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Moldability of Nano Size Zirconia for Powder Injection Molding Process by Using PEG and PMMA Binders

Al Basir*, Abu Bakar Sulong, Etta Eshak, Najlaa Nazihah Mas'ood, Nashrah Hani Jamadon & Norhamidi Muhamad

Mechanical Engineering Programme, Centre for Engineering Materials and Smart Manufacturing (MERCU), Faculty of Engineering & Built Environment, Universiti Kebangsaan Malaysia, Malaysia
**Corresponding author: al.basir005@yahoo.com*

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ABSTRACT

Powder injection molding (PIM) is a well-known manufacturing technique for the production of metal and ceramic near net shapes. Now-a-days, this technology is largely used in electronics, biomedical, aerospace, automotive, defence and telecommunication industries. In this paper, green parts of ZrO_2 with polyethylene glycol (PEG), polymethyl methacrylate (PMMA) and stearic acid (SA) binders were prepared by PIM process. The average particle size of ZrO_2 powder was 50 nm with pycnometer density of 6.054 g/cm^3. The ZrO_2 powder was mixed with binder content of 73 wt.% PEG, 25 wt.% PMMA and 2 wt.% SA. The rheological results showed pseudoplastic properties of the feedstock at 140 °C and 160 °C, which was suitable for PIM process. The suitable injection molding parameters for feedstock at 51 vol.% powder loading such as mold temperature, injection temperature, injection pressure and holding time were 60 °C, 160 °C, 10 bar and 8 s, respectively. At the same powder loading, the green part density of 3.60 g/cm^3 was measured, whereas for the three-point flexural, the measured strength was in the range of 13-15 MPa. For structural analysis, the morphological properties of the powder as well as the surface and the cross-section of the green part was examined.

Keywords: Powder injection molding; Zirconia; Green part; Density

INTRODUCTION

Powder injection molding (PIM) is a manufacturing technique for producing metals, ceramics and carbide products. PIM consists of two processes, namely plastic injection molding and powder metallurgy (German & Bose, 1997). PIM has its own advantages and widely used in medical, dental, automotive, telecom, electronics, space and instrumentation industries (Choi et al. 2017; Daudt et al. 2017; Fu et al. 2005; Fu et al. 2007; Lin et al. 2017). PIM is capable of producing net-shape from complex shapes and different materials including super alloy, stainless steel and carbide. Notable features of PIM are: low cost, appreciable design options, flexibility, high mechanical properties, good surface finish and rapid production (Choi et al. 2017; Dehghan-Manshadi et al. 2018). In PIM process, there are four levels that need to be passed to produce the products. The stages are mixing, injection molding, debinding and sintering. In the mixing process, the metal powder or the ceramic powder is mixed with the binders at certain composition to produce the feedstock. The function of binder is to coat the metal or ceramic powder to ensure fluidity during the injection process. The feedstock is then injected into the mold and the resulting product is called green part. The debinding process is then carried out to remove the binders from the green part. At the stage, the part is known as brown part. Finally, the brown part will go through sintering process.

Zirconia (ZrO_2) is widely used in high temperature applications. It also has a very high level of thermal expansion and often used to combine with ceramic or steel. ZrO_2 powder is used in heat-resistant compositions to improve heat shock resistance and abrasion resistance. ZrO_2 materials are employed in sliding plates for steel steering and in steel immersion applications. Nano ZrO_2 can be used for medical applications because of its high level of bio-properties and strength (Piconi & Maccauro, 1999).

EXPERIMENTAL PROCEDURES

ZrO_2 powder with binders consist of polyethylene glycol (PEG), polymethyl methacrylate (PMMA) and stearic acid (SA) were used as feedstock. ZrO_2 powder was nearly spherical in shape and the mean particle size was 50 nm. The pycnometer density 6.054 g/cm^3 was measured by using

Ultrapycnometer 1000 (Quantachrome Instrument Ltd). The scanning electron microscope image of ZrO_2 powder is shown in Figure 1. The binder system was consisted of 73 % PEG, 25 % PMMA and 2 % SA based on the volume fraction.

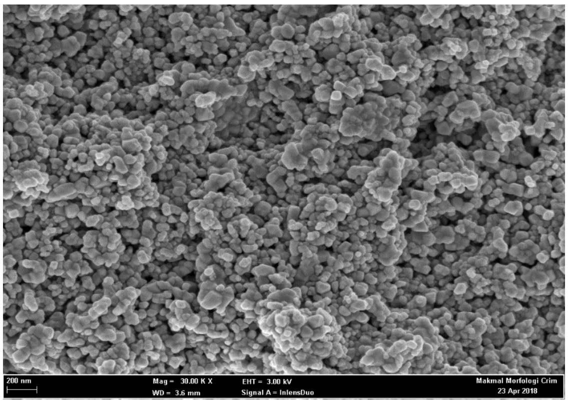

FIGURE 1. Morphology of ZrO_2 powder

A Brabender mixer (W50 EHT) was employed for the mixing process. In order to achieve a dough-like mixture, the applied mixing temperature, speed and time were 150 °C, 25 rpm and 1.5 h, respectively. Then it was crushed to make feedstock in granulated form. The rheological measurements of the ZrO_2 feedstock were carried out by employing a CIMB-500D Shimadzu model capillary rheometer at temperatures of 140 °C, 160 °C and 180 °C. The injection process was performed employing DSM Xplore injection molding machine. Injection parameters were manipulated to get the best possible results without developing any defects or cracks.

5567 Instron Universal Testing Machine was used to examine the flexural strength of the injection molded parts with powder loading of 51 vol.%.

RESULTS AND DISCUSSION

MATERIAL CHARACTERIZATION

The measured critical powder loading (CPVP) value for ZrO_2 powder was 53 vol.% with 27 mL oleic acid (Figure 2). In this case, the optimal solid loading was 2 to 5 vol.% less than the critical loading which was 48 to 51 vol.%. The obtained value was found to be higher than the previous report, where the critical powder loading of 41.4 vol% was found for 3 mol% YSZ with average particle size 50 nm (Foudzi et al. 2011). Zakaria et al. (2014) experimentally found the value of solid loading was 56 vol.%. German & Bose (1997) stated that most ceramics have powder loading in the range between 50-55 vol.%. Therefore, 51 vol.% of ZrO_2 was considered as optimal powder loading during experiment.

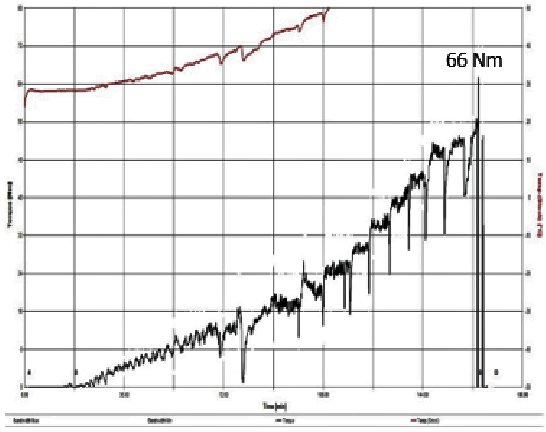

FIGURE 2. CPVP with critical peak value

RHEOLOGICAL PROPERTIES

Figure 3 displays the viscosity relationship with the shear rate at temperatures 140 °C, 160 °C and 180 °C which denotes the rheological properties. Generally, the viscosity of feedstock decreases as the shear rate increases and this indicates that the feedstock displays a pseudo-plastic behavior (Ani et al. 2014). Feedstock with powder loading 51 vol.% had high viscosity values in the range of around 1000 ~ 8000 Pa.s. During PIM, the appropriate shear rate of feedstock is within the range of 100 to 100,000 s^{-1} whereas the viscosity value of the feedstock must be less than 1000 Pa.s to facilitate the injection process and to avoid any defects occurring (German & Bose, 1997). Zakaria et al. (2014) also found higher viscosity while carried out rheological investigation on feedstock made by ZrO_2 powder with mean particle size 50 nm and PEG, PMMA and SA binders. Resende et al. (2001) explained that fine powder will contribute to higher viscosity compared to coarse powders. This will make the injection molding process difficult to inject the feedstock.

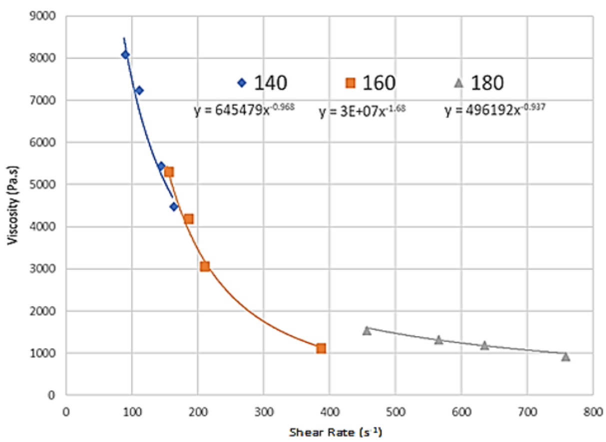

FIGURE 3. A variation of viscosity with shear rate at different temperatures

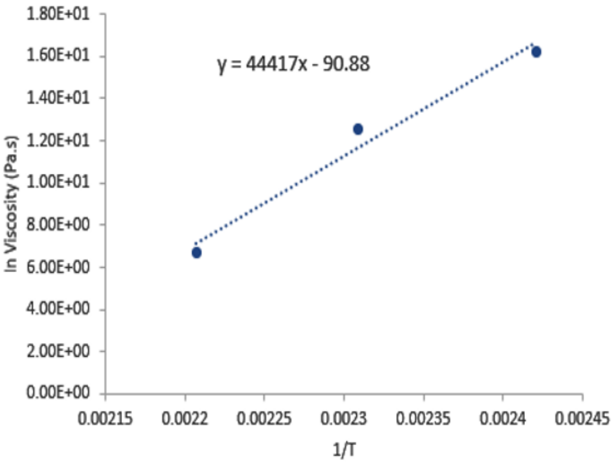

FIGURE 4. Correlation between viscosity and temperature

Table 1 shows the value of flowability index n for ZrO_2 powder. Here, the value of n at different temperatures for the feedstock is less than 1. This indicates that the feedstock has suitable pseudoplastic properties for PIM (Karatas et al. 2004).

TABLE 1. Flowability index of 51 vol.% ZrO_2 powder

Temperature (°C)	Flowability index (n)
140	0.032
160	-0.68
180	0.063

The calculation of the activating energy E is obtained by using the Arrhenius equation, which is given below (German & Bose, 1997):

$$\eta(T) = \eta_o \exp\,(E/RT)$$

where η_o is the viscosity at the reference temperature, R is the gas constant, and T is the temperature. Figure 4 shows the graph of $ln\eta$ versus $1/T$. The effect of temperature on the viscosity of the feedstock is indicated by the value of E. Low activation energy value indicates low sensitivity to temperature and consequently flow instability can be avoided during injection process (Ani et al. 2014). High value of E promotes premature freezing (Agote et al. 2001). The activation energy value, E for the 51 vol.% powder load is 3.69E + 05 kJ/mol.

INJECTION PROCESS

In the study, the injection parameters values were chosen based on the tried-and-tested method. In addition, the rheological test parameter was also used as a reference to this method. In the injection process, the maximum injection temperature shall not exceed the lowest decomposition temperature of the binder.

TABLE 2. Injection Parameter for 51 vol.% ZrO_2

Injection Temperature (°C)	Injection Pressure (Bar)	Holding Time (s)	Mold Temperature (°C)
160	10	8	60

Table 2 represents the best values obtained from the tried-and-tested method. With powder loading of 51 vol.%, the feedstock required slightly higher pressure and temperature. This is because of the low volume content of binder. It was found that the injection molded parts had good appearance and no defects or cracks were observed (Figure 5).

FIGURE 5. Green part after injection process

PHYSICAL AND MECHANICAL PROPERTIES

The value of density was obtained using the principle of Archimedes. The density of the green part at 51 vol.% powder loading was 3.60 g/cm^3. The density values for all green parts were found to be in the range of 3.58-3.61 g/cm^3. Therefore, the density for green part was 3.60 g/cm^3 based on the average value.

The green body should have enough strength to facilitate the handling of the substance or sample for the next process. Experiment on strength was carried out using three-point bending test methods. Loads were uniformly applied to the green body in the center where the tip of the sample was placed in the support span. During the test, the load rate set in the software was 5 mm/min. The value obtained was the maximum flexural strength. The flexural strength of the green part in this study was within the average of 16 MPa at injection temperature of 160 °C. Therefore, powder loading plays an important role. At lower powder loading, the binder will act more responsively at high temperatures which will reduce the ability of the powder to formulate particles during molding.

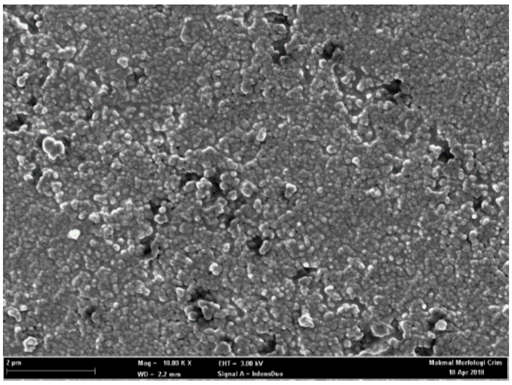

FIGURE 6. The FESEM image of green part, at 10000X magnificent

Figure 6 shows the FESEM image of the green part that was successfully injected. Based on the figure, ZrO_2 powder is nearly coated with the binders due to small particle size of ZrO_2. With a small size of powder, the ZrO_2 powder is entirely mixed with the binder. It can also be seen that there are several pores on the surface of the green part. Such pores can cause the green part to become brittle. This also leads to lower flexural strength of the green part due to presence of such pores.

CONCLUSION

This study was initiated by obtaining the value of critical powder loading. Optimal powder loading applied during experiment is 51 vol.%. Feedstock with powder loading 51 vol.% has a high value of viscosity within range of 1000 ~ 8000 Pa.s. This causes the feedstock required high pressure to inject completely into the mold. The injection temperature, injection pressure, mold temperature and holding time employed in this study were 160 °C, 10 bar, 60 °C and 8 s respectively. By using these parameters, this study produced adequate good injectd samples. The measured density of the green part was 3.60 g/cm^3. Furthermore, the flexural strength of the green part was within the average of 16 MPa at 160 °C. This study will help to understand the injection molding process of nano-sized zirconia more precisely.

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