Powder Technology 320 (2017) 273–284

Contents lists available at ScienceDirect

Powder Technology

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

# Influence of segregation on rheological properties of wax-based feedstocks

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ARTICLE INFO

*Article history:*
Received 31 October 2016
Received in revised form 3 April 2017
Accepted 18 July 2017
Available online 21 July 2017

*Keywords:*
Powder injection molding (PIM)
Viscosity
Segregation
Feedstock
Metallic powder
Binder

ABSTRACT

The rheological behavior of wax-based feedstocks has a direct impact on successful mold filling for parts produced by low-pressure powder injection molding. During a rheological test, segregation may occur within low-viscosity feedstocks, leading to errors in results, and to an improper evaluation of the flowability of powder-binder mixtures. The segregation occurring during rheological tests is not generally considered when measuring the viscosity profiles of such mixtures. In this study, the impact of testing time, testing protocol (increasing or decreasing shear rate), polymer degradation, powder deagglomeration, and temperature on the rheological properties of feedstocks was investigated. The segregation occurring during rheological testing produces a meaningful effect in low-viscosity feedstocks. Because the segregation is driven by the time spent in the molten state, the effects of segregation on viscosity were visible, particularly at the end of a long rheological test. During a short rheological test, the pseudoplastic effect occurring in wax-based feedstocks was only attributable to the binder molecules' orientation with respect to the flow. In this respect, and contrary to the information reported in literature, it was demonstrated that the dilatant effect observed was in fact more likely due to segregation occurring during the rheological test, rather than as a result of the elimination of the preferential layer formed during the pseudoplastic regime. Because the rheological properties of low-viscosity feedstocks were significantly influenced by the test duration, a rheological test duration of a few minutes must be used to precisely quantify the flowability of such feedstocks.

## 1. Introduction

Low-pressure powder injection molding (LPIM) is a cost-effective emerging technology for producing small and complex parts, either in high or low production volumes. This rapid manufacturing process consists in mixing metallic or ceramic powder with molten polymer binders to obtain a feedstock which is injected into a mold cavity to generate a complex shape. During debinding and sintering treatments, the binder is completely removed to obtain a near-net-shape dense metallic component [1,2]. The conventional high-pressure powder injection molding (HPIM) process using an injection pressure up to 200 MPa has transitioned to LPIM by taking advantage of low-viscosity feedstocks to achieve high moldability during the injection at a pressure lower than 1 MPa [3]. Initially used in ceramics shaping [4,5], the LPIM technology has quickly become attractive for the development of high value-added metallic parts in the aerospace and medical industries [6–8].

A key to the successful injection of feedstock at low pressure lies in the low-viscosity properties of the wax-based binder. Paraffin wax, microcrystalline wax, beeswax, and carnauba wax are widely used as the main constituents to form commercial and development feedstocks [9–11]. Surfactant and thickening agents are generally added to enhance the homogeneity of the feedstock as well as to prevent powder-binder separation. The surfactant agents act as a bridge between the metallic powder and the other constituents to enhance the homogeneity and the mixing properties of the feedstock. The thickening agent for its part is generally used to increase the viscosity of the mixture in order to prevent powder-binder separation. Stearic acid, ethylene vinyl acetate, and low-density polyethylene are extensively used in LPIM feedstocks [12–15]. Although the binder is not present in the final LPIM component, it is important for controlling the rheological properties of feedstocks during and after injection.

Feedstock viscosity is one of the most important parameters influencing the success of the molding stage. The rheological properties of several feedstocks used in conventional HPIM are well known, as are those of some feedstocks used for LPIM. The main variables influencing

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http://dx.doi.org/10.1016/j.powtec.2017.07.056
0032-5910/

the viscosity of powder-binder mixtures are the shear rate, temperature, solid loading, powder characteristics (shape and size) and binder composition. Flow characteristics of feedstocks can be described by a power law as widely reported in the literature (Eq. (1)). This model shows how the shear rate depends on the viscosity, and can be used to study the impact of the binder on the rheological behavior of feedstocks [16,17].

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

where $\eta$ is the feedstock viscosity, $\dot{\gamma}$ the shear rate, $K$ a constant, and $n$ is the shear sensitivity index. The slope of the log $\eta$ - log $\dot{\gamma}$ graph is $n - 1$, from which $n$ can be calculated. The rheological behavior of the feedstocks used in metal injection molding is generally pseudoplastic ($n<1$) or Newtonian ($n = 1$). The relationship between the temperature and viscosity has also been widely studied [18–20]. This temperature-dependence of viscosity can be described by the Arrhenius equation, indicating that the viscosity of a feedstock decreases as the temperature increases (Eq. (2)).

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right) \tag{2}$$

where $\eta_0$ is a constant, $E$ the activation energy, $R$ the gas, constant and $T$ is the temperature. The slope of the log $\eta$ - $1/T$ graph is $E/R$, from which $E$ can be calculated. This activation energy quantifies the dependence of temperature on viscosity, which should be as small as possible in order to minimize the significant changes of feedstock viscosity between the hot and cold zones in the injection press or in the mold. It is well accepted that the viscosity of a feedstock increases with an increase in the volume fraction of powder. Several models similar to the one presented by Quemada [21] (Eq. (3)) have been used to predict this solid loading dependence [22,23]:

$$\eta = \eta_b \left(1 - \frac{\phi}{\phi_{max}}\right)^{-2} \tag{3}$$

where $\eta_b$ is the binder viscosity, $\phi$ the solid loading, and $\phi_{\max}$ is the maximum solid loading. It has also been demonstrated that the viscosity of a feedstock decreases with an increase in particles size and with an increase in particles sphericity [24,25]. When properly designed, a homogenous HPIM feedstock shows smooth and stable values of viscosity over time [26]. However, the influence of segregation on viscosity properties has previously not clearly been demonstrated for LPIM feedstocks.

Segregation refers to the inhomogeneous distribution of powder particles in feedstocks. This fluctuation in solid loading within the feedstock has only been superficially examined in a conventional HPIM due to the inherently high viscosity of feedstocks, which prevents the occurrence of this phenomenon. It well accepted that the separation of the binder from the powder is generated mainly by gravity, an improper mixing method, or high-pressure gradient during the molding process [27–31]. This parameter must be minimized in order to prevent distortions, cracks, voids, warping and the heterogeneous shrinkage of sintered parts [32]. It was recently shown that the intensity of segregation in LPIM feedstocks depends significantly on the binder constituents, as well as on the time spent in the molten state [33]. Segregation may occur within the injection machine because a trapped feedstock could remain idle within the injection press during dead times of the process. In general, while the segregation of LPIM feedstocks is prevented by adding thickening agents to increase viscosity, this results in a decrease in the flowability of the feedstocks. The recent development of a new injection concept leads to the injection of very low-viscosity feedstocks, while avoiding segregation within the injection machine [34]. As mentioned previously, it is important to evaluate the rheological properties of the feedstocks in order to control its flowability during the molding stage. However, the related rheological tests can be long, and segregation may occur during testing, leading to errors in results. Consequently, the segregation occurring during extended rheological tests is not generally considered in the viscosity profiles of such mixtures. The aim of this study was to investigate the influence of segregation occurring during rheological testing on the rheological properties of wax-based feedstocks used in the LPIM process.

## 2. Experimental procedures

### 2.1. Materials

A gas-atomized Inconel 718 superalloy powder (Sandvik Osprey, Neath, UK) with a typical spherical shape and an average particle size of 12 μm was used (Fig. 1). Due to their extensive use in LPIM, paraffin wax (PW), stearic acid (SA) and ethylene vinyl acetate (EVA) were selected as the major constituent, surfactant and thickening agent, respectively. These organic constituents were mixed with the metallic powder to form homogeneous feedstocks according to the powder-binder formulations given in Table 1. In this study, simple feedstocks (single- or dual-binder constituents) were used to provide a better understanding of the impact of segregation on viscosity measurements. Feedstock containing only paraffin wax (40PW) was used as the reference feedstock, while those containing stearic acid (35PW-5SA) or ethylene vinyl acetate (35PW-5EVA) were selected due to their very low and relatively high viscosity values. Solid loading of feedstocks was kept constant at 60 vol% in order to ensure the wettability of metallic powder with a single-binder constituent (e.g., feedstock 40PW) and obtain homogeneous powder-binder mixtures. The volume fractions of powder presented in this study are the values determined at room temperature, and the feedstock identification is referenced by their polymer volume fraction. For example, the feedstock 35PW-5SA is a mixture containing 60 vol% of powder with 35 vol% of paraffin wax and 5 vol% of stearic acid. Finally, an uncommon powder-honey feedstock (solid loading of 50 vol%) was tested at 30, 40 and 70 °C to produce a Newtonian feedstock and quantify the impact of deagglomeration or powder alignment on the viscosity values.

### 2.2. Measurements

The viscosity of the feedstocks was evaluated using an Anton Paar MCR 501 rotational rheometer with a concentric-cylinder geometry C-PTD200, and a Peltier temperature-controlled measuring system. The feedstock, the cylinder, and the container were preheated to reach the

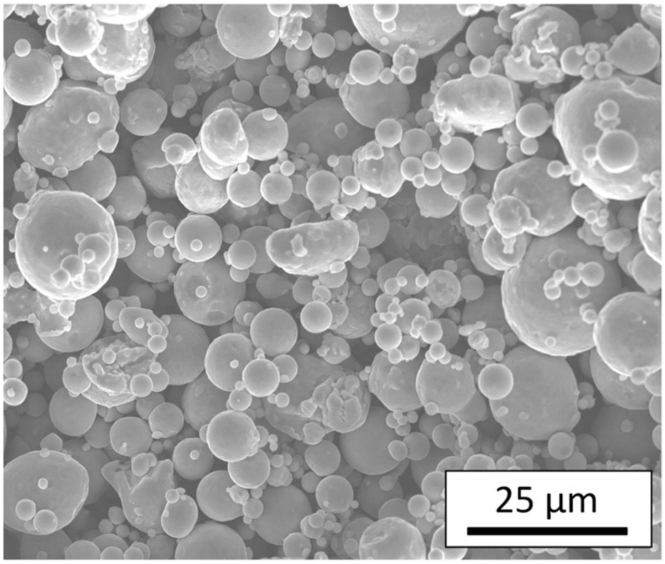

**Fig. 1.** SEM micrograph of Inconel 718 powder.