

Influence of stearic acid on the structure and rheological behavior of injection-molded ZTA suspensions

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The zirconia-toughened-alumina (ZTA) composite powder was exposed to a prior ball milling treatment with a small amount of stearic acid (SA) before the traditional blending process. The effect of different amounts of stearic acid on surface properties of the powder, the particle size distribution of the powder, and the rheological properties of the suspension were systematically studied within the design of experiments. Fourier transformation infrared spectroscopy (FTIR) analysis was used to prove the chemical interaction between the stearic acid and the ZTA powder. The effects of SA content on the particle sizes and their distribution were carefully examined. Rheological properties such as viscosity, yield stress, and power law exponent of the suspensions were determined within a temperature range of 140 - 170 °C. The optimal content of SA to improve the properties of the suspensions was found to be 3 wt.%.

Keywords: ZTA suspension; ceramic injection molding; rheological property

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1. Introduction

Ceramic injection molding (CIM) has received more and more attention due to its advantages in producing complex components on a large scale [1]. It is a near-net-shaping technology which can minimize the expensive finishing expenses of sintered parts. The typical ceramic injection molding process involves the preparation of suspensions, injection molding, debinding and sintering. Many studies have been devoted to the monophase ceramics such as Al₂O₃, ZrO₂ or Si₃N₄. As a widely used multiphase ceramics, zirconia toughened alumina (ZTA) ceramics attracted considerable attention in recent years mainly because of their excellent mechanical properties, but only few studies were focused on the fabrication of ZTA composites by the CIM process.

One of the most critical issues in CIM process is to obtain low viscosity suspensions with high solid loadings, which are primarily composed of ceramic powders, organic vehicles, and a small amount of surfactant [2, 3]. Since a perfect binder system for various powders is still difficult to attain, many researches focused on the surfactants including carboxylic acids (such as oleic acid, stearic acid, 12hydroxystearic acid and so on), titanate coupling agent [4], amines [5], menhaden fish oil, and some other commercial surfactants [6–8].

Among all these surfactants, the suspension modified by stearic acid (SA) exhibits a relatively low viscosity and yield stress [9]. Due to its particular structure, stearic acid can decrease the friction force among the powder particles, and disperse the powder particles much more easily, meanwhile enhancing the adhesion strength between the binder and the powders [3]. However, the content of stearic acid as a dispersant in a suspension is one of the most crucial parameters for the suspension preparation. Tseng [10] found that the viscosity and yield stress in the suspension decreased proportionally with the increase in the stearic acid fraction. Dean [11] also found that the increasing amount of SA would greatly enhance the characteristics of the suspension. Although most results encourage to increasing the amount of stearic acid in the suspension, there are also some conflicting views on this point. Li Yiming [12] discovered that while the content of SA exceeds 5 %, only little decrease in viscosity

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Stearic acid fraction	Composition (wt.%)				
(wt.%, with respect	Alumina	Zirconia	Stearic	Paraffin	high-density
to powder loading)			acid	wax	polyethylene
1	72.74	12.39	0.85	8.41	5.61
2	72.74	12.39	1.70	7.90	5.27
3	72.74	12.39	2.55	7.39	4.93
4	72.74	12.39	3.40	6.88	4.59

Table 1. Composition of ceramics/binder mixtures.

can be observed. Thomas [13] considered that the suspension containing a moderate stearic acid concentration had the best characteristics. An excessive stearic acid concentration leads to a multilayer coverage of the surface with the particles, and the outer layer of the stearic acid, which shows higher viscosity compared to paraffin, only fulfills the function of low viscous paraffin. S. Novak [5] also confirmed by sedimentation tests that the most stable suspension contained moderate stearic acid concentration. Although the studies on the rheological behavior of suspension with SA are comprehensive, the influence of stearic acid on the suspension structure is still on debate, especially when the amount of SA is excessive. In terms of the analysis of the surface modification and the particle size distribution of ZTA powder, the influence of SA amount on the suspension structure is carefully explored in this study, and the rheological behavior of the suspension is studied based on the suspension structure.

2. Experimental procedures

Prior to being mixed with the polymer binders, zirconia (QZ-3Y-T, Guangdong oriental zirconium Co., China) and alumina (UPC998F, Zhejiang chemical Co., China) the powders were dried at 105 °C for 180 min and then milling treated together with different amounts from 1 wt.% (basis of powder) to 4 wt.% of stearic acid (reagent grade, chemical reagent Co., China). The volume ratio of alumina to zirconia powder was 9:1. Wet milling was performed for 16 h in alcohol medium with rubber lining and ZrO₂ milling balls. Subsequently, the powders were dried at 130 °C for 24 h and then were kneaded in a two-blade kneader (NH-1500, Rugao Machinery, China) with organic vehicle. The ceramics powder was first mixed with high-density polyethylene (HDPE, 5000S, China Petrochemical Co., China) at 160 °C until all the HDPE had melted. After that, the paraffin wax (PW, China petrochemical Co., China) was added at 140 °C for half an hour. The ceramic suspensions contained 55 vol.% of ceramic powder. The composition details of the binder mixtures are shown in Table 1.

The rheological behavior of the suspensions were characterized by high pressure capillary rheometry (XLY-II, Jilin University Instrument Co., China) through a 20 mm long nozzle, 1 mm in diameter, in the shear stress range from 3.92 to 11.76 MPa and at temperatures of 140 to 170 °C. The shear rate was corrected for the non-Newtonian behaviour of suspensions using the Weissenberg-Rabinowitsch method [14],

$$n = d \lg \tau_w / d \lg \gamma_a \tag{1}$$

$$\gamma = (3n+1)\gamma_a/4n \tag{2}$$

where γ is the shear rate, γ_a is the apparent shear rate. The chemical characteristics of ZTA powders before and after surface modification were analyzed by Fourier transformation infrared spectrometer (FTIR-6700, Nicolet, USA) operated from 4000 to 400 cm⁻¹. Particle sizes and their distribution were determined with a laser diffraction analyzer (Winner 2000 B, Jinan Micro-nano, China). The shape and the dispersity of the powder specimens were examined with the aid of scanning electron microscopy (JXA-840, Jeol, Japan).

3. Results and discussion

3.1. FTIR analysis

FTIR analysis was performed to confirm the binding mechanism of stearic acid with the surface



Fig. 1. Infrared absorption spectra of (a) Al₂O₃ powder and ZTA powders with (b) 1.0 wt.% SA;
(c) 2.0 wt.% SA; (d) 3.0 wt.% SA; (e) 4.0 wt.% SA; (f) pure SA, respectively.

of the powders. Fig. 1 shows the infrared absorption spectra for pure SA, pure alumina powder and ZTA powders with different amounts of SA. Fig. 1(a) is the infrared absorption spectrum of pure alumina powder. As for inorganic matter, only a strong peak appeared at 3446 cm^{-1} , which denotes the vibration peak of hydroxyl (-OH). It indicates that the surface of alumina powder is abundant in hydroxyl group resulting from the unsaturated bonds on the powder surface. Fig. 1(f) is the infrared absorption spectrum of pure stearic acid; the characteristic peak of the carbonyl group in the stearic acid appears at 1704 cm^{-1} which confirms that the carbonyl group of SA is in a dimerized state. The exact frequency of this group depends upon the nature of the neighboring groups. The peaks at 2918 and 2850 cm^{-1} correspond to the antisymmetric and symmetrical stretch vibration absorption peaks of CH₂, respectively, which remained in the powders modified by SA as shown in Fig. 1(b - e). However, the peak at 1704 cm^{-1} has disappeared compared with the pure SA, which indicates that the groups adjacent to carbonyl group (C=O) were changed and no COOH groups remained. Moreover, the intensity of the vibration peak of hydroxyl weakened, implying that there might be a reaction between hydroxyl and SA. Meanwhile, one new peak at about 1638 cm^{-1} emerged instead, representing the absorption of SA on ceramics to form metal–O–CO–bond, since a metal-stearate stretching frequency is usually at about 1560 – 1650 cm⁻¹ [15–18]. In addition, with the increase of SA amount, the intensity of the new peak obviously enhanced, which indicates that the degree of chemical adsorption of SA with alumina powders increased. The above analysis of FTIR indicates that the surface of the ceramics powders was chemically modified by stearic acid through the esterification reactions between the carboxyl group of SA and hydroxyl group of the powder surface, which may greatly improve the surface properties of the inorganic powders.

3.2. Particle size analysis

The microstructure of ZTA powders modified by stearic acid is shown in Fig. 2. Combined with the data of the particles size distributions (Fig. 3), it can be easily concluded that the particles with 3 wt.% SA are characterized by more uniform dispersity and narrow distribution compared to the other compositions. However, irregular particles sizes and distributions can be observed in the powders with 4 wt.% SA content. Generally speaking, the surfactants such as SA can cover the surface of the particles as a result of the permeation pressure caused by the capillary pores, which can be expressed as follows:

$$\Delta P = 2\gamma_{LV}\cos\theta/R \tag{3}$$

where R is the radius of the capillary pipe, γ_{IV} is the interfacial tension of the binder and θ is the wetting angle of the powder by the liquid binder. It has been reported that increasing of the SA amount can significantly decrease the wetting angle [12], and consequently increase the permeation pressure. In other words, the rise of SA content can not only increase the surface coverage in order to form the adsorption layers, but also can play a positive role in enhancing the covering efficiency by increasing the permeation pressure, and thereby greatly prevent the powders from reagglomeration, and finally reduce the particle size of the powders. Wenjea found that the stearic acid coverage on the particle surface shows a typical Langmuir behavior and rises above 90 % when the acid fraction is about 3 wt.%. Nevertheless, when the adsorption monolayer reaches



Fig. 2. SEM micrographs of the ZTA powders modified with (a) 2.0 wt.% SA; (b) 3.0 wt.% SA; (c) 4.0 wt.% SA.



Fig. 3. Particle size distribution of ZTA powders with the varying addition of SA.

a saturated level and multilayers occur on the powder surface, the agglomerates become much more serious [10–12], which might happen in the case of the samples with 4 wt.% SA, as shown in Fig. 2(c).

It seems that a large excess of stearic acid exists when the amount of SA approaches 4 wt.%. The crosslinking of the polar ends of the superfluous molecules or winding their nonpolar chains could influence the particle agglomeration [19].

3.3. Rheological properties

3.3.1. Viscosity

The dependence of viscosity on shear rate could be described using the Oswald-de Waele power law:

$$\eta = K\gamma^{n-1} \tag{4}$$

where η is the viscosity, *K* is the consistence coefficient, γ is the shear rate, and *n* is the power law exponent giving the deviation from the Newtonian behavior (for *n* = 1 a Newtonian liquid is concerned). Similar to the previous investigations [19–21], the highly concentrated suspensions exhibited a pseudoplastic behavior over the shear-rate range of this study. As shown in Fig. 4, when the addition of SA



Fig. 4. Viscosity of suspensions with the varying addition of SA at powder volume fraction V = 0.55 as a function of shear rate at a temperature of 140 °C.

varied from 1 wt.% to 3 wt.%, the viscosity of the suspension decreased, which may also result from the dispersing effects of stearic acid addition. In this sense, the use of SA leads to more uniform powder packing and homogeneous suspension, and the suspension containing 3 wt.% SA has the lowest viscosity. The suspension with 4 wt.% SA shows the highest viscosity when compared with other suspensions, which is not in in accord with the view of Sotomayor [22], who considered that a relatively wide particle size distribution led to relatively low viscosity, based on a well-known model of relative viscosity:

$$\eta_{\gamma} = A (1 - \delta / \delta_{MAX})^{-m} \tag{5}$$

where η_{γ} is the viscosity of binder, δ is the volume fraction of powder, and δ_{MAX} is the maximum volume fraction of powder, *m* is a constant varying from 21 to 3 when the curve of the particle size distribution changes from a narrow peak to a wide peak. Therefore, a relatively wide particle size distribution leads to a relatively low viscosity. However, it is worth noting that the particle size distribution of the suspensions with 4 wt.% SA has an irregular shape and is relatively wide because of the bulky agglomerates, which may have limited the rotation of the particles during flowing. Moreover, it could lead to the entrapment of plasticizer components



Fig. 5. Temperature dependence of power law exponent for suspensions with the varying addition of SA.

within the agglomerates, and then to the reduction of the effective volume fraction of those media which are necessary to enhance the mobility of suspension [23, 24]. To sum up, the suspension containing 4 wt.% SA exhibited the highest viscosity due to the agglomerates.

3.3.2. The power law exponent

The power law exponent *n* can be used to judge the degree of the deviation from the Newtonian behavior (n = 1). The lower value of the exponent of power law indicates that the suspension exhibits appreciable shear-rate dependence, that is, the suspension viscosity will greatly decrease under certain shear intensity. The *n* values for individual types of suspensions, which are also temperature dependent, are given in Fig. 5. The values for the ceramic mixtures range between 0.477 and 0.641, which suggests a change in suspension structure. The power law exponents decrease obviously with the increasing amount of SA, which suggests the weakening of the interaction of the particles network. The lowest values, at which the suspensions exhibit the obvious pseudoplasticity, were established for the mixture with 3 wt.% SA. However, as mentioned above, bulky agglomerates are not beneficial to reduce the viscosity, which leads to the highest value of n in the suspension with 4 wt.% SA. Furthermore, it is obvious that the increase in temperature causes the rise

of the *n* value, which is indicative of the increasing tendency toward Newtonian behavior (where n = 1).

3.3.3. Yield stress

The τ_y represents the minimum stress which needs to be overcome before particles in the media are able to slide over adjacent particles for the flow to occur. One of these models was proposed by Casson, who related the shear stress (τ) to the shear rate (γ) for a nonlinear Bingham-type suspension by the equation [23, 24]:

$$\tau^{1/2} = \tau_v^{1/2} + (c\gamma)^{1/2} \tag{6}$$

The yield stress τ_v can be determined at a zero shear rate. Yield stress variation versus temperature from 140 to 170 °C is shown in Fig. 6. The values for the suspensions ranged from 8 to 20 kPa, and the acceptable level of yield stress for these suspensions was estimated to be about 5 - 10 kPa from the injection moulding and debinding experiments. A suspension with high yield stress is hard to be injection moulded because of the reduced laminar flow ability, whereas the suspension with yield stress too low to preserve enough strength may be subject to deformation during the binder removal stage. The yield stress of the suspensions (except the suspension with 4 wt.% SA) decreased slightly with the increasing amount of SA. It can be concluded that the strength of interparticle attraction is reduced as the fraction of SA increases, which leads the particles to roll over the neighboring particles more easily in compliance with the applied shear in the suspension. Similarly, the mutual occlusion and hard rotation of irregular agglomerates bring about the highest yield stress in the case of the suspension with 4 wt.% SA. As a result, because of its low viscosity and proper flow yield stress, the suspension with modest content of SA additions is more suitable for injection molding.

4. Conclusions

ZTA powder pretreated with different amounts of SA was blended with the binder system, including HDPE binder and PW plasticizer. All the suspensions contained 55 vol.% of ceramic powder. Experimental results indicated that stearic acid was



Fig. 6. Effect of temperature on the yield stress of the suspensions with the varying addition of SA.

chemically adsorbed onto the powders surface. With the increasing fraction of SA, the mean particle size decreased and the particle size distribution got narrower. It was accompanied with the decrease in the viscosity, yield stress and the power law exponent of the suspensions because of the reduced particle network strength. On the other hand, the excess of SA led to particle agglomeration, and consequently the suspension exhibited the highest viscosity and yield stress.

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