7B.

During thermal decomposition, sintering necks between nanosilica (melting temperature 1600°C) were formed due to diffusion, and bonds were also formed between hybrid fillers. This allows the particles to bind together, reducing the “particle packing” pore size, and maximizing the mechanical strength of the final monolith. At the same time, the filler decomposed further, forming more bonds. Since filler has been prepyrolyzed, the reaction during the second pyrolysis was very limited, therefore, mesopores can be preserved. In case of higher pyrolysis (1000°C or even higher) temperature, the mesopores collapse as shown in Figure 7B. The development of micropores is ascribed to the thermal decomposition of the cross-linked polymer. The hierarchical porous structure was produced by

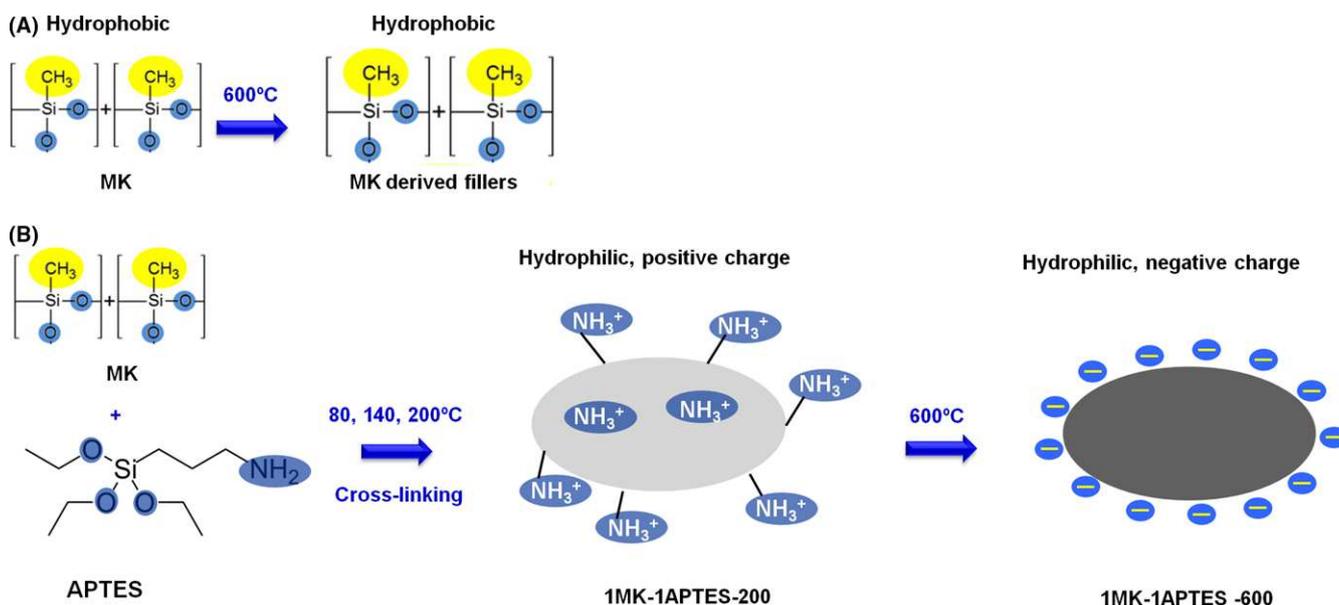


FIGURE 9 Change of chemical structure during pyrolytic conversion. Coloring of functional groups according to Ref. [43]: yellow color and blue color represent hydrophobic interactions and hydrophilic interactions, respectively. Decomposition products are not completely released, but hydrocarbons remain partly in the matrix (A) Surface modification by thermal decomposition and (B) Surface modification by compositing and thermal decomposition [Color figure can be viewed at wileyonlinelibrary.com]

combining the preceramic polymer with the water-based freeze casting. Similar micro/meso/macrostructures can be formed when 1MK-APTES-200 particles are suspended in pure water (as they were positively charged, they were not compatible with silica sol) for freeze casting and finally pyrolyzed at 600°C (see Figure S 2-4). The use of 1MK-APTES-200 with water led to the similar porous structure, which may simplify the preparation by excluding the pyrolysis steps, however, during the slurry preparation, the surface of 1MK-1APTES-200 particles are only mostly wetted (not completely wetted, since there will be dry powders floating on the slurry surface), even after a very long stirring times and high speed, which gives relatively inhomogeneous slurry. Besides, the wet particles were found to be partially dissolvable in water, due to the complexity of this system, it was not investigated further.

4.3 | Influences of silica sol

When silica sol was used during the freeze casting process with filler, the suspension stability of the slurry can be improved. Due to the more negative zeta potential value of silica nanoparticles, the repulsion between the negative particles are stronger, therefore the filler in silica sol were more stable than in water.

The use of silica sol affects the monoliths in terms of surface characteristics (vapor adsorption), and SSA (nitrogen adsorption/desorption) and mesopores. Due to the high hydrophilicity of the silica particles in the sol, the resulting monolith is more hydrophilic. Since silica sol acts as binder, the condensation of silica particles will influence the packing of the filler particles by the binding force, therefore influenced mesopores. The amounts of mesopores and the pore size accordingly influenced SSA. The use of silica sol was expected to have no obvious influence on micropores and macropores size, however, the silica particles contributed to the solid content, which decreased the macroporosity.

4.4 | Influences of process parameters

The microstructure (pore size, pore morphology, porosity, unidirectional or radial pore structure, etc.) of a monolith can be varied by the altering the freeze casting conditions (freezing rate, temperature gradient directions, solid loading).¹⁰ The filler powders were produced by planetary ball milling; there is the possibility that some particles may not be ground down smaller than 1 μm . Due to the high specific surface area and surface charges on the surface, particle sizes separation by sieving is unsuccessful. However, even the bigger particle sizes are much smaller than the pore sizes, given that they are small in quantity, they could hardly disturb the ice growth. The freezing process was done in a deep freeze, and the temperature gradient and

lamellae growth direction are controlled by the mold configuration; thermal isolation (PVC) vs conducting aluminum. Thus, the temperature gradient may not be perfectly linear along the freeze direction. If a copper cold finger with an accurately controllable temperature gradient is used, a highly unidirectional structure can be obtained.⁴⁸ In this work, the ice tends to grow along the temperature gradient, but heterogeneous nucleation results in the formation of randomly oriented lamellar domains perpendicular to the ice front propagation. There has been at least one report using the unidirectional pattern on the cooling surface to manipulate the ice lamellae direction and obtain long-range ordering with well-oriented structures on the length scale of the sample.¹⁹

5 | CONCLUSION

Altering surface characteristics by compositing hydrophobic methyl polysiloxane with hydrophilic agent and a pyrolysis step turned out to be a strategy, which not only enlarges methods for preparing PDCs using various kinds of polysiloxanes, but also may extend the usage of polysiloxanes in aqueous system. The hydrophobic MK was successfully altered to hydrophilic fillers by introducing APTES and a pyrolysis to apply in water-based freeze casting. The hierarchically ordered micro/meso/macroporous SiOC macroporous monoliths were created due to thermal decomposition of precursors and freeze casting process. This method enables the adjustment of porosity at different scales, alteration of surface characteristics, and maximization of specific surface areas of final monoliths by varying precursor ratios and pyrolysis temperatures. The incorporation of APTES also raises the possibility to introduce metal salts into the structure; especially useful for catalysis applications.

ACKNOWLEDGMENTS

This work was supported by German Research Foundation (DFG) within the Research Training Group GRK 1860 “Micro-, meso- and macroporous nonmetallic Materials: Fundamentals and Applications” (MIMENIMA).

REFERENCES

1. Zhang J, Jin Y, Li CY, Shen YN, Han L, et al. Creation of three-dimensionally ordered macroporous Au/CeO₂ catalysts with controlled pore sizes and their enhanced catalytic performance for formaldehyde oxidation. *Appl Catal B*. 2009;91:11-20.
2. Ribeiro RP, Sauer TP, Lopes FV, Moreira RF, Grande CA, et al. Adsorption of CO₂, CH₄, and N₂ in activated carbon honeycomb monolith. *J Chem Eng Data*. 2008;53:2311-2317.

3. Aiken GR, Mcknight DM, Thorn KA, Thurman EM. Isolation of hydrophilic organic acids from water using nonionic macroporous resins. *Org Geochem.* 1992;18:567-573.
4. Taslicukur Z, Balaban C, Kuskonmaz N. Production of ceramic foam filters for molten metal filtration using expanded polystyrene. *J Eur Ceram Soc.* 2007;27:637-640.
5. Wei J, Jia JF, Wu F, Wei SC, Zhou HJ, et al. Hierarchically microporous/macroporous scaffold of magnesium-calcium phosphate for bone tissue regeneration. *Biomaterials.* 2010;31:1260-1269.
6. Chen Y, Bunch J, Li TS, Mao ZP, Chen FL. Novel functionally graded acicular electrode for solid oxide cells fabricated by the freeze-tape-casting process. *J Power Sources.* 2012;213:93-99.
7. Estevez L, Dua R, Bhandari N, Ramanujapuram A, Wang P, et al. A facile approach for the synthesis of monolithic hierarchical porous carbons—high performance materials for amine based CO₂ capture and supercapacitor electrode. *Energy Environ Sci.* 2013;6:1785-1790.
8. Kim YW, Jin YJ, Chun YS, Song IH, Kim HD. A simple pressing route to closed-cell microcellular ceramics. *Scripta Mater.* 2005;53:921-925.
9. Gonzenbach UT, Studart AR, Tervoort E, Gauckler LJ. Macroporous ceramics from particle-stabilized wet foams. *J Am Ceram Soc.* 2007;90:16-22.
10. Studart AR, Gonzenbach UT, Tervoort E, Gauckler LJ. Processing routes to macroporous ceramics: a review. *J Am Ceram Soc.* 2006;89:1771-1789.
11. Wegst UGK, Bai H, Saiz E, Tomsia AP, Ritchie RO. Bioinspired structural materials. *Nature Mater.* 2015;14:23-36.
12. Colombo P, Vakifahmetoglu C, Costacurta S. Fabrication of ceramic components with hierarchical porosity. *J Mater Sci.* 2010;45:5425-5455.
13. Ohji T, Fukushima M. Macro porous ceramics: processing and properties. *Int Mater Rev.* 2012;57:115-131.
14. Deville S. Freeze-casting of porous ceramics: a review of current achievements and issues. *Adv Eng Mater.* 2008;10:155-169.
15. Fukasawa T, Deng ZY, Ando M. Pore structure of porous ceramics synthesized from water-based slurry by freeze-dry process. *J Mater Sci.* 2001;36:2523-2527.
16. Chen RF, Wang CA, Huang Y, Ma LG, Lin WY. Ceramics with special porous structures fabricated by freeze-gelcasting: using tert-butyl alcohol as a template. *J Am Ceram Soc.* 2007;90:3478-3484.
17. Tang YF, Qiu S, Wu C, Miao Q, Zhao K. Freeze cast fabrication of porous ceramics using tert-butyl alcohol-water crystals as template. *J Eur Ceram Soc.* 2016;36:1513-1518.
18. Fukasawa T, Ando M, Ohji T, Kanzaki S. Synthesis of porous ceramics with complex pore structure by freeze-dry processing. *J Am Ceram Soc.* 2001;84:230-232.
19. Munch E, Saiz E, Tomsia AP. Architectural control of freeze-cast ceramics through additives and templating. *J Am Ceram Soc.* 2009;92:1534-1539.
20. Colombo P, Modesti M. Silicon oxycarbide ceramic foams from a preceramic polymer. *J Am Ceram Soc.* 1999;82:573-578.
21. Hojamberdiev M, Prasad RM, Morita K, Zhu YF, Schiavon MA, et al. Template-free synthesis of polymer-derived mesoporous SiOC/TiO₂ and SiOC/N-Doped TiO₂ ceramic composites for application in the removal of organic dyes from contaminated water. *Appl Catal B.* 2012;115–116:303-313.
22. Vakifahmetoglu C, Colombo P, Pauletti A, Martin CF, Babonneau F. SiOC ceramic monoliths with hierarchical porosity. *Int J Appl Ceram Technol.* 2010;7:528-535.
23. Schmidt H, Koch D, Grathwohl G, Colombo P. Micro-/macroporous ceramics from preceramic precursors. *J Am Ceram Soc.* 2001;84:2252-2255.
24. Vakifahmetoglu C, Menapace I, Hirsch A, Biasetto L, Hauser R, et al. Highly porous macro- and micro-cellular ceramics from a Polysilazane precursor. *Ceram Int.* 2009;35:3281-3290.
25. Adam M, Kocanis S, Fey T, Wilhelm M, Grathwohl G. Hierarchically ordered foams derived from polysiloxanes with catalytically active coatings. *J Eur Ceram Soc.* 2014;34:1715-1725.
26. Hong CQ, Zhang XH, Han JC, Du JC, Han WB. Ultra-high-porosity zirconia ceramics fabricated by novel room-temperature freeze-casting. *Scripta Mater.* 2009;60:563-566.
27. Yoon BH, Park CS, Kim HE, Koh YH. In situ synthesis of porous silicon carbide (SiC) ceramics decorated with SiC nanowires. *J Am Ceram Soc.* 2007;90:3759-3766.
28. Fukasawa T, Deng ZY, Ando M, Ohji T, Kanzaki S. Synthesis of porous silicon nitride with unidirectionally aligned channels using freeze-drying process. *J Am Ceram Soc.* 2002;85:2151-2155.
29. Yoon BH, Lee EJ, Kim HE, Koh YH. Highly aligned porous silicon carbide ceramics by freezing, polycarbosilane/camphene solution. *J Am Ceram Soc.* 2007;90:1753-1759.
30. Naviroj M, Miller SM, Colombo P, Faber KT. Directionally aligned macroporous SiOC via freeze casting of preceramic polymers. *J Eur Ceram Soc.* 2015;35:2225-2232.
31. Zhang HX, Nunes PD, Wilhelm M, Rezwan K. Hierarchically ordered micro/meso/macroporous polymer-derived ceramic monoliths fabricated by freeze-casting. *J Eur Ceram Soc.* 2016;36:51-58.
32. Rao AP, Rao AV. Modifying the surface energy and hydrophobicity of the low-density silica aerogels through the use of combinations of surface-modification agents. *J Mater Sci.* 2010; 45:51-63.
33. Owen MJ, Smith PJ. Plasma treatment of polydimethylsiloxane. *J Adhesion Sci Technol.* 1994;8:1063-1075.
34. Kim JH, Park PK, Lee CH, Kwon HH. Surface modification of nanofiltration membranes to improve the removal of organic micro-pollutants (EDCs and PhACs) in drinking water treatment: graft polymerization and cross-linking followed by functional group substitution. *J Membrane Sci.* 2008;321:190-198.
35. Duman O, Tunc S. Electrokinetic and rheological properties of Na-bentonite in some electrolyte solutions. *Micropor Mesopor Mat.* 2009;117:331-338.
36. Scheffler M, Gambaryan-Roisman T, Takahashi T, Kaschta J, Muenstedt H, et al. Pyrolytic decomposition of preceramic organo polysiloxanes. *Ceram Trans.* 2000;115:239-250.
37. Prenzel T, Wilhelm M, Rezwan K. Tailoring amine functionalized hybrid ceramics to control CO₂ adsorption. *Chem Eng J.* 2014;235:198-206.
38. Prenzel T, Wilhelm M, Rezwan K. Pyrolyzed polysiloxane membranes with tailorable hydrophobicity, porosity and high specific surface area. *Micropor Mesopor Mat.* 2013;169:160-167.
39. Deville S, Saiz E, Tomsia AP. Ice-templated porous alumina structures. *Acta Mater.* 2007;55:1965-1974.
40. Esfahanian M, Oberacker R, Fett T, Hoffmann MJ. Development of dense filler-free polymer-derived SiOC ceramics by field-assisted sintering. *J Am Ceram Soc.* 2008;91:3803-3805.

41. Halfer T, Rei A, Ciacchi LC, Treccani L, Rezwan K. Selective covalent immobilization of ferritin on alumina. *Biointerphases*. 2014;9:031018, 9 pp.
42. Barabanova AI, Pryakhina TA, Afanas'ev ES, Zavin BG, Vygodskii YS, et al. Anhydride modified silica nanoparticles: preparation and characterization. *Appl Surf Sci*. 2012;258:3168-3172.
43. Jastorff B, Störmann R, Ranke J. Thinking in structure-activity relationships-a way forward towards sustainable chemistry. *Clean*. 2007;35:399-405.
44. Jean G, Sciamanna V, Demuyneck M, Cambier F, Gonon M. Macroporous ceramics: novel route using partial sintering of alumina-powder agglomerates obtained by spray-drying. *Ceram Int*. 2014;40:10197-10203.
45. Brandes C, Treccani L, Kroll S, Rezwan K. Gel casting of free-shapeable ceramic membranes with adjustable Pore size for ultra- and microfiltration. *J Am Ceram Soc*. 2014;97:1393-1401.
46. Besser B, Veltzke T, Dreyer JAH, Bartels J, Baune M. A comparative experimental study on the deviation of the ideal selectivity in DTMS-functionalized and untreated ceramic structures with pores in the upper mesoporous range. *Micropor Mesopor Mat*. 2015;217:253-261.
47. Bartels J, Souza MN, Schaper A, Árki P, Kroll S, et al. Amino-functionalized ceramic capillary membranes for controlled virus retention. *Environ Sci Technol*. 2016;50:1973-1981.
48. Wicklein B, Kocjan A, Salazar-Alvarez G, Carosio F, Camino G, et al. Thermally insulating and fire-retardant lightweight anisotropic foams based on nanocellulose and graphene oxide. *Nat Nanotech*. 2015;10:277-283.

SUPPORTING INFORMATION

Additional Supporting Information may be found online in the supporting information tab for this article.

How to cite this article: Zhang H, Fidelis CL, Serva ALT, Wilhelm M, Rezwan K. Water-based freeze casting: Adjusting hydrophobic polymethylsiloxane for obtaining hierarchically ordered porous SiOC. *J Am Ceram Soc*. 2017;100:1907–1918.