

The effect of water on the behaviour of alumina–paraffin suspensions for low-pressure injection moulding (LPIM)

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Abstract

The properties of ceramic powder–paraffin suspensions for low-pressure injection moulding (LPIM) is of critical importance to the successful production of high quality ceramic parts. Due to the high hygroscopicity of fine alumina powder, water introduced into the suspension at any stage of the production prior to sintering, may significantly influence its rheological behaviour and hence determine the process parameters as well as the properties of the sintered ceramics. In the industrial environment humidity cannot easily be avoided. Its effect is usually detrimental — it causes flocculation, which is usually the source of defects in sintered ceramics. However, according to the results of the present work, the effect can also be put to good use. Penetration of water into the as-moulded green parts facilitates binder removal and prevents defect formation during this processing step. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Low-pressure injection moulding (LPIM) is a cost-effective near-net-shaping method for producing complex shaped ceramics, and offers several advantages over other methods of ceramics forming.^{1,2} In contrast to the competing high-pressure powder injection moulding (PIM), low injection pressures are used which guaranties a low wear rate of the mould. One of its major advantages is relatively easy (however slow) and environmentally friendly binder removal by thermally activated capillary flow of a liquefied binder that is collected in a bed of adsorbent powder or simply by evaporating. Several disadvantages limit the use of this process, in particular, defects which remain in the moulded sintered parts. A catalogue of the defects arising from different steps of production have been reviewed by Zhang et al.,³ other workers have discussed their sources as well as the possibilities for avoiding them.^{4,5} Literature data indicate that defects mostly appear during

binder removal but result from the inhomogeneity introduced or remaining from the early stages of the process.

The overall success of low-pressure injection moulding of ceramics relies primarily on the properties of the starting suspension. It is well known, that it must contain a high solids loading to assure low shrinkage during sintering and low final porosity. The powder must be homogeneously dispersed in a liquid carrier and, simultaneously, the rheological properties of the suspension must be suitable for moulding.^{1,2,6,7} The appropriate addition of surfactants is therefore one of the most important requirements that significantly enhances the dispersion of powder in the binder which in turn results in enhanced powder loading at reasonably low viscosity. Due to their favourable price and properties, fatty acids are probably the most widely used surfactants, they are introduced to disperse powder-paraffin suspensions in many industrial procedures.^{8,9} Stearic acid seems to be one of the most appropriate due to functional group anchoring at the powder surface and a carbon chain containing 18 C atoms dissolving into the binder matrix. Adsorption of the organic surfactant is usually via hydrogen bonding, although covalent bonding is also possible.¹⁰

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The binder in a paraffin-based system for LPIM typically makes up 30 to 40 vol% of the composition. This is one of the certain drawbacks of this system, since a large amount of organic material must be removed which increases the probability of introducing defects or distortion. During thermal extraction, outward diffusion of a molten binder can cause migration of solid particles, resulting in non-homogeneous density of the as moulded part. In spite of its non-polar character, paraffin does not prevent hygroscopic ceramic powders from interacting with water present in the surroundings.¹¹ Water in fact exhibits an adverse effect on the stability of the dispersant chain on the alumina surface. Consequently, flocculation may occur at different stages of the process, either in a suspension ready to mould or even in the already moulded part.^{12,13} The destructive effect of high environmental humidity is not unknown to the manufacturers since it periodically causes difficulties during injection moulding of paraffin suspensions of ceramic powder.

In the present study the influence of water on the properties of alumina–paraffin suspensions was analysed. Its detrimental as well as advantageous effects at different stages of the LPIM process are discussed.

2. Experimental

The suspensions were prepared by blending alumina powders in molten paraffin KX1313 (Zschimmer & Schwarz, 20 to 40 carbon atoms, melting point of approximately of 51°C) in a heated three-roll mill (Exact 80S). Most of the experiments were performed with Alcoa A-16 SG alumina powder ($d \approx 0.5 \mu\text{m}$), while for comparison a mixture containing 1/3 of Alcoa A16 SG and 2/3 of Alcoa CL3000SG alumina ($d \approx 5 \mu\text{m}$) was also used. Stearic acid (SA) was added as a surface-active agent. Before de-agglomeration a part of the powder was dried by heating at 300°C for 24 h (“dry powder”), while another part was used after exposure to environmental humidity, i.e. 55% RH, temperature was 25°C (“non-dried powder”). Due to its hygroscopicity, after a few days the powder exposed to humid air contained 0.8% of moisture. The third part of the powder (“hydrophobic powder”) was coated by stearic acid prior to blending, according to the following procedure.^{10,14} The powder was de-agglomerated in a ball mill in dimethyl ketone in which 0.6% of SA (referred to the mass of powder) was dissolved. After de-agglomeration the liquid was removed and the powder was heated at a temperature of 130°C for 2 h. The hydrophobic powder coated by SA was then homogenised in the molten paraffin. The highly loaded suspensions (up to 87.5 wt% of powder) were injection moulded at 0.4 MPa and a temperature of 65–70°C, to form rectangular bars of dimension 5 × 5 × 50 mm.

Water as a disturbing factor was introduced at three stages of the process. In the first case, a suspension was prepared with the non-dried alumina powder. In the second case, small quantities of water were admixed into the suspension of dry alumina powder. In the third experiment the as-moulded green parts were immersed in water in order to simulate the effect of high environmental humidity during the ageing of green parts. The rheological properties of the suspensions were analysed with a Haake rotational viscotester (VT500) using the MV2 or cone-and-plate PK 100D measuring system. The temperature of the suspensions during measurement was 66°C, and the shear rate was increased up to 1000/s. Viscoelastic properties were analysed under oscillatory shear conditions with a Physica MC200 rheometer. In order to determine the elastic and viscous contributions, amplitude sweep experiments were performed over a range of shear rates from 0.1 to 1000 and a frequency of 1 Hz.

The susceptibility of the green parts during thermal de-binding toward deformation was estimated by heating the bars (5 × 5 × 50 mm) at 200°C for 4 h, heating rate was 0.2°C/min. During the test ceramic bars supported the samples, so that they were loaded by their own weight.

3. Results and discussion

3.1. The effect of powder humidity

The first requirement that has to be taken into account in the preparation of the feedstock for LPIM is the addition of the proper amount of surface-active agent, characterised by a minimum in the suspension viscosity. The effect of stearic acid (SA) addition on the viscosity of the dry or non-dried A16 alumina suspensions in molten paraffin is shown in Fig. 1. The viscosity sharply decreases up to 0.3–0.35 wt% SA while further addition result in a gradual increase. The relation holds for both the suspensions analysed, however the absolute value of the viscosity minimum is lower for the suspension of the dry alumina than for the non-dried one. Fig. 2 shows corresponding up and down flow curves for the dry and non-dried A16SG powder suspensions, containing the same solids content and SA addition (i.e. 87 and 0.35 wt%, respectively). Both the suspensions exhibit pseudo-plastic behaviour (shear thinning) with a yield point. The suspension of non-dried powder also exhibits time dependency (thixotropy), while in the case of the dry powder suspension this is not observed.

In the as-received state, fine alumina particles, (like most minerals and technological powders) are covered by a thin surface layer of hydroxyl groups that serve as anchoring points for the attachment of surface modifying agents. The molecules of carboxylic acid added to

disperse the alumina powder in a paraffin suspension adsorb across their carboxylic group onto the free hydroxyl groups at the surface of alumina particle. In the case of the non-dried alumina powder the adsorbed water molecules limit the ability of the acid to adsorb and hence determine interactions of the powder with the surrounding non-polar media. This is reflected in higher viscosities of paraffin suspensions as shown in the diagram in Fig. 1. The minimum viscosity is obtained when the powder surfaces of the solid are completely covered by a mono-layer of SA that corresponds to a minimum interfacial energy between the solid and liquid in the system.

The use of non-dried powder therefore results in a higher viscosity for a given solids loading which results in a lower possible solids content. The results clearly suggest the need for drying the alumina powder prior to admixing into paraffin in order to obtain a suspension containing the highest possible solids loading.

3.2. The effect of water introduced into the alumina–paraffin suspension

Water affects the properties of the alumina–paraffin suspension not only as the humidity of the powder used; it can also change the suspension's properties when dry alumina powder is used while water is somehow introduced into the as-prepared suspension. There are two common possibilities: (1) water is accidentally introduced and admixed into the molten suspension during the homogenisation, pouring or re-melting prior to moulding, (2) the suspension (in the molten or even in the solid state) is exposed to very humid surroundings for some time.

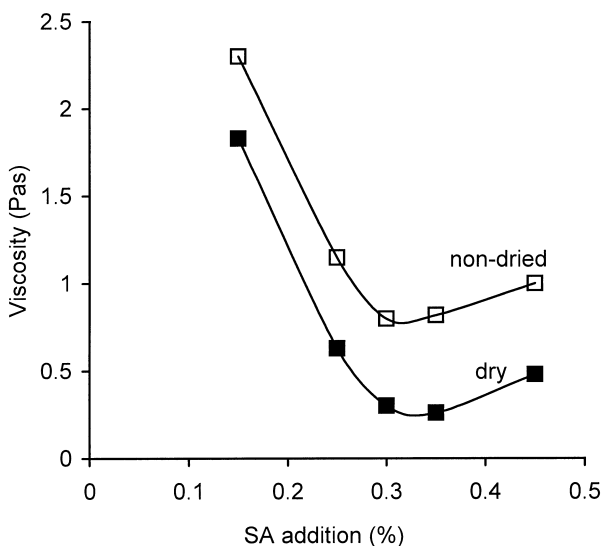


Fig. 1. Effect of stearic acid addition on the viscosity of the paraffin suspension of dry and non-dried A16SG powder; solids content = 60 vol.%, measuring system: cone-plate, shear rate = 300/s, temperature = 66°C.

3.2.1. The effect of water introduced into the as-prepared liquid suspension

The effect of water introduced into an alumina–paraffin suspension in the molten state on the viscosities measured at shear rates up to $D = 1000 \text{ s}^{-1}$ is illustrated in Fig. 3. The viscosity of the alumina–paraffin suspension, containing 87 wt.% of solids, increased significantly with a small (0.2%) addition of water. An order of magnitude increase was observed when 0.4 wt.% of water was admixed, and the thixotropic behaviour appears to be more pronounced. Furthermore, the visual inspection of the suspension after water admixing strongly suggests

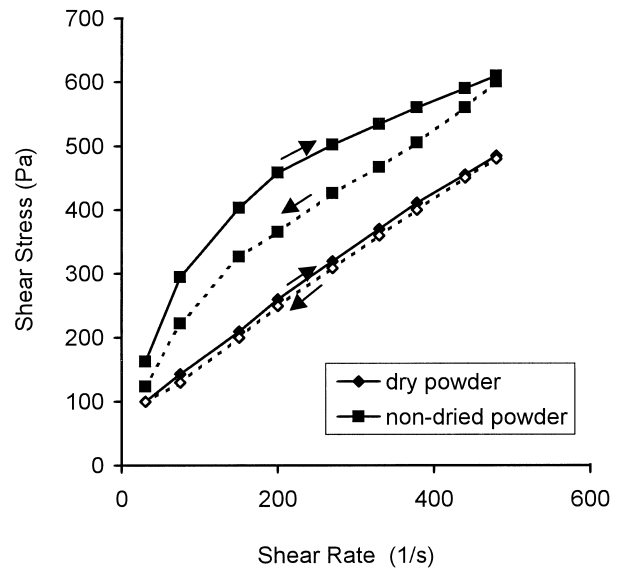


Fig. 2. Flow curves of the suspensions of dry and non-dried A16SG powder; solids content = 60 vol.%, 0.35 wt.% SA addition, measuring system: cone-plate, temperature = 66°C.

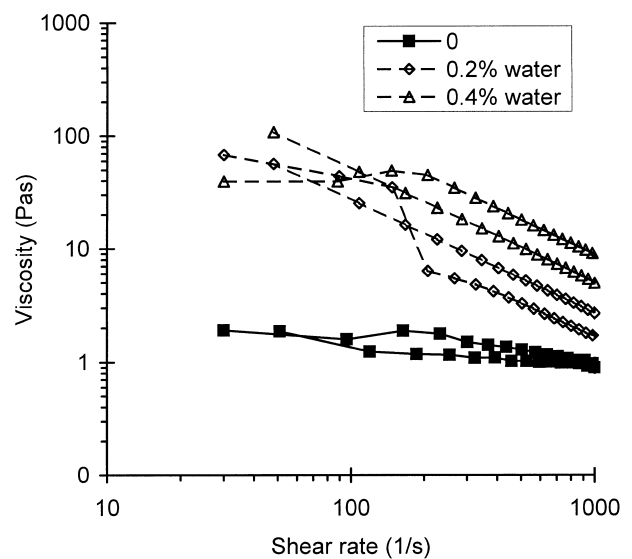


Fig. 3. The effect of admixed water on the viscosity of the dry A16SG alumina–paraffin suspension containing 60 vol.% solids and 0.35 wt.% SA; measuring system: cone-plate, temperature = 66°C.

that flocculation takes place. This can be explained by the replacement of the SA attached to the surface by a weak Van der Waals bond with water molecules.

Destabilisation of an alumina–paraffin suspension can be successfully prevented by using hydrophobic powder. As reported,^{13,14} the carboxylic acids can be chemically bonded to hydroxylated oxide particle surfaces via a condensation reaction. When the stearic acid is covalently bonded to a particle's surface, then the water cannot break the bond between the SA and the particle surface and so the suspension is not sensitive to any kind of water introduction. The latter is confirmed by a constant value of viscosity even at higher levels of water admixed into the suspension of the hydrophobic alumina powder (Fig. 4).

3.2.2. The immersion of the solid suspension into water

After the suspension of dry alumina powder in paraffin with the adsorbed SA is solidified (either before moulding or after it), water can still enter by diffusion. If the suspension is exposed to a highly humid environment for a longer period, water penetrates into the surface layer of the solid part. When re-melted, the part of the suspension from this layer exhibits a much higher viscosity and may effect the viscosity of the bulk sample as well.

The diffusion of water into the solid alumina–paraffin suspension was studied by immersion of the as-moulded ceramic parts in water for 5 to 24 h. After the immersion, the samples were aged for a few days, than re-melted, stirred and the viscosity was measured, as well as this, weight change was controlled. As shown in Fig. 5a, after 5 h the viscosity of the suspension of A16SG powder increased by an order of magnitude and the suspension also became more thixotropic. Immersion

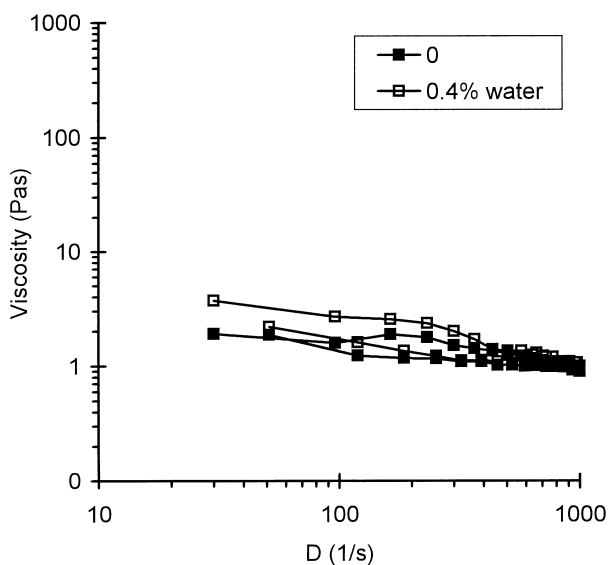


Fig. 4. The effect of admixed water on the viscosity of the hydrophobic A16SG alumina–paraffin suspension containing 60 vol.% solids and 0.35 wt.% SA; measuring system: cone-plate, temperature = 66°C.

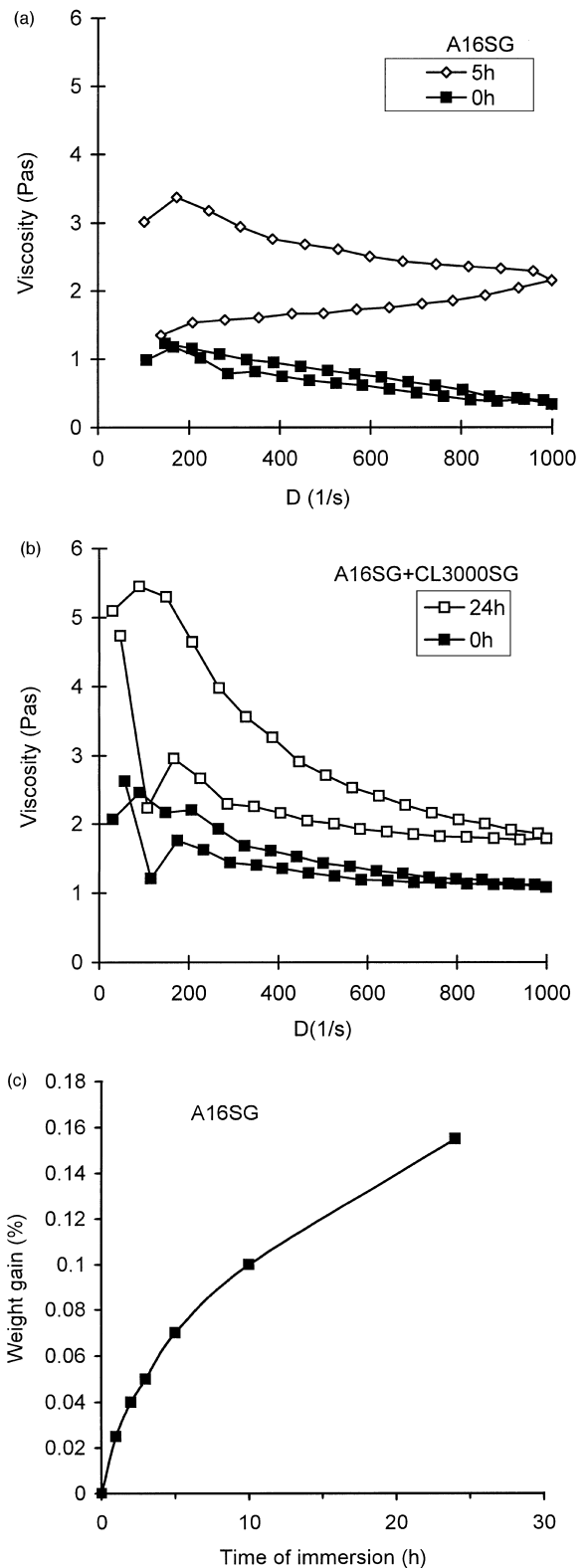


Fig. 5. The effect of immersion in water on the viscosity of re-melted green parts: (a) dry A16SG alumina–paraffin, (b) dry powder mixture–paraffin suspension; solids content = 60 vol.%, measuring system: cone-plate, temperature = 66°C; (c) the effect of immersion time on the weight gain for the dry A16SG alumina–paraffin suspension; solids content = 60 vol.%, 0.35 wt.% SA addition, measuring system: cone-plate, temperature = 66°C.

for longer times resulted in viscosities out of measuring range, the slurry appeared as clotted substance implying extensive flocculation. The suspension of the A16SG and CL3000SG powder mixture appeared to be less sensitive to the water, which can be ascribed to the lower total surface area of the powder and the lower sensitivity to water of a coarser powder. A significant increase in viscosity was observed only after 24 h of immersion (Fig. 5b).

With respect to the observed increase in viscosity and weight gain for the suspension of A16SG alumina (Fig. 5c), it is clear that water diffuses into the samples rather quickly. Obviously, the water molecules diffuse into the bulk material intrude into the Van der Waals bond between the hydroxylic groups at the particle surface and the carboxylic group of the stearic acid and hence diminish its effect.

In contrast, the effect of water is minor if the hydrophobic powder is used. The viscosity of the hydrophobic A16 powder suspension slightly increased after 24 h of immersion in water (Fig. 6a), while no increase was observed for the suspension of hydrophobic powder mixture (Fig. 6b).

The results therefore imply that water has a detrimental effect on the rheological properties of alumina–paraffin suspensions for LPIM if the powder is not made hydrophobic. It can enter either into a molten suspension or it can penetrate into a solid part. In both cases the result is higher viscosity which can in many cases cause difficulties during moulding or in extreme cases even make the moulding impossible due to low flowability of the feedstock. However, the water-induced flocculation of the solid suspension of alumina in paraffin can also be put to a good use as described in the following section.

3.3. Improvement of the properties of the as-moulded green parts

As described above, the rheological properties of re-melted parts after immersion were observed to change significantly. It was reasonable to conclude that the increase in viscosity can facilitate binder removal by preventing deformation in green parts heated above the melting point of paraffin during this processing step. In order to get more information on the deformation properties of green parts during binder removal, viscoelastic properties under amplitude sweep conditions of the re-melted sample prior and after immersion were analysed. The results are represented in Fig. 7 as a loss factor ($\tan \delta$) that characterises the ratio between the loss modulus (G'') and the storage modulus (G') as a function of shear stress. According to the results, the loss factor increases with increasing shear stress, which implies changing from a predominantly elastic to a more viscous behaviour. In a first approximation the

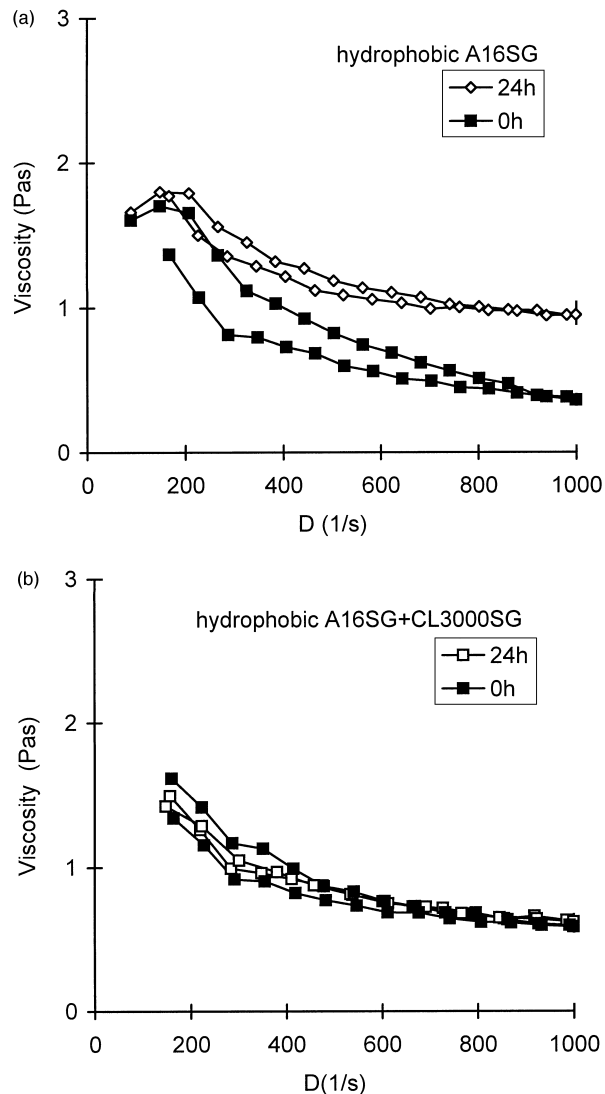


Fig. 6. The effect of immersion in water on the viscosity of re-melted green parts: (a) hydrophobic A16SG alumina–paraffin, (b) hydrophobic powder mixture–paraffin suspension; solids content = 60 vol.%, measuring system: cone-plate, temperature = 66°C.

critical shear stress, τ_c , for the elastic-to-viscous transition can be estimated as the stress at which the storage modulus becomes lower than the loss modulus, i.e. the loss factor increases above a value of 1. It is shown in Fig. 7 that the A16SG powder suspension changes to a viscous liquid at a much higher shear stress than the mixed A16SG + CL3000SG suspension. For comparison, the suspension of the CL3000SG powder was also analysed and the obtained τ_c is two orders of magnitude lower than that of the A16SG powder (see Table 1). One could also see from the diagram, that hydrophobisation does not influence the visco-elastic properties of the suspension except in that it prevents water from interfering (compare bulk triangles and crosses in Fig. 7). As is also evident, the elastic contribution of viscosity increases significantly after the immersion of non-treated powder suspension in water for 5 h, which shifts the

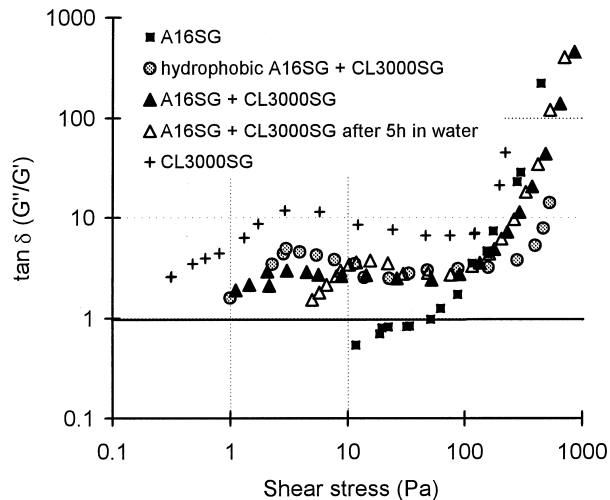


Fig. 7. Loss factor, $\tan \delta$, for the paraffin suspensions of dry or hydrophobic alumina powders as a function of shear stress in amplitude sweep; $f = 1$ Hz, $T = 70^\circ\text{C}$, solids content = 60 vol%.

critical shear stress to a value which is higher by an order of magnitude. The immersion of the A16SG powder suspension resulted in a drastic change in the visco-elastic properties such that the measurements were not possible under the given conditions. The obtained values for τ_c obtained for the analysed samples are collected in Table 1.

The results suggest that water penetrates into the green parts and causes an enhanced elastic contribution to viscosity at least in the surface region of the green part. This contributes to improved stability of the formulations that tend to deform due to a low critical shear stress at temperatures above the melting point of the paraffin.

In order to verify the relationship between critical shear stress and defect formation during de-binding, the samples were subjected to higher temperatures. During the test, they were supported by ceramic bars so that they were loaded by their own weight. After heating above the melting point for few hours, the samples characterised by the τ_c lower than 1 were plastically deformed (Fig. 8). The results therefore confirm the decisive importance of the elastic contribution to viscosity, which can be, according to the above shown results, increased by immersion of green parts in water.

Table 1
Critical shear stress, τ_c , for the analysed suspensions

Powder	Powder treatment	Suspension treatment	τ_c (Pa)
A16SG	–	–	50
A16 SG+CL3000SG	–	–	0.8
A16 SG+CL3000SG	–	Immersion 5 h	3
A16 SG+CL3000SG	Hydrophobised	–	0.8
CL3000SG	–	–	0.2

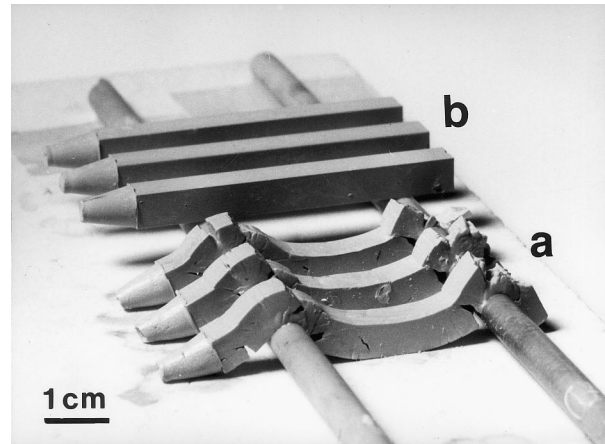


Fig. 8. Green parts (A16SG+CL3000SG powders mixture) after thermal de-binding: (a) without immersion in water, $\tau_c \approx 0.8$; (b) immersed in water for 5 h prior de-binding, $\tau_c \approx 3$.

4. Conclusions

The rheological properties of an alumina–paraffin suspension largely depend on the humidity of the used powder. Water molecules interfere with the stearic acid–powder bond at three stages of the process: 1. Water molecules attached to the surface of wet powder prevent the stearic acid from adhering in a monolayer that results in a higher viscosity for a given solids loading. 2. Water effects the properties of the alumina–paraffin suspension not only as the humidity of the powder used but can also change its properties when dry alumina is used by replacing the SA molecules attached to the surface by a weak Van der Waals bond. Water induced destabilisation of an alumina–paraffin suspension can be successfully prevented by chemically bonding the SA, i.e. powder hydrophobisation. 3. Water also penetrates into the green parts and causes an enhanced elastic contribution to viscosity: the critical shear stress for elastic to viscous transition, τ_c , increases after immersion the green parts in water for 5 h. During thermal de-binding this contributes to improved stability of the formulations, which tend to deform due to a low critical shear stress at temperatures above the melting point of the paraffin.

The critical shear stress for elastic-to-viscous transition, τ_c , is preferentially governed by the particle size distribution. When compared to the suspension of the A16SG + CL3000SG alumina mixture, the τ_c for the A16SG alumina is almost two orders of magnitude higher. When non-hydrophobic powder is used, the immersion of the as-moulded green parts in water significantly increases the τ_c which is caused by water induced flocculation. This helps to prevent the green parts from deformation during thermal de-binding. The effect of hydrophobisation, which prevents the water from interfering with the SA–powder bond, on τ_c is minor.

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