

# Plastic Forming of Preceramic Polymers

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## Abstract

*The method of plastic forming for the preparation of green bodies from different polymeric precursors is discussed. Experiments on the influence of the pressure, the temperature and the grain size of the powders were carried out with different precursors of the system Si–C–N and the system Si–B–C–N. Optimised conditions led to lower porosities in the pyrolysed ceramic for the specimen prepared by plastic forming (PF) than for the specimen prepared by cold isostatic pressing (CIP) of the preceramic polymer. It was also possible to form dense green bodies from polymers which could not be shaped by CIP. Furthermore, the mechanism of the plastic forming behaviour of the preceramic polymers is shown for the first time. © 1998 Elsevier Science Limited. All rights reserved*

**Keywords:** precursors: organic, pressing, porosity, plasticity.

## 1 Introduction

Monolithic ceramics can be obtained by the pyrolysis of elementorganic polymers without the use of any sintering aids.<sup>1–9</sup> Precursors, leading to SiC and Si<sub>3</sub>N<sub>4</sub> ceramics as well as to the ternary system Si–C–N are well investigated. In recent time precursors for ceramics in the quaternary Si–B–C–N system have also become of interest, because of their extraordinary thermal stability.<sup>1,12–24</sup> To get bulk materials, polymers were shaped by cold isostatic pressing (CIP) to form green bodies which were then transformed into amorphous ceramics by subsequent pyrolyses (temperature range between 1000 and 1400°C).<sup>25</sup> With this method a

minimum porosity of 7% of the bulk ceramic was achieved with a Si–C–N-precursor. This porosity originates on the one hand from the incomplete densification by the cold compaction procedure of the polymer powder and on the other hand from the evaporation of gaseous species during the pyrolyses.

Additionally, CIP is not applicable for many kinds of polymeric precursors. Especially highly crosslinked polymer powders can often not be transformed into green bodies by CIP due to their brittle nature.

Therefore, a new technique for the shaping of green bodies has already been developed.<sup>26</sup> Thermomechanical analysis (TMA) on green bodies obtained by CIP show that crosslinked polymers have a softening range where the polymer powders become formable but do not melt. In order to overcome the brittleness and to decrease the porosity of the green bodies the precursors were compacted at their softening temperature. With this new method of plastic forming it was possible to lower the open porosity of polysilazane derived ceramics to a minimum of 3%.

In the present work this technique was applied to several polymer powders of the Si–C–N and Si–B–C–N system; these powders could not be densified so far in the crosslinked stage by CIP.

## 2 Experimental

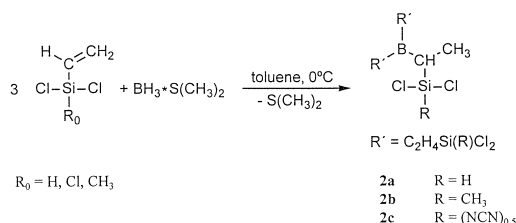
Three types of polymers have been investigated: a polyvinylsilazane (PVS),<sup>10</sup> a polyhydridomethylsilazane (PHMS)<sup>11</sup> and different boron containing polysilylcarbodi-imides.<sup>21,22</sup>

In order to get an infusible polymer which can easily be ground, the PVS and PHMS were substantially crosslinked. PVS was heat treated at 240°C in argon and in vacuum for 1 h each. PHMS

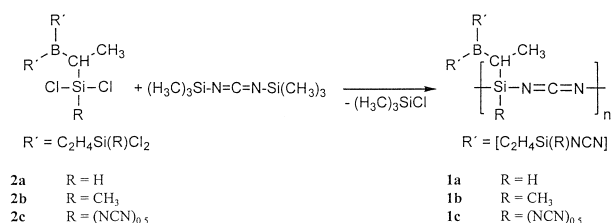
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was crosslinked at 400°C in argon and vacuum for 2 h each.

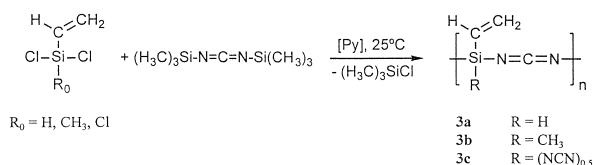
The synthesis of the boron containing polysilylcarbodi-imides of general type  $\{B[C_2H_4Si(R)NCN]\}_n$  [1] where R is a singly bonded ligand [**a** R = H, **b** R = CH<sub>3</sub>, **c** R = (NCN)<sub>0.5</sub>] is, according to Refs 21 and 22, possible by two different reaction pathways. The first possibility is the hydroboration of the vinyl-substituted chlorosilanes (H<sub>2</sub>C = CH)(R)SiCl<sub>2</sub> with borane dimethylsulphide to yield the tris[(chlorosilyl)ethyl]boranes B[C<sub>2</sub>H<sub>4</sub>Si(R)Cl<sub>2</sub>]<sub>3</sub>.



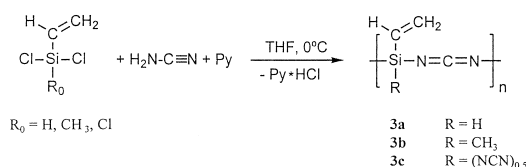
In a second reaction step the as-obtained compounds were treated with bis(trimethylsilyl)carbodi-imide which results in the formation of the hydroborated polysilylcarbodi-imides **1a–1c**.



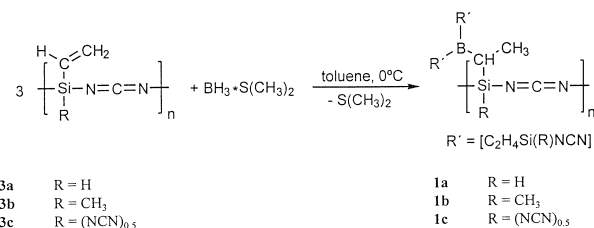
The second possible reaction pathway is given by the reaction of the vinyl-substituted chlorosilanes with either bis(trimethylsilyl)carbodi-imide



or cyanamide to yield vinylated polysilylcarbodi-imides  $[\text{H}_2\text{C}=\text{CH}(\text{R})\text{SiNCN}]_n$ .



The hydroboration of these compounds with borane dimethylsulphide results in the formation of the compounds **1a–1c**.



These boron containing polysilylcarbodi-imides are infusible and do not require any further cross-linkage. The polymers used in this investigation were all prepared according to the first described reaction pathway.

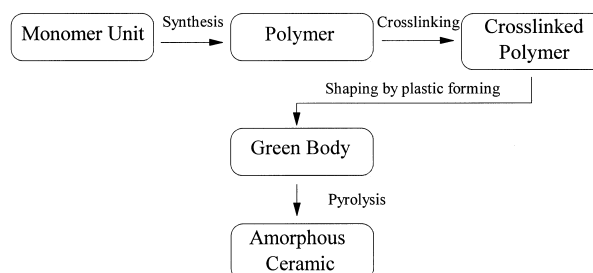
From the raw precursors, hydrogenated powders were produced using a ball mill. Compaction of the powders was performed by uniaxial pressing in graphite dies (diameter 25 mm) in vacuum using a hot-pressing equipment (DSP 475, Dr. Fritsch, Germany). The pyrolyses of the green parts were carried out in tubes of quartz or alumina using the Schlenk technique.\* The complete process scheme is shown in Fig. 1.

If not specified differently all experiments including polymer synthesis, milling, sieving, pyrolyses, etc., were performed in an inert atmosphere (argon) due to the oxidation sensitive nature of the material in the polymer stage.

The pyrolysed ceramic materials were investigated by mercury porosimetry, scanning electron microscopy (SEM) and thermo mechanical analysis (TMA).

### 3 Results and Discussion

Preliminary experiments using both methods CIP and PF had already shown that the grain size of the polymer powders had no or only little influence on the resulting porosity of the pyrolysed product, but a strong effect on the stability of the green



**Fig. 1.** Process pathway for the preparation of precursor-derived ceramics.

\*This preparative method is based on experiments developed by the German chemist Wilhelm Schlenk. All apparatus are equipped with sidearms for pumping out the air and moisture and introducing inert gas.

body. However green bodies prepared from polymer powders with small grain sizes ( $< 0.028$  mm) often tend to break because of compression cracks. On the other hand green bodies prepared from powders with grain sizes  $> 0.08$  mm seldom show compression cracks. Therefore, CIP and PF were carried out using polymer powders with a grain size  $> 0.08$  mm.

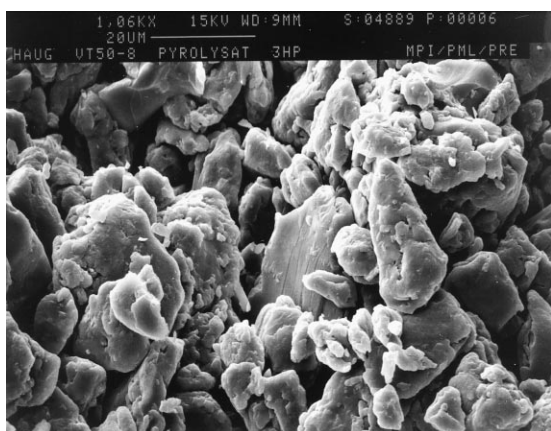
To study the plastic forming process in detail, powder compaction was performed under different conditions. PVS powder was plastically formed by warm pressing at 45 MPa at different temperatures (30–200°C), the boron containing polymers [1a–1c] were treated at different pressures (31–43 MPa) and at different temperatures (100–180°C) and PHMS was treated at 200°C at different pressures (28–52 MPa).

The results showed the same mechanism of densification by plastic forming for all polymers which have been investigated. At low temperatures the polymer powders were densified only because of some rearrangements of the particles (Figs 2 and 3). With increasing temperature the polymer started to soften. With an even more increased temperature

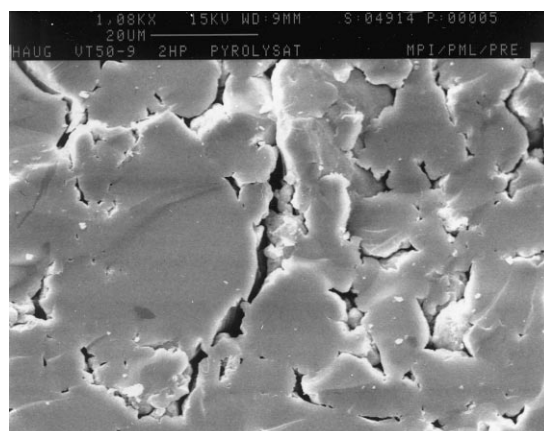
the particles were deformed and melt together as can be seen from the microstructure shown in Fig. 4.

At higher pressing temperatures the remaining porosity was further reduced resulting in dense ceramic monoliths (Fig. 5). However, it has to be mentioned that a fully densified green body does not yield a completely densified ceramic. Due to the need for the evaporation of gaseous species during pyrolyses the green bodies always resulted always in ceramic monoliths which were either cracked, contained holes, or were even totally destroyed after pyrolysis. As a consequence, some open porosity has to be left in the green body in order to allow proper degassing.

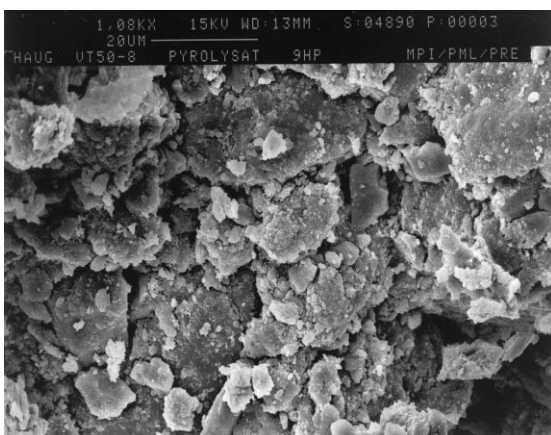
The limited temperature range for obtaining dense and crackfree ceramic monoliths is shown by the set of experiments with PVS (Fig. 6). After pyrolyses at 1050°C the sample which had been plastically formed at 185°C (45 MPa) yielded a ceramic material with a porosity of about 11% (Fig. 4). Densification at 200°C (45 MPa) resulted in a porosity of only 0.97%. However this sample had lots of cracks and macropores formed by the



**Fig. 2.** SEM (1000×) fracture surface of a PVS-derived ceramic. Prepared by densification at 30°C and 45 MPa and subsequent pyrolysis at 1050°C for 4h.



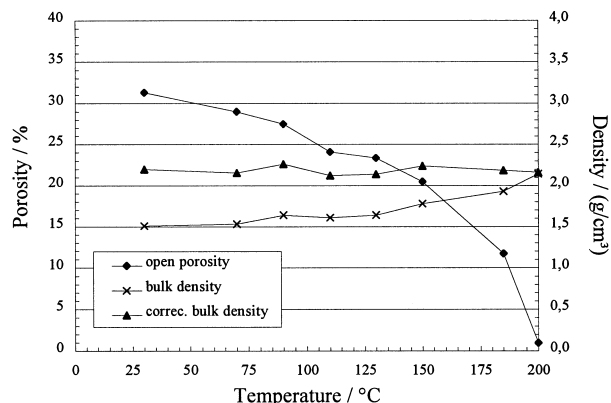
**Fig. 4.** SEM (1000×) fracture surface of a PVS-derived ceramic. Prepared by densification at 185°C and 45 MPa and subsequent pyrolysis at 1050°C for 4h.



**Fig. 3.** SEM (1000×) fracture surface of a PVS-derived ceramic. Prepared by densification at 130°C and 45 MPa and subsequent pyrolysis at 1050°C for 4h.



**Fig. 5.** SEM (70.5×) fracture surface of a PVS-derived ceramic. Prepared by densification at 200°C and 45 MPa and subsequent pyrolysis at 1050°C for 4h.



**Fig. 6.** Porosity of as pyrolysed PVS-derived ceramics; dependent on the temperature applied for plastic forming of the polymer powders at 45 MPa.

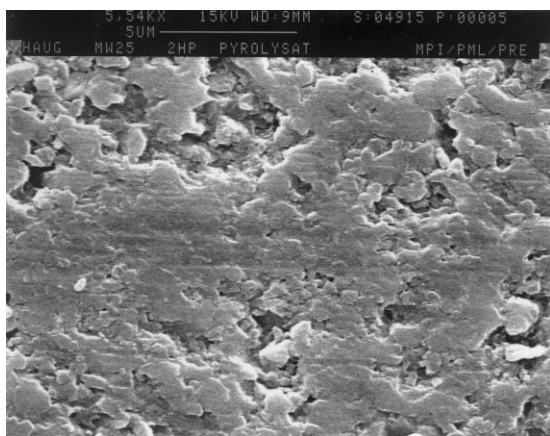
gases which had been evaporated during pyrolysis (Fig. 5).

In Fig. 6 the open porosity, the bulk density (with pores) and the corrected bulk density (without pores) are shown as a function of the temperature applied for PF. As expected the bulk density is increasing with a decreasing porosity while the corrected bulk density stays at an overall constant level.

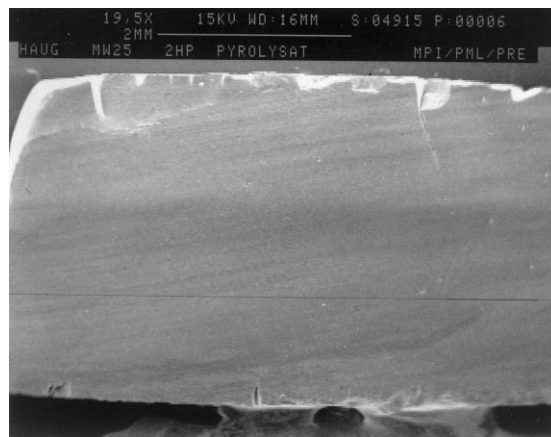
Similar results were obtained for the PHMS polymers and the boron-modified polysilylcarbodi-imides. Plastic forming of the boron containing polysilylcarbodi-imide [1a] at 120°C and 31 MPa and subsequent pyrolysis of the obtained green bodies at 1400°C yielded a crackfree ceramic monolith with about 6% porosity left (Figs 7 and 8).

The same polymer densified at 180°C and 31 MPa formed a dense green body, but similar to the PVS-material showed many cracks after pyrolysis.

TMA-Investigations (Fig. 9) of crosslinked PHMS green bodies obtained by CIP showed vibrations in a temperature range from 320°C up to 450°C (Fig. 10). These vibrations are according



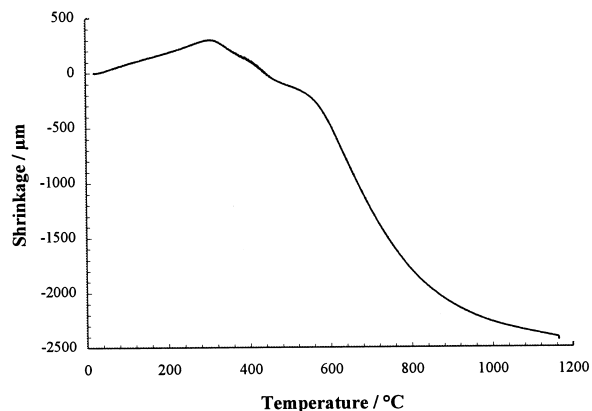
**Fig. 7.** SEM (5540×) intersection of a ceramic derived from [1a]. Prepared by densification at 120°C and 31 MPa and subsequent pyrolysis at 1400°C for 2 h.



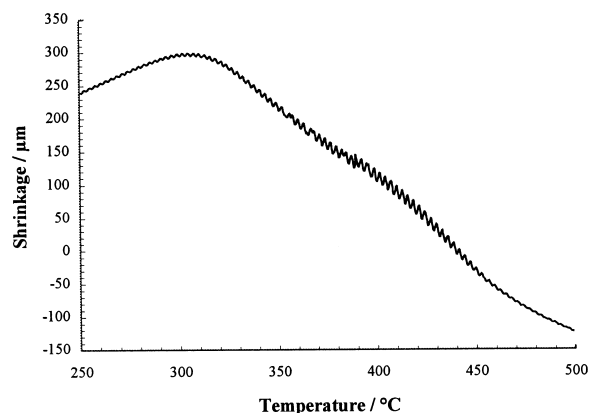
**Fig. 8.** SEM (20x) intersection of a ceramic derived from [1a]. Prepared by densification at 120°C and 31 MPa and subsequent pyrolysis at 1400°C for 2 h.

to Ref. 26 caused by a softening of the green body. However, plastic forming experiments on the PHMS-polymer powder showed that due to the higher pressure during the plastic forming process as compared to the TMA-investigations the polymers can already be densified at lower temperatures (150–250°C).

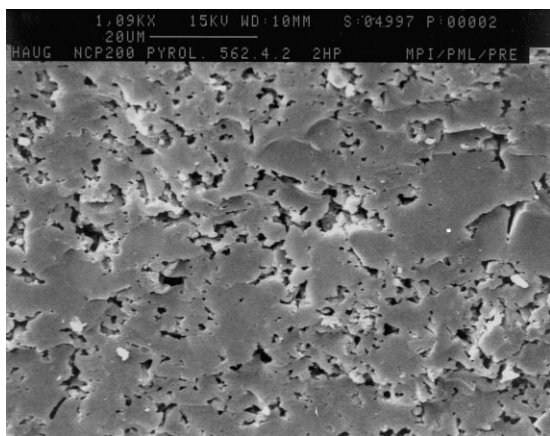
The experiments showed furthermore that the PHMS-polymer powders can also be densified by an increase of the pressure without a further increase of temperature. The porosity of the ceramic



**Fig. 9.** TMA-investigation on a PHMS-green body obtained by CIP.



**Fig. 10.** Enlarged section (250–500°C) of Fig. 9.



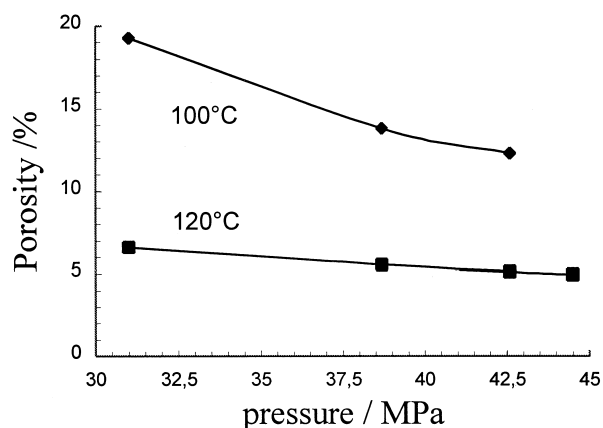
**Fig. 11.** SEM (1000 $\times$ ) fracture surface of a PHMS-derived ceramic. Prepared by densification at 200 $^{\circ}$ C and 52 MPa and subsequent pyrolysis at 1050 $^{\circ}$ C for 4 h.

decreased from 15% when plastically formed at 200 $^{\circ}$ C at a pressure of 28 MPa to a porosity of 5% by increasing the pressure to 52 MPa (Fig. 11).

The same results were obtained for the boron containing polysilylcarbodi-imide [1a] where the open porosity of samples prepared at 100 $^{\circ}$ C decreased from about 20% when warm pressed at 31 MPa to 12% if a pressure of 43 MPa was applied. If the same polymer was plastically formed at 120 $^{\circ}$ C the porosity decreased from 6.6 to 5% within the same pressure range (Fig. 12).

These experiments showed that the temperature during plastic forming of the polymer powders has a much bigger effect on the resulting open porosity of the ceramic specimens than the pressure has. Nevertheless, it is also possible to decrease the porosity of the resulting ceramic by increasing the pressure.

Finally, it has to be mentioned that the parameters for plastic forming concerning pressure and temperature are specific for each of the polymers. These parameters are strongly dependent on the stage of crosslinkage of the polymers and also on



**Fig. 12.** Porosity of ceramics derived from the boron containing polysilylcarbodi-imide [1a]; prepared by plastic forming of the polymer powder at different pyrolysis temperatures and pressures and subsequent pyrolysis at 1400 $^{\circ}$ C for 2 h.

the chemistry of the polymers. Experiments with the boron containing polysilylcarbodi-imides [1a–1c] showed that only little changes, like the exchange of an H [1a] by a methyl group [1b] lead to different plastic forming parameters. First experiments showed that a pressure of 31 MPa and a temperature 120 $^{\circ}$ C lead for polymer [1a] to an open porosity of 6.6%, while for polymer [1b] a temperature of 140 $^{\circ}$ C (pressure 31 > MPa) was necessary to obtain a ceramic with about 8% of porosity. Higher pressing temperatures in both cases led to the destruction of the original shape. However, further experiments have to be carried out in order to gain more insight on this matter.

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