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Superplastic Behaviour of a Zirconia Powder–Binder Blend

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Abstract: A zirconia powder (ZrO_2–3 mol%Y_2O_3) blended with an organic binder was prepared for injection moulding. In the temperature range investigated (120–200°C), the blend exhibited a flow pattern similar to that of a Newtonian fluid with a low activation energy of flow (3.2 kJ/mol). Subsequent to extrusion at temperatures between 120 and 200°C, the blend could be drawn from more than 3 mm in diameter down to less than 0.1 mm in diameter, indicating a local reduction of area by a factor of more than 1000. Such a superplastic phenomenon was attributed to a strong interfacial adhesion between powder and binder arising from the utilization of an acrylic resin as one of the binder components.

1 INTRODUCTION

Powder injection moulding is a fabrication process used for mass production of parts with thin walls and complex shapes.[1] In this process, the binder chemistry has a major influence on the success of the process. The binder has to be properly designed such that a homogeneous powder–binder blend can be attained during mixing, integrated parts can be moulded under an appropriate rheological pattern, and clean binder burnout can be achieved during debinding. For the above cited considerations, compatibility of binder and powder is required. Generally speaking, compatibility of binder and powder means an appropriate degree of binder components adsorbing onto the powder surface. The consequences of such an adsorption event are improving the dispersion of powder in the binder, minimizing the separation of binder from the blend during moulding, but possibly enhancing the content of binder burnout residue.[2]

The binder used for powder injection moulding usually comprises of a major filler (wax or oil), a backbone polymer, a plasticizer, and a surface active agent.[1] Among these components, the surface active agent has the most dramatic effect on the process. Usually, a low molecular weight component is used as a surface active agent, which consists of a functional group adhering to the powder surface and an oriented molecular chain extending into the binder to prevent aggregation of powder. It serves as a bridge between the binder and powder and creates the stabilization of the particles when they are broken apart by mechanical shearing during mixing. Enhanced adhesion of binder components onto the powder surface is primarily realized by hydrogen bonding between the powder surface and the surface active agent through a Lewis acid (electron acceptor)–base (electron donor) reaction.[2]

The adsorption of the binder components onto the powder surface is competitive such that patterns similar to the Langmuir adsorption and desorption isotherms usually take place.[3] In such a competitive adsorption phenomenon, a good surface active agent can easily reach the monolayer coverage on the powder surface, or the plateau of the adsorption isotherm with a small amount of addition. The surface active agent can be a high molecular weight polar wax, such as carnauba wax or montan wax, or a low molecular weight material, such as fish oil or stearic acid.[1] The low molecular weight surface active agents are usually more effective in reducing the melt viscosity of the powder–binder blends than the high molecular weight ones due to their lower intrinsic

Table 1. Binder composition and characteristics of each component.

	Weight fraction	Density (g/cm^3)	Molecular weight (g/mol)	Melting point (°C)
Poly(butyl methacrylate)	0.35	1.03	100,000	156
Paraffin wax	0.60	0.90	350–420	59
Stearic acid	0.05	0.94	285	74

viscosities and higher polarities. However, interlinking strength among binder components is weak, due to the short chain lengths of the low molecular weight surface active agents, and necking during plastic forming occurs easily. On the other hand, a polymer having suitable functional groups in each repeating unit can enhance the interlinking strength among binder components, in addition to improving the adhesion force with the powder surface.

In this study, an acrylic resin was used as the backbone polymer. The intention of such a substitution was to enhance the adhesion strength between binder and powder, and the interlinking strength among the binder components by increasing the number of functional groups and the chain length of the surface active agent. The interaction between the binder and powder, as well as the rheological behaviour of the blend, are correlated with the plastic deformation behaviour of the blend.

2 EXPERIMENTAL

The powder used in this study was a commercial grade yttria doped zirconia powder (ZrO_2–3 mol%Y_2O_3, HYS 3.0, Daiich Kigenso Kagaku Kogyo Co. Ltd., Japan). The purity of this powder was 99.4%. It had an average particle size of 0.6 μm and a specific surface area of 6.9 m^2/g. The electrophoretic mobility of the powder determined in deionized water (pH = 7.2) was -2.96×10^{-8} m^2/V·s (zeta potential: −36.24 mV), indicating an average acidic powder surface.[4] The binder consisted of the components of an acrylic resin (poly(butyl methacrylate)), paraffin wax, and stearic acid. Table 1 shows the composition of this binder and some respective properties of each component.

The powder–binder blend, which had a fractional powder loading of 0.48 by volume or 0.85 by weight, was prepared with a Z-blade mixer, operated at 170°C for 1 h. The rheological behaviour of the blend was determined using a capillary rheometer 42 mm long and 2 mm in diameter. Rectangular bending specimens with dimensions of 72mm × 12 mm × 4 mm were moulded with a 120 ton reciprocating screw injection moulding machine.

The interaction between the binder components and powder was monitored using infrared (IR) spectroscopy. The transmission spectrum of the molecular bonds was recorded in the form of wavenumber, which is the reciprocal value of the wavelength (cm). The wavenumber was varied between 400 and 4000 cm^{-1}. The specimens were

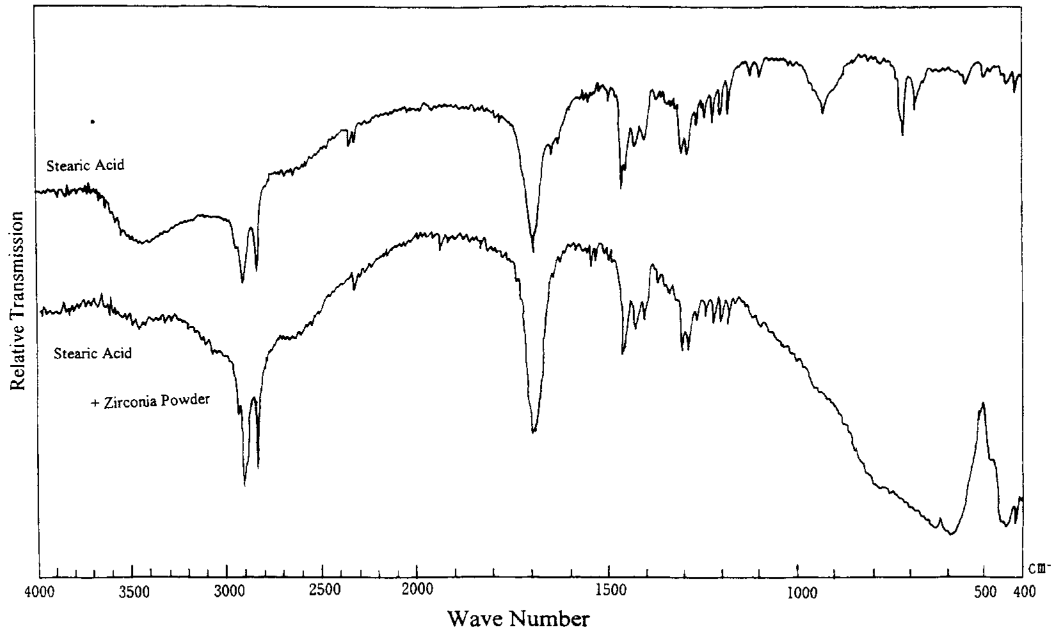

Fig. 1. IR absorption spectra of stearic acid and stearic acid mixed with zirconia powder.

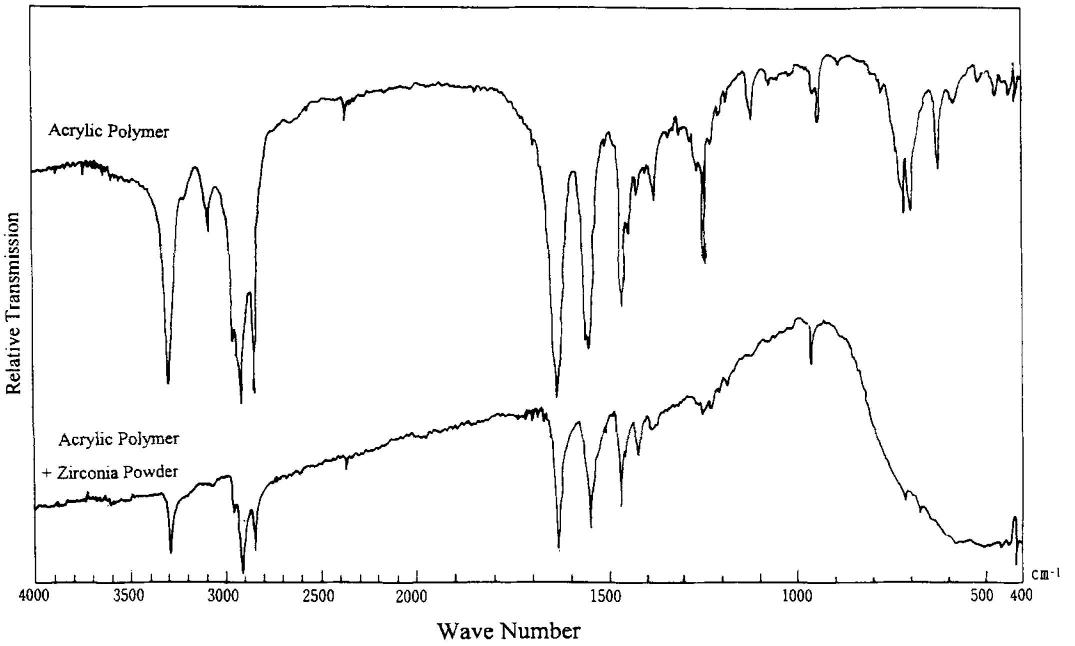

Fig. 2. IR absorption spectra of acrylic resin (PBMA) and acrylic resin mixed with zirconia powder.

prepared in the form of a thin film with the addition of KBr, which diluted the concentrations of the tested materials and assisted film formation. The wavenumber of the characteristic absorption peak of KBr was smaller than 400 cm^{-1}, so it did not interfere with the absorption patterns of interest.[5] The intensity change and the wavenumber shift of the characteristic absorption peaks were used as an indication of the change of the molecular bonding states.

3 RESULTS AND DISCUSSION

3.1 Interaction

The IR absorption spectra of stearic acid and stearic acid mixed with the zirconia powder are shown in Fig. 1. There was no shifting in wavenumber or significant change in intensity for the characteristic absorption peaks when stearic acid was mixed with the zirconia powder. In comparison, preferred adsorption of stearic acid onto an alumina powder surface by a Lewis acid–base reaction was justified by the shifting of the characteristic peak of the carbonyl functional group (CO) and change in intensity of the characteristic peak of hydroxyl functional group (O–H) in IR absorption spectra.[2] The different observations for stearic acid interacting with alumina powder and zirconia powder in the IR spectra could have arisen from the different surface charges for these two powders. The isoelectric point of alumina is about 9 (electrophoretic mobility $=0.22\times10^{-8}$ $m^2/V{\cdot}s$, zeta potential = 2.6 mV), indicating an average basic powder surface.[4] On the other hand, the zirconia powder used in this study had an average acidic powder surface (electrophoretic mobility = -2.96×10^{-8} $m^2/V{\cdot}s$, zeta potential = −36.24 mV). Therefore, the acid–base reaction occurs only when an appropriate powder–binder pair is used, which is the essential for achieving a homogeneous blend having a high interfacial binding strength.[6]

Figure 2 shows the IR spectra of PBMA and PBMA mixed with the zirconia powder. The intensities of the characteristic absorption peaks of the acrylate functional group (1150 cm^{-1} and 1250 cm^{-1})[5] weakened and almost disappeared when the acrylic resin was mixed with the zirconia powder. Such an observation indicated that an acid–base interaction event occurred between the acrylate functional group and the zirconia powder surface. The acrylate functional group is usually treated as a basic group (an electron donor) in polymer–solvent pairs.[7] Consequently, preferred adsorption of the acrylic resin onto the zirconia powder surface through a Lewis acid–base reaction is anticipated.

The effect of the acrylic resin as a surface active agent, in addition to as a backbone polymer, is different from the low molecular weight polar molecules such as stearic acid and fish oil. A schematic illustration of the difference is shown in Fig. 3. The acrylic resin was a long-chain polymer (MW = 100,000 g/mol), having an acrylate functional group in each repeating unit. Therefore, the same polymer chain of the acrylic resin can strongly adhere onto many particles and maintain

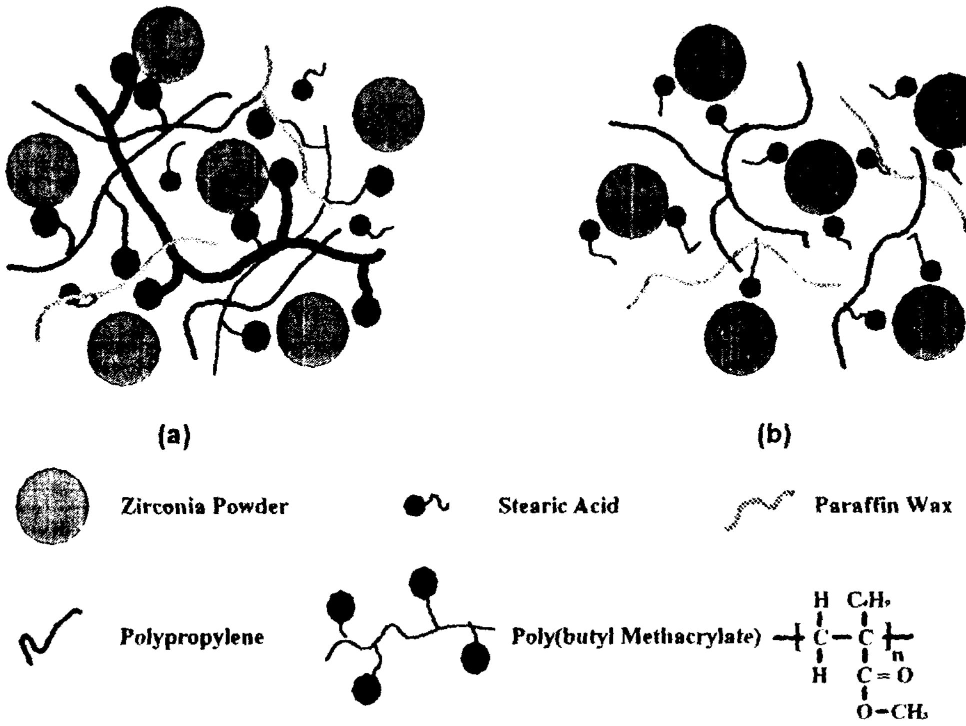

Fig. 3. A schematic illustration of the functions of surface active agents having different molecular weights on the interlinking of particles.

a strong interlinking strength with the other binder components. On the other hand, low molecular weight surface active agents can only adhere to a single particle without a strong interlinking strength among binder components.

3.2 Rheology

For the lack of a better approach, the rheological properties of a particulate-filled polymer are usually related in terms of apparent shear stress (τ_a) and apparent shear rate ($\dot{\gamma}_a$) through the power law:[8]

$$\tau_a = K\dot{\gamma}_a^n \tag{1}$$

where K is defined as the fluid consistency index and n is the flow behaviour index. The apparent viscosity (η_a) is defined as the ratio of apparent shear stress to apparent shear rate.

$$\eta_a = \frac{\tau_a}{\dot{\gamma}_a} = K\dot{\gamma}_a^{n-1} = K_0 e^{\frac{E}{RT}}\dot{\gamma}_a^{n-1} \tag{2}$$

where K_0 is a constant coefficient, E is the activation energy of flow, R is the gas constant, and T is the absolute temperature.

The flow curves for the blend at temperatures ranging from 120 to 200°C are shown in Fig. 4. Linear regression of these curves in log–log scale yielded values of fluid consistency index and flow behaviour index, which are listed in Table 2. The flow behaviour indices varied in the neighbourhood of one, indicating very consistent apparent viscosity values with respect to the variation of apparent shear rate. These flow curves were thus very similar to that of a Newtonian fluid. In comparison, the flow behaviour indices for most injection moulding blends using stearic acid as the surface active agent and a non-polar polypropylene as the backbone polymer lie in the range of 0.06[9] and 0.4–0.7.[10,11] A blend having a flow behaviour index in the neighbourhood of zero displays a shear thinning manner, by which the apparent viscosity is infinitely large at low apparent shear rates.

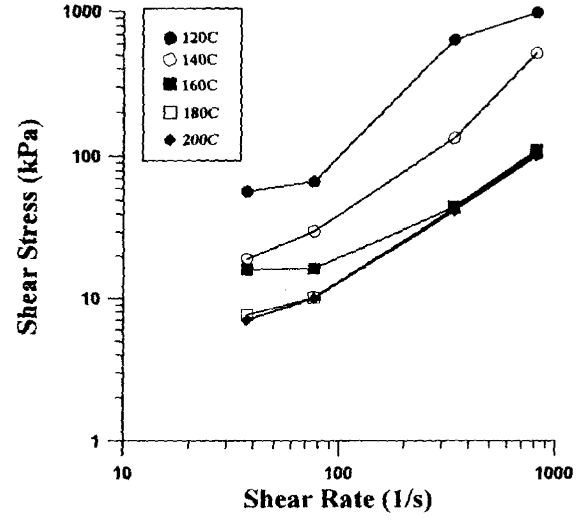

Fig. 4. Flow curves of the zirconia powder–binder blend at temperatures ranging from 120–200°C.

Table 2. Fluid consistency index (*K*) and flow behaviour index (*n*) for the zirconia powder–binder blend at different test temperatures

Temperature (°C)	*K* (Pa·s)	*n*
120	704	1.14
140	258	1.13
160	359	0.93
180	171	0.98
200	183	0.96

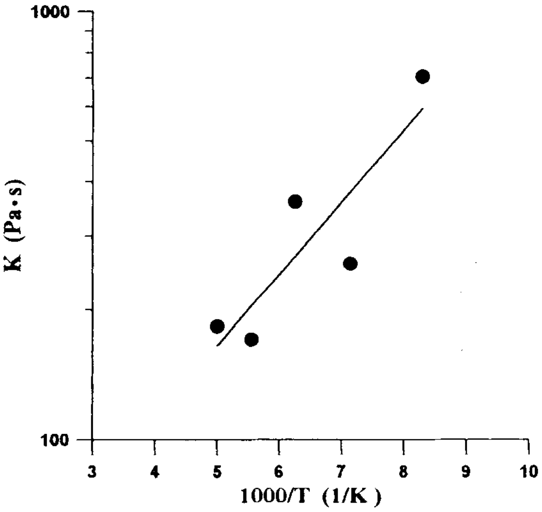

Fig. 5. Temperature dependency of fluid consistency index (*K*) in the form of an Arrhenius expression.

The interpretation of the distinctly different rheological patterns for the blends using the acrylic resin and stearic acid as the surface active agents can be derived from the conceptual illustration shown in Fig. 3. For the blend using stearic acid as the surface active agent, there is no strong binding force among particles due to a weak interlinking strength within the binder components that the friction coefficient decreases with the increase of the relative velocity of particles, a typical phenomenon of boundary lubrication effect.[12] On the other hand, the strong interlinking strength among particles due to the use of the acrylic resin caused a close to constant friction coefficient among particles, and, therefore, a close to constant viscosity with the variation of shear rate.

Figure 5 shows the temperature dependency of the fluid consistency index in the form of an Arrhenius expression. In the temperature range between 120 and 200°C, the activation energy of flow was 3.2 kJ/mol. Such a small value indicated that the dependence of the blend viscosity on temperature was very weak, even at temperatures lower than the melting point of the acrylic resin (156°C). In comparison, the activation energies of flow for various injection moulding blends lie in the range of 20 kJ/mol in the moulding temperature range.[13] Frequently, the activation energy of flow depends strongly on the melting point of the backbone polymer. For example, the activation energies of flow for a blend using polypropylene as the backbone polymer were 140 kJ/mol and 3.1 kJ/mol for temperatures lower and higher than the melting point of polypropylene, respectively.[9]

3.3 Superplastic behaviour

The weak dependence of the melt viscosity of the zirconia powder–binder blend on shear rate and temperature induced superplastic deformation behaviour under elongation. Figure 6 shows the zirconia fibres drawn at 140°C, one of which was sintered at 1400°C for 1 h. A reduction in diameter of more than 40 times (or more than 1000 times reduction in area) was experienced prior to necking down during drawing. The drawn fibres typically had diameters in the range of 20–100 μm. In addition, it was also viable to form ceramic springs by extruding the blend onto a rotating axe. Similarly, injection moulding of large parts having thin cross-sections was feasible as the chance of experiencing pre-matured freezing was reduced owing to the low activation energy of flow for the blend in the temperature range of interest. Such a superplastic deformation observation was not experienced previously for blends using stearic acid as the surface active agent.[9]

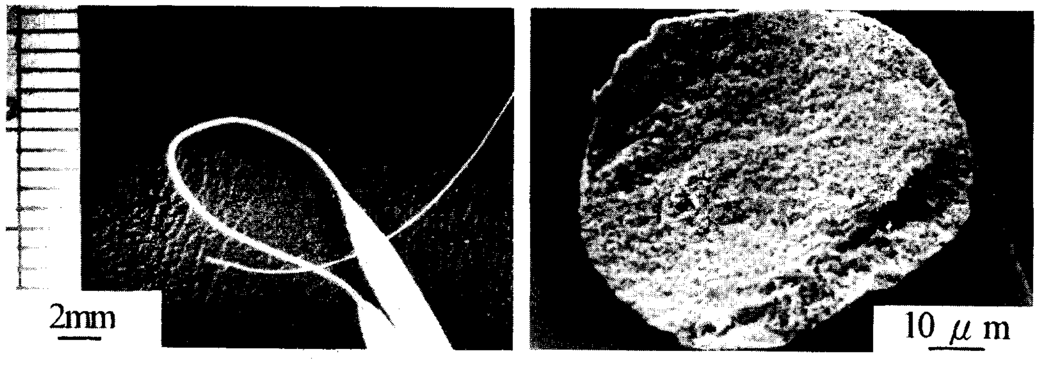

Fig. 6. Micrographs of polycrystalline zirconia fibres.

The required characteristics of the superplastic behaviour for a powder–binder blend during deformation are discussed in the following paragraphs and are contrasted to those for polycrystalline metals and ceramics.

Continuity of the powder–binder blend during deformation is a major factor determining the degree of elongation prior to necking down. A strong adhesion strength between the binder and powder, and a strong interlinking strength among binder components in a blend with homogeneous powder dispersion are required to achieve the continuity during deformation. The enhanced adhesion and interlinking strengths can also yield a high green strength. For example, the average green strength of the moulded specimens was 26 MPa, much higher than that (18 MPa) using stearic acid as the surface active agent.[9]

A guideline for accentuating superplastic behaviour for polycrystalline materials is testing the mateirals at low strain rates to avoid cavitation. Similarly, drawing the zirconia powder–binder blend to a large elongation required a low strain rate operation. Since the flow behaviour index of the blend lay in the neighbourhood of one in the temperature range of interest, the apparent viscosity of the blend was weakly dependent on the strain rate and could be approximated by the fluid consistency index (*K*). Therefore, the apparent viscosities at low strain rates (1–10 s^{-1}) lay in the range of 200–800 Pa·s, while those of blends exhibiting shear thinning behaviour were in the range of 2,000–30,000 Pa·s.[9] Cavitation or creep crack growth during tensile deformation can be induced at low shear rates by the high melt viscosity.[14]

The equation describing the superplasticity of polycrystalline metals and ceramics can be expressed by the power law:[14,15]

$$\sigma = c\,\dot{\epsilon}^{m} \qquad (3)$$

where σ is the normal stress, $\dot{\epsilon}$ is the normal strain rate, c is a constant, and m is strain rate sensitivity. The strain rate sensitivity (m) is equivalent to the flow behaviour index (n), through appropriate substitutions of normal stress and normal strain rate into shear stress and shear rate.[15] Based on eqn (3), large elongations result from the suppression of necking in polycrystalline materials with high values of strain rate sensitivity.[15] Typical values of strain rate sensitivity lie in the range of 0.5–0.7 for polycrystalline materials exhibiting superplastic behaviour.[14,15] An extreme case is hot glass (strain rate sensitivity = 1), which exhibits a Newtonian viscous flow pattern and can be drawn from the melt into glass fibres without the fibres necking down.[15] Therefore, the tensile elongation behaviour for the hot zirconia powder–binder blend was analogous to that for hot glass in that both have a similar rheological pattern and can be drawn into very thin fibres.

The mechanism for the superplasticity of single phase polycrystalline materials is usually attributed to grain shape accommodation by grain boundary sliding, with minor contributions from dislocation motion and diffusion creep.[16] The flow pattern for such a system is usually non-Newtonian. For the superplasticity of two phase polycrystalline materials containing a liquid phase, a liquid phase enhanced diffusion mechanism (solution–precipitation) is proposed.[17] The flow pattern for such a system is usually Newtonian. The powder–binder blend investigated in this study was a two phase system exhibiting close to Newtonian flow behaviour. However, there was no liquid phase enhanced diffusion mechanism involved in this system due to the mutual insolubility between the zirconia powder and the binder. A strong interfacial cohesion in the powder–binder blend was the principal mechanism in achieving the observed superplastic behaviour.

4 CONCLUSION

This research illustrated the possibility of using a functional polymer as the surface active agent and backbone polymer in powder injection moulding blends. A strong adhesion between powder and binder could be achieved through the interaction between the functional polymer and the powder surface, which in turn resulted in a rheological pattern similar to that of a Newtonian fluid. A blend exhibiting a superplastic pattern during tensile elongation was thus developed.

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