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The Properties of a Ceramic Injection Moulding Suspension Based on a Preceramic Polymer

T. Zhang & J. R. G. Evans*

Department of Materials Technology, Brunel University, Uxbridge, Middlesex, UB8 3PH, UK

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Abstract

A ceramic suspension incorporating fine sinterable silicon carbide powder in a polycarbosilane vehicle has been modified by additions of paraffin wax to make it suitable for plastic forming operations. The diluent enables higher volume fractions of ceramic to be incorporated and lowers the softening point of the suspension. The danger of temperature-induced crosslinking in processing machinery is alleviated.

Eine keramische Suspension aus feinem sinterfähigem Siliziumcarbidpulver in Polycarbosilan wurde durch Zugabe von Paraffin dahingehend verändert, daß plastische Formgebungsverfahren angewandt werden können. Der Zusatz ermöglicht einen höheren keramischen Feststoffanteil und setzt den Erweichungspunkt der Suspension herab. Die Gefahr einer temperaturinduzierten Vernetzung in der Apparatur vermindert sich.

On a modifié une suspension de céramique constituée de poudre fine frittable de carbure de silicium en milieu polycarbosilane à l'aide d'additions de cire de paraffine dans le but de la rendre appropriée aux opérations de formage plastique. Le diluant permet d'augmenter la fraction volumique de céramique et provoque un abaissement du point de ramolissement de la suspension. On réduit ainsi les risques de réticulation induite par la température lors de l'élaboration de la céramique.

1 Introduction

A wide range of plastic forming processes are now available for preparing arrangements of ceramic particles in complex shapes. These include injection moulding,[1,2] extrusion,[3] vacuum forming[4] and blow moulding.[5] They are each potentially augmented by operations which allow joining before firing.[6] However, they require that interstitial space be filled with an organic fluid which must then be removed prior to firing. It follows that if the organic vehicle is selected such that it deposits the relevant ceramic on pyrolysis, prefired relative density could be increased, less matter must be removed from interstitial space and mechanical strength before firing may be increased. Unfortunately, few organic species are available which deposit ceramic residues with sufficient volumetric efficiency and combine the necessary properties for plastic forming processes.

Yajima, who pioneered the fabrication of continuous silicon carbide fibre from polycarbosilane (PCS), suggested that it could also form a suitable binder for silicon carbide.[7] Mutsuddy[8] showed that this was indeed possible and extruded suspensions of silicon carbide powder in PCS which subsequently sintered to 97% relative density. Silicon carbide precursors have also been used to prepare ceramic fibre reinforced ceramics with unidirectional fibres.[9] Subsequently, Mutsuddy[10] showed that silicon carbide whiskers could be incorporated at 30 vol.% in PCS for injection moulding. In this way, a ceramic composite can be prepared without the use of powder.

The logical consequence of these developments as mentioned previously[1] is that ceramics could be manufactured by plastic forming of polymer ceramic precursors, thus dispensing with powders and the difficulties associated with them. A number of reviews discuss this possibility,[11–13] but considerable problems remain with the volumetric efficiency of deposition, high shrinkage and removal of volatile products of pyrolysis without damage.

The present work is confined to the realisation of

PCS as a major binder component in suspensions suitable for injection moulding. Mutsuddy[8] showed quite clearly the problem of temperature-induced crosslinking in this material, whereby viscosity decreased in the temperature range 150–230°C but thereafter increased sharply. Such a composition presents a serious risk of machine seizure caused by minor temperature control problems or long residence times caused by occasional machine faults. The answer lies in carefully tailoring the composition to offer more forgiving properties.

2 Experimental details

2.1 Preparation of suspensions

The silicon carbide (Superior Graphite Co., Kentucky, USA) had a particle size distribution as shown in Fig. 1. A sample of PCS was kindly prepared by Changsha Institute of Technology (China) with a number average molecular weight of 928. The method of synthesis was similar to that used by Yajima[7] and polyborodiphenylsiloxane was used as a reaction accelerator. The paraffin wax was grade 130/135 from Shell Chemicals UK. The compositions are given in Table 1.

The suspensions were prepared by ball milling in a plastic container in *n*-hexane (Analar grade, BDH Chemicals). The weight ratio *n*-hexane: composition:grinding medium was 1:1:2. Mixing was continued on rollers for 4 h and the suspension was dried with final expulsion of solvent being carried out in a vacuum oven at 80°C for 4 h. A Perkin Elmer TMS-1 thermomechanical analyser was used to obtain dilatometric softening points.

2.2 Viscosity measurements

The apparent viscosity of composition 2 was measured using a Davenport Capillary Rheometer fitted with a 2 mm diameter die, 40 mm in length. The measurements were carried out at temperatures from 170–230°C and shear rates from 36 to 717 s^{-1}. Ten minutes were allowed for temperature equilibration in the barrel and end corrections were not applied.

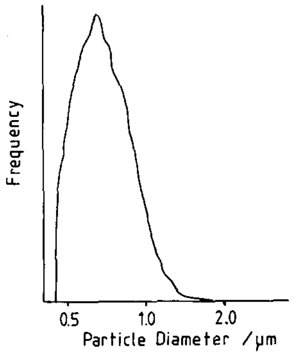


Fig. 1. Particle size distribution for the SiC powder.

Table 1. Composition of ceramic suspensions

	Density (*kgm^{-3}*)	*Weight (%)*	
		Composition 1	*Composition 2*
Silicon carbide	3 200	75	80
Polycarbosilane	1 070	25	16
Paraffin wax	916	—	4
SiC, vol.% (calculated)		50	56

2.3 Pyrolysis and thermogravimetry

Discs for pyrolysis were prepared by compression moulding at 190–200°C and at 170–180°C for compositions 1 and 2 respectively. The discs were 25 mm in diameter and 5 or 10 mm in height.

Compression moulded discs were pyrolysed in flowing oxygen-free nitrogen at various heating rates in an Inconel tube furnace controlled by a Eurotherm 818P programmable temperature controller.

Pyrolysed samples were examined by X-ray diffraction, using a Phillips PW1050 diffractometer with stepper motor drive. A complete pattern for 8–80° of 2θ was recorded at a scan speed of 6°C/min. Subsequent scans for quantitative interpretation were recorded at 0·3°C/min in the range 32–38° of 2θ.

A Perkin-Elmer Model TGS-2 thermogravimetric balance was used to analyse both compositions 1 and 2 as well as polycarbosilane in the as-received state and blended with paraffin wax. A heating rate of 2·5°C/min up to 900°C was used in flowing oxygen-free nitrogen. This thermogravimetric balance was used in an attempt to estimate free carbon in the pyrolysed polycarbosilane. Samples of pure PCS and PCS with paraffin wax in the weight ratios 4:1 were pyrolysed in the tube furnace to 900°C. These samples were first heated in flowing oxygen at 20°C/min in the thermogravimetric balance to 740°C and held for 1 h. They were then raised to 950°C in flowing oxygen and held for 10 min.

A Kratos ES300 X-ray photoelectron spectrophotometer (XPS) was used to detect free silicon in the pyrolysed products in the absence of silicon carbide powder. The device was operated at 14 kV using Al Kα X-rays. The depth of penetration was 3–10 nm.

A Perkin-Elmer Model 683 infra-red spectrophotometer was used to obtain spectra of polycarbosilane samples in KBr discs. The KBr was dried before use to avoid spurious absorptions from water.

Flexural strength of composition 2 before and after pyrolysis was measured by three-point bending in an Instron 4206 machine with a cross-head speed of 0·2 mm/min. Bars were approximately 3 mm × 5 mm and a span of 20 mm between outer loading points was used.

3 Results and discussion

3.1 Structure and pyrolysis of polycarbosilane

The infra-red spectrum of the PCS is shown in Fig. 2. It is very similar to the material used by Mutsuddy[8] and the absorption peaks are identified in Table 2 from Refs 14 and 15.

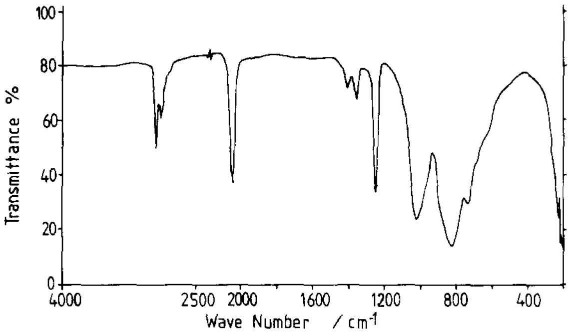
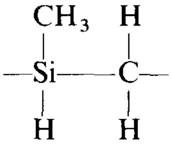


Fig. 2. Infra-red spectra of as-received polycarbosilane.

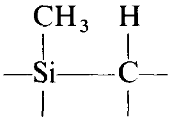
The pyrolysis process was studied by thermogravimetric analysis and the weight losses of the organic binders are shown individually and as mixtures in Fig. 3. The weight loss of PCS occurs in two short stages from 180–370°C and from 370–500°C followed by steady weight loss up to 900°C where the experiment was terminated. The total weight loss of PCS was 34%. The main structural units of PCS are:



$-\overset{CH_3}{\underset{H}{Si}}-\overset{H}{\underset{H}{C}}-$

Type I

and



$-\overset{CH_3}{\underset{CH_3}{Si}}-\overset{H}{\underset{H}{C}}-$

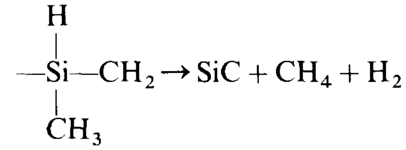
Type II

and an analysis of the material supplied suggests that Type I predominates. The theoretical yield of silicon carbide is relatively insensitive to the proportions of Type I and Type II units when the fraction of Type I exceeds 0·8.

Table 2. Identification of infra-red absorption peaks for polycarbosilane (from data in Refs 14 and 15)

Wavenumber (*cm*$^{-1}$)	*Mode*
2 950, 2 870	CH_3 stretching
2 090	Si—H stretching
1 460	—CH_2— and C—CH_3
1 350	CH_2 deformation in Si—CH_2—Si
1 250	Si—CH_3 deformation
1 020	CH_2 deformation in Si—CH_2—Si; Si—O—Si; Si—O—C
840	Si—H bending and Si—C stretching

During pyrolysis the main reaction is therefore expected to be:[16]



$$-\overset{H}{\underset{CH_3}{Si}}-CH_2 \rightarrow SiC + CH_4 + H_2$$

giving a theoretical yield of 68 wt%, slightly larger than that observed. The discrepancy may be due to the evaporation of low molecular weight species.[8]

Figure 3 also shows the pyrolysis of a mixture of 80 wt% PCS and 20 wt% paraffin wax mixed with *n*-hexane as solvent. When the experimental curve for the mixture is compared with the theoretical curve, calculated assuming no interference between the two species, the agreement is close and is comparable to the agreement for a range of organic mixtures previously investigated in this way.[17]

The thermogravimetric analysis for free carbon showed that for both pure PCS and PCS–paraffin wax, the weight loss from the pyrolysed product after heating in oxygen to 950°C was less than 0·3%. This is within the error of the method so that the amount of free carbon was considered to be low. The constituents of the complex XPS peaks for Si (2*p*) were identified by the Kratos DS300

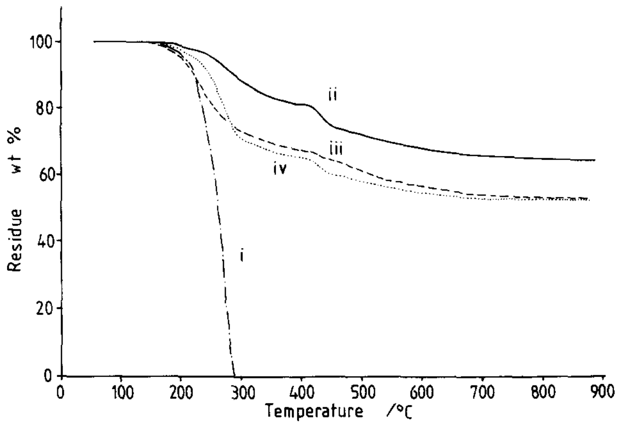


Fig. 3. Thermogravimetric loss of: i, wax; ii, polycarbosilane; iii, wax + polycarbosilane in weight ratio 1:4; iv, theoretical curve for the mixture.

curve fitting routine. No peak at 99 eV for free silicon could be identified. The main silicon peak corresponded to SiC at 101·6 eV and a small peak associated with Si–O was noted, corresponding partly to surface silica, since the assay is surface-specific.

The weight loss of composition 2, which incorporates SiC powder, PCS and wax is shown in Fig. 4. The total weight loss is 9·3% which corresponds to a weight loss from PCS of 33% and is close to theoretical. The calculated weight loss curve is also shown in Fig. 4 and although the overall weight loss is the same, there is some evidence of acceleration of the reaction in the presence of SiC powder; an effect which may be associated with the catalytic effects of the silicon carbide surface. Such effects have been noted for oxide powders.[18]

The conversion to SiC was also studied by X-ray diffraction. Figure 5(a) shows the (111) reflection for β-SiC obtained from the as-received powder while Fig. 5(b) shows the corresponding band associated with the amorphous product of pyrolysis of PCS after heating to 900°C in flowing nitrogen. Under the same conditions the (111) reflection for composition 2 before pyrolysis is shown in Fig. 5(c). The intensity of this band is increased after pyrolysis at 900°C (Fig. 5(d)) suggesting that pyrolysis in the presence of SiC powder yields a crystalline product.

The crystalline fraction X_j can be deducted from the intensities using direct analysis by absorption–diffraction,[19] which does not require an internal standard, as long as the mass absorption of the mixture and its constituents are known:

$$X_j = \frac{\bar{\mu}^*}{\mu_j^*} \cdot \frac{I_{ij}}{(I_{ij})_0} \qquad (1)$$

where I_{ij} and $(I_{ij})_0$ are the intensities of line i of phase j in the mixture and in the pure state respectively. $\bar{\mu}^*$ and μ_j^* are the mass absorption coefficients of the mixture and phase j respectively. For the unpyrolysed composition 2, $\bar{\mu}^*$ was found from the sum of the phases by using the mass absorption coefficients of elements given in reference 19 to be $4{\cdot}091 \times 10^{-3}\,m^2/g$ to CuKα. In the same way, the mass absorption of SiC is given as $4{\cdot}38 \times 10^{-3}\,m^2/g$. From the intensity given in Fig. 5, by using eqn (1), the crystalline SiC in the original composition 2 is 79·9 wt%, which agrees with the composition as mixed.

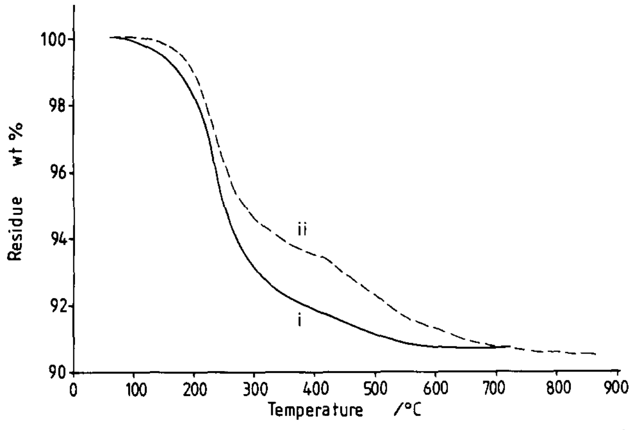
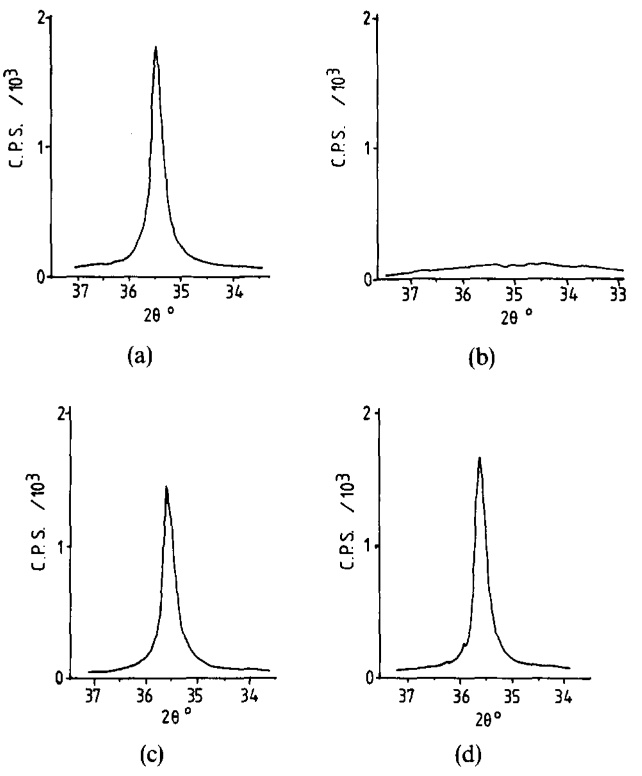


Fig. 4. Thermogravimetric loss from composition 2: i, experimental, ii, calculated.



(a) (b) (c) (d)

Fig. 5. XRD reflections for the (111) plane in β-SiC for (a) as-received powder, (b) PCS pyrolysed to 900°C, (c) composition 2 before pyrolysis, (d) composition 2 after pyrolysis to 900°C.

After heating to 900°C, no free carbon or silicon could be detected, therefore $\bar{\mu}^* = \mu_j^*$. From eqn (1), the crystalline fraction rises to 94%. Since 9·2 wt% of the sample has been lost after heating to 900°C, the original crystalline SiC powder in the sample represents 88%. The extra 6 wt% crystalline SiC appears to originate from the product of PCS pyrolysis. Although this calculation rests on detection of a small change in intensity (about 10%) it suggests that approximately 55 wt% of the PCS product is present in crystalline form and the implication is that the presence of SiC powder encourages crystallinity of the PCS product.

Previous work on the crystallinity of the products of pyrolysis of PCS is contradictory. Kodama & Miyoshi[20] found a product which was amorphous up to temperatures of 1300°C while Yajima[7] obtained substantial crystallinity after heating to

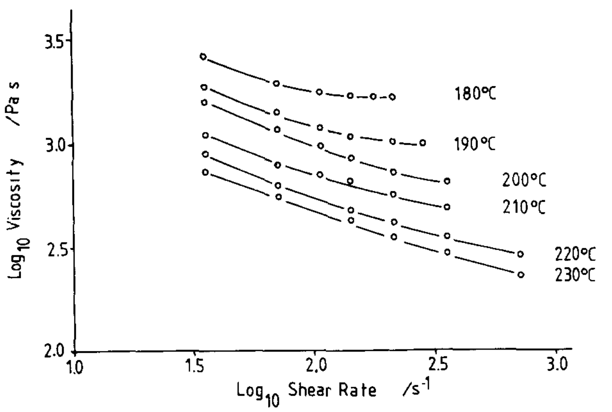


Fig. 6. Apparent viscosity as a function of shear rate for composition 2 at various temperatures.

900°C. Soraru *et al.*[21] observed the onset of crystallinity between 840°C and 1000°C.

3.2 Viscosity of suspensions

The viscosity of composition 1 could only be measured by using a 6·8 mm diameter die. At a shear rate of 2·3 s^{-1} and at 240°C the apparent viscosity was 4·7 × 10^4 Pa s. Since PCS undergoes crosslinking above 190°C[20] further heating to reduce viscosity is inappropriate. The composition is therefore unsuitable for injection moulding.

The flow curves for composition 2 are shown in Fig. 6 for a range of temperatures. At 200°C and at a shear rate of 100 s^{-1} the apparent viscosity is less than 1000 Pa s. The material extrudes evenly to give extrudate with smooth surface finish (Fig. 7). In order to check the stability of the viscosity of composition 2 at these temperatures, samples were retested in the capillary rheometer ten times and similar apparent viscosity results were obtained. Thus, the rate of crosslinking is slow and the composition is suitable for injection moulding without the risk of setting in the machine barrel for normal residence times. The suspension is pseudoplastic above 200°C in the shear rate range 30–730 s^{-1} with a flow behaviour index of 0·6 at 230°C.

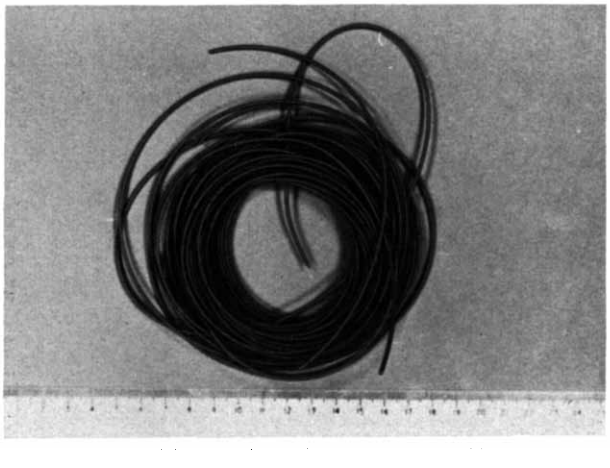


Fig. 7. The appearance of the rheometer extrudate showing excellent surface finish and hence suitability for plastic forming operations.

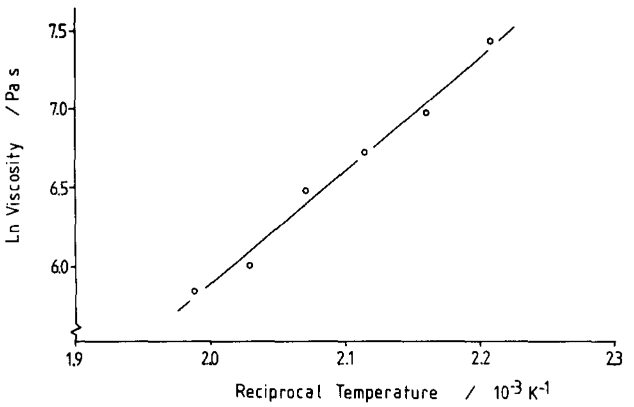


Fig. 8. Logarithm of viscosity at a shear rate of 143 s^{-1} as a function of reciprocal temperature.

Noting the theoretical objections of Hildebrand[22] to the use of activation energy to describe viscous flow of polymers, but recognising the predictive value of the concept, the natural logarithm of viscosity at 143 s^{-1} was plotted against reciprocal temperature (Fig. 8) to obtain constants in the equation:

$$\eta = \eta_0 \exp\frac{E}{RT} \tag{2}$$

From Fig. 8, $\eta_0 = 1{\cdot}4 \times 10^{-3}$ Pa s and $E = 52$ kJ mol^{-1}, indicating a rather high temperature dependence of viscosity.

While composition 1 is inappropriate for injection moulding, having both a high apparent viscosity and subject to the danger of crosslinking in the machine, the wax modification yields a material with excellent flow properties in which a higher particulate volume fraction can be incorporated. The high viscosity of composition 1 is therefore attributable to the viscosity of the PCS not to an excessive ceramic volume loading.

The wax addition also has a beneficial effect in lowering the softening point. The unfilled PCS presented a softening point of 102°C, whereas that for composition 2 was 50°C and close to the softening point of paraffin wax. This has the effect of reducing the thermal stresses which are set up in an injection moulded body between its solidification point and room temperature.

The wax presents its own melting endotherm in the DSC trace (Fig. 9) at the expected temperature, suggesting it is present as a discrete phase in the solid blend. The PCS presents a continuous curve without

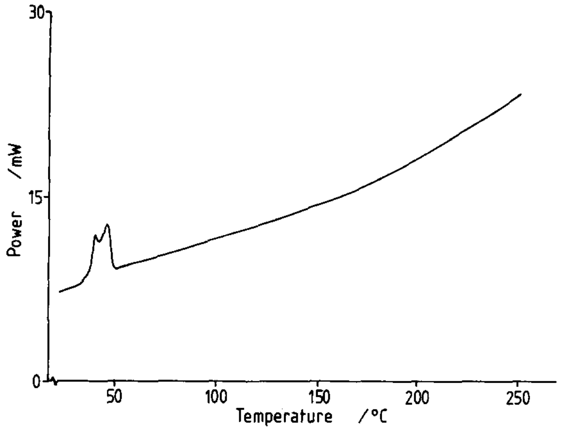


Fig. 9. DSC trace for the polycarbosilane-wax blend with weight ratio 4:1.

a clear change of gradient at T_g, probably because of wide molecular weight distribution.

3.3 Evaluation of pyrolysed composites

Composition 1 could not be compression moulded with pressures in the range 10–100 MPa and temperatures 190–230°C without the appearance of cracks and this can be attributed to the high softening point and brittle nature of PCS; brittleness which is enhanced by the incorporation of powder. However, composition 2 could be compression moulded with ease at 12 MPa and the resulting discs were free from macroscopic defects.

The organic binder of composition 2 decomposes over a wide temperature range which is advantageous for process control and, although it occupies 44 vol.% of the body, only 34 vol.% is displaced on pyrolysis, which is considerably smaller than the amount of material which must be displaced from conventional injection moulded ceramic bodies. During pyrolysis, PCS has a tendency to crosslink which increases the cohesive strength of the body at this critical stage. This meant that a heating rate of 10°C/h to 900°C was acceptable and discs examined by X-ray contact radiography were free from macroscopic defects under these conditions (Fig. 10).

The average strength of three bars of composition 2 before pyrolysis was 10 MPa, which is typical of the strength of ceramic–polymer compositions at these volume loadings. Unlike conventional compositions whose strength decays to extremely low values after pyrolysis of the vehicle, composition 2 presented a mean strength of 35 MPa from five samples after pyrolysis.

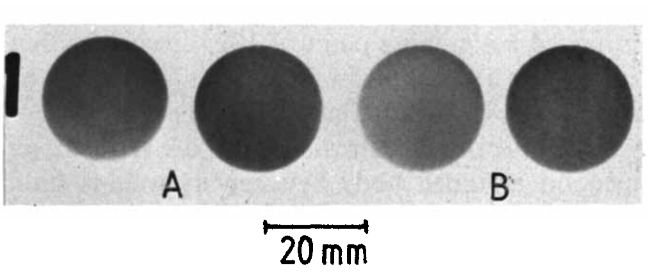


Fig. 10. Prints of contact radiographs of composition 2 compression moulded at 12 MPa: (a) before pyrolysis, (b) after heating to 900°C at 10°C/h.

In conventional injection moulding with a transient wax or polymer binder, a ceramic content of 50 vol.% could be expected to yield a prefired density of ≈52% after taking account of the shrinkage on binder removal. With 50 vol.% of the interstitial space occupied by PCS (composition 1) the prefired density was 72%. The incorporation of the wax diluent allowed the loading of SiC to be increased to 56 vol.% without exceeding viscosity limits for plastic forming processes. After pyrolysis, the relative density of the prefired body was 67%. The weight losses from the compression moulded discs were 32·0% for both compositions and are close to the results from thermogravimetric measurements on small samples of 10–30 mg. The heating rate did not systematically affect the weight loss in the range 10–90°C/h.

The fracture surface of a disc of composition 1 before pyrolysis is shown in Fig. 11. The individual particles of ceramic powder are not easily distinguished from the polycarbosilane which fills interstitial space. After pyrolysis to 900°C the fracture surface (Fig. 12) is very similar but slightly rougher and particles can just be distinguished but the product of pyrolysis also fills a large proportion of interstitial space cementing the particles together, although it may itself contain porosity on a much finer scale.

In contrast, the fracture surface of composition 2 before pyrolysis (Fig. 13) shows particles covered with a layer of the vehicle. The true appearance of the fracture surface has been lost as a result of

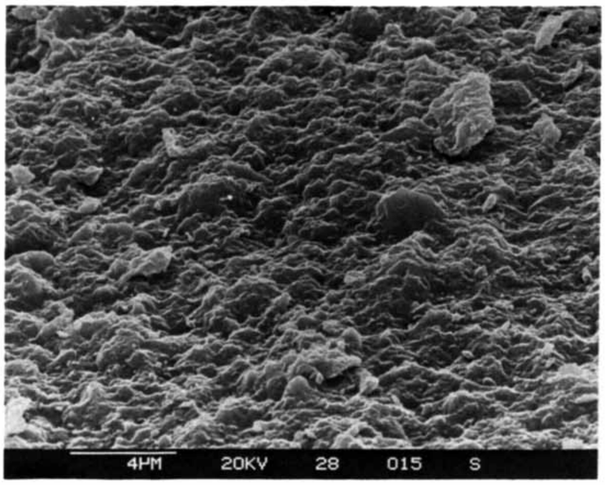


Fig. 11. Fracture surface of composition 1 before pyrolysis.

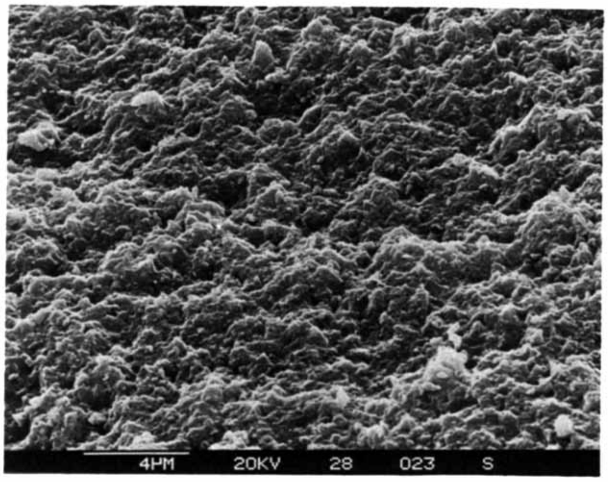


Fig. 12. Fracture surface of composition 1 after pyrolysis.

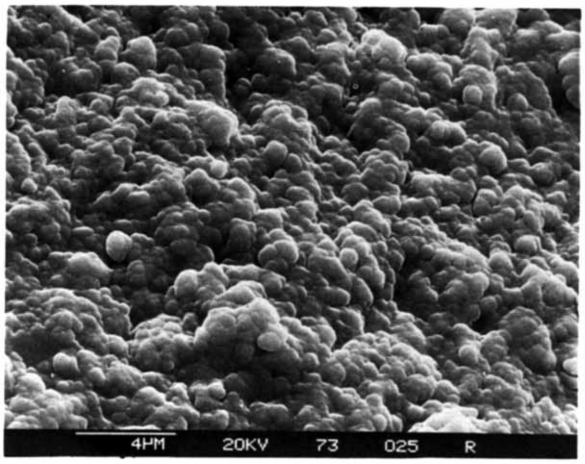


Fig. 13. Fracture surface of composition 2 before pyrolysis (surface subject to incipient melting from sputter coating).

incipient surface melting in the sputter coating equipment. This occurs because of the low softening point of 50°C and is extremely difficult to avoid in this coating technique. The appearance is therefore artificial. The interesting difference in appearance caused by the wax addition is seen in Fig. 14, which shows composition 2 after pyrolysis and should be compared with Fig. 12. This time, the individual particles can be discerned, although weight changes indicate that substantial SiC residue from the PCS is present. The investigation was repeated twice with the same result, and the implication is that the PCS recedes locally in the pore space as pyrolysis progresses. The apparently greater porosity compared with Fig. 12 is thus a result of the morphological difference of the product, not its content.

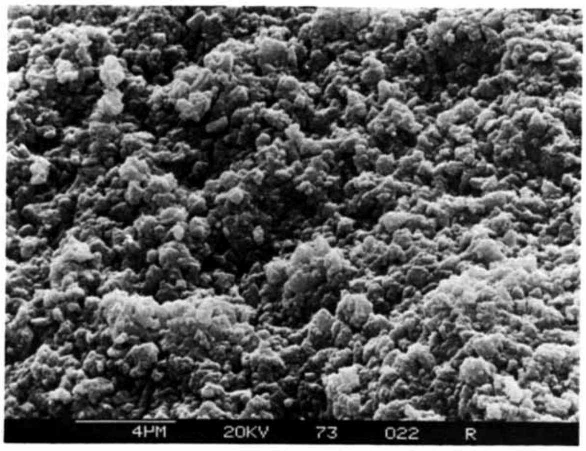


Fig. 14. Fracture surface of composition 2 after pyrolysis.

The two compositions also present different shrinkage on pyrolysis (Table 3). Composition 2 shows a linear shrinkage of only 2% and this results in a slightly lower relative density after pyrolysis. Thus, although the higher powder loading of composition 2 should compensate for the replacement of PCS by wax and give a higher relative density (column 3 of Table 3), the higher shrinkage of composition 1 just offsets this advantage. Nevertheless, this is a small price to pay for enhanced processability. The difference in shrinkage is related to the different ceramic powder volume loadings.[23]

4 Conclusions

By modification of polycarbosilane using a paraffin wax diluent, a ceramic suspension has been obtained

Table 3. Changes on conversion of PCS to SiC

	Loss on pyrolysis		*Calculated relative density after pyrolysis* (%)[a,b]	*Linear shrinkage on pyrolysis* (%)	*Measured relative density after pyrolysis* (%)[b]
	Weight loss based on PCS (%)	*Volume loss based on original volume* (%)			
Composition 1	31·6 ± 1·6 (8)	38·5 ± 0·3 (8)	61·4 ± 0·3 (8)	4·2 ± 0·3 (3)	72 (2)
Composition 2	32·2 ± 1·3 (14)	36·3 ± 0·1 (14)	63·7 ± 0·1 (14)	2·1 ± 0·2 (5)	67 (4)

[a] Assuming no shrinkage.
[b] Assuming all SiC has a density of $3\,200\,\mathrm{kg\,m^{-3}}$.
Number of experiments are given in parentheses.
95% confidence limits are given.

which is predicted to be suitable for plastic forming operations such as injection moulding without the danger of crosslinking in the machine. It combines a low softening point and viscosity which allows greater ceramic powder loading. The enhanced cohesive strength during pyrolysis of the binder offers greater resistance to the production of defects than would be obtained from a fugitive binder.

Acknowledgements

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