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Original Article

Tape casting of polysiloxane-derived ceramic with controlled porosity and surface properties

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ABSTRACT

Tape casting has been applied to produce porous hybrid and SiOC ceramic tapes using ceramic precursors and commercially available polysiloxanes as polymeric binders. SiC particles of two different mean sizes (4.5 or 6.5 μm) were used as inert fillers to prevent shrinkage and increase mechanical stability. Macroporosity was adjusted by varying the azodicarbonamide (ADA) content from 0 to 30 wt.%. Decomposition of the polysiloxanes at 600 °C resulted in the generation of micropores with high specific surface area (187–267 $m^2 g^{-1}$) and a predominant hydrophobic behavior. At 1000 °C mainly meso/macroporosity were observed (SSA: 32–162 $m^2 g^{-1}$) accompanied by increased hydrophilicity. The influence of ADA content, SiC size, and pyrolysis temperature on open porosity (2.5–37%), average pore size (< 0.01–1.76 μm), surface characteristics, and flexural strength (10.5–121 MPa) were investigated. The porous tapes with different surface characteristics and controlled structure are highly promising for applications involving membrane processes, particularly microfiltration systems (0.1–10 μm).

1. Introduction

Tape casting is a well-established wet shaping process at industrial and laboratory scales. Conventionally, a tape casting slurry is composed of a solvent, organic polymers as binders and plasticizers, surfactants, and ceramic particles which are left after burning out the organic compounds [1,2]. This technique is traditionally applied to produce planar thin ceramic tapes (10–1000 μm) for electronic components such as dense multilayered substrates [3].

The advances in ceramic processing and the increasing interest in developing porous ceramic materials allowed the fabrication of thin ceramic tapes for a wide range of applications, such as: solid oxide fuel cells [4–6], photocatalysis [7], supports/substrates [8–10], and microfiltration [11,12]. There are plenty of strategies to produce macroporous ceramic tapes which include sacrificial pore formers, freeze casting, phase-inversion, and partial sintering [13].

However, depending on the application, a hierarchical structure with micro-meso-macropores may be required. Macropores (> 50 nm) are responsible for providing mechanical stability and improved mass transport, while micro (< 2 nm) and mesopores (2–50 nm) have a major influence on the functional properties and specific surface area (SSA) [14]. To this end, the incorporation of micro-mesopores and functional properties is feasible by using preceramic polymers (PCPs) such as polysiloxanes. PCPs are capable of undergoing different shaping processing routes due to their polymeric nature [15–17]. Furthermore, these precursors can be converted into hybrid ceramics (at 500–700 °C) [18], when parts of the polymers remain unreacted. When ceramic materials (SiC, SiOC, SiCN) are formed from silicon-based polymers by heat treatment (≥1000 °C) under inert atmospheres [19], those products are described as polymer-derived ceramics (PDCs).

Sacrificial templating, direct foaming, freeze casting, emulsion based or etching methods have been applied to shape porous polymer-derived ceramics [20,21]. Most of those studies are mainly focused on the production of bulk systems like monolithic or foam structures. Therefore, there are only a few mentions in the literature regarding the use of polysiloxanes as polymeric binder for the tape casting process [10,22,23]. Ceramic tapes from silanes/polysiloxanes have been fabricated using PCPs as binders and ceramic precursors, eventually including SiC as inert filler to avoid shrinkage, and Si as active filler to generate pores [10,22]. After pyrolysis at high temperatures (1200–1600 °C) under inert atmosphere (Ar or N_2), a Si-O-C-(N) ceramic system was obtained. Nevertheless, to the best of our

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knowledge, the capability of producing tape casted hybrid ceramic was not investigated.

Polysiloxanes may result in hybrid ceramics with high specific surface area, due to the formation of micropores, when pyrolyzed below 700 °C [18], keeping the hydrophobic character of the polymers. On the other hand, pyrolysis at higher temperatures (≥1000 °C) leads to a collapse of micropores and a hydrophilic behavior is developed due to the decomposition and ceramization process [24]. Macroporosity can be produced by adding sacrificial pore formers like azodicarbonamide (ADA) [25,26].

Therefore, the present study focuses on the processability of polysiloxanes to produce PCP-based tapes with adjustable porosity and surface properties in terms of hydrophilicity or hydrophobicity.

2. Material and methods

2.1. Precursors, solvent and additives

All experiments were performed using commercially available chemicals with no additional purification step. Powders of methylphenyl polysiloxane (Silres® H44, Wacker Chemie) and methyl polysiloxane (Silres® MK, Wacker Chemie) were used as binders and ceramic precursors. Silicon carbide powders (SiC F800, d_{50} = 6.5 µm; and SiC F1000, d_{50} = 4.5 µm; EKS) were used as inert fillers to increase processability, reduce cracking due to shrinkage, and provide mechanical stability after pyrolysis. Azodicarbonamide (ADA, 97%, CAS 123-77-3, Sigma–Aldrich) was used as pore former. Imidazole (99%, A10221, CAS 288-32-4, Alfa Aesar) was applied as a cross-linking catalyst for the polysiloxanes. Xylene (98.5%, CAS 1330-20-7, Sigma–Aldrich) was the solvent for the polysiloxanes and the liquid medium to disperse the other components.

2.2. Preparation of the polysiloxane-based tapes

The preparation procedure of the polysiloxane-based tapes is shown in Fig. 1. The first step comprises the slurry preparation, which was conducted at room temperature (r.t.) using magnetic stirrer. Firstly, MK (20 wt.%) and H44 (20 wt.%) powders were dissolved in xylene to get a clear solution. SiC (59 wt.%; d_{50} = 4.5 or 6.5 µm) was then added into the obtained solution and stirred for 60 min to produce a homogeneous slurry. Finally cross-linking catalyst, imidazole (1 wt.%) was added and stirred for further 60 min. In order to understand the effect of ADA, this pore former agent was added in various amounts. It was added in the obtained clear solution of MK and H44 before the addition of SiC. The calculation of the ADA (0, 10, 20, and 30 wt.%) was based on the total weight of the other solid components in the composition (MK + H44 + SiC + imidazole = 100 wt.%). The slurry was casted over a polyethylene terephthalate carrier film (Mylar, G10JRM, Richard E. Mistler, Inc.) using a doctor blade with the gap set at 1.5 mm. The tape was dried at room temperature in a fume hood for 24 h prior to cutting. Afterward, the cut pieces were dried for at least more 24 h before pyrolysis. The tapes were pyrolyzed at 600 and 1000 °C in an atmosphere of nitrogen. The heating rate was 120 °C h^{-1} to 100 °C below the final temperature and 30 °C h^{-1} to the final temperature with a dwelling time of 4 h. The overall appearance of the pyrolyzed tapes at 600 and 1000 °C is shown in Fig. 1.

2.3. Sample notation

Tapes were composed by varying the particle size of SiC and the weight percentage of ADA regarding the total amount of the other solids in the slurry. Sample notation was based on the following construction: SiCX –AY–Z, where X means the silicon carbide average particle size in µm; A stands for ADA; Y refers to the ADA weight percentage (wt.%); and Z is the pyrolysis temperature in °C.

2.4. Characterization

The macrostructure was analyzed by Scanning Electron Microscopy (SEM, 20 kV; Series 2, Obducat CamScan). For this purpose, the samples were sputtered with gold (K550, Emitech, Judges Scientific). The surface roughness (Ra) was determined in triplicate with an optical profilometer (Pll2300, Sensofar). Porosity and mean pore size of the tapes were determined using mercury intrusion porosimetry (Pascal 140/440, Porotec). Specific BET surface area (SSA) was determined by nitrogen adsorption and desorption isotherms measured at 77 K (Belsorp-Mini, Bel Japan). The samples were degassed at 120 °C for 3 h. Before degassing, the pyrolyzed tapes were ground and sieved with a 300 µm mesh sieve in order to diminish the limitation of nitrogen diffusion within the timeframe of the experiment. Hydrophilicity and

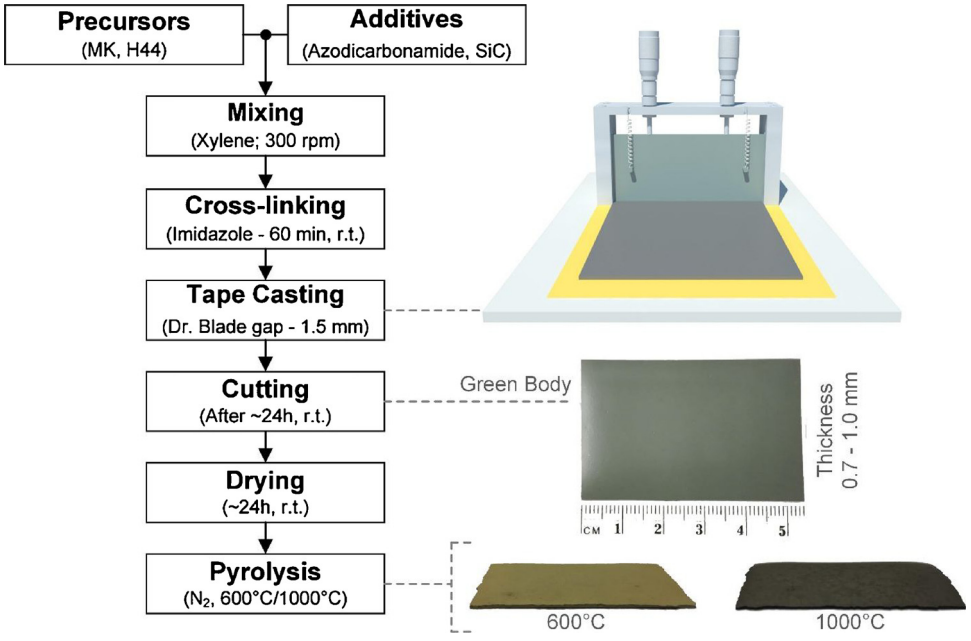

Fig. 1. Flowchart of polysiloxane-derived, casted and pyrolyzed tapes (600/1000 °C).