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Injection Moulding of Polysiloxane/Filler Mixtures for Oxycarbide Ceramic Composites

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Abstract

A complex shaped preceramic part has been prepared from polysiloxane/$MoSi_2$ mixtures via the injection moulding process. Processing of the system requires granulation of the powders prior to injection moulding through a separate extrusion step and the addition of carboxylic acids as surfactants to adjust the viscosity. Polymerization temperatures are effected through catalytic behaviour of the filler particles. Viscosity measurements have been applied to determine an appropriate viscosity, temperature and time-frame for this novel thermosetting system. The presence of Mo^{5+} oxidation states on the filler surface and interaction with the carboxyl groups of the carboxylic acids were detected.

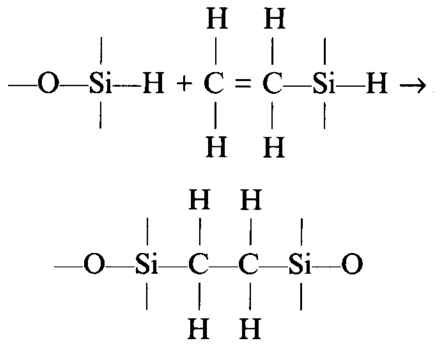
1 Introduction

Injection moulding is a suitable method for economic manufacturing of complex shaped ceramic parts.[1] Usually organic binder systems are added to the ceramic powder to obtain a mouldable mixture with the appropriate viscosity. The binder system usually consists of the major binder, a minor binder, a plasticizer/lubricant (or hardener) and a surfactant for particle wetting. The organic binder has to be removed very carefully to avoid the creation of porosity afterwards.[2–5] The minor binder is burned out at a lower temperature to provide pore channels for the escape of gaseous species produced on decomposition of the major binder. The green body is then sintered with typical linear shrinkages of up to 20%. Especially complex geometries are susceptible to tolerance deviations due to inhomogeneities and the large degree of sintering shrinkage, leading to increased machining costs or even rendering the part useless.[7] The development of easily removable binder systems and lowering the sintering shrinkages are therefore important issues.

Recently, Zhang and Evans[8] reported on the properties of a ceramic injection moulding suspension which is based on an organometallic polymer. A ceramic suspension was prepared by adding a fine sinterable silicon carbide powder to a polycarbosilane vehicle which had been modified by additions of paraffin wax to make it suitable for plastic forming operations.

By using organometallic polymers like polysiloxanes, polysilazanes or polycarbosilanes as a binder no binder burn-out is necessary, since these polymers are converting into SiO_2/SiC, Si_3N_4, SiC or Si–O–C–(N) glasses upon pyrolysis depending on the pyrolysis temperature.[9] Large weight loss and corresponding shrinkage, porositiy formation and fragmentation upon pyrolysis are obstacles for the realization of monolithic ceramic parts from pure organometallic polymers. The addition of reactive fillers like the transition metals of groups IV–VI is a possibility to obtain samples with structural integrity. When sintered in a reactive atmosphere like N_2, the filler components react with the decomposition products of the polymer and the atmosphere to constitute a ceramic matrix consisting of the corresponding metal carbides and nitrides and a Si–O–C–(N) glass.[10–12] By appropriate choice of the amount and type of the polymer and filler component, a positive volume change upon carburization or nitridation can be achieved, leading to very low shrinkages.[13]

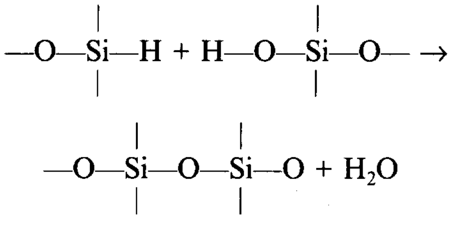
The use of organometallic polymers necessitates thermosetting systems, thereby retaining the shape during the early stages of the pyrolysis. Another requirement with respect to processing is the handling of the polymer in an ambient atmosphere, making hydrolysis sensitive silazanes difficult binder candidates. Polysiloxanes are easy to handle and are commercially available in a large variety of forms, and have thus been chosen for this work. The crosslinking mechanism is of importance, depending on the forming methods. Using pressureless forming methods like moulding, a polymer which undergoes crosslinking via an addition mechanism is the choice, since no gaseous products are evolved, which would lead to bloating of the part. The most common reaction is based on the hydrosilylation of a vinyl group:[14–16]



$$-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{H}+\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}=\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{H}\rightarrow$$

$$-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{\mathrm{H}}{\overset{\mathrm{H}}{\mathrm{C}}}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O} \qquad (1)$$

In the case of the injection moulding process, polycondensating systems, giving off water during polymerization, can be used as well due to the applied pressure. The reaction involves two silanol groups:



$$-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{H}+\mathrm{H}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\rightarrow$$

$$-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{O}+\mathrm{H_2O} \qquad (2)$$

Compensation of the shrinkage during pyrolysis depends on the filler loading and, in general, filler loadings are of the order of 40–60 vol% depending on the filler type. The use of solid polymeric precursors in powder form with a defined melting point simplifies the processing as compared to liquid precursors and enables high filler loadings, since filler and polymer can be dry mixed and granulated in a separate extrusion step before injection moulding.

Pyrolysed polysiloxane/$MoSi_2$ mixtures have shown the potential for high temperature applications with excellent oxidation stability and creep resistance up to 1550°C. This paper summarizes the processing of such a preceramic part with complex geometry through injection moulding, i.e. a screw 70 mm in length with a diameter of 8 mm and a fine thread (M8 with respect to DIN 601).

2 Experimental Procedures

A commercially available solid polycondensating polymethylsiloxane (NH 2100, Hüls Corp., Germany) with a melting point of 54°C and a setting temperature of 230°C was chosen as the polymeric precursor. This polymer exhibits a high ceramic yield of 90 wt% and is decomposing with the evolution of environmentally uncritical species like hydrogen and methane. $MoSi_2$ (Grade C, HC Starck Corp., Germany) (d_{50} = 2·0 μm) was used as the reactive filler. Citric acid (CA) and tartaric acid (TA) (Merck Corp., Germany) (1–5 wt%) were used as surfactants.

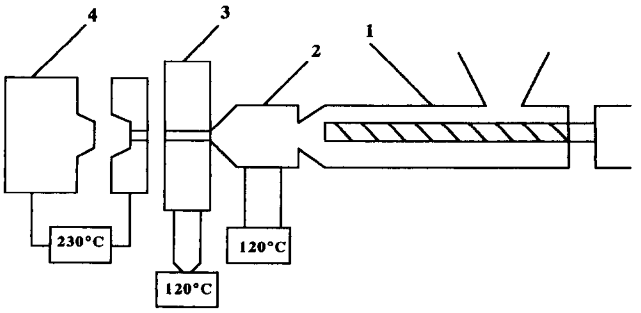


Fig. 1. Set-up of modified injection moulding unit: 1, injection moulding unit; 2, nozzle; 3, thermal barrier; 4, injection moulding die.

Polymer (60 vol%), filler (40 vol%) and surfactant were dry mixed and homogenized in a polyethylene bottle with Al_2O_3 milling media for 12 h. Preliminary experiments had shown that direct feeding of the powder mixture into the injection moulding unit was inappropriate due to electrostatic charging of the polymer powder and subsequent inhomogeneous melting and homogenization. It was therefore necessary to prepare a granulate by extruding the powder mixture through a double-screw extruder (LSM 30.34.GI, Leistritz Corp., Germany) at 120°C. The surfactant was either added as a powder to the mixture or directly precipitated on to the filler surface by dissolving the acid in acetone, adding the filler, ultrasonically dispersing the powder and evaporating the acetone. The granulate was then fed into a modified injection moulding machine (ES 200/50, Engel Corp., Germany). A thermal barrier was installed between the injection unit and the die to prevent thermal flux from the die (230°C) to the injection unit tip (120°C); Fig. 1. The injection velocity was chosen as 5 mm s^{-1} at a maximum injection pressure of 16 MPa, a post-pressure of 4 MPa, post-pressure time of 250 s and curing time of 400 s.

The viscosities of the polymer/filler mixtures were measured with a cone/plate system (SR 200, Bohlin Corp., UK) in the dynamic mode (shear rates of: $2{\cdot}9 \times 10^{-3}$–$2{\cdot}7$ cm^{-1}) at shear stresses ranging from 100 to 3000 Pa and temperatures ranging from 100 to 240°C to determine an appropriate η–t–T-frame. A viscosity range of 100–100000 Pa s, a temperature range of 100–140°C and a time-frame of 60 min were used.

The effect of the carboxylic acids on the catalytic behaviour of $MoSi_2$ and the rheology was examined by EPR spectroscopy (B-K 70, Bruker Corp., UK). The microwave frequency (9·67 GHz), microwave power (63·6 mW) and measurement time (335 s) were kept constant, while the magnetic field strength was varied between $33{\cdot}0 \times 10^6$ and $37{\cdot}5 \times 10^6$ T.

Thermogravimetric analysis (Model 409, Netzsch

Inc., Selb, Germany) was employed to monitor the oxidation behaviour. Density and porosity were determined using a helium pycnometer (AccuPyc 1330, Micromeritics Inc., Germany) by measuring the pressure change in a calibrated volume. The electrical conductivity was examined by impedance spectroscopy (4192A LF Impedance Analyser, Hewlett-Packard, USA). The pyrolysed samples were tested in four-point-flexure with a universal testing machine (Instron, UK) and a fixture with a 24 mm outer span and 12 mm inner span. A constant displacement rate of 1 mm min^{-1} was used. Creep behaviour was monitored by a compression test with a constant load of 100 MPa at 1500°C in air.

3 Results and Discussion

3.1 Rheology

Figure 2 shows the viscosity as a function of temperature of the filler-free polysiloxane. Figure 3 shows the thermosetting temperature T^* as a function of filler loading. A minimum of the viscosity is observed at 230°C with $\eta \sim 1$ Pa s. At higher temperatures the viscosity increases, again due to crosslinking of the polymer. With a solid loading of 20 vol% $MoSi_2$ the viscosity increased by five orders of magnitude and the polymerization temperature decreased by more than 120°C. Although a viscosity drop can be expected, the polymerization temperature should remain constant. From catalysis, however, it is known that transition metals and transition metal compounds, especially oxides, can act as catalysts in various polymerization processes.[17] Molybdenum oxides are widely used for such purposes.

With 40 vol% solid loading it was therefore necessary to inhibit the catalytic effect and to decrease the viscosity in order to adjust the system to the desired η–t–T-frame. Carboxylic acids can be used as surfactants which react with the filler surface via the carboxyl groups. Furthermore, it was expected that the carboxyl groups would reduce the catalytic effect of the filler. The effect of adding 3 wt% CA on the η–T dependency is shown in Fig. 4. The polymerization temperature increases by more than 40°C to 150°C, which is close to the decomposition temperature of the acid (T_{dec} = 153°C). At the same time the viscosity decreased to 3×10^4 Pa s. The η–t dependency at constant shear stress (2200 Pa) and temperature (120°C), i.e. the stability of the mixture in the injection unit, is shown in Fig. 5.

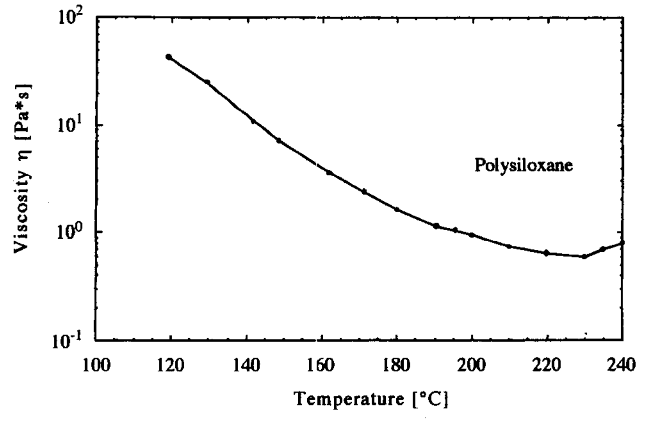


Fig. 2. Viscosity as a function of temperature of the filler-free polysiloxane measured with a constant shear rate of 5·15 cm^{-1}.

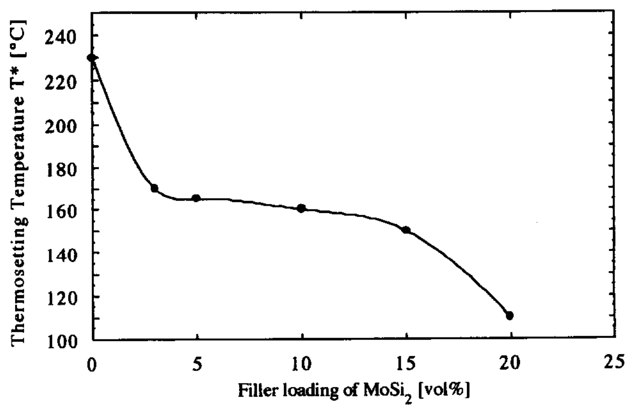


Fig. 3 Thermosetting temperature T^* as a function of filler loading between 0 and 20 vol% $MoSi_2$.

Immediately after remelting of the mixture, an overlapping of two processes is noticed: (1) a decrease of the viscosity due to homogenization of the melting mixture and (2) an increase of the viscosity due to the onset of thermosetting. With increasing CA content (from 3 to 5 vol%) the time-frame (time until polymerization commences) increases from 17 to 25 min. The addition of 3 vol% TA instead of CA further decreases the viscosity by an order of magnitude and prolongs the time-frame to 30 min; Fig. 6. Coating of the filler surfaces with 1 wt% TA is sufficient to achieve a constant viscosity of 50 000 Pa s for at least 1 h at 120°C and a shear stress of 2200 Pa.

Figure 7 shows the viscosity as a function of temperature with increasing shear stress of a mixture containing 20 vol% filler (1 wt% CA). A decrease in

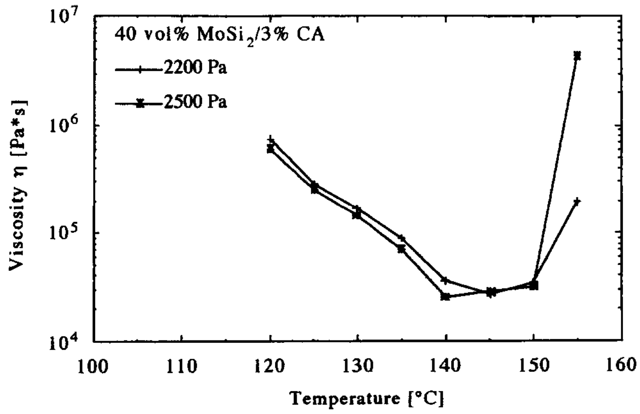


Fig. 4. Viscosity as a function of temperature for 40 vol% solid loading with 3 wt% CA, shear stresses of 2200 and 2500 Pa and shear rates of $2{\cdot}9 \times 10^{-3}$–$1{\cdot}1 \times 10^{-2}$ cm^{-1}.

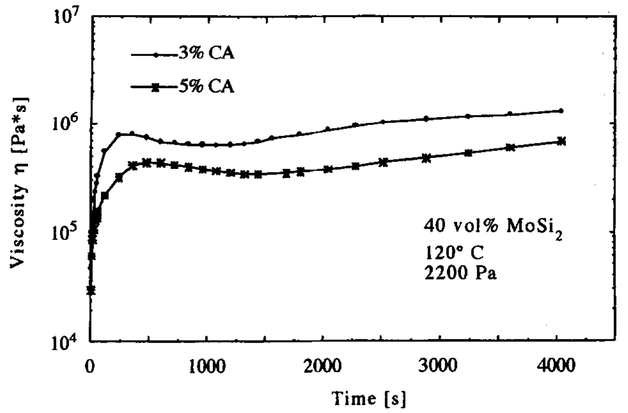


Fig. 5. Viscosity as a function of time for 40 vol% solid loading with 3 and 5 wt% CA, shear stress of 2200 Pa and constant temperature of 120°C.

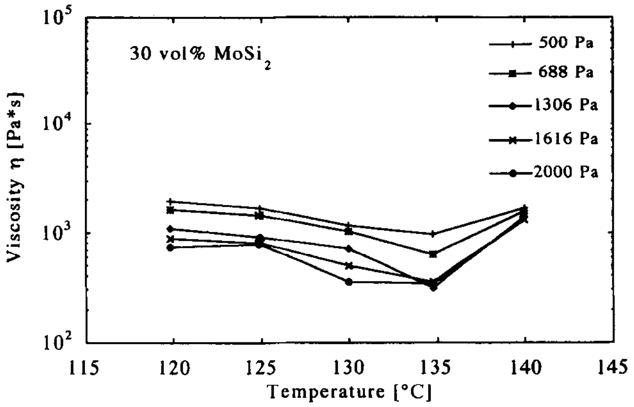


Fig. 7. Viscosity as a function of temperature and different shear stresses (500–2000 Pa) for 30 vol% solid loading with 1 wt% CA and shear rate of $2{\cdot}5 \times 10^{-1}$–$2{\cdot}7 \times 10^{-1}$ cm^{-1}.

viscosity is noted for increasing temperatures and increasing shear stresses. The temperature-dependent viscosity minimum is shifted to lower temperatures with increasing shear stresses. This behaviour is observed for filler loadings higher than 30 vol%. High filler loadings result in frictional heat and hence decreasing polymerization temperatures. This behaviour has been confirmed by viscosity measurements in the oscillation mode (frequency 20 Hz), where only small volume elements are moved in the gap of the cone/plate system. In the oscillation mode the real polymerization temperature can be determined. High filler loadings beyond the percolation limit and subsequent enhanced shear stresses are therefore responsible for local frictional heat and apparently lower polymerization temperatures. An oil tempered injection moulding nozzle was subsequently installed in the injection moulding unit tip to absorb the frictional heat from the polymer mixture during remelting and homogenization of the granulate.

The first injection moulding trials were performed by injecting the granulate in the heated die at 250°C. These parts showed a distinct core–shell structure, whereby the outer parts, which are in direct contact with the die wall, had undergone instantaneous crosslinking, while the inner parts were still fluid. Consequently, the parts usually showed distinct fracture lines along the interface of the outer and inner region. Subsequently the die temperature was reduced to 230°C, enabling more homogeneous crosslinking across the screw cross-section. Figure 8(a) shows the screw and Fig. 8(b) a magnification of the thread part, demonstrating the well-defined contours.

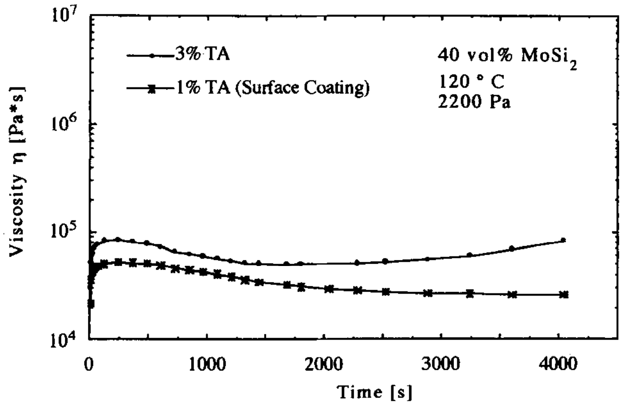
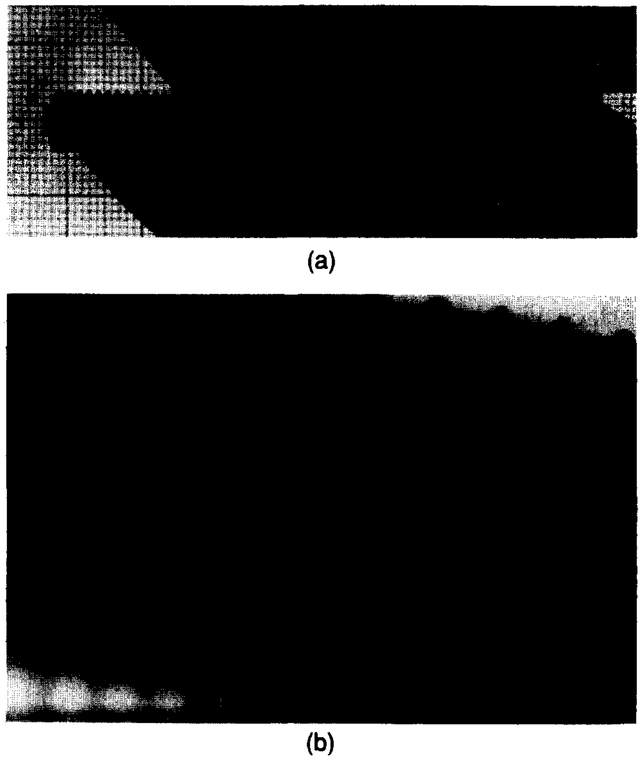


Fig. 6. Viscosity as a function of time for 40 vol% solid loading with 1 (surface coating) and 3 wt% TA, shear stress of 2200 Pa and constant temperature of 10°C.

3.2 Filler surface coating

EPR spectrum of MoSi$_2$ powders is shown in Fig. 9. The narrow peak at $34{\cdot}5 \times 10^6$ T corresponding to a g-value of 2·003 may be attributed to dangling bonds[18] of free carbon.[19] Carbon is used for the synthesis of MoSi$_2$.[20] The broad


(a)

(b)

Fig. 8. (a) Injection moulded screw with 40 vol% solid loading. The screw was cured at 230°C for 400 s. (b) Magnification of the screw thread

absorption between 35·0 × 10^6 and 36·0 × 10^6 T is assigned to pentavalent Mo^{5+} oxidation states in the $MoSi_2$ powder, because the determined *g*-value of ~1·95 is typical for Mo^{5+}.[21]

Transition metal compounds of groups IV–VI (V, Nb, Ta, Cr, Mo), mainly Cr-complexes, are used for catalytic processes in the chemical industry. They are all capable of catalysing the reactions of hydrogen and olefins, alkynes and polymerization reactions.[22] The determined *g*-value confirms the presence of Mo^{5+} oxidation states.[21] Further investigations of monoalkene polymerization[23] showed that the valence states and the structures of the transition metal active centres of Cr^{5+}-complexes are responsible for the polymerization process. Based on these observations, we suggest that Mo^{5+} shows similar catalytic behaviour to Cr^{5+} and is therefore (unless other active sides are present) responsible for decreasing the thermosetting temperature of the polysiloxane/filler mixture.

The mechanisms of surface adsorption of carboxylic acids from liquid solutions have been discussed previously.[24–26] The adsorbate molecules are amphiphilic, i.e. they contain both a hydrophobic non-polar part (aliphatic chain) and a hydrophilic polar ionic carboxyl group. Depending on the relative magnitude of the hydrophobic part and the polarity or non-polarity of the particle surface and of the solvent, these solutes may be adsorbed primarily either due to the hydrophobic effect or by electrostatic or co-ordinative interaction (attraction between functional groups of the solute and the particle surface).[27]

The first step in the adsorption mechanism of tartaric acid in acetone on $MoSi_2$ is orientation of the hydrophilic group of the surfactant (carboxyl groups) towards the particle surface; Fig. 10. Similar to the adsorption mechanism of stearic acid in cyclohexane on AlN [Fig. 10(a)] for making AlN powders[27] or benzoic acid on Al_2O_3 [Fig. 10(b)][28,29] hydrophobic, such behaviour can be related to the adsorption of tartaric acid on polar surfaces [Fig. 10(c)] and is in agreement with the chemisorption hypothesis.[30] Tartaric acid is a dipolar molecule, with two carboxyl groups and the two hydroxyl groups. Due to inductive effects and electrostatic interactions, the acidity of the carboxyl groups is stronger than that of the hydroxyl groups.[31] The carboxyl groups are orientated towards the polar particle surface and the weak hydroxyl groups act as hydrophobic units. Since tartaric acid is a two-teeth ligand, two positive surface charges will be compensated.

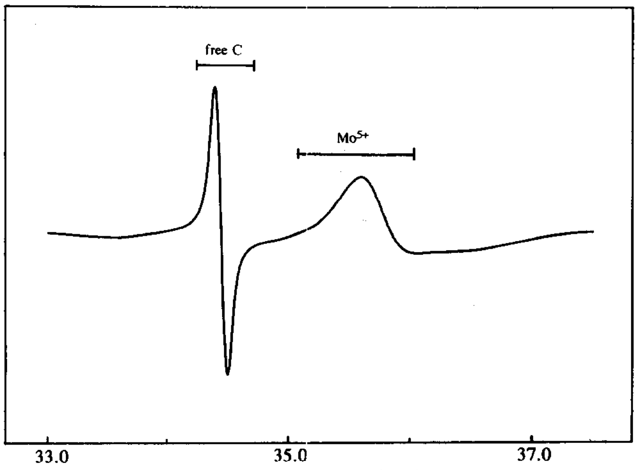


Fig. 9. EPR spectra of dry $MoSi_2$ powder with d_{50} = 2·0 μm at a microwave frequency of 9·67 GHz.

3.3 Pyrolysis

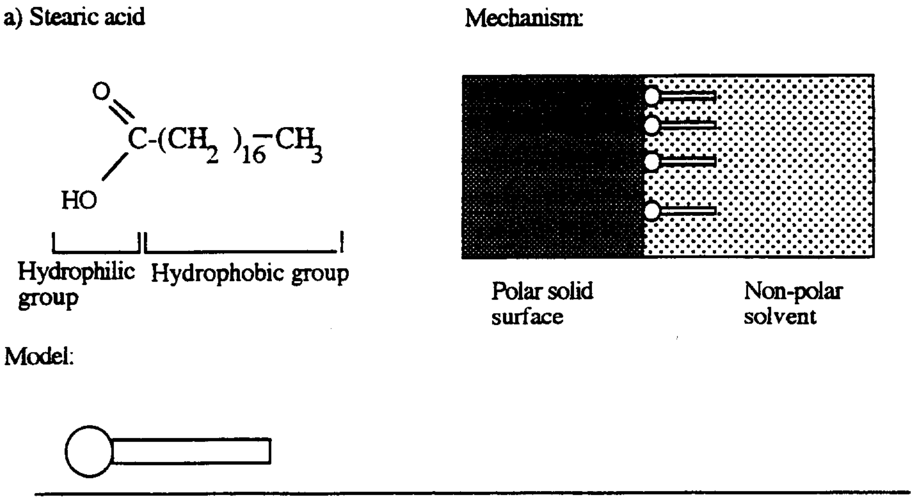
The injection moulded parts are easily transformed into ceramic composites by subsequent pyrolysis using a N_2 atmosphere (99·99% purity, 0·1 mPa). The samples were heated to 1200°C at a rate of 5 K min^{-1}, held at temperature for 4 h, and then cooled to room temperature at a rate of 10 K min^{-1}. The reaction of the active filler $MoSi_2$ can be described by:

$$6\,MoSi_2 + 3\,C + 8\,N_2 \rightarrow 3\,Mo_2C + 4\,Si_3N_4$$
$$\Delta G = -66{\cdot}74 \text{ kJ mol}^{-1} \text{ (1200°C)} \qquad (3)$$

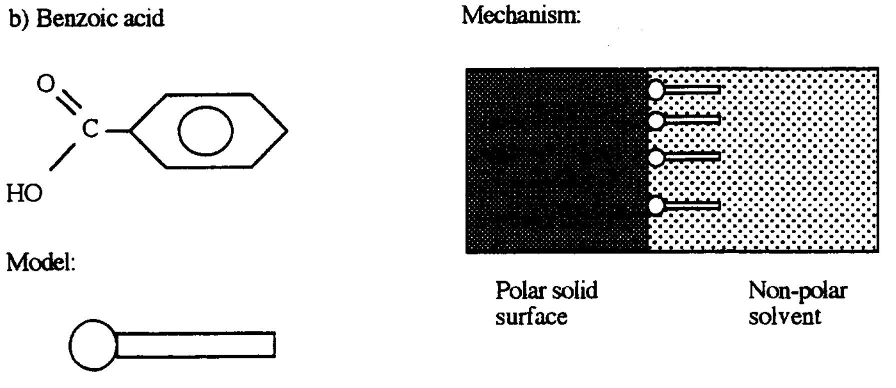
Through the large volume expansion of 67 vol% for eqn (3) the inherent polymer shrinkage can be significantly reduced; using a volume content of 40 vol% $MoSi_2$ filler phase a linear shrinkage of 5% results after pyrolysis at 1200°C. The microstructure of the ceramic composite consists mainly of Mo_2C and Si_3N_4 particles which are embedded in a nanocrystalline oxycarbide/oxynitride matrix; Fig. 11. Residual pores due to insufficient solvent removal, however, were frequently found in the pyrolysed screws. To avoid surface cracking as a result of inhomogeneous shrinkage during pyrolysis a uniform curing process throughout the cross-section of the screw is required.

Due to the formation of a protective SiO_2 layer on the sample surface, the ceramic composites reveal an excellent oxidation resistance. Thermogravimetric experiments showed a small weight increase of 0·30 wt% after oxidation at 1500°C for 100 h. Furthermore, the pyrolysis samples (density 4300 kg m^{-3}, porosity 8 vol%) show excellent creep behaviour ($\dot{\epsilon}_{sec}$ = 1 × 10^{-7} s^{-1},100 MPa, 1500°C) and a high electrical conductivity of σ = 0·1 × 10^6 S m^{-1} at 1400°C. The pyrolysed material exhibits a four-point bending strength of MOR = 390±10 MPa, a fracture toughness of K_{IC} = 3·2 MPa $m^{1/2}$ and an average linear thermal expansion coefficient of $\bar{\alpha}$ = 8·2 × 10^{-6} K^{-1} (RT–1000°C). These properties, in combination with the shaping capabilities, offer a high potential for net shape production of low cost ceramic bulk materials for high temperature applications such as heating

a) Stearic acid



b) Benzoic acid



c) Tartaric acid

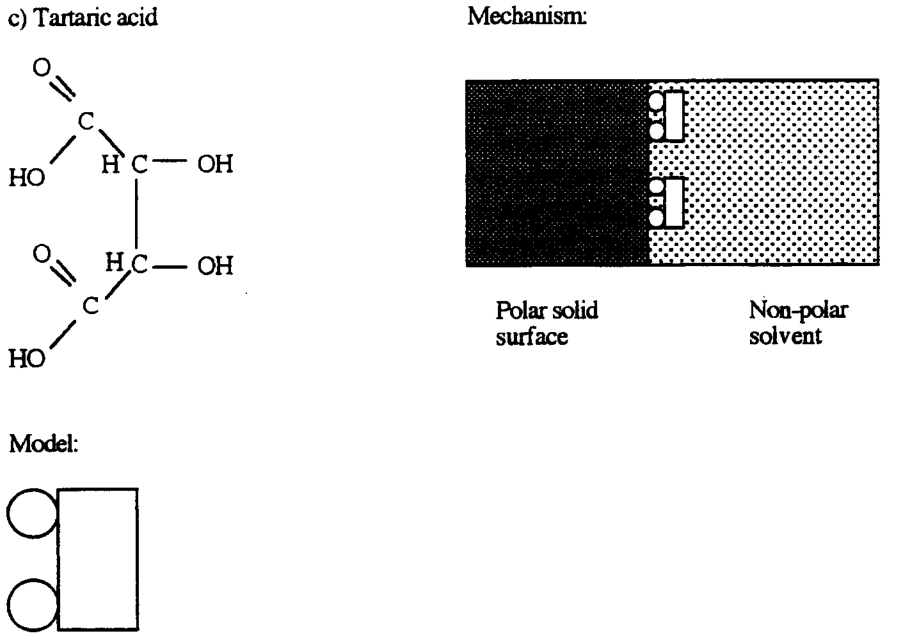


Fig. 10. Adsorption mechanisms of carboxylic acids: (a) Stearic acid; (b) benzoic acid; (c) tartaric acid.

elements, high temperature electrical contacts, wear resistant coatings and thermal barriers.

4 Conclusions

Polysiloxane/$MoSi_2$ mixtures can be injection moulded into complex preceramic parts. Filler surface chemistry has a strong impact on polymerization temperatures and viscosity/time and viscosity/temperature dependencies due to catalytic effects. Processing requires the granulation of powderous polymer/filler mixtures in a separate extrusion step before injection moulding. Mo^{5+} oxidation states are suggested to account for the catalytic behaviour of $MoSi_2$, leading to charging

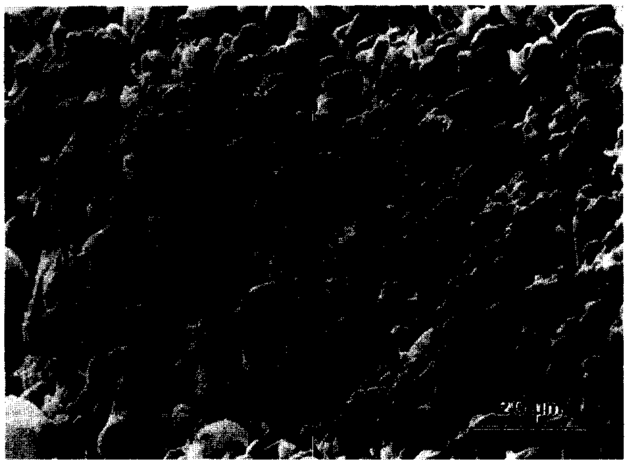


Fig. 11. SEM micrograph of composite microstructure (fracture surface) with 40 vol% $MoSi_2$ after pyrolysis in N_2 atmosphere at 1500°C.

effects on the surface and causing interaction with the hydroxyl groups of the polymer. Positive surface charges were compensated by shielding with carboxylic acids, which was achieved by coating the filler surface. Appropriate surfactants are citric acid and tartaric acid. They are most effective if precipitated on to the filler surface, enabling high filler loadings by lowering the viscosity and increasing the polymerization temperatures.

Acknowledgements

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