Rheological Behaviour of Metal Powder Suspensions Under Dynamic Loading

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A B S T R A C T

The dynamic rheological properties of injection moulding of feedstock powder-binder blends (suspension) based on iron powder and HDPE (High Density Polyethylene) were investigated by using a parallel plate rheometer. The solid content ranging from 30 to 60 vol% of the total volume of loaded metal powder, compatibilizer, stearic acid, and stearamide. The dynamic rheological response of the materials was used to analysis the effect of the mentioned factors on the material functions of the mixtures (dynamic viscosity $\eta^*$, storage modulus $G'$, and loss modulus $G''$) at frequency range 0.1-100 s$^{-1}$. These parameters showed large differences in the response of the suspensions with changes in loading and addition of compatibilizer. All dynamic parameters increase by increasing the volume fraction of solid loading. As compatibilizer, stearamide shows a significant effect on rheological behaviour of suspensions. Falkner-Schmit models were used to fit the experimental rheological data. It was found that our experimental data and modified composition fit the modified forms of these models.

Key Words: rheology; HDPE; Falkner-Schmit's model; PIM; Powder injection molding.

INTRODUCTION

Injection moulding is receiving attention as a method of shaping engineering artifacts from metallic and ceramic powders. Because it offers near net shape production by an automated process. Homogeneous feedstock granules for injection moulding are produced by blending powders of the desired material with a molten wax or polymer binder. It is done often under vacuum to eliminate voids in the granules and in the final part. Although, both thermosetting [1-3]
and low and high molecular weight thermoplastics [3-5] have been investigated. But much attention has been paid to high molecular weight thermoplastics, which are fabricated routinely by injection moulding.

The selecting process of organic vehicle compositions has been recently reviewed [1-5]. Two dominant criteria are (1) the rheological properties of the binder and (2) pyrolyse in a non-catastrophic manner during sintering step that permit defect-free moulding and elimination of binder from sintering metallic part. In this study, the rheological properties of high density polyethylene suspensions filled with various loadings of iron powder, and two kinds of compatibilizer were investigated. The physical properties of the used organic binder (vehicle) is reported elsewhere [6].

Useable moulding compositions generally include, the metal powder, several organic components [7]; the major binder component, which determines the general range of properties; minor components such as plasticizers for the main polymer which behave as flow modifiers; oils that are claimed to modify pyrolysis; and processing aids which are supposed to act as surfactant and improve wetting of the metal powder particles.

The interaction of the two criteria for choosing the organic vehicle compositions described above and the selection of the binder are complex and time-consuming. In both cases there is a need for simple tests which guide on the likely performance of the final composition in moulding trials [8]. The flow behaviour of feedstock during moulding can vary considerably due to wide variations in particle characteristics including density, mean particle size, width of size distribution, and particle shape [9]. In terms of characterizing the rheological properties, which are relevant to moulding behaviour, three routes are available: (1) measurement of viscosity using a rheometer over a range of temperature and shear rate, (2) spiral flow moulding trials, (3) pressure, time, and temperature adjustment during the moulding of a relevant artifact. Both (2) and (3) routes involve considerable processing time and large quantity of materials. Therefore, the present work chooses to characterize some prospective metal injection moulding suspensions by parallel plate rheometry.

EXPERIMENTAL

Materials
Iron powder supplied by IPMC (Iran Powder Metallurgy Complex Co.) was used as metallic powder. As seen in Figure 1a, the original powders are highly agglomerated and should be de-agglomerated. For this reason we milled the powder in a ball mill for 24 h. Milled powder micrograph (SEM, Cambridge Instrument, Stereoscan 360) and its particle size distribution (Fritsch Particle sizer) curve are shown in Figures 1b and 2, respectively. Its average particle size was 28.48 micron.

For selection of major binder we achieved the flow curves of some the commercial polyethylenes that are produced in IPPC (Iran Petrochemical Products Co.). The grade 5218 that has the lowest MFI among the other grades selected as major binder and technical grade paraffin wax used as minor binder [6]. Stearic

Figure 1. SEM Micrographs of (a) received iron powder and (b) milled powder.
acid was used to compatibilize metallic powder and the binders. Data on the used materials are shown in Table 1. Also a synthesized amide compound (stearamide from the reaction of diethanolamine and stearic acid in toluene, Scheme I) was used to characterize the effect of compatibilizer on the rheological behaviour of the suspensions. Figure 3 shows the FTIR spectrum (Bruker, Equinox 55) of the synthesized compound. Adsorption peak at 3302 cm⁻¹ represents the N-H bond of stearamide.

### Procedures
Binder and powder-binder suspensions were mixed in a jacketed mixing chamber with a mixer (Kinematica Switzerland) at 6000 rpm coupled with two mechanical stirrers polytron (Kinematica) at 170°C. At first we admixed the binder (using a high shear mixer, the composition of binder was set at PE/wax/compatibilizer: 60/35/5) and then added iron powder gradually to binder during the next 30 minutes. A simple scheme of the chamber, its high shear mixer,

### Table 1. Characteristics of used materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Property</th>
<th>Details</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyethylene (5218)¹</td>
<td>Melt flow index</td>
<td>17-19</td>
</tr>
<tr>
<td></td>
<td>Density (g/cm³)</td>
<td>0.951-0.953</td>
</tr>
<tr>
<td></td>
<td>Impact resistance (J/mm)</td>
<td>0.019</td>
</tr>
<tr>
<td>Paraffin wax²</td>
<td>Density (g/cm³)</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>Melting point (°C)</td>
<td>60-63</td>
</tr>
<tr>
<td>Stearic acid²</td>
<td>Density (g/cm³)</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td>Melting point (°C)</td>
<td>53</td>
</tr>
<tr>
<td>Polyethylene wax³</td>
<td>Density (g/cm³)</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>Melting point (°C)</td>
<td>98-108</td>
</tr>
<tr>
<td>Iron powder⁴</td>
<td>Apparent density (g/cm³)*</td>
<td>2.16</td>
</tr>
<tr>
<td></td>
<td>Apparent density (g/cm³)**</td>
<td>3.17</td>
</tr>
<tr>
<td></td>
<td>Flow rate (g/50sec)*</td>
<td>25.13</td>
</tr>
<tr>
<td></td>
<td>Flow rate (g/50sec)**</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Particle shape***</td>
<td>Irregular</td>
</tr>
</tbody>
</table>

¹ IPPC catalogue; ² Experimentally determined; ³ BASF Co.; ⁴ IPMC catalogue.

⁴ Before milling, ⁵ After milling, ⁶ By scanning electron microscopy.
and stirrers assembly are shown in Figure 4. Powder loading ranges between 50 and 60 vol% and the mixing time was fixed at 30 min.

After mixing the suspension was cooled down to room temperature and then was powdered by free hand crasher. The powder was melted and moulded to $(25 \times 2.5 \text{ mm})$ rheological test disk samples. The rheological properties of the suspensions were measured on a parallel plate rheometer (Paar Physica, D300) at $150^\circ \text{C}$.

RESULTS AND DISCUSSION

Figure 5 is a plot of $\eta^*$ versus frequency ($\omega$) of HDPE paraffin wax binder filled with iron powder of 50, 55, and 60 vol%. Several conclusions can be inferred from this Figure. All three compositions show a very shear dependence behaviour over the entire range of investigated frequency. The highest loaded mixture exhibits a yield stress at frequency up to 20 rad/s. Existence of a yield stress is exemplified by slope of -1 on the $\ln \eta^*-\ln \omega$ plot [10]. The curves of other concentrations do not show any yield stress at frequencies above 0.1 rad/s. An interesting feature of the data in Figure 5 is that the viscosity curves of the 55 and 60 vol% loaded suspensions are only modestly higher than that of the suspension containing 50 vol%.

Figure 6 is a plot of $G'$ vs $\omega$ for these three compositions. Similar to the viscosity curves of Figure 5 the highest loaded composition behaves differently from the others. Its $G'$ curve is quite flat at frequencies above 5 rad/s. The other compositions show a continuous increase in $G'$ with frequency. At low frequencies, the response of the polymer dominates the behaviour of the system. This accounts for the lower shear modulus at low frequencies. The time scale of the experiment allows for movement of the particles in the molten polymer before the motion of the oscillating disc changes. At higher frequencies, the particles have less time to move and since their motions are hindered by the close proximity of neighboring particles, the material responds as a solid. Hence, $G'$ increases with increasing $\omega$.

In PIM we are always looking for the highest possible solid loading. This is for being able to achieve the highest experimental density. Therefore, we studied the effect of the compatibilizers on 60 vol% suspension.

Figure 7 contains viscosity-frequency data for 60 vol% compositions containing two additives investigated in this study. From these data, it is clear that the additives affect the mixtures in different ways and to different extents. Stearamide increases the suspension viscosity compared to stearic acid. The reduction of shear sensitivity of the suspension is a non-favorable
The effect of stearamide. The composition containing stearamide exhibits a yield stress at frequencies lower than 1 rad/s. It is concluded that stearamide couples polymer to iron particles in a more effective manner rather than stearic acid.

The shear storage modulus of two compositions is shown in Figure 7. As expected, the stearamide sharply increases the storage modulus of the composition. This is another evidence for the conclusion that the stearamide effectively bridges between polymer and metallic particles. Such a chemical bridge not only would increase the viscosity, as it has done, but also would increase the stiffness, or modulus of the system. The $G'$ curve for this composition is rather flat.

The $G'$ curve for the suspension containing stear-

Figure 7. Rheological parameters vs. angular frequency for two different compatibilizers for 60 vol% powder loading (open symbols = stearamide, solid symbols = stearic acid).

amide also shows the evidence of coupling between metal particles and polymer. The magnitude or strength of the network formed using stearamide is higher than that of stearic acid. This phenomenon is related to a stronger organic functionality-polymer linkage in the former system. The organic functionality polymer bridge yields easily at low deformation rates. At high frequencies this linkage does not have time to yield, and the system modulus remains high.

Rheological Model

Model for Storage and Loss Modulus

Falkner and Schmit [11] suggested two equations to express the effect of solid phase volume fraction on the ratios of storage and loss modulus of suspension to those of binder. The models are as follows:

$$G'(\phi, \omega) = 1 + 1.8\phi$$

(1)

$$G''(\phi, \omega) = 1 + 2\phi + 3.3\phi^2$$

(2)

The ability of Falkner-Schmit models (eqs. 1 and 2) to predict suspension rheological properties was investigated.

As seen in Figures 8 and 9, the studied system does not fit in the model at any angular frequency. A probable reason for this observation is that, Falkner-Schmit models are proposed for suspensions of glass beads in mixes.
in which the particles are spherical, isolated, and non-agglomerated. As seen, much more deviation is observed at high volume fraction and high frequency as well. To fit experimental data into the models at 10 s\(^{-1}\) frequency we modified Falkner-Schmit models due to a better fitting as compared with other frequencies. As shown in Figures 8 and 9 we have reached to a suitable comparison between modified models and obtained data.

The modified forms of the Falkner-Schmit models are as follows:

\[
\frac{G'(\phi,\omega)}{G'(0,\omega)} = 1 + 1.07\phi \\
\frac{G''(\phi,\omega)}{G''(0,\omega)} = 1 - 2.07\phi + 6.61\phi^2
\]

As seen, the modification of the model is limited to changing in numerical constants and algebraic sign.

**Flow Index**

The flow behaviour of the PE-metallic powder suspensions could be characterized by a shear rate (\(\gamma\))-viscosity (\(\eta\)) curve (derived simply from \(\eta = k\gamma^{n-1}\)), as shown in a log-log plot of Figure 10.

It is evident that the suspensions posses the shear-thinning character and their flow behaviour of the suspensions is as a function of concentration of the iron powders. The flow index generally increasing in the range 1.50-1.80 for the suspensions with 50, 55, and 60 vol% solid particles. This increasing indicates that the flow behaviour changes due to increasing the inter-particle interaction, including surface attraction or friction.

On the other hand, for the composition with larger solid loading, it may have an open network structure with voids between the closely connected framework filled with binder melt. With such interconnected structure, the flow ability of the molten binder is then effectively retarded and a higher shear viscosity could be expected under an identical shear rate. It is leading to a shear dependent character higher than that of the lower solid concentration [12].

**Viscosity model**

There are two methods, i.e., experimental and theoretical methods to measure maximum solid fraction (\(\phi_m\)). In experimental method usually relative or complex viscosity at various volume fractions of solid are measured and plotted. A sharp increase in viscosity at high volume fractions of solid is observed by projecting a line from maximum volume fraction point to the solid loading axis. For the system under investigation it was found that \(\phi_m = 0.61\) (Figure 11).

The theoretical method has been proposed by Liu to predict the maximum solid fraction in filed materials [13]. This theoretical method involves relative viscosity \(\eta_r\) as follows:

**Table 2. Composition of binders.**

<table>
<thead>
<tr>
<th>Component</th>
<th>PE 5218</th>
<th>Wax</th>
<th>Compatibilizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight percentage</td>
<td>15</td>
<td>80</td>
<td>5</td>
</tr>
</tbody>
</table>

**Figure 10.** Shear rate-shear viscosity relationship for different loaded suspensions.

**Figure 11.** Practical measuring of maximum powder loading (\(\phi_m\)) in studied range of powder loading.
\[
\eta_r = \frac{\eta_{\text{suspension}}}{\eta_{\text{binder}}}
\]  

(5)

As shown in Figure 12, the experimentally determined \(1 - \eta_r^{-1/2}\) is a linear function of \(\phi\) with a reasonable correlation factor \(R^2 = 0.990\) over rather broad range of solid loading (0.5, 0.55, 0.6, 0.61).

The maximum solid fraction was then determined by extrapolating the fitted line to \(1 - \eta_r^{-1/2}\) from which, the \(\phi_m\) was found to be 0.614 for the given suspension system. This value is low when it is compared with what is achievable by the random close packing of mono-size spheres (\(\phi_m = 0.64\)). It is presumably due to the apparent particle agglomerations found in the starting powder (Figure 1b) that exist persistently in the suspension to an unspecified extent even after high-shear ball milling.

CONCLUSION

The rheological behaviour of a series of suspensions made from iron powder particles suspended in binders has been investigated over a volumetric solid concentration range 30-60%. The dynamic viscosity and storage and loss modulus increased with increasing solid content due to strong interaction between particles in the high volume percentage suspensions. It was found that using stearamide as compatibilizer increases all three dynamic parameters that could be attributed to strong interactions between polymer and iron powder. Maximum solid loading (\(\phi_m\)) was determined experimentally and theoretically. In theoretical method it was determined from the \((1 - \eta_r^{-1/2}) - \phi\) linear relationship that for this suspension system \(\phi_m = 0.614\). Maximum solid loading (\(\phi_m\)) value was experimentally found to be 0.61. The probable reason for difference between theoretical and experimental values of \(\phi_m\) could be the agglomeration of particles in which small quantities of binder are trapped in cavities inside agglomerated particles.

Falkner-Schmit models were modified to fit experimental data of the studied metal-powder suspension system. In the absence of a good fit it can be said that, Falkner-Schmit models are for non-agglomerated and isolated particles, whereas, the studied powder is highly agglomerated.

REFERENCES


