ELSEVIER

Ceramics International 25 (1999) 587–592

CERAMICS INTERNATIONAL

Control of yield stress in low-pressure ceramic injection moldings

D.-M. Liu*

Materials Research Laboratories, Industrial Technology Research Institute, Chutung, Hsinchu 31015, Taiwan

Received 25 May 1998; received in revised form 23 August 1998; accepted 13 October 1998

Abstract

Wax-based zirconia mixtures with solid content ranging from 55 to 60 vol% were prepared for low-pressure injection molding (LPIM) application. In LPIM, an appropriate yield stress of the suspension may be critical for two specific processes, namely, molding and thermolytic debinding. The former requires a low viscosity and yield stress which facilitates conveying and molding of the suspension at elevated temperatures. However, the latter requires the molded artifacts to have sufficient yield stress preventing deformation on thermolytic debinding. Therefore, to properly manipulate the suspension property, a better understanding and control of the yield stress of the suspensions becomes critical for optimization between the two processing stages in the LPIM process. In this investigation, the yield value of the suspensions together with the corresponding value for a successful LPIM application is described with an additional help by visual examination of the molded specimens during thermal debinding. The yield stress is correlated linearly with a dimensionless parameter, $\phi/A - \phi$ defined as flow resistance parameter, where A represents the maximum particle packing density and is shown to be related dynamically to the shear force. A further analysis also explain the yield stress as a result of the van der Waals attraction in the suspensions. A model is proposed for the determination of interparticle distance (λ) which produces the λ consistent in magnitude with those reported in literature. © 1999 Elsevier Science Ltd and Techna S.r.l. All rights reserved

Keywords: Low-pressure injection molding; Yield stress; Particle packing; Interparticle distance

1. Introduction

Low-pressure injection molding (LPIM) has recently been recognized as an attractive forming technique in the fabrication of high-precision, complex-geometry ceramic/metal parts in comparison to conventional injection molding. The latter technique usually requires a higher temperature and particularly a much higher pressure than those in LPIM. This would cause a number of drawbacks such as higher friction rate along molding system and particularly higher residual stresses within the molded artifacts in conventional injection moldings [1,2], which would frequently cause defects formation in subsequent thermal processing and damage final property [3].

In LPIM, the mixture must possess relatively high flowability at elevated temperatures typically in the neighbourhood of around 100°C. More specifically, the mixture should have a viscosity that is low enough to facilitate easy injection into the mold cavity, typically by a pressure source, such as compressed air, with a pressure frequently below 0.7 MPa [1]. In contrast, the molded parts should have enough strength, despite its low viscosity, which enables the parts to be survived during handling and subsequent thermal debinding without deformation. The former requires a lower yield stress; however, the latter, a higher yield stress. Therefore, some strength in between seems to be critical. In view of the literature, many efforts can be used to adjust suspension strength, for instance, solid concentration, degree of powder dispersion, particle property, and binder property, for specific green-shaping application. In this investigation, the solid concentration is chosen as the major variable for tailoring the suspension strength. Increase in solid concentration offers advantages such as better particle packing efficiency, improving shape retention ability, and ease of binder removal; however, it causes an increase in yield strength which enhances risk of molding ability in the LPIM process.

In practical LPIM application, binder removal of the molded parts is frequently carried out in a powder bed where both organic extraction by thermal wicking and

* Corresponding author at present address: Department of Materials Science and Engineering, University of Pennsylvania, 3231 Walnut Street, Philadelphia, PA19104, USA.

PII: S0272-8842(98)00066-2

shape retention of the parts can be achieved simultaneously. This is not a cost-effective process and in some cases particularly for parts requiring a delicate dimensional control, an improper embedding of the parts in powder bed may cause undesired deformation after debinding. Therefore, an optimization of suspension strength, or, in other words, the yield stress of the suspension under the LPIM process is critically required and this is the focus of the current investigation. As one realized, the yield stress of a powder suspension is a direct reflection of the forces between particles, such as interparticle repulsive/attractive forces and friction forces [4] provided that the stress of matrix fluid is negligible. These forces can be manipulated through the use of dispersant/additives [5,6] and/or solid content in the suspension [7,8]. In this study, we characterize the rheological behavior, particularly the yield stress, of the suspension as a function of solid content. An optimal strength for a successful LPIM application is determined.

2. Experimental procedures

In this investigation, mixtures containing yttria-stabilized zirconia powder (Tosoh-3YS, Japan, average particle size = 0.25 μm, Fig. 1) in 55%–60% solid fraction and paraffin wax (Echo Chemicals, Taiwan, melting point = 56°C and average molecular weight = 500) were prepared. A proprietary dispersant, 12-hydroxystearic acid (Tokyo Chemicals Inc. Japan) (~1 wt% on powder basis), was used, which is a derivative of stearic acid. The rheological data of the suspensions are determined using a cone-and-plate viscometer with shear rate ranging from $0.1\,s^{-1}$ to $10\,s^{-1}$ at a temperature of 85°C. The yield stress (τ_y) can be calculated by extrapolation at zero shear rate, $\gamma = 0$ with the help of Casson's model [9] which has been successfully applied to a number of suspension systems [7,8,10],

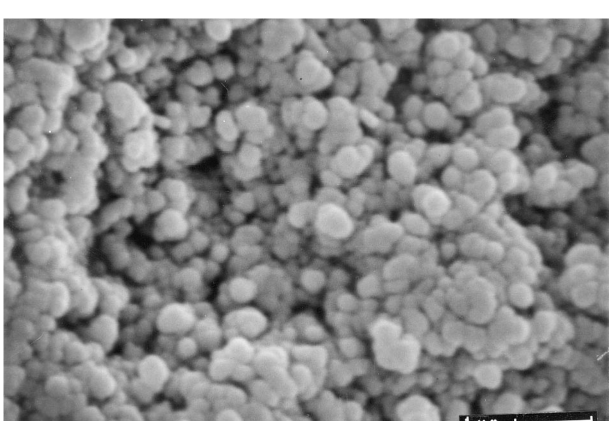

Fig. 1. Morphology of the zirconia powder used in this study.

$$\tau^{1/2} = \tau_y^{1/2} + c\gamma^{1/2} \quad (1)$$

The mixtures were processed through a low-pressure injection molding equipment (Peltsman Corp., USA). Prior to molding, the mixtures were vigorously stirring and degassing for 20 min in a container. The temperature was kept at 85°C and the pressure, 0.5 MPa, was supplied by an air compressor. The metal mold with a predetermined cylindrical-shape cavity has a temperature of 30°C though a water cooling system. Some of the successfully molded artifacts were placed into an oven under 100°C for a period of time for shape retention test by visual examination. In the molding operation, mixtures containing higher solid fraction were too viscous to be processed and thus were abandoned in subsequent visual test.

3. Results and discussion

3.1. Flow behavior

Fig. 2 illustrates a typical shear rate (γ)-viscosity (η) relation of the suspensions. lie suspensions are shear-thinning and the linearity in the logarithmic $\gamma - \nu$ plot indicates that the suspensions follows a power law dependence, i.e. $\nu = k\gamma^{n-1}$. The change in flow index (n), from $n = 0.64$ for 55% to nearly 0 for 60% loading, suggests a significant change in suspension structure. This change in the flow index is considerably different from the suspensions previously prepared using stearic acid as dispersant where the n values determined were only slightly decreased with solid fraction [11] which suggests the presence of strong interaction of the adsorbed macromolecules between approaching particles in the suspensions. However, a detailed study of this subject is not the focus of current investigation and will be reported elsewhere.

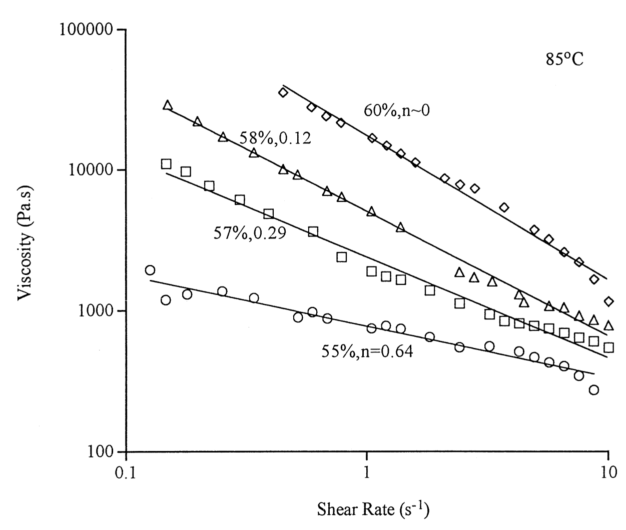

Fig. 2. Flow curves of the suspensions with varying solid concentrations and corresponding flow index, n.

One interesting phenomenon is observed in the 55% suspension which behaves much more like a Newtonian fluid (strictly, it is non-Newtonian) than others and appears to exhibit desirable fluidity (good flowability) under gravity as visually observed. The observed fluid-like nature for 55% suspension at 85°C indicates the least ability of shape retention, i.e. the molded parts are easily collapsed, upon heating. However, increase in solid content improves shape retention ability but it shows a gradual disappearance of fluid-like nature as the solid fraction is above 57%; that is, the shape of the molded parts was almost perfectly kept at rest upon heating when the solid content is greater than 57%. This observation indicates the small operation window (from the viewpoint of solid content) between moldability and shape retention of the mixtures currently prepared for LPIM.

Fig. 3 displays the result of shape retention test before and after thermal treatment at 100°C. The solid concentration is limited to the range of 55–57 vol%. Clearly, at solid fractions below 57%, the molded specimens behaved like fluid and collapsed easily; however, a better shape retention ability is observed for 57%-loading suspension over the same treatment. This suggests a better suspension strength can be produced to meet, to some extent, both the molding and the thermal debinding requirements. Therefore, a quantitative understanding of the suspension strength is critical, especially in terms of a more fundamental aspect such as the potential between particles which will be elucidated in later discussion.

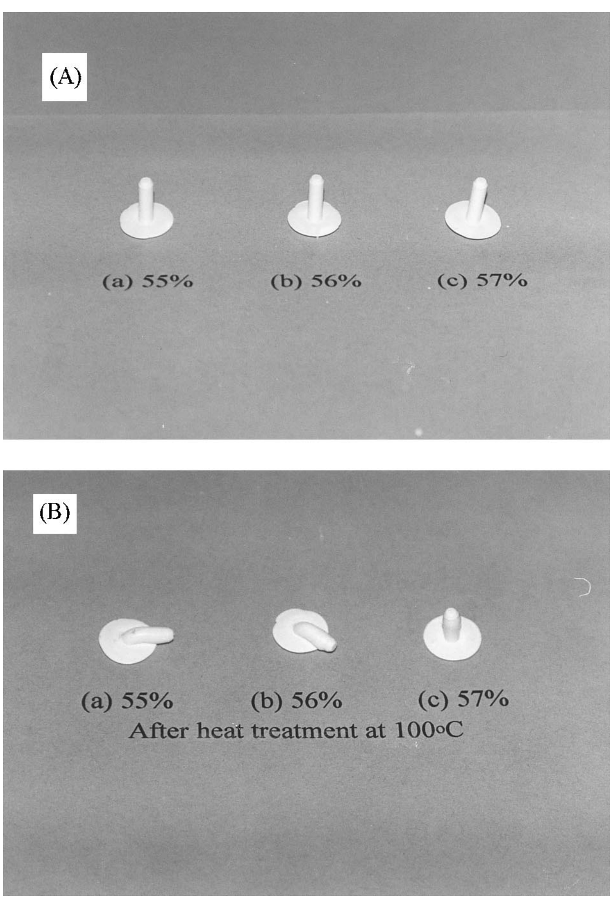

Fig. 3. The photographs showing the deformation of the molded artifacts (ceramic ferrules) (A) before and (B) after thermal treatment.

3.2. Yield behavior

These suspensions are non-Newtonian and can be analyzed using Casson's model [9], shown in Fig. 4. All the suspensions exhibit a linear $\tau^{1/2} - \gamma^{1/2}$ relationship which accordingly suggests the presence of connected particle networks. These particle networks are believed to be a result of interparticle attraction. That is to say, these suspensions are flocculated in different levels depending on solid content. If this statement is correct, it is suggested that the dispersant can only provide some sufficient level of steric: stabilization rather than a complete steric stabilization. This can further be evidenced both by visual examination on its good fluidity in 55% suspension and from its relatively low yield value (in coming discussion). These particle networks impart different levels of strength upon suspensions, resulting in different yield stresses, i.e. the intercept values in $\tau^{1/2} - \gamma^{1/2}$ straight lines. The higher the suspension strength, e.g. 60% loading, indicates a stronger panicle network structure (i.e. highly flocculated due to stronger interparticle attraction) and a better shape retention ability of the molded parts is expected. However, the suspension with increased solid concentration gradually loses its fluid-like nature untill a critical loading is attained where the suspension behaves somewhat like a solid and can hardly be moldable under the LPIM process.

By extrapolation of the $\tau^{1/2} - \gamma^{1/2}$ straight lines to zero shear rate and plugging the obtained yield stress in

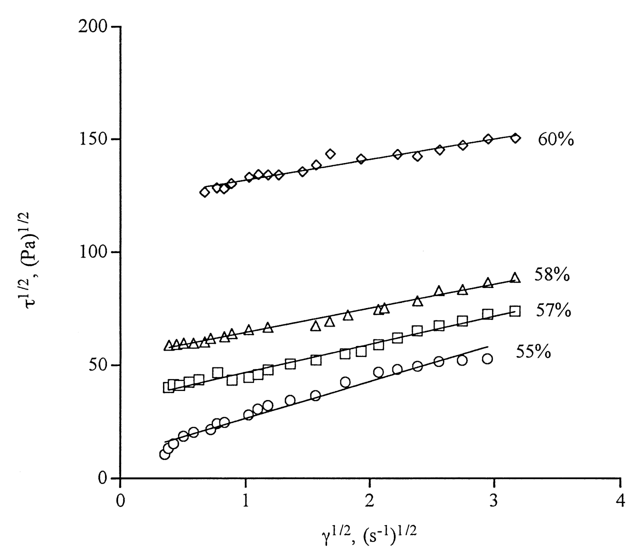

Fig. 4. A Casson's plot for the suspensions with different solid concentrations.

terms of the solid fraction (ϕ), Fig. 5 shows the resulting correlation. The yield stress increases roughly in a power manner with solid fraction, i.e. $\tau_y \sim \phi^m$, which is consistent with other reports in different suspensions [5,12,13]. From the viewpoint of moldability, suspensions with solid concentration within the range of 55–57%, corresponding to a suspension strength from 0. 1 kPa–1 kPa at rest, exhibits fluidity best for the LPIM. However, by taking the shape retention ability into account, we find a suspension strength in the neighbourhood of 1 kPa is more suitable whilst the molded parts were easily deformed when the solid concentration is below 57%, as has been revealed in Fig. 3. These findings suggest an optimal solid concentration for the LPIM process to be approximately 57%.

The increased yield stress with increasing solid concentration indicates an increase in the particle network strength. This suggests a more fundamental relation between the yield stress and suspension microstructure that has to be realized. One important parameter to characterize the suspension microstructure is the maximum particle packing density (ϕ_m) This parameter has been reported as a function of shear in flocculated suspensions [13]. At high shear, the corresponding ϕ_m would be higher than that attainable at low shear. This is primarily because a higher shear force is able to overcome a higher network strength compared to that using lower shear force until a point, i.e. ϕ_m at which the movement of particles (or particle networks or clusters) in the matrix fluid is highly inhibited and suspension viscosity becomes infinite. This indicates a dynamic nature of the ϕ_m, with respect to shear. In this case, we correlate the suspension viscosity with solid concentration under shear rates of $0.5\,s^{-1}$ and $5\,s^{-1}$, as illustrated in Fig. 6. The data appear to follow a power law dependence as denoted in corresponding solid curves.

It is interesting to note that at lower shear, suspension viscosity increases significantly when the solid fraction is greater than $\phi \sim 0.6$ and the viscosity tends to approach infinity when ϕ is close to 0.615. However, this is not the case at higher shear rate, i.e. $5\,s^{-1}$, where ϕ_m, is apparently greater than that observed at lower shear. These findings strongly suggest that the maximum packing density of the suspension should behave as a function of shear and should not be taken as a constant value in given flocculated suspensions as commonly used in the literature. Kitano et al. [14] have defined an apparent maximum packing density with a capital letter A instead of ϕ_m. As they suggested that, in practical cases, the term A appears to involve more generalized and physically meaningful interpretation on particle packing efficiency for a given suspension structure than does the term ϕ_m. With this in mind, it may be reasonably to realize that the value A is basically a suspension-structured dependent which is strongly related to the size and spatial arrangement of particle networks in a suspension. In other words, the value A represents essentially a dynamic packing structure under which a maximum packing density is attainable over a given spatial distribution of particle networks of different sizes in a given suspension.

In a previous communication [7], the present author proposed an empirical model to correlate the yield stress of suspensions with the apparent maximum packing density A by the equation;

$$\tau_y = C_1 \frac{\phi}{A - \phi} - C_2 \tag{2}$$

where constants C_1 and C_2 represent attractive and repulsive components of the suspension, respectively, which can be determined experimentally. The dimensionless term $\phi/A - \phi$ defined as the flow resistance

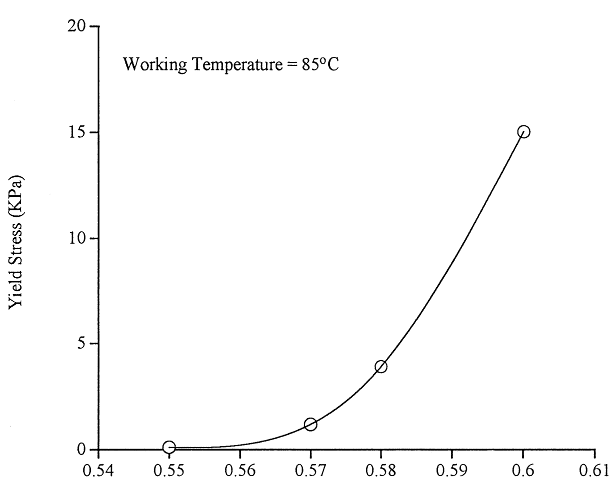

Fig. 5. Yield stress of the suspensions as an increasing function of solid concentration.

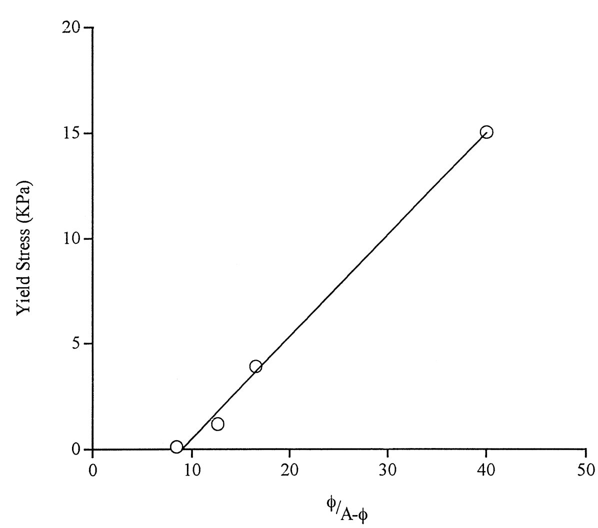

Fig. 6. Yield stress of the suspensions as a linear function of the flow resistance parameter, $\phi/A - \phi$.

parameter of the system, indicating the effective space available for the particles to move freely in a matrix fluid. Therefore, Eq. (2) involves both the interparticle potentials and friction effect among particles/clusters as well. The yield stress becomes infinite only when $\phi => A$, wherein the particles "lock" in position relative to their nearest neighbors. For the suspensions currently prepared, as expected from Eq. (2), a straight line was obtained in a $\tau_y - \phi/A - \phi$ plot, as shown in Fig. 7 with $A = 0.615$.

3.3. Correlation between τ_y and interparticle attractions

According to a recent article by Song et al. [16], who indicated that the interparticle attractions play critical role in the yield stress in these non-polar, wax-based suspensions. This attractive force (F_{vdw}) should arise from the Van der Waals potential which can be expressed between two identical spheres of radius r by,

$$F_{\text{vdw}} = -\frac{\text{H}r}{12\lambda^2} \quad (3)$$

where H represents the effective Hamaker constant between the medium and solid and λ is the interparticle distance. In the suspensions of different solid concentrations, the interparticle distance should be accurately determined. In a recent paper by Agarwala et al. [17] who used an equation by modifying a computation model deduced from stereological technology [18] to calculate the mean surface-to-surface distance (λ) of two identical spheres of radius r in a given suspension, which has a form related to the solid fraction (ϕ) by,

$$\lambda = \frac{4}{3} r \frac{1-\phi}{\phi} \quad (4)$$

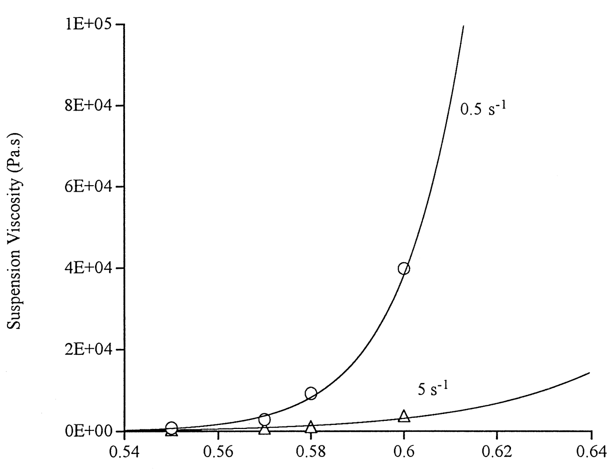

Fig. 7. Suspension viscosity increases exponentially with solid concentration and exhibits different behaviors under different shear rates.

However, this equation may be too optimistically to give a true representation of interpartilclve distance primarily because it averages the fraction of the matrix phase, i.e. the term $(1 - \phi)$, over the fraction of particulate phase in a given suspension without considering the realistic particle packing structure. That is, the particles are closely in contact when $\phi => A$ or ϕ_m and the value λ should be approached to 0 rather than some finite value based on Eq. (4). In other words, the effective space for particles to move in a suspension should be $(A - \phi)$ rather than $(1 - \phi)$. The value λ calculated from Eq. (4) would certainly be an overestimate value. Therefore, by taking the concept of particle packing efficiency into account, Eq. (4) can be re-formulated in terms of $(A - \phi)$ as;

$$\lambda = \frac{4}{3} r \frac{A-\phi}{\phi} \quad (5)$$

A comparison of λ calculated from Eqs. (4) and (5) for the suspensions under investigation is given in Table 1 with $r = 125$ nm and $A = 0.615$. Obviously, Eq. (4) produces an interparticle distance greater by over an order of magnitude than that from Eq. (5). In comparison with a recent paper on estimate of interparticle distance in Al_2O_3 suspensions over similar range of solid contents [18], the λ computed from Eq. (5) in current suspensions is close in order-of-magnitude to the value reported. Furthermore, when the particles are closely in contact at some critical concentration, i.e. $\phi = A = 0.615$ in this case, the λ should be zero rather than 104 nm, a value near the size of particle radius. Therefore, from the viewpoint of particle packing, Eq. (5) appears to provide more reasonable estimation on interparticle distance in particularly highly-concentrated and flocculated suspensions.

As a rough approximation, we may take the resulting yield stress of the suspensions as a function proportional to F_{vdw}, which gives

$$\tau_y \sim cF_{\text{vdw}} \quad (6)$$

From Eqs. (5) and (6) together with the obtained λ, it is possible to correlate the τ_Y with the inverse square of λ

Table 1
A comparison of the interparticle distance (λ in nm) calculated from Eqs. (4) and (5)

Solid fraction (ϕ)	λ from Eq. (4)	λ from Eq. (5)
0.55	136.4	19.7
0.57	125.7	13.2
0.58	120.7	10.1
0.60	111.1	4.2
0.615[a]	104.3	0

[a] A fraction corresponding to the maximum packing density of the particles in the suspensions under a shear rate of $0.5\,s^{-1}$.

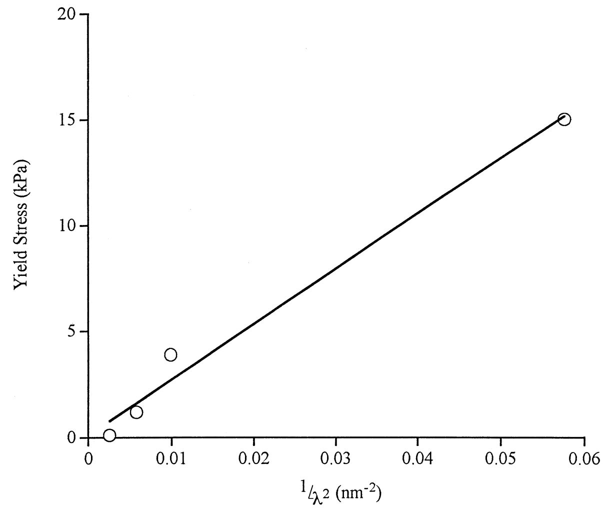

Fig. 8. Yield stress of the suspensions increases linearly with the inverse square of interparticle distance ($1/\lambda^2$).

and this is shown in Fig. 8 where a straight line with a correlation coefficient as good as 0.985 results. This finding suggests that the van der Waals attraction should be responsible for the yield stress in the suspensions to a significant extent. This can also be verified by both the rheological behavior illustrated in Fig. 2 and the calculated yield values through Casson's equation.

4. Concluding remarks

The present investigation demonstrates the importance of yield stress on a control criterion for low-pressure ceramic injection moldings. Suitable solid fraction for a given powder can be obtained with consideration of both moldability of the mixture and shape retention of molded parts during subsequent thermolysis and in this case, the best solid fraction in the suspensions is in the neighbor of 57% in volume, corresponding to a yield stress of ~1 kPa. Molded parts with solid fractions lower than 57% are easily collapsed on thermolysis, however, higher than the critical value, the mixtures can hardly be moldable.

The yield stress of the suspension can be linearly related to a newly-defined parameter $\phi/A - \phi$, termed flow resistance parameter, where A is the apparent maximum packing density of a suspension. In this study, we find that A is strongly related to suspension structure and is dynamically affected by the shear rate; a lower A is apparently attributed to low shear rate and vise versa. With incorporation of the A into a model for particle-to-particle distance (λ) calculation, the λ obtained appears to present a more reasonable and physically meaningful value in a given real suspension.

Acknowledgement

The author is gratefully indebted to the Minister of Economic Affairs, Taiwan, for financial support towards the research work under contract no. 863QB1000.

References

[1] J.A. Mangels, Low pressure injection molding, Am. Ceram. Soc. Bulletin 73 (5) (1994) 37–41.
[2] E. Morales, J.R. White, Residual stress and molecular orientation in particulate-filled polypropylene, J. Mater. Sci. 23 (1988) 3612–3622.
[3] M.S. Thomas, J.R.G. Evans, Non-uniform shrinkage in ceramic injection moldings, Br. Ceram. Trans. J. 87 (1988) 22–26.
[4] V. Ramakrishnan, S.G. Pradip, Malghan, Yield stress of alumina-zirconia suspensions, J. Am. Ceram. Soc. 79 (10) (1996) 2567–2576.
[5] D.M. Liu, Effect of dispersant on the rheological properties in zirconia-wax suspensions, J. Am. Ceram. Soc. in press.
[6] S. Novak, K. Vidovic, M. Sajko, T. Kosmac, Surface modification of alumina powder for LPIM, J. Europ. Ceram. Soc. 17 (1997) 217–223.
[7] D.M. Liu, W.J. Tseng, Yield behavior in zirconia-wax suspensions, Mater. Sci. Eng.254(1–2) (1998) 136–146.
[8] M.J. Edirisinghe, H.M. Shaw, K.L. Tornkins, Flow behavior of ceramic injection molding suspensions, Ceram. Int. 18 (1992) 193–200.
[9] N. Casson, A Flow equation for pigment oil suspensions of the printing ink types, in: C.C. Mill (Ed.), Rheology of Disperse Systems, Pergamon Press, London, 1959, pp. 84–104.
[10] J.C. Chang, F.F. Lange, D.S. Pearson, Viscosity and yield stress of alumina slurries containing large concentrations of electrolyte, J. Am. Ceram. Soc. 71 (1) (1994) 19–26.
[11] D.M. Liu, W.J. Tseng, Rheology of zirconia-wax suspensions, J. Mater. Sci. in press.
[12] T. Kataoka, T. Kitano, M. Sasahara, K. Nishijima, Viscosity of particle filled polymer melts, Rheol. Acta. 17 (1978) 149–155.
[13] C.R. Wildemuth, M.C. Williams, A new interpretation of viscosity and yield stress in dense slurries: coal and other irregular particles, Rheol. Acta. 24 (1985) 75–91.
[14] T. Kitano, T. Kataoka, T. Shirota, An empirical equation of the relative viscosity of polymer melts with various inorganic fillers, Rheol. Acta. 20 (1981) 207–209.
[15] T. Dabak, O. Yucel, Shear viscosity behavior of highly concentrated suspensions at low and high shear rates, Rheol. Acta. 25 (1986) 527–533.
[16] J.H. Song, J.R.G. Evans, Flocculation after injection molding in ceramic suspensions, J. Mater. Res. 9 (1994) 2386–2397.
[17] M.K. Agarwala, B.R. Patterson, P.E. Clark, Rheological behavior of powder injection molding model slurries, J. Rheol. 36 (21) (1992) 319–334.
[18] R.T. Defloff, F.N. Rhines, Quantitative Microscopy, McGraw-Hill, New York, 1968.
[19] S. Novak, U. Kunaver, A. Zupancic, Effect of interparticle distance on rheological properties of ceramic formulation for LPIM, Proceedings in Powder Injection Molding, German, 1997, pp. 97–104.