

# Mechanical and tribological properties of polymer-derived Si/C/N sub-millimetre thick miniaturized components fabricated by direct casting

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## Abstract

The utilization of silicon-based polymers as a source of amorphous non-oxide ceramics obtained upon pyrolytic treatment of them is increasingly gaining attention in research and is currently expanding into the field of commercial products. This work is focused on the near-net shaped fabrication, mechanical and tribological properties of a polymer-derived Si/C/N system.

Small sub-millimetre thick ceramic test discs and bars were fabricated by casting of polysilazane and/or polycarbosilane precursor mixtures into elastomeric polydimethylsiloxane forms, thermal cross-linking and subsequent pyrolysis. Additional carbon was introduced on the molecular level using triphenylvinylsilane as the precursor, its cross-linking with the polymers via hydrosilylation prohibits phase separation of graphite within the amorphous matrix. The characteristic strength of nearly 700 MPa along with stable low friction coefficients in sliding against similar polymer-derived ceramics testifies to their potential in micro electro mechanical system applications.

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## 1. Introduction

Polymer-derived ceramics (PDCs) – are a relatively new class of non-oxide structural and functional materials gaining increasing interest from research and industry.<sup>1,2</sup> The soft nature of the starting polymeric materials provides a unique opportunity for fabrication of various shapes (e.g. by liquid moulding), which are converted into rigid ceramic structures upon curing and subsequent pyrolytic treatment at 600–1000 °C. The tailoring of the chemical structure of the starting polymeric precursor at the molecular level and varying pyrolysis conditions enables adjustment of the resulting composition, microstructure and properties. This approach was successfully commercialized

for fibres (e.g. Tyranno Fiber<sup>®</sup>, Nicalon<sup>™</sup>)<sup>1a,3</sup> and ceramic matrix composites.<sup>4,1b</sup> It is currently extending into the fields of protective<sup>5,1c</sup> and functional<sup>6,7</sup> coatings, porous bodies,<sup>8,9</sup> filaments<sup>10</sup> and is anticipated to gain a niche in fabrication of miniaturized components. Current micro electro mechanical system (MEMS) technology is mostly based on silicon, whose modest mechanical and tribological properties necessitate the identification and development of new alternative materials.<sup>11,12</sup> Fabrication of various PDC fine structures based on variations in lithographic and soft lithographic techniques was reported over the last decade.<sup>1d,13–16</sup> However, in order to pave the way for a broad use of PDC MEMS, the state of their mechanical and application-specific properties, (e.g. tribological) should be validated. Similar to diamond and DLC,<sup>11</sup> PDCs show low wear friction coefficient in mild operating conditions<sup>17,18</sup> and seem to be promising candidates for MEMS. However, the contact pressures in small moving and sliding parts can exceed

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maximal acceptable Hertzian stresses and lead to severe friction and wear conditions, causing failure.

Among the broad spectrum of preceramic polymers, the family of liquid CERASET<sup>®</sup> polysilazane<sup>19</sup> precursors which lead to silicon carbonitrides has so far attracted highest attention in the PDC research community, being as well the material of choice for most of the works devoted to PDC MEMS. Additionally silicon oxycarbide<sup>20</sup> and glassy carbon<sup>21</sup> MEMS were presented. Remarkably, polycarbosilane<sup>22</sup> which is industrially used for fabrication of the SiC matrix in disc brakes and is thus promising for other frictional applications has not yet come into the focus of MEMS research.

In the few systematic studies on tribology of PDCs it was shown in the CERASET<sup>®</sup>-derived Si/C/N system that a transition from mild to severe wear regime occurs after reaching a threshold contact pressure.<sup>17,18</sup> The attractive frictional properties in a mild wear regime were attributed to the free carbon. However, the question of optimal composition in the Si/C/N with respect to strength, friction and wear as well as the requirements and limitations imposed by these materials on engineering applications remain open.

Perhaps the main obstacle which precludes comprehensive and exhaustive characterization of intrinsic properties of PDCs is the difficulty in fabrication of monolithic macro-sized test specimens, the latter is due to cracking caused by substantial gas evolution and shrinkage during pyrolysis.<sup>2d</sup> As already mentioned above, PDC components are made by a number of techniques including, photolithography, soft lithography, moulding and casting of liquid polymers and for larger components using a powder route by warm pressing of partially cross linked (sometimes with fillers) and re-crushed preceramic polymeric powder.<sup>2b</sup> The majority of large bulk test specimens (e.g. 3 mm × 4 mm × 50 mm in dimension) containing a PDC matrix were produced using this powder route.<sup>1e,2a,2b</sup> This technique is not suitable for MEMS fabrication and the mechanical results of these studies are affected by the powder route processing steps. The method of pressure casting reported by Shah and Raj<sup>23</sup> and modified by Janakiraman and Aldinger<sup>24</sup> seems to present a breakthrough in the problem to obtain data which is more relevant to liquid route processed MEMS components. Its applicability for MEMS is however yet to be proven. Test specimens using MEMS fabrication routes tend to have much smaller dimensions e.g. for bending strength specimens these might be typically 1 mm × 3 mm × 0.5 mm in dimension.<sup>25</sup>

Here we report on fabrication of polymer-derived ceramic sub-millimetre-thick components by a direct casting method suitable for production of MEMS test specimens in a size range approximately in between those mentioned above and their characterization with respect to strength, fracture toughness and friction behaviour.

## 2. Experimental

### 2.1. Materials

Commercially available liquid preceramic polymers selected for this study were Ceraset<sup>®</sup> polysilazane 20 (Clariant Charlotte,

NC, USA) and allylhydridopolycarbosilane SMP-10 (Starfire<sup>®</sup> Systems, Malta, NY, USA). Triphenylvinylsilane (TPVS) – the source of additional free carbon was purchased at ABCR GmbH (Karlsruhe, Germany). 1,1'-Azobis(cyclohexanecarbonitrile) was used as radical initiator for thermal cross-linking of polymeric precursors (Sigma–Aldrich, Buchs, Switzerland). Two-component elastomeric polydimethylsiloxane (PDMS) Sylgard<sup>®</sup>-184 (Dow Corning, Midland, USA) was used for replication of soft moulds from a SU-8 (MicroChem Corp., Newton, USA) photoresist master. All chemicals were used as received without any purification or modification.

### 2.2. Fabrication

The master SU-8 structures with dimensions of 20 mm × 2.1 mm × 0.3 mm (bars) and 20 mm (diameter) × 0.3 mm (discs) on silicon wafers were created by means of lithography. For the fabrication of PDMS moulds, two components of Sylgard<sup>®</sup>-184 with mass ratio 1:10 as prescribed by the vendor were mixed, degassed under 2–4 mbar vacuum for 15 min and poured onto a silicon wafer bearing the complementary SU-8 master pattern. After manual tilting of the wafer for a uniform distribution of PDMS, the wafer was placed into a drying box and the temperature was increased to 140 °C with a heating rate of 20–40 °C/h and held for 2 h. After cooling the PDMS replica was gently peeled off, cut into circles of 50 mm diameter and glued with the unstructured side onto 7 mm thick PTFE discs, which act as a rigid support for flexible PDMS. For the fabrication of thicker (0.6 mm) PDC specimens the corresponding cavities were ground directly in PTFE discs (depth ~0.8 mm). The precursors were mixed in the proportions given in Table 1, using for the sake of homogeneity and process acceleration a small ultrasonic horn (5 W) for 30–60 s (liquid is heated up to 60 °C). The mixtures were degassed at 0.3–0.5 mbar for 20–30 min whilst intensively stirring (800–1100 rpm) and thereafter cast using a micropipette into previously lubricated (with silicon grease) PDMS moulds. The usefulness of the degassing procedure is dictated by the fact that both preceramic polymers contain volatile oligomers and slowly expel hydrogen and/or ammonia even during normal storage, causing macroporosity and even bloating of the samples upon heating and evaporation of dissolved volatile species. Caution was paid to the volume injected into the mould cavities in order to minimize the meniscus built on the top. For the fabrication of PDC counter bodies for tribological tests, drops of precursor were placed directly onto PTFE support without PDMS. Due to the high contact angle between polymers and PTFE the drops do not spread and solidify during cross-linking in the form of hemispheres. The latter being pyrolytically converted into ceramics were glued onto an aluminium pin and fixed to a strain gauge in a tribometer (see next paragraph). The filled supported moulds are stacked onto each other and transferred into a hermetically tight Büchi miniclave chamber (Büchi AG, Uster, Switzerland) which is evacuated and flushed with argon twice. Thereafter, Ar pressure of 3 bar is

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