Powder Technology 291 (2016) 1–6

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Predicting the yield stress of paraffin-wax suspensions

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ARTICLE INFO

Article history:
Received 3 October 2015
Received in revised form 27 November 2015
Accepted 2 December 2015
Available online 3 December 2015

Keywords:
Injection moulding
Paraffin-wax suspensions
Alumina
Zirconia
Yodel model
Particle size distribution

ABSTRACT

An empirical modification of the Yodel model was developed for the prediction of the yield stress of concentrated, particulate, paraffin-wax suspensions, with a solids loading in the range of 47–57 vol.%, used in the low-pressure injection moulding (LPIM). The Yodel model takes into account the volume fraction of the solids, the particle size distribution (PSD), the maximum packing, the percolation threshold and the interparticle forces. However, yield-stress prediction over a broader range of volume fractions, for systems with a low interparticle attraction (<5 kT), is difficult to achieve without fitting at least one of the parameters. Here, we adjusted the dependence of the volume fraction of solids (X) to get a better fit to the experimental data in the volume fraction range used in LPIM and introduced the characteristic median number particle size radius (R_n), which is a function of both the PSD and the shape of the particles. A practical validation of the empirical model, in terms of predicting the yield stress of paraffin-wax suspensions made from several alumina powders and one zirconia powder yielded excellent agreement with the experimental results. It is shown that it is possible to predict realistic yield stresses across the whole of the solids-loading range suitable for LPIM just by making a single yield-stress measurement for the desired volume fraction of solids in the paraffin-wax suspension.

1. Introduction

Low-pressure injection moulding (LPIM) is a promising processing technique that is gaining advantage over the high-pressure injection moulding (HPIM) technique mostly used for the shaping of relatively small parts with complex shapes in the production of ceramics as well as metal parts [1,2]. One of the LPIM's main advantages is in the lower production costs. The rheological properties of suspensions play a crucial role in the successful shaping of a specimen using the LPIM process, determining the filling ability of the “cold” mould. An additional efficiency-limiting factor also represents the separation of powder and binder components during injection moulding stage, where interfacial adhesion of ceramic suspension and processing tools plays an important role [3].

Paraffin waxes with melting points between 50 and 80 °C are predominantly used as a dispersing medium for the preparation of a suspension. Short carboxylic amines or acids are added to make the polar surface of the particles compatible with the non-polar, dispersing, paraffin-wax medium. These molecules adsorb with their polar head onto the polar surfaces of the particles, while the non-polar tail is accommodated within the paraffin-wax medium. In this way, an adsorbed layer is formed on the particle surface, which prevents any direct contact between the neighbouring particles. The thickness of the adsorbed layer of stearic acid, for example, which is the most commonly used surface-active agent, is around 2.4 nm. Such a thickness is insufficient to provide complete stabilization of the particles in the suspension. However, it does enable some shielding of the attractive van der Waals forces. The thin adsorbed layer prevents any direct contact between the particles [4], but it is insufficient to prevent a weak attraction of the particles, resulting in a secondary minimum [5]. This attractive interaction is the origin of the yield stress, which was already determined with rheological measurements of paraffin-wax suspensions [6]. Therefore, the yield stress of such suspensions is an extremely important parameter. It determines the stress needed to induce the flow, as well as the flow itself (viscosity), which consequently determines the suspension's mouldability.

However, in order to be successful with the LPIM process a high enough yield stress for the paraffin-wax suspension needs to be achieved, enabling the shaping of specimens at high solids content [7]. However, it should not be too high because of the importance of the thermal de-binding step, where a wick embedment composed of granulated powder with a high specific surface area is used [8]. The binder is composed solely of paraffin wax and does not contain a high-melting-point backbone polymer that would hold the particles firmly in place after re-melting the samples during the thermal de-binding. Presumably, the attractive interactions between the particles after re-melting must be high enough to retain their shape and also sustain the capillary-driven suction of the molten dispersing medium into a highly porous embedment prior to the sintering in order to keep the

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http://dx.doi.org/10.1016/j.powtec.2015.12.002
0032-5910/

form of the shaped specimens intact. As was already reported, the yield stress of such suspensions after the re-melting of the shaped specimens is increased by at least an order of magnitude compared to the as-prepared suspension [6].

Due to the decisive role of the yield stress in the successful implementation of the LPIM process prediction could be an easy way to foreseeing the range of solids loading for paraffin-wax suspensions. In the literature several models for the yield-stress prediction can be found, and these fit well with the experimental data [9–11]. However, they are mainly used in a specific system for which the dependence of the yield stress was already determined. Moreover, an important drawback of these models is that they only take into account the median volume or the average particle diameter, oversimplifying the microstructural contribution to the final yield-stress value.

A model for yield-stress prediction, known as the Yodel model, was recently introduced [12]. It was derived from fundamental particle properties, taking into account the interparticle forces, the suspension microstructure and the particle size distribution (PSD). More recently, it was extended to include multimodal powder suspensions [13]. The Yodel model was initially validated using data from the literature on four different alumina powder suspensions [10]. The broader applicability of the presented model was then shown by applying it to suspensions made from MgO [14], cement and alumina for spray granulation [15], that is, from powders that can be well described by using the relevant physical parameters. However, it is important to note that besides the broad applicability and convenience of the Yodel model, at least one of its parameters, i.e., maximum packing, percolation threshold, pre-factor linked to interparticle forces and PSD, has to be fitted to an initial set of experimental data in order to predict the yield-stress values for a broader range of volume fractions, which might cause uncertainties for specific systems., e.g. low ionic strength systems [16].

The goal of the present study was to modify the Yodel model in such a way that it would enable the yield-stress prediction of paraffin-wax-based suspensions used in the LPIM shaping process. The modification takes account of the PSD and the microstructure of the suspension. When the appropriate PSD was introduced into the calculations, the values of the calculated yield stresses were in line with the experimental results and effectively covered the solids-loading range of 47–57 vol.%, the range most commonly used in the LPIM process. Furthermore, the empirically modified Yodel model makes it possible to predict legitimate yield stresses across the whole solids-loading range suitable for LPIM, by making a single yield-stress measurement for the desired volume fraction of solids in the suspension.

2. Materials and methods

The alumina powders and the zirconia powder used in this study for the preparation of the suspensions, differing in their respective PSDs, are listed in Table 1. The particle size measurements were made using laser diffraction [17]. The powder suspensions were then prepared using INA 58/62 paraffin wax (INA, Croatia), having melting points in the temperature range of 58–62 °C, where the paraffin-wax served as a solvent medium, while short carboxylic acids were used as the surface-active agents. For the determination of the solids loading the dependence of the yield stress of the stearic acid C18 (Carlo Erba, Italy) was used. To determine the effect of the length of the carboxylic acids (interparticle distance) on the yield stress of the paraffin-wax suspensions, palmitic acid C16 (Sigma-Aldrich, USA), myristic acid C14 (Sigma-Aldrich, USA) and lauric acid C12 (Sigma-Aldrich, USA) were used. The particle volume fractions in the suspensions were calculated by taking the density of the paraffin wax to be 0.76 g/cm^3 (at 70 °C) [18]. The powders were oven-dried at 140 °C for 4 h before being compounded in a molten mixture of paraffin wax and carboxylic acids. After the compounding, the suspensions were homogenised at 80 °C using a water-heated, three-roller mill (Exact, Germany). Three passes through the gap between the rollers were sufficient for the preparation of homogeneous suspensions, which was experimentally determined in our laboratory [19].

The amount of surface-active agent per surface area of the used powder was 0.175 μmol/m^2. The volume fractions of the solids in the suspensions at 70 °C were between 47 and 57 vol.%. After the preparation of the paraffin-wax suspensions their rheological properties were measured with an Anton Paar MCR 301 rheometer (Anton Paar, Austria) using a cone-and-plate geometry and a CP-25-1 sensor system. The rheological measurements were performed at 70 °C. Prior to the yield-stress measurements the suspensions were conditioned by measuring the flow curves in the range of shear rates from 1 to 100 s^{-1} until reproducible results were obtained. The suspensions were further conditioned by applying a shear rate of 50 s^{-1} for 2 min prior to the measurement of the yield stress. After conditioning the suspensions at a constant shear rate, the yield-stress measurements were performed by increasing the shear stress and measuring the strain of the sample. Each yield-stress value reported in the paper is an average of three measurements. The differences between the measurements were less than 5%.

3. Theory

The Yodel model is based on basic principles and takes into account the PSD, the interparticle forces, and the microstructural features in an aqueous concentrated, agglomerated suspensions [12]. The Yodel model is represented by the yield-stress function

$$\tau_0 = m_1 \frac{\theta(\theta-\theta_0)^2}{\theta_{max}(\theta_{max}-\theta)} \tag{1}$$

where θ is the volume fraction of the powder in the suspension, θ_0 is the percolation threshold, θ_{max} is the geometrical maximum packing of these powders, and m_1 is a pre-factor that accounts for PSD of nonspherical particles with spherical contact points written as

$$m_1 = \frac{0.15 u_{k,k} a^* A_0}{\pi^4 H^2} \frac{f^*_{\sigma,\Delta}}{R^2_{v,50}} \tag{2}$$

while for the spherical particles it is written as

$$m_1 = \frac{0.15 u_{k,k} A_0}{\pi^4 H^2} \frac{f_{\sigma,\Delta}}{R_{v,50}} \tag{3}$$

where A_0 is the Hamaker constant, $f_{\sigma,\Delta}$ and $f^*_{\sigma,\Delta}$ are the normalized size-distribution function, $u_{k,k}$ is the limit value for the volume increment — enclosing sphere diameter (for a detailed development of $f_{\sigma,\Delta}$, $f^*_{\sigma,\Delta}$ and

Table 1
Powders used in the study for the preparation of the suspensions together with their respective measured particle size volume distributions; d_{10}, d_{50} and d_{90} along with the corresponding span of the particle size distribution, $(d_{90} - d_{10}) / d_{50}$.

Material	Type	Producer	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)	$(d_{90} - d_{10}) / d_{50}$
Alumina	A16	Alcoa, USA	0.31	0.53	1.29	1.85
	AA04	Sumitomo, Japan	0.24	0.41	0.57	0.89
	AKP 30	Sumitomo, Japan	0.21	0.29	0.38	0.58
	AKP 50	Sumitomo, Japan	0.12	0.18	0.26	0.77
Zirconia	TZ-3YS	Tosoh, Japan	0.26	0.40	0.81	1.37