

# The use of silane coupling agents in ceramic injection moulding

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Ceramic injection-moulding blends containing 56 vol% fine silicon nitride and 65 vol% coarse silicon powder in a polypropylene and wax vehicle were prepared by dispersive mixing with and without 2 p.p.h. silane coupling agent based on the weight of powder. The addition of silane reduced the viscosity and the pseudoplasticity of the suspensions considerably. The mechanical strength of the moulding compositions, which may influence the tendency to crack during solidification in the cavity, was marginally increased. The treated silicon powder was strongly hydrophobic but this was not the case with the silicon nitride powder.

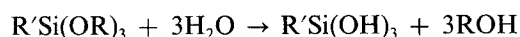
## 1. Introduction

There is considerable interest in the use of coupling agents in modifying the interface in fibre- or particle-reinforced polymers [1] and in adhesive joints [2] where they are known to adjust the viscosity or influence interfacial shear strength. The objective of the present work was to examine the advantages to be gained from incorporating such surface-active species in compositions intended for the injection moulding of engineering ceramics where a concentrated polymer-ceramic suspension is required to flow into a cavity and solidify to withstand thermal stresses [3, 4].

There are three potential benefits from exploiting the current range of coupling agents in ceramic injection-moulding technology. These are

- (i) The protection, prior to blending, of hydrolysable fine powders from the capillary condensation of water at particle junctions and subsequent surface reaction to produce solid-bridge agglomeration.
- (ii) The action of some coupling agents as flow modifiers for suspensions, reducing the viscosity of highly filled polymers.
- (iii) The improvement in adhesive strength of the polymer-ceramic interface, which may enhance the toughness of the moulded material and reduce the tendency to crack during shrinkage in the mould.

For silicon-based ceramics, silane coupling agents are acceptable since after pyrolysis they may leave a small SiO<sub>2</sub> or SiC residue. For other ceramic powders where silicon-containing species are undesirable, there is a range of titanates [5], zirconates [6] and zirconaluminates [7]. As is the case for silanes, these are claimed to form either primary bonding or hydrogen bonding to high-energy surfaces. In the case of silanes the alkoxy groups are first hydrolysed in the presence of ambient or adsorbed water:



The silanol groups are then available for either

condensation with adsorbed hydroxy groups on the substrate or hydrogen bonding. A further possibility is the condensation of silanol groups to produce oligomers, and this hinders adsorption on the substrate.

In general, coupling agents are also selected to produce primary bonding to the polymer phase via the R' group. However, in the present work polypropylene was selected for the main component of the binder system [8]. When the polymer is intrinsically unreactive, and polyolefins are the most widely used example, the situation near the polymer-ceramic interface is ill defined and the relevant literature contradictory.

A number of studies have shown the effect of coupling agents on the viscosity modification of particle-filled polymers [9-12], but reduced viscosity is sometimes accompanied by reduced mechanical properties [10].

Plueddemann and Stark [13] have advanced a theory of coupling-agent action based on the secondary forces acting between interpenetrating polymer networks. They give examples of the adhesion of glassy polymers to silane-modified substrates, based on solubility of the organic group of the coupling agent in the polymer interfacial region in the absence of chemical reaction. It is well known that in the diffusion of high polymers [14], short diffusion distances of the order of a few molecular segments can contribute to high strength and that chain-end diffusion contributes significantly to the development of strength [15]. Both conditions are favourable for the development of strength between an unreactive condensed silane layer and a compatible polymer, and indeed the interpenetrating network theory can be regarded as a modification of the diffusion theory of adhesion [16].

Unfortunately, this mechanism of silane action is thought to be ineffective with semicrystalline polymers because of the low solubility of low molecular weight species in crystalline regions [13]. In the case of polypropylene, therefore, Plueddemann and Stark

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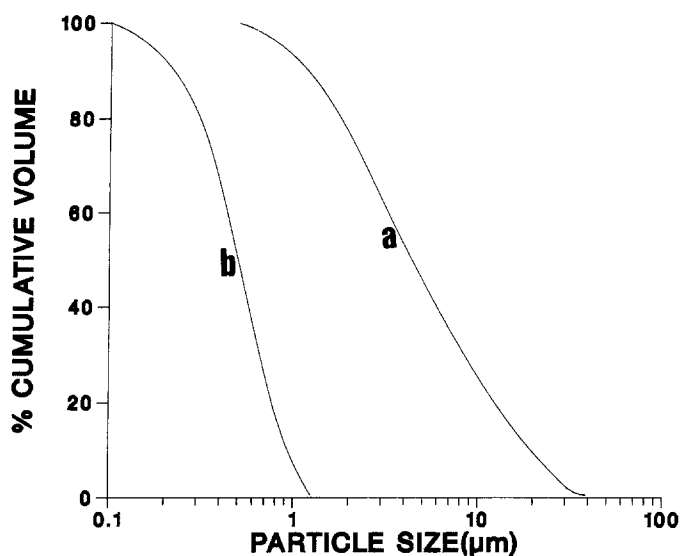


Figure 1 Particle size distribution of (a) silicon powder, (b) silicon nitride powder.

proceeded to increase the reactivity by using functional silanes and peroxide additions to generate reactive sites in the polymer [13]. The more recently developed azidosilanes are also claimed to react chemically with polyolefins [17].

In contrast, an oriented monolayer of stearic acid adsorbed on an aluminium surface has been shown to increase the adhesion of polyethylene to aluminium [18], the improvement in tensile strength being of the order of 24%.

Similarly  $\gamma$ -aminopropyl triethoxysilane ( $\gamma$ -APS) is claimed to increase the adhesion of polyethylene to alumina considerably in the absence of polyethylene oxidation, by a diffusion mechanism [19].

These precedents suggest that long-chain alkyl silanes which would be expected, from polarity considerations, to be more compatible with unoxidized polyolefins than  $\gamma$ -APS, should function as coupling agents in the absence of primary bonding. It must be recognized, however, that the rate of hydrolysis of alkyl silanes is slow in comparison with the rate of polymerization of the silane [20]. Moreover, since isotactic polypropylene was used, the solubility of the alkyl group may be limited [13]. Under such circumstances it is not possible to predict the behaviour of silane coupling agents.

The silanes selected for study were n-octyltriethoxysilane, which may present an unreactive alkyl chain to the polymer phase, and the proprietary blend PCIA/PCIB which is specifically marketed for filled polypropylene systems.

## 2. Experimental details

### 2.1. Materials

Silicon powder (specific surface area  $5.7\text{ m}^2\text{ g}^{-1}$ ), suitable for the production of reaction-bonded silicon nitride (RBSN), was vibratory-milled by Pilamec Ltd, Lydney, Glos., UK. The powder has a wide particle size distribution as shown in Fig. 1. The silicon nitride powder was Starck LC12 which has a much narrower size distribution (Fig. 1), and a specific surface area of 21 to  $25\text{ m}^2\text{ g}^{-1}$ .

The silicon nitride powder was used without sintering aids. The polypropylene was grade GY545M (ICI

and Astor Chemicals supplied the 1865Q microcrystalline wax. n-octyltriethoxysilane (tradename: Octeo) was donated by Dynamit-Nobel and the proprietary silane blend PCIA/PCIB was donated by Union Carbide UK.

### 2.2. Silane treatment

Silicon powder was treated in a solution consisting of 2 parts n-octyltriethoxysilane based on 100 parts of powder dissolved in sufficient methanol to form a slurry. The methanol was slowly evaporated. The silicon nitride was treated with a solution of 1.5 parts PCIA and 0.5 parts PCIB based on 100 parts of powder, in sufficient 10% water + 90% methanol to form a slurry prior to drying.

In order to calculate the polymer additions to blends containing silane coupling agents to give the desired volume fractions of ceramic powder, several additional experiments were needed. The residual silanol on the treated powder was less than the added amount because of the loss of alcohol as a product of hydrolysis. This was determined by adding weighed amounts of coupling agent to samples of powder at the 2 p.p.h. level in methanol or 10% water + 90% methanol solutions and drying before re-weighing. The results are given in Table I. Furthermore, the loss on ignition for the silane-treated powder was recorded in order to correct for any silicon-containing residue which may not be removed at  $600^\circ\text{C}$ . These results, which are discussed below, also appear in Table I and make possible the accurate calculation of powder volume fractions derived from the ashing of samples of compounded material which are given in Table II.

### 2.3. Mixing

Formulations with compositions given in Table II were prepared by preblending in a Henschel high-speed mixer followed by twin-screw extrusion using a Gay's co-rotating twin screw extruder (now manufactured by Betol Machinery, Luton, Beds., UK) using a method previously described [21] with barrel temperatures (feed to die) of  $220\text{--}225\text{--}240\text{--}235\text{--}225^\circ\text{C}$  and a screw speed of 60 r.p.m. These were subsequently ashed to give the exact filler loading.

TABLE I Percentage of added silane remaining after application to the powder and loss on ignition of the powder associated with silane (number of experiments in brackets)

	n-octyltriethoxysilane on silicon	PCIA/PCIB on silicon nitride
Residual silane after drying (wt %)	59	66
Standard deviation	± 13 (5)	± 7 (5)
Loss on ignition for the silane- treated powder (wt %)	1.14	1.34
Standard deviation	± 0.50 (10)	± 0.24 (10)

## 2.4. Rheology

The viscosity as a function of shear rate was recorded on a Davenport Capillary Rheometer with a die diameter of 1.5 mm and length 35 mm in the shear rate range 100 to 1000 sec<sup>-1</sup> at 195 and 225°C. The procedure has been previously described [8].

## 2.5. Mechanical testing

Samples for three-point flexural testing were prepared by single-ended die pressing at 200°C in a die 10 mm × 70 mm, at a pressure of 13.4 MPa. These were slowly cooled under constant pressure to 100°C whereupon the pressure was allowed to subside to avoid shrinkage-related defects. The bars were tested at a crosshead speed of 10 mm min<sup>-1</sup> in an Instron testing machine (Model 1195) with a three-point bending jig of span 60 mm.

## 3. Results and discussion

### 3.1. Silane treatment

Fig. 2 shows the extent to which the treated powders were rendered hydrophobic. The silicon powder, initially wetted by water (A) became completely hydrophobic after treatment with n-octyltriethoxysilane (B). On the other hand the silicon nitride powder (C) could still be dispersed in water after treatment with the commercial silane blend PCIA/PCIB (D). This may be a characteristic of the silane used or it may indicate that the amount added was insufficient. For the silicon nitride of specific surface area 25 m<sup>2</sup> g<sup>-1</sup>, taking the adsorption area of the silanol group as 50 × 10<sup>-20</sup> m<sup>2</sup> per molecule ([1] p. 83), 2.3 wt % of n-octyltriethoxysilane would be needed for monolayer coverage. The molecular weight

of the commercial blend is unknown and so the corresponding amount cannot be calculated. Nevertheless this illustrates the large amount of these materials needed for the treatment of fine powders. In contrast, for the relatively coarse silicon powder of specific area 5.7 m<sup>2</sup> g<sup>-1</sup>, 0.5 wt % n-octyltriethoxysilane is needed to produce a monolayer and nearly four times this amount was applied.

However, when 8 wt % n-octyltriethoxysilane was blended with the silicon nitride powder, giving similar surface coverage to the treated silicon, it was rendered hydrophobic, but only after storage for 24 h. This suggests that adsorption on the silicon nitride powder is slower than on the silicon surface.

### 3.2. Effect on viscosity

Figs 3 and 4 show the viscosity–shear rate characteristics for the silicon (F3, F13) and silicon nitride (F14, F15) suspensions at 195 and 225°C. In order to achieve a viscosity of about 1000 Pa sec at 100 sec<sup>-1</sup> at the nozzle temperature of 225°C [21] which is suitable for injection moulding, a much lower volume fraction of the fine uniform silicon nitride powder was acceptable compared with the relatively coarse, wide particle size distribution silicon powder (Fig. 1). The volume fraction of powder is almost identical with the prefired relative density, and hence determines the sintering shrinkage of the silicon nitride and the nitrified density of the RBSN.

In each composition the polypropylene, wax and stearic acid were kept in the same ratio. The compositions were adjusted to keep the volume fraction of powder in silane-treated and untreated blends the same as far as possible.

TABLE II Composition of ceramic suspensions

Component	Density (kg m <sup>-3</sup> )	Composition (wt %)			
		F3	F13	F14	F15
Silicon	2300	82.44*	82.11*	–	–
Si <sub>3</sub> N <sub>4</sub>	3147 <sup>†</sup>	–	–	81.51*	80.69*
Polypropylene	905	11.71	11.29	12.33	12.17
Wax	904	3.90	3.76	4.11	4.06
Stearic acid	941	1.95	1.88	2.05	2.03
Silane (Octeo)	880	–	0.95 <sup>‡</sup>	–	–
Silane (PCIA)	1079 <sup>§</sup>	–	–	–	0.79 <sup>‡</sup>
Silane (PCIB)	924 <sup>§</sup>	–	–	–	0.25 <sup>‡</sup>
Calculated volume percentage of powder		64.9	64.4	56.0	54.8

\* Average of three ashings.

<sup>†</sup> Density corrected for quoted silicon and oxygen levels.

<sup>‡</sup> Amount after hydrolysis based on data in Table I.

<sup>§</sup> Average of three density-bottle determinations.

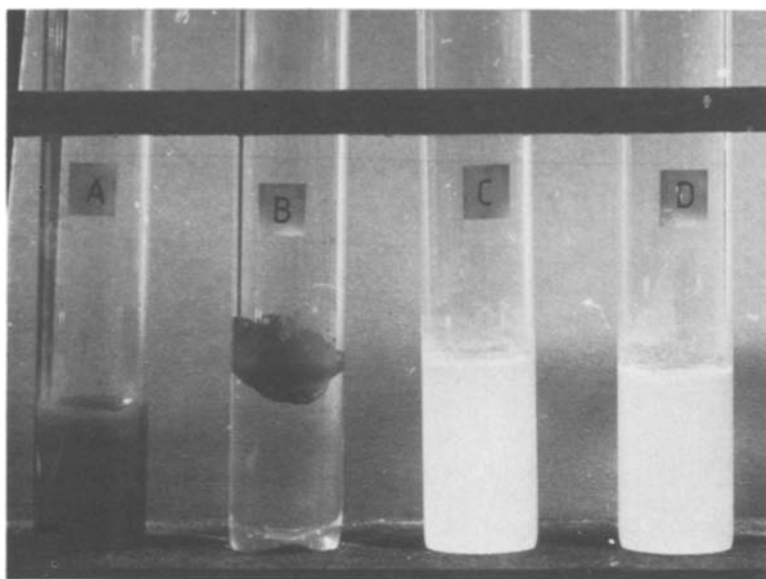
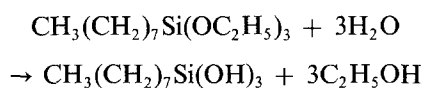


Figure 2 Ceramic powders mixed with distilled water: (A) silicon as-received, (B) silicon + 2 p.p.h. n-octyltriethoxysilane, (C) silicon nitride as-received, (D) silicon nitride + 2 p.p.h. PCIA/PCIB.

Care is needed in the calculation of volume fractions of powder for the silane-containing compositions. All the volume fractions were calculated from ashing results, since some error is always introduced on blending and mixing in the twin-screw extruder.

After blending 1.97 wt % n-octyltriethoxysilane with the silicon powder and drying, the composition must be adjusted for loss of alcohol:



The loss on drying for both silanes was determined experimentally and is given in Table I. The loss of 41 wt % for the n-octyltriethoxysilanes should be compared with the loss of 30 wt % predicted by stoichiometry, the discrepancy probably being caused by error in weight-change determinations on a component which represents less than 2 wt % of the sample. The proprietary combination PCIA/PCIB presents a loss of 34 wt % and the stoichiometric value is not available for this material. These values were used in calculating the volume fractions in Table II. The loss-on-ignition data are also given in Table I and in both

cases, despite a large error caused by the measurement of small weight changes, correspond to the losses expected for the silanol resident after treatment and drying. This is 1.16 wt % for the n-octyltriethoxysilane and 1.30 wt % for the PCIA/PCIB system, taking the loss of alcohols into account. This suggests that coupling agents are sufficiently volatile to avoid leaving a substantial silicon-containing deposit.

The assumption made in determining precise volume fractions for the silane-containing blends was that the density of the deposited silane was the same as the density of the liquid reagent. In view of the small amount involved and the likelihood that any deviation would be small the assumption is reasonable.

For the silicon powder there was a reduction in viscosity from 886 Pa sec at a shear rate of 108 sec<sup>-1</sup> and a temperature of 225°C (Composition F3) to 524 Pa sec for the formulation containing silane (F13). This represents a reduction of 41%. For the silicon nitride powder the corresponding reduction was from 1164 Pa sec for F14 to 561 Pa sec for F15, corresponding to 52%. This is in agreement with other observations on filled polymers, albeit at lower volume

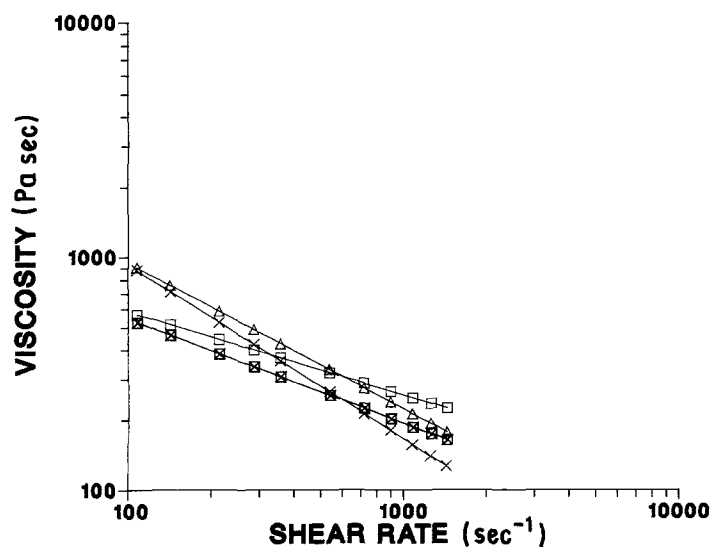


Figure 3 Viscosity–shear rate plots for silicon powder with and without silane addition. (Δ) F3, 195°C; (×) Fe, 225°C; (□) F13, 195°C; (⊠) F13, 225°C.

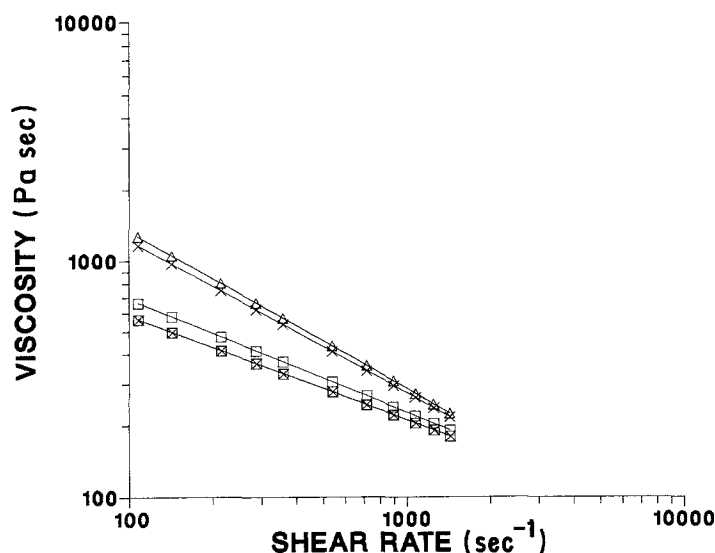


Figure 4 Viscosity-shear rate plots for silicon nitride powder with and without silane addition. ( $\Delta$ ) F14, 195°C; ( $\times$ ) F14, 225°C; ( $\square$ ) F15, 195°C; ( $\boxtimes$ ) F15, 225°C.

loadings of powder than those used here [10, 11]. In the case of the silicon nitride, the 1.2 vol % difference in powder volume fraction between F14 and F15 would be expected to make a small contribution to the reduced viscosity.

The action of the silane on the suspension is not entirely clear. It may enhance deagglomeration and improve the wetting of the particles by the polymer blend, thus improving the stability of the dispersed system, especially under pressure. On the other hand it may be present in the polymer bulk as a flow modifier. The apparent difficulty of coupling agents to adsorb on the silicon nitride focuses attention on the latter possibility. The silane, perhaps in the form of siloxane oligomers, may be an effective lubricant or processing aid for the polymer. It is pertinent to note that the silanes make up approximately 5 vol % of the organic component of the blends.

The pseudoplasticity of the suspension was substantially reduced by the silane addition, as evidenced by the rise in the value of the flow behaviour index  $n$  at 225°C, from 0.35 for silicon nitride and 0.25 for silicon suspensions to about 0.55 in both cases with silane coupling agents present.

The temperature dependence of viscosity of both powder suspensions was slightly increased by the silane coupling agents and although this is unfavourable [21], it is a small price to pay for considerably enhanced fluidity. The enhancement of fluidity suggests that higher volume fractions of powder could be tolerated.

### 3.3. Effect on mechanical properties

The mechanical strength data for the four compositions in the as-moulded state are presented in Table III. The presence of silane produces a 10 to 15% increase in flexural strength of the composite and the

difference is significant at the 1% level of probability. The difference is unlikely to be caused by moulding defects. Since the flexural strength test-bars were each compression-moulded in the same die under identical conditions, the influence of fabrication defects is likely to be small. The alternative explanations are an increase in strength effected by enhanced adhesion at the ceramic-polymer interface, or an effect of the silane on the mechanical properties of bulk polymer. Independent experiments are needed to decide between these explanations.

### 4. Conclusions

The use of silane coupling agents was shown to be an effective means of substantially increasing the fluidity of ceramic injection-moulding blends. This increase was accompanied by other rheological changes, in particular the fluids become more Newtonian. The mechanical strength of the as-moulded materials was not reduced by these additions, in fact there was a modest increase in strength. These additions also offer a means of protecting hydrolysable fine powders from moisture, provided a sufficient quantity of silane based on the specific surface area of the powder is added at the milling stage.

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TABLE III Flexural strength of as-moulded materials

Property	Compositions			
	F3	F13	F14	F15
Flexural strength (MPa)	13.53	15.12	12.72	14.65
Standard deviation	0.92	0.88	1.10	0.96
No. of tests	8	8	8	8
$t$	3.31		3.50	

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