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Surface Modification of Alumina Powder for LPIM

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Abstract

To utilise all the advantages of the low-pressure powder injection moulding (LPIM) technique in the production of complex-shaped high-performance ceramics, a stable suspension with a high solids loading and appropriate rheological properties is needed. In this investigation different surface active agents were either physisorbed or chemisorbed to modify the surface of alumina powder. To introduce the proper amount of the surfactants homogeneously into the powder–paraffin system, different techniques were applied including direct admixing into the melted paraffin, as well as coating of the alumina particles during milling in a solution of the surfactant in an organic liquid. The efficiency of the physisorbed or chemisorbed surfactants was examined in terms of the apparent viscosity of highly loaded powder–paraffin suspensions. Moreover, the hydrophobicity of the powders as well as the sensitivity of alumina–paraffin suspensions and of moulded green parts to destabilisation with water were estimated. © 1996 Elsevier Science Limited.

Introduction

Low-pressure powder injection moulding (LPIM) is a cost-effective near-net-shape process that offers automated production of complex-shaped ceramic parts. The process consists of several stages at which different defects can be introduced. For this reason, control of each of these steps and appropriate selection of the starting materials are critically important to the overall success of the process. In recent years a number of publications have addressed basic aspects of ceramic and metal injection moulding.[1–3] However, most of the relations reported are typical for the so-called high-pressure regime, where a high-viscosity organic vehicle is used.

In order to produce dense, defect-free injection moulded ceramics several requirements have to be satisfied. Generally, feedstocks should consist of a high volume loading of fine ceramic powder, yet still exhibit satisfactory rheological behaviour under injection moulding conditions. The basic principle to meet these requirements is to modify the properties of the powder surface with different surfactants.[1,4] Among these, carboxylic acids and amines, as well as menhaden fish oil are most frequently used; however the interactions of the ceramic powder particles and these additives are not yet well understood. Johnson *et al.*[5] suggested that fatty acids adsorbed onto an alumina surface reduce the viscosity of the slurry compared to uncoated powders, but they do not produce stable nonaqueous dispersions since the molecules are not long enough for steric stabilisation. Additionally, the polar nature of fatty acids and amines weakly bonded to the powder surface makes them susceptible to water and they could be pushed away during the process.[6] On the other hand, it has been shown that chemically bonded alcohol makes the coated powders resistant to water,[7,8] but the coated powders do not form a stable suspension.[7]

Due to the well-known hygroscopicity of fine alumina powder, water molecules are generally present at the surface of the powder. Furthermore, water is also present as environmental humidity during the production of the injection moulded parts and can theoretically influence the rheological properties of the feedstock during the process. The aim of our work was twofold: (a) to verify the influence of water present at the powder surface and of subsequently introduced water on the viscosity and stability of alumina powder–paraffin suspensions for LPIM, and (b) to confirm the proposed possibility of stabilising the suspension by a proper modification of the powder by chemically bonded surfactants.

Experimental Procedures

The suspensions were prepared by deagglomeration of Alcoa A-16 SG alumina powder in a melted paraffin characterised by 20 to 40 carbon atoms and a melting point of approximately 51°C (Zschimmer & Schwarz). Fatty acids (stearic and oleic acid), octadecylamine and menhaden fish oil were used as surfactants. Deagglomeration was performed in a heated ball mill and three-roll mill (Exact 80 S). Before deagglomeration a part of the alumina powder was dried by heating at 300°C for 24 h (dry powder), while part of the powder was used after long exposure to room atmosphere ($\approx$50% humidity). The humidity of the so called wet powder was determined to be above 1%.

Two different methods were used for the preparation of suspensions. In the first the proper amount of surfactant was simply admixed into a suspension of a dry or wet alumina in melted paraffin, so that the surfactant was only physisorbed onto the powder surface. In the second method the powder was previously deagglomerated in *n*-hexane or in dimethyl ketone in which a proper amount of surfactant was dissolved. After removal of the liquid, the powder was heated at a temperature of 90 to 150°C for 6 h in order to achieve a chemical bond of surfactant on the powder. The powder was then homogenised in the melted paraffin. The hydrophobicity of these powders and hence the success of chemisorption of the surfactant, were estimated by immersing the powders in water for a few days, while the interaction of the surfactant with the powder surface was analysed by FTIR spectroscopy.

The sensitivity of the alumina–paraffin suspensions to destabilisation was analysed by measuring the viscosity increase during addition of a small amount of water into a melted suspension where the surfactant was either physisorbed or chemisorbed onto the powder surface.

The suspensions of dry or coated alumina powders, characterised by a high solids loading and low viscosity, were injection-moulded at 0·4 MPa and a temperature of about 60°C. Some of the moulded parts were then immersed in water for a few days, which should simulate the effect of high environmental humidity during storage of the green parts. In order to estimate the proposed sensitivity to humidity, the viscosity of the melted green parts after immersion was measured. Additionally, the green parts were visually controlled after thermal debinding. Mechanical properties (three-point bending) were analysed using an Instron machine.

Viscosities were measured with a Haake rotational viscotester (VT500) using the NV2 or cone-and-plate PK 100D measuring system at temperatures from 60 to 70°C and shear rates up to 1000 s.$^{-1}$ The stability of the suspensions containing different amounts of surfactants was estimated after two days of sedimentation of suspensions with 10 wt% of solids in paraffin at 70°C.

Results and Discussion

One of the most important requirements to achieve a well-dispersed suspension is the appropriate addition of a suitable surfactant. It has been shown many times that the optimum addition coincides with the well-defined minimum of suspension viscosity that characterises high repulsive forces between particles and low interparticle friction. Small amounts of stearic (SA) and/or oleic acid (OA) (Fig. 1: curves SA, OA), as well as of octadecylamine (ODA) dramatically decrease the viscosity of suspensions of dry alumina. A surplus of SA, OA or ODA causes an increase of viscosity, which can be explained by crosslinking of polar ends of the surfactant molecules. The effect of the surfactant was observed to be much lower when wet powder was used (curve SA-wet). We suppose that molecular water present on the surface of wet alumina (peaks at $\approx$1580 cm^{-1} and 1392 cm^{-1} in the FTIR spectra, Fig. 2) hinders adsorption of the surfactant molecules, which makes the suspension unsuitable for moulding due to a high viscosity. Fish oil (curve FO, Fig. 1) shows only a small influence on the viscosity, although the effect of a small addition was reported to be significant.[9]

As evident from Fig. 3, suspensions of dry alumina with an optimal quantity of a suitable surfactant are nearly Newtonian in behaviour. A small surplus increases the shear stress and pseudoplasticity of the suspension. Furthermore,

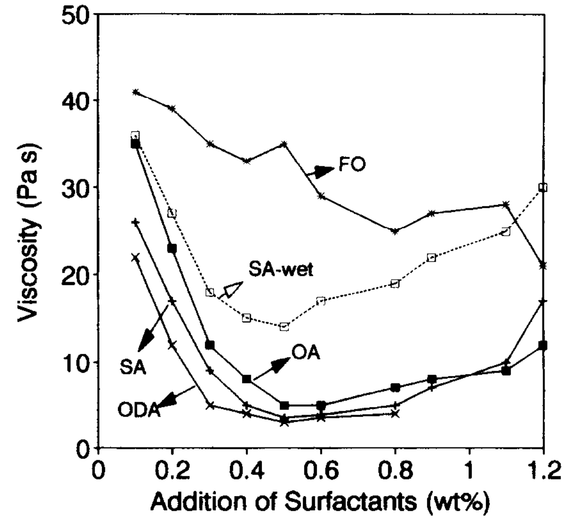


Fig. 1. Influence of surfactants on the viscosity of suspensions of dry or wet alumina in melted paraffin; solids content: 60 vol%, temperature: 64°C, shear rate: 500 s^{-1}; (SA: stearic aid, OA: oleic acid, ODA: octadecylamine, FO: fish oil, SA-wet: stearic acid – wet alumina powder), cone-and-plate measuring system.

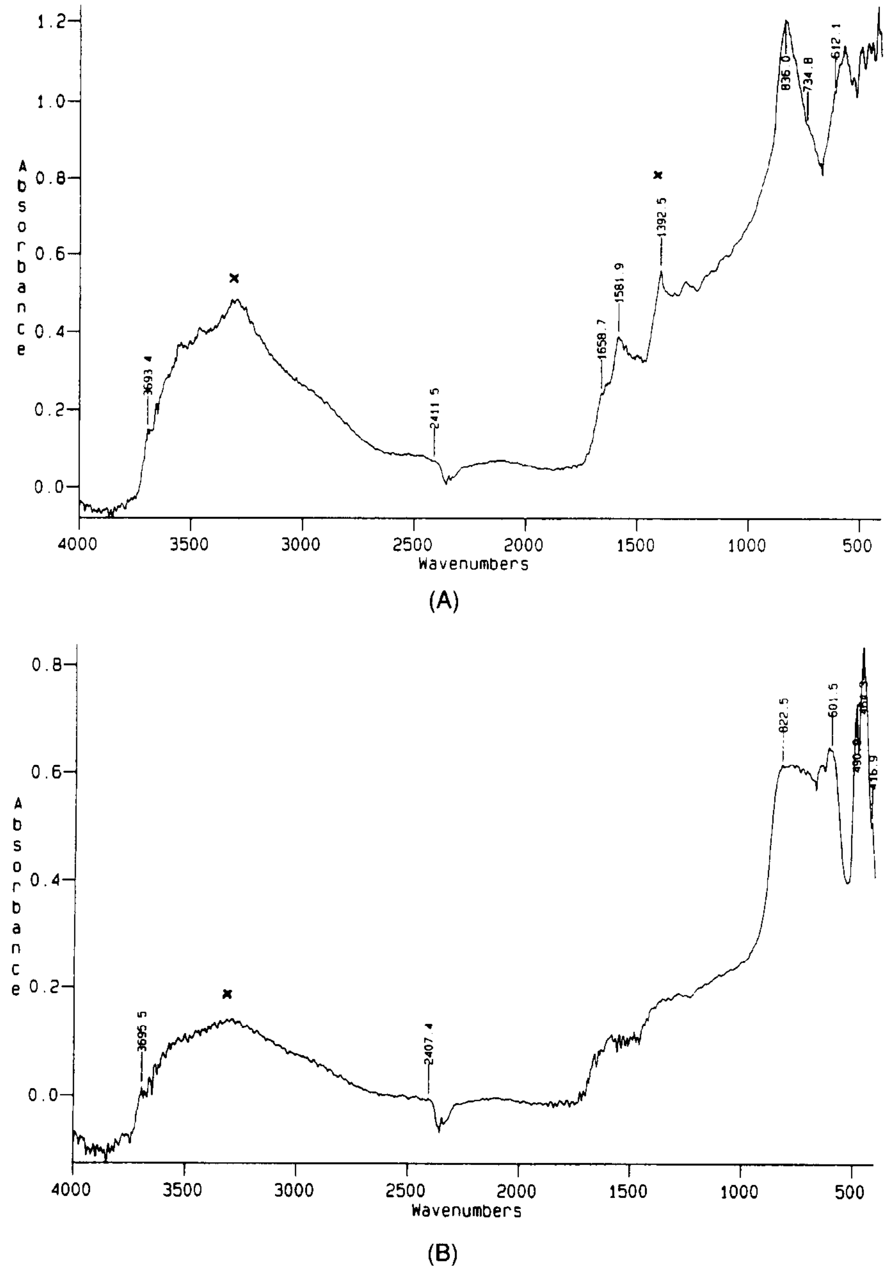


Fig. 2. FTIR spectra of (A) wet and (B) dry alumina powder.

sedimentation tests confirmed that the most stable suspension is one containing dry alumina powder and 0·5 wt% of stearic or oleic acid or the same quantity of octadecylamine, while a deficit or a surplus results in less stable suspensions. This implies, that the suspension prepared with a proper amount of surfactant can contain a high solids loading of a well-dispersed dry powder and still exhibit satisfactory rheological properties for low-pressure injection moulding.

In further experiments, the influence of environmental humidity or accidentally introduced water on the stability of the melted suspension, ready to mould, was established. The results confirmed that not only the presence of adsorbed water molecules on the surface of the starting powder but also water subsequently introduced into a well-dispersed suspension of dry alumina can detrimentally affect the viscosity. Figure 4 shows the viscosity of a dispersed suspension with 15 vol% of solids after admixing different amounts of water. As shown, a small amount of water considerably increases the viscosity of the suspension of alumina with physisorbed stearic acid (admixed only). This implies that, due to its hygroscopic nature, alumina powder tends to interact with water rather than with carboxylic groups, which causes the release of fatty acid.

In order to prevent desorption of surfactant from the powder surface during processing, optimal quantities were chemically bonded to alumina powder according to the above-mentioned procedure.

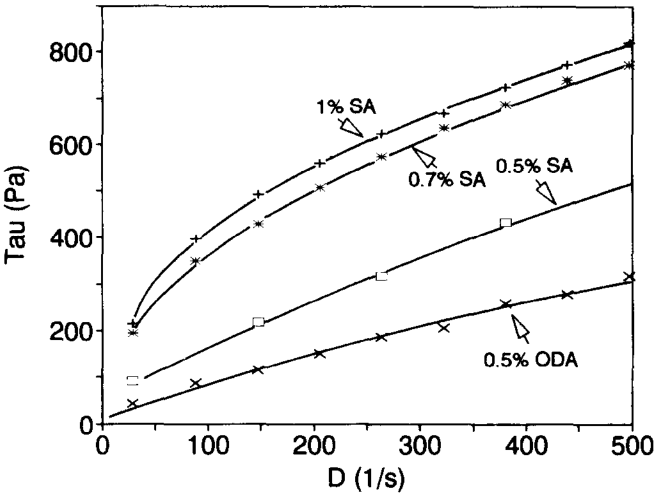


Fig. 3. Influence of the surfactant on the rheological properties of suspensions with (a) 0·5% ODA, (b) 0·5% SA, (c) 0·7% SA; (d) 1·0% SA; solids content: 60 vol%, T = 70°C, cone-and-plate measuring system.

Table 1. Properties of the powders with optimal addition of stearic acid

Powder	*Heating* T (°C)	t (h)	*Floating on water*	*Estimation of hydrophobicity*
1[a]	—	—	No	/
2	90	6	Partly, ≈4 days	Not successful
3	110	6	Mostly, ≈4 days	Not successful
4	130	6	> 10 days	OK
5	150	6	> 10 days	OK

[a] SA admixed into the suspension of alumina in melted paraffin.

Table 1 shows the properties of powders with stearic acid physisorbed or chemisorbed at temperatures from 90 to 150°C. As expected, powders with stearic acid admixed only (powder 1) do not float on water, while powders coated and heated at above 130°C are more or less hydrophobic (powders 4 and 5). The surfactant is therefore successfully chemisorbed on the powder surface. If the temperature of heating is too low (powders 2 and 3), the powder floats on water from a few seconds to four days, while successfully hydrophobised powders float on water indefinitely. When dispersed in melted paraffin, a suspension with a low viscosity was achieved.

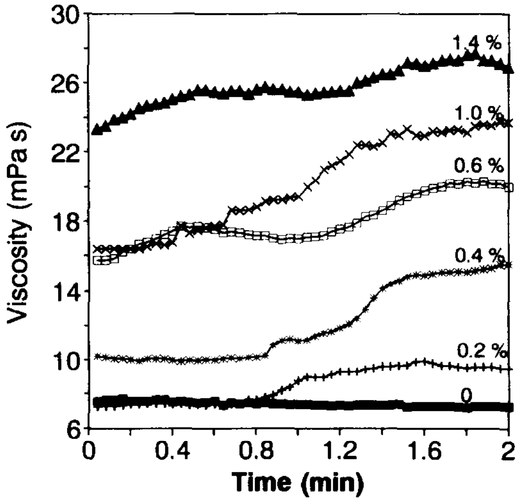


Fig. 4. The influence of water addition into the dispersed suspension of alumina, when SA is admixed only. The measurements were performed one minute after water admixing; solids content: 15 vol%, T = 70°C, shear rate: 500 s^{-1}, NV measuring system.

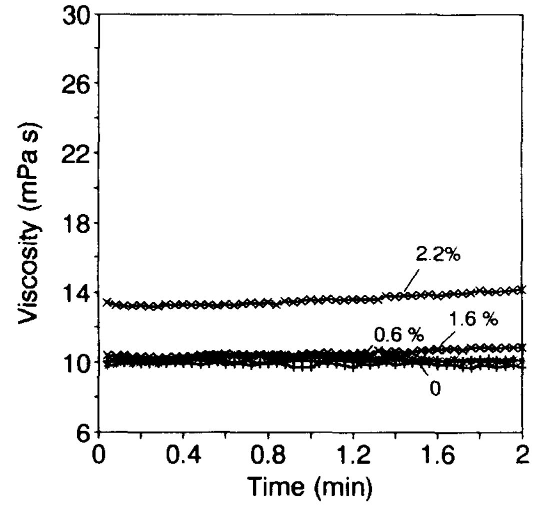


Fig. 5. Increase of viscosity after water addition into the dispersed suspension of alumina, when SA is chemisorbed by heating at 130°C; solids content: 15 vol%, T = 70°C, shear rate: 500 s^{-1}, NV measuring system.

The suspensions of powders coated by chemisorbed stearic acid are resistant toward destabilisation with water. In contrast to the suspension with only physisorbed stearic acid (Fig. 4), viscosities were not affected by water addition in this case. As evident from Fig. 5, the viscosity of the suspension of alumina coated with chemisorbed stearic acid by heating at 130°C remains low even

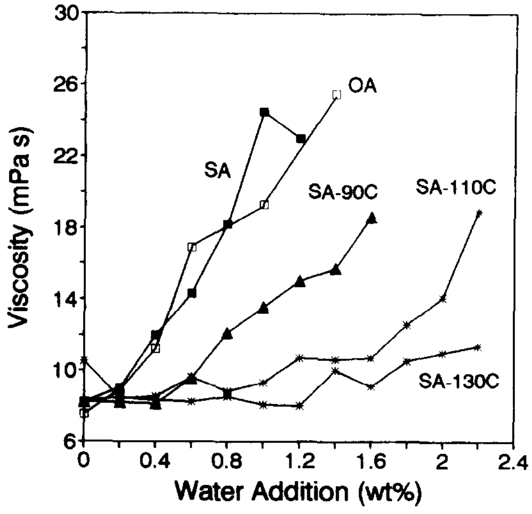


Fig. 6. Resistance of suspensions toward destabilisation with water: SA: physisorbed stearic acid, OA: physisorbed oleic acid, SA-90C: stearic acid bonded at 90°C, SA-110C: bonded at 110°C, SA-130C: bonded at 130°C; solids content: 15 vol%, shear rate: 500 s^{-1}, T = 70°C.

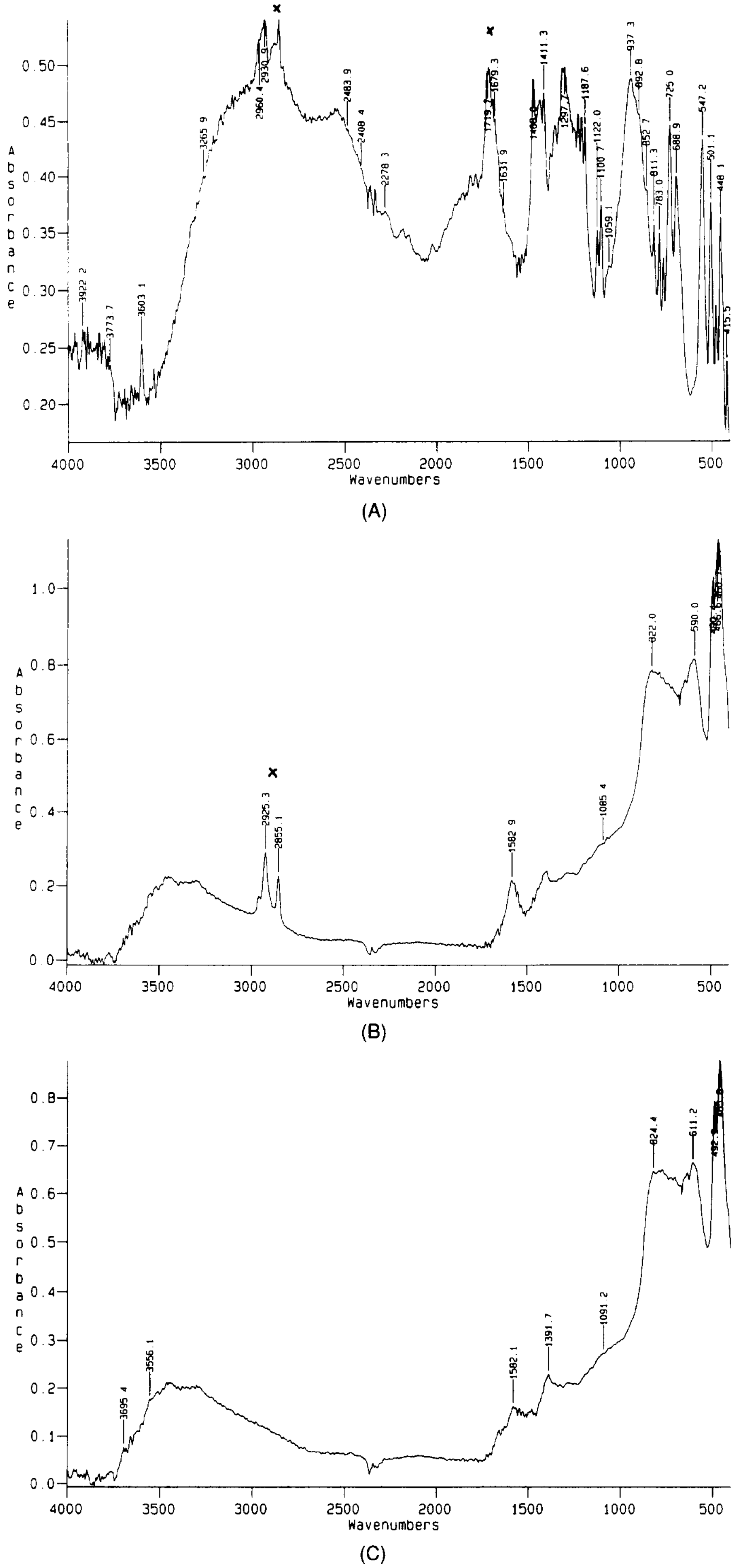
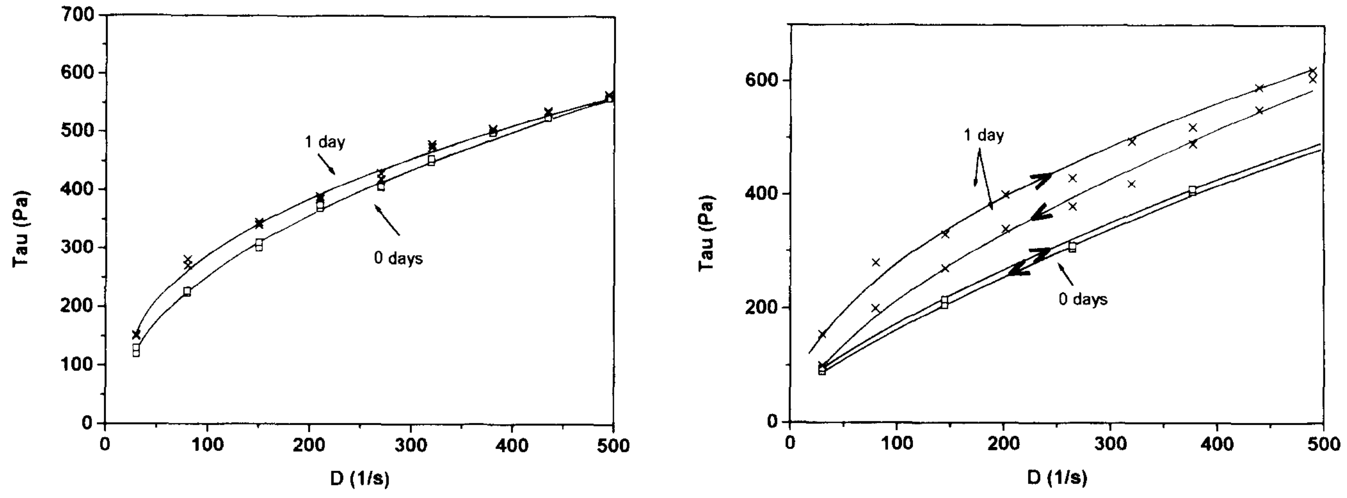


Fig. 7. FTIR spectra of (A) stearic acid, (B) alumina powder with chemisorbed stearic acid after washing, (C) alumina powder with physisorbed stearic acid after washing.



(A) (B)

Fig. 8. Rheological properties of the suspensions of the powder with SA (A) chemisorbed at 130°C and (B) bonded at 110°C; solids content 60 vol%, $T = 70°C$, cone-and-plate measuring system.

after admixing more than 1 wt% of water into the melted suspension.

The results of the experiments where water was added to the powder-paraffin suspension are summarised in Fig. 6. As shown, a small amount of water considerably increases the viscosity of a suspension of dry alumina powder dispersed by simple admixing of stearic (SA) or oleic acid (OA). A similar effect was also observed for other surfactants used in this study. Obviously, water molecules replace the surfactant molecules at the powder surface which causes a decrease of surface charge and hence flocculation. In contrast, suspensions prepared from hydrophobic powder (SA–130C) were not affected by water. Some degree of moisture sensitivity is evident only for a suspension of powder for which chemisorption was not complete due to an insufficiently high temperature of reaction (SA–90C).

In order to confirm chemical or physical bonding of stearic acid onto the alumina powder surface, FTIR analysis was performed with the starting materials and powders with physisorbed or chemisorbed SA. The powders were washed with dimethyl ketone prior to analysis. The results are shown in Fig. 7. The presence of the peak at approximately 2900 cm^{-1} (CH_2-units of stearic acid) in the case of coated alumina (Fig. 7B), confirms the bonding of SA onto the alumina surface. However, the characteristic peak of the carbonyl group in stearic acid at approximately 1700 cm^{-1} is absent in the case of the coated powder. This confirms bonding of the polar end of the SA onto the alumina and additionally, that no free acid has remained. When the SA was only admixed into the suspension, the FTIR spectrum of the washed powder showed no evidence of groups characteristic of the SA. The spectrum is the same as the spectrum of the alumina powder without surfactant (Fig. 7C).

A similar phenomenon was observed in the case of the powder coated with oleic acid. In the case of octadecylamine coating, interaction of NH_2 groups with the OH– groups of the powder was proposed, but is not yet clearly understood.

Based on the observed sensitivity of the powder suspension with physisorbed surfactant to the presence of water, it was hypothesised that moulded green parts should also be sensitive to destabilisation when subjected to a highly humid environment (during storage). In order to establish this hypothesis, some of the green injection moulded parts were immersed in water. After a few days the viscosities of the melted parts were measured and compared to the viscosity before immersion. The results confirmed the proposed behaviour. The viscosity of a melted suspension with physisorbed surfactant increased above measurable value after one day of immersion. In contrast, water had no effect on the rheological properties of the green parts with chemisorbed stearic acid (Fig. 8A). When the chemisorption was not complete due to an insufficient temperature of reaction, a small increase of viscosity was observed after one day of immersion. Additionally, as evident from Fig. 8B, after one day of immersion a suspension exhibits a pseudoplastic and more thixotropic nature as distinct from its nearly Newtonian behaviour before immersion. As proposed, the relatively high volume percentage of hygroscopic alumina powder (> 60 vol%) enables the water to enter into the moulded part. After heating above the melting point of the paraffin a similar phenomenon was observed as in the case

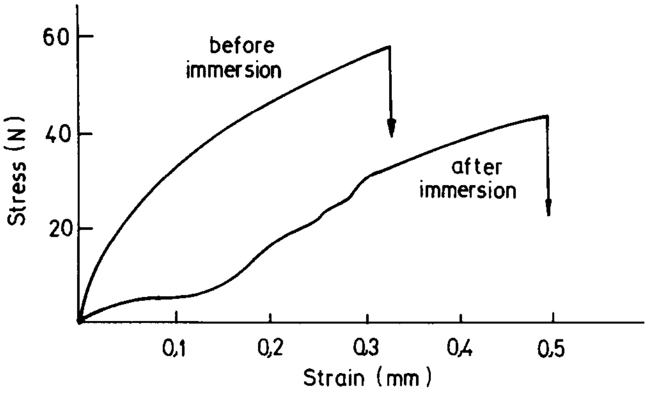


Fig. 9. Stress–strain curve of the green parts before and after immersion.

of mixing water into the suspension — the vicosity is much higher compared to the viscosity prior to immersion. This suggests that the water has diffused into the green part and caused flocculation of the suspension in a melted state.

The parts which were immersed in water for two days and for which an increase of the viscosity was characteristic showed much more plastic behaviour than before immersion. The stress–strain curves of the test bars prior to and after two days of immersion are shown in Fig. 9. Obviously, bend strength has decreased from 10·5 to 7·7 MPa after immersion, while deformation before fracture was 50% higher. This confirms that water is not only adsorbed on the surface of the immersed samples, but has diffused into the interior thus causing modification of mechanical and rheological properties of the green parts. Additionally, after thermal debinding, cracks were typically observed on the immersed samples which is another confirmation of flocculation in the green parts. Similarly, Song and Evans[10] suggested flocculation as one of the main causes of cracking during debinding.

Conclusions

The results imply that in the system of fine alumina-paraffin either a ready-to-mould suspension or even injection moulded parts are subjected to destabilisation due to high moisture in the environment when the surfactant is only physisorbed on the powder surface. In the first case, the consequence can be unsuitable properties of the suspension for injection moulding, while in the second case flocculation in the moulded part results in its plasticity and in cracking during debinding. This can be prevented by chemical bonding of a proper amount of surfactant. This implies that not only the activity and quantity of the surfactant, but also the type of bond between the surfactant and the powder surface is of essential importance for the success of low-pressure injection moulding of ceramics.

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