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Effect of Stearic Acid on Rheological Properties of 316L Feedstock for Metal injection Moulding

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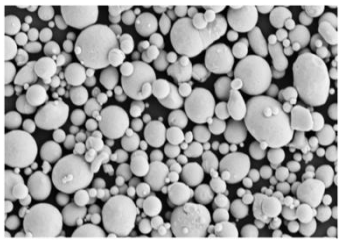
Graphical abstract



Abstract

Stearic acid (SA) was used as an additive in the process of metal injection moulding (MIM). It was added to the wax/polymer mixture in order to modify the powder wetting, mould lubrication, mixture viscosity, residual stress and debinding behaviour. In this study, the effect of SA in feedstock formulation on mixing torque and rheological properties was investigated. Further, it's correlation on the as-moulded and as-debound parts behaviour was also investigated. The results showed that addition of SA significantly reduced the mixing torque value and viscosity which correspond to decreasing in inter-particle friction. As a result, injection moulding could be carried out at a lower temperature to achieve sound moulded parts and increased the removal rate of binder during solvent extraction process. However, it seemed that increasing the SA had a little negative effect on the as-moulded density.

*Keywords:*Metal Injection Moulding; rheological properties; palm stearin; stearic acid; feedstock

Abstrak

Asid stearik (SA) telah digunakan sebagai bahan penambah dalam proses pengacuan suntikan logam. Bahan ini ditambah ke dalam campuran lilin / polimer untuk mengubah tahap pembasahan serbuk, pelinciran acuan, kelikatan campuran, tegasan baki dan tingkah laku semasa proses penyahikatan. Dalam kajian ini, kesan SA dalam formulasi bahan suapan terhadap nilai tork campuran dan sifat reologi telah diselidiki. Di samping itu, hubungan terhadap tingkah laku semasa pengacuan suntikan dan juga semasa penyahikatan larutan juga dikaji. Hasil kajian yang diperolehi menunjukkan bahawa penambahan SA dapat mengurangkan nilai tork yang ketara semasa proses pencampuran yang mana kesannya dapat mengurangkan tahap geseran antara serbuk logam yang diaduk. Signifikannya adalah proses pengacuan suntikan boleh dijalankan pada suhu yang lebih rendah untuk mendapatkan produk yang bebas kecacatan. Selain itu, ianya juga dapat meningkatkan kadar penyingkiran bahan pengikat dalam proses pengekstrakan pelarut. Walau bagaimanapun, peningkatan SA dilihat memberikan implikasi yang amat minima terhadap tahap kebolehpadatan jasad yang disuntik.

Kata kunci: Pengacuan Suntikan Logam; sifat reologi; stearin sawit, asid stearik; bahan suapan

1.0 INTRODUCTION

The importance of binder formulation in evaluating the success of the MIM process has been recognized by many. This has given rise to the development of many patented systems. Table 1 shows a selection of some patented binder systems.

Two major observations could be made from Table 1. First, almost all systems are multi-component. Having more than one component allows one binder component to be preferentially removed prior for the thermal degradation of the other components. The rationale is that the remaining component can then hold the particle in the moulded specimens against the stress resulted from the removal of the first component. It thus helps to retain the specimen and open pores in the component which form the channels for the remaining binder to vaporize [5]. The sequential debinding method allows a more rapid debinding as compared with a single component binder system. This inhibits the formation of an internal vapor pressure that might cause specimen failure [6]. It is interesting to note that, as shown in Table 1, stearic acid seems to be one of the important components in the binder system.

Table 1 Some patented binder systems

No	Composition	Ref.	No	Composition	Ref.
1	56% Water 25% Methyl Cellulose 13% Glycerin 6% Boric acid	[1]	3	50% Paraffin wax 35% Polyethylene 14% Candelilla wax 1% Stearic acid	[3]
2	65% Polystyrene 15% Polyethylene 12% Stearic acid 7% Diethyl phthalate	[2]	4	69% Paraffin wax 20% Polypropylene 10% Carnauba wax 1% Stearic acid	[4]

It is well known in the powder injection moulding process that SA can serve as a plasticizer for polymers, as a lubricant between powder and machine die walls and as a surfactant between powder and binder [7]. Paul Lin and German [8] claimed that a bulk mixture of powder and binder is difficult to obtain without the addition of SA in the binder system. Strongly preferred, adhesion of SA to the powder surface significantly reduces the binder/powder interfacial energy and contact angle but their usefulness increases as the particle surface area increases. These resulted in the reduction of viscosity of the feedstock, accounted for the reduction of iron pickup arising from the machine wear during mixing [8]. Presumably, hydrogen bonding occurred between the acidic hydroxyl functional group and the basic calcium carbonate powder surface [5]. In many cases, SA can be removed simultaneously with the primary binder component by solvent extraction process, whereas n-heptane solution has been widely used as a solvent.

In this present study, the effect of SA in feedstock formulation on mixing torque, rheological properties and injection moulded parts behaviour were systematically studied. Besides that, its effect on the solvent extraction kinetics was also investigated.

2.0 EXPERIMENTAL PROCEDURE

In this study, the gas atomized 316L grade stainless steel powder, which is almost spherical in shape as shown in Figure 1 was used. A set of 6 feedstock formulation with different amount of SA and powder loadings were prepared and can be summarized in Table 2.

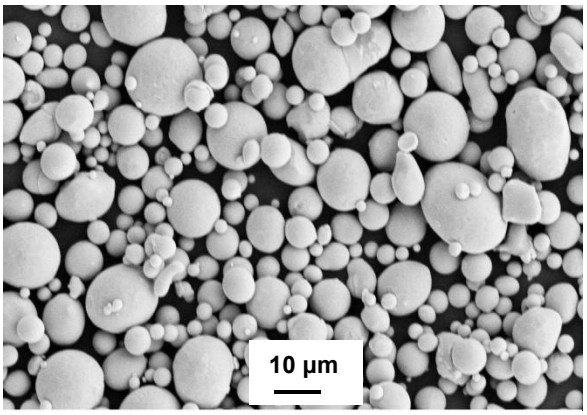


Figure 1 SEM of 316L gas atomised stainless steel powder

Table 2 Binder composition used to study the effect of varying the SA additions

Label	Powder volume fraction (%)	Binder component weight fraction (wt.%)		
		PS	PP	SA
PSPP-65	65	50	50	0
PSPPSA-4	65	50	46	4
PSPPSA-6	65	50	44	6
PSPPSA-8	65	50	42	8
PSPPSA-10	65	50	40	10
PSPP-63	63	50	50	0

Mixing was based on feedstock batch of approximately 250 g in a Brabender Plasticorder, manufactured by M-Brabender OHG Germany. The mixing was carried out at a preset temperature of 190^{o}C held for 2 hours with a rotational speed of 50 rpm. The sequence of addition of the binder components for producing all sets of the feedstock is as follows; first, when the required mixing temperature was reached, a quarter amount of polymer comprised of PP was loaded into the bowl. Then, the powder was loaded gradually together with the remaining binder components of PP, SA and PS. This is to ensure the homogeneity of the mixture. The powder-binder mixture was assumed to be uniformly mixed when the mixing torque yielded a stable and consistent value.

All feedstocks were then characterized by a CFT-500D capillary rheometer, manufactured by Shimadzu accordance with the ASTM Standard D 3835-02. The die orifice made from tungsten carbide and having a dimension of 1.0 mm in diameter and 10 mm in length, resulting in an aspect ratio (L/d) of 10. The rheological data such as shear rate, shear stress and viscosity were recorded and analysed as a function of different test load and setting temperatures.

Two feedstock formulations of PSPP-65 and PSPPSA-10 were injection moulded using a vertical MCP-100KSA injection moulding, manufactured by MCP, Germany for comparison. During moulding, the temperature and injection pressure were adjusted until the optimum condition was obtained. The green parts present a very good homogeneity as deduced from the microstructural analysis and from green density values. The binder of palm stearin and stearic acid was then removed by means of solvent extraction by immersing the samples in an n-heptane solution for 5 hours at the temperature of 60^{o}C.

3.0 RESULTS AND DISCUSSION

3.1 Torque Evolution

Figure 2 shows the influence of SA addition and different powder loadings on the mixing behaviour. It clearly shows that, varying the amount of powder loading, as well as the SA addition resulted in variation in torque stability, in which the torque value decreases with SA addition and decreased powder loading. This is because of the differences in mixture viscosity. Compared the feedstock between the 65 and 63vol% without SA addition, the difference in torque values are clearly evident, in which the torque value is almost 6 times greater for case of greater powder loading. It is well known that, greater amount of powder volume fraction result in greater inter-particle friction, therefore, a greater torque is desired to stabilize the mixture for ensuring uniform mixing.

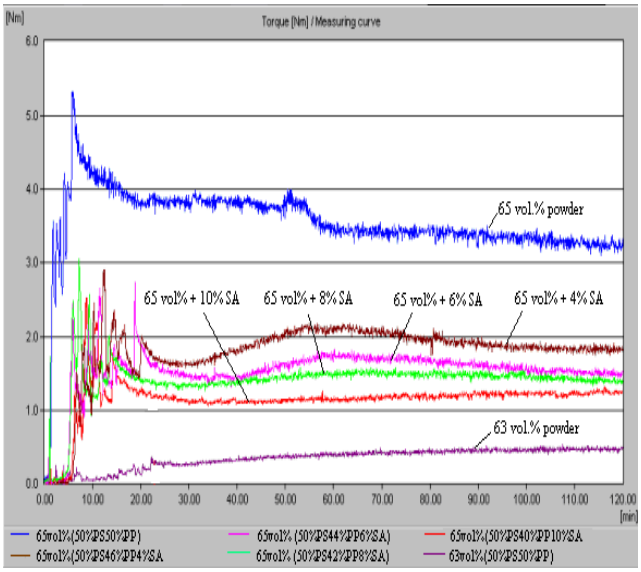


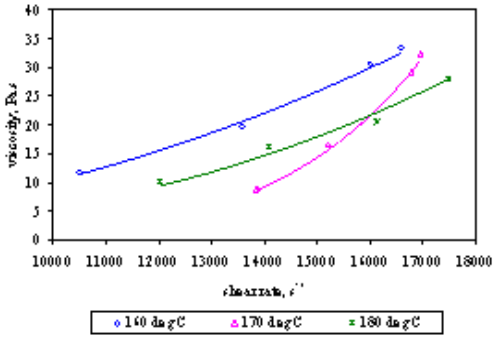
Figure 2 Different torque rheometer with addition of different amount of stearic acid

Mixing torque is basically proportional to the shear stress of the mixer, indicates the work energy consumed to disperse and distribute the powder-binder mixture [8]. When the SA was added in the feedstock comprised of 65vol%, it is clear that the torque values decreases gradually, attributed to better lubrication of the mixture while mixed. As a result, viscosity of the powder-binder mixture decreases to a great degree, nearly approaching the feedstock with the lowest powder loading (63vol%). A similar pattern was also observed by Merz *et al*. [9] who claimed that by adding 5% surfactant, the torque of a feedstock with a 55 vol.% powder fraction could be lowered to the same value as a feedstock with a powder fraction of 50 vol.% showed without surfactant. Moreover, with the addition of 10% SA in the binder formulation, it seemed that a much better feedstock homogeneity was achieved, corresponded to a shorter time (less than 20 minutes) for the feedstock to attain a steady state torque condition. The reason being that was the SA content improves the interaction between the powder and the binder. In short, enhancement of the interaction will decrease the usage of the binder and more powder can be contained in the feedstock in a determinate volume. It is important to use a greater powder loading in MIM as it could minimize sample shrinkage after sintering, as well to improve sintered density and the performance of the final products.

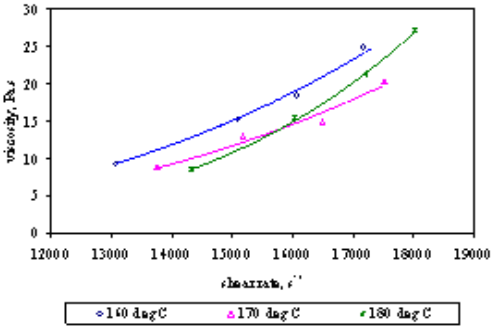
This method, however, suggested that is based essentially on the degree of mixing of the powder with the binder before reaching a steady state. Therefore, the rheological characteristics of the feedstock should be characterized, following the mixing process after reaching a steady state value.

3.2 Rheological Properties

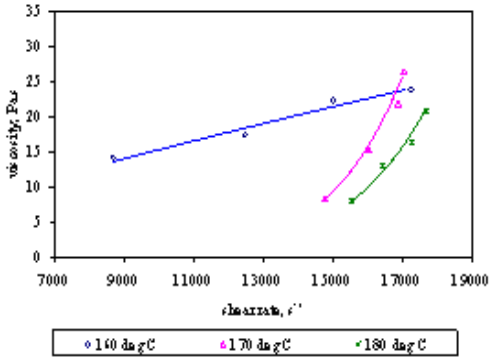
Figure 3 shows the rheological behaviour of the feedstock with different SA additions. It is clear that all of the feedstock show dilatant behaviour, viscosity increases with shear rates for all temperatures tested, unlike many feedstock used in MIM practice, viscosity decreases with shear rates is generally observed [10-13]. The viscosity data seems to be not consistent, particularly at the higher shear rates. Generally, the viscosity and shear rate of feedstock will decrease by adding SA in the binder formulation and this would change the dilatant to pseudoplastic flow under applied stress at lower temperature [11]. However, an addition of SA from 4 % to 10% in this binder formulation resulted in a very small deviation of flow behaviour from the counterpart. Even thought all samples show dilatant characteristis, the viscosity data are relatively lower in comparison with many feedstock used in MIM works [10,12, 13]



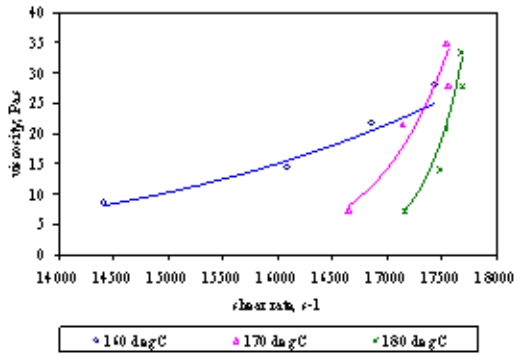
(a) PSPPSA-4



(b) PSPPSA-6



(c) PSPPSA-8



(d) PSPPSA-10

Figure 3 The viscosity against shear rate curves for different binder formulations of PS/PP/SA

Figure 4 shows the viscosity over shear rate, examined at various compositions of SA at 160 °C. As the amount of SA was increased, the viscosity decreased rather exponentially. This indicates that addition of SA in the binder formulation plays a leading part in decreasing the viscosity where it reinforced the wetting property for the powder.

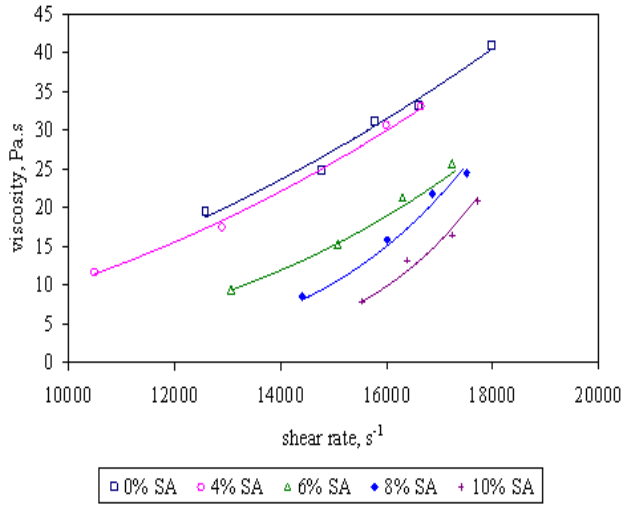


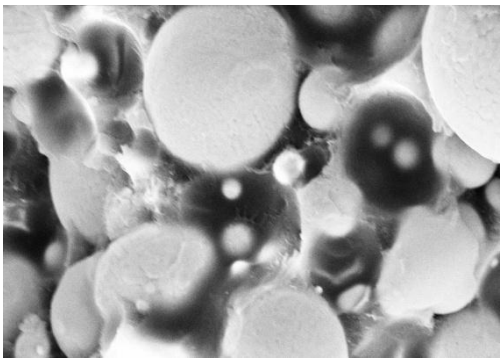
Figure 4 Viscosity vs shear rate curves for various surfactant compositions at temperature 160°C

It is clear that, for the proposed feedstock formulation in the present work, SA may serve significantly as a lubricant in the mixing process to produce a homogeneous blend. This is because the SA helps the metal powder and the binder to have a better cohesion by increasing the wetting of the binder on the powder. Thus, it improves the injection mouldability of the feedstock.

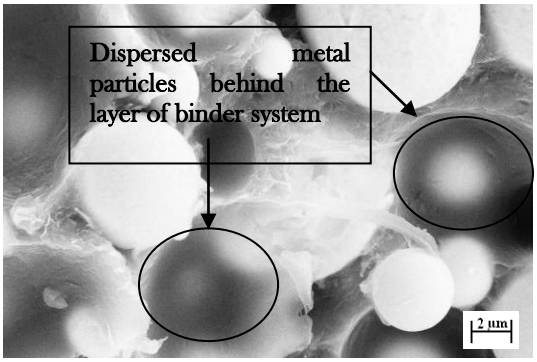
3.3 Injection Moulding

When two batches of feedstock (PSPP-65 and PSPPSA-10) were injection moulded for comparison, it was observed that with the addition of a surfactant in the feedstock, it is possible to reduce the injection moulding temperature, a reduction of 40-50°C. The PSPPSA-10 feedstock was successfully injection moulded at 220°C with an injection pressure of 30 MPa. Addition of the SA in the feedstock could decrease the powder-binder mixture viscosity, therefore increases the ability of the mixtures to flow at a lower moulding temperature.

Figure 5 shows the morphology of the fracture surface of the green specimen of PSPP-65 and PSPPSA-10. The fracture pattern of PSPP-65 is more rounded as a result of pull-out of particle breaking. Both fracture surface shows that the binder are completely melted and uniformly distributed in a powder matrix. Moreover, the fracture surface of PSPPSA-10 shows that the SA surfactant is prone to spread on the powder surface as clearly shown in the Figure 5 (b). These effects significantly prevented the particles from making a direct surface-to-surface contact.



(a) fracture surface of PSPP-65



(b) fracture surface of PSPPSA-10

Figure 5 SEM of green specimen of PSPP-65 and PSPPSA-10

From the experimental observation, it was found that the green specimens were quite gentle and flexible, and the specimens could easily be removed from the mould. Although the addition of SA could improve the mouldability, it was found that the green density was slightly reduced as reported in the previous work [14]. The reduction in green density could be attributed to the lower viscosity of feedstock made with the addition of SA (refer to Figure 4) compared to feedstock without SA addition. Less viscosity resulted in lower packing density.

3.4 Solvent Extraction Study

Figure 6 shows the kinetic study of solvent extraction of the moulded samples of PSPP-65 and PSPPSA-10. It clearly shows that for the case of 10% SA, all the soluble binder, particularly PS was completely leached away in just 150 minutes, while for samples without SA, the leaching time was prolonged for another 50 minutes to remove them. This is attributed to the lower amount of PS in the latter green parts. A lower rate of binder

removal in PSPP-65 was due to a greater amount of PS. Furthermore, a greater content of insoluble binder, PP, presumably creates a physical barrier, which retarded the diffusion of the PS and SA molecules from the moulding by clogging the pores and thus the debinding rate was impeded. Hence, it would be intuitive to use as little backbone binder as possible. However, there must be a minimum, otherwise, there will not be enough backbone binder to prevent compacts from slumping and distorting.

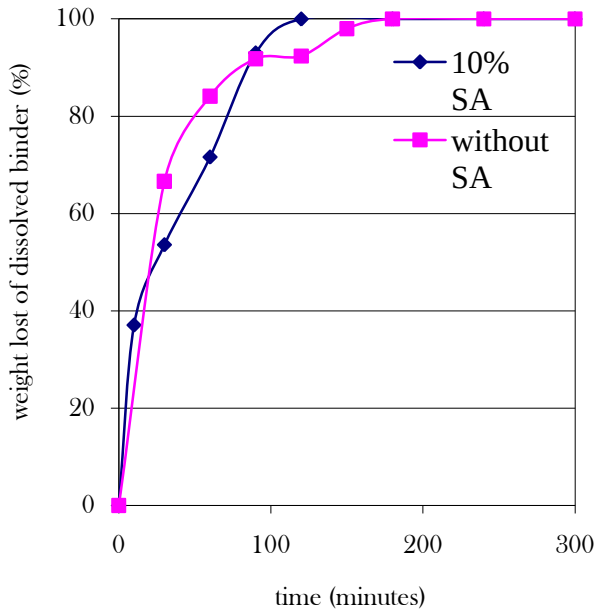


Figure 6 The percentage of soluble binder removed from moulded specimen

4.0 CONCLUSIONS

Addition of SA could modify the powder wetting, in which the torque value could be significantly reduced, manifest to increased lubrication. Furthermore, due to decreased viscosity, the mixing could reach a steady state in a relatively short period of time. Even though, all formulations exhibited a dilatant characteristic in rheological test, their viscosity are relatively lower in comparison with many feedstock used in MIM. Furthermore, the samples could be easily injection moulded without any problems. Adding SA has several advantageous during moulding and solvent extraction, in which lowered moulding temperature could be used and the rate of binder removal during solvent extraction could be significantly increased.

Acknowledgement

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