Characteristic Of The YTTRIA Stabilized Zirconia (YSZ) for Ceramic Injection Moulding by Using Palm Stearin as a Primary Binder

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ABSTRACT

Ceramic injection moulding (CIM) is a near net shape process to produce smaller and intricate parts at a competitive cost. However, fine particle size (nano scale) used for such injection moulding process generally leads to agglomeration, higher binder content and critical dimensional shrinkage, which result in defects on the sintered components. This study extensively investigates the characteristics of YSZ for CIM process. YSZ parts were moulded by CIM process that utilized a multi-component binder system using palm stearin (PS) and polyethylene (PE) in 60:40 (vol %) ratio. The powders were characterized using particle size analyzer, pycnometer density and scanning electron microscopic (SEM). The binders were characterized by the pycnometer density, differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). Powders loading were chosen by the critical powder volume percentage (CPVP) through an oil absorption test. YSZ powder was mixed with the binders at different powder loadings ranging from 58 to 60 vol% based on CPVP. The parts were injected moulded, thermal debound, pre-sintered and sintered. The microstructure, green strength and hardness of the sintered part at different powder loadings were investigated. A large porous region was clearly observed at 58 vol% compared to 60 vol%. All samples were sintered at 1350 ^{O}C, with the highest green strength and hardness was 13MPa and 357.42 HV respectively were given by the sintered part at powder loading of 60 vol%.

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Introduction

Ceramic injection molding (CIM) is a combination of powder technology and injection molding that involves several stages including mixing, debinding, and sintering [1]. Characterization of the powders and binders were important and should be done as a prior before proceed to further process. Through the characterization, the suitable characteristics of the powder for injection moulding can be identified such as spherical particle shape, particle size and good particle size distribution. In addition, the parameters used for mixing, injecting and debinding were selected by characterization of the binders. During mixing, ceramic powder is blended with binders to form a homogeneous compound. Binders provide viscosity to the powder, thereby simplifying the process of filling feedstock into the molds during injection molding. In addition, binders help in maintaining the original shape of the ceramic powder until the early stage of the sintering process [2]. Optimum powder loading ratio is also important to the success of PIM [3]. Commanly, the powder to binder ratio ranges from 45% to 75% by volume [4]. A high powder loading ratio will cause inconsistencies in the injected parts, which can subsequently damage the injection machine. In contrast, a low powder loading ratio can cause separation of binders from powder during injection, thus prolonging debinding leads to considerable shrinkage during sintering [5,6]. An optimum percentage of powder loading can minimize shrinkage, prevent cracking, and increase the mechanical properties of materials [7]. Therefore, the characterization of the materials give an effect to obtain the optimum powder loading ratio for injection by critical powder volume concentration (CPVP) to avoid unfavorable samples.

Experimental Set Up

The YSZ powders were white in colour and its particle shape is nearly spherical (Figure 1). The average particle size is 13µm was determined by the malven particle sze analyzer (Table 1) where its pycnometer density is 5.60 g/cm^3. Such powder was mixed with binders of palm stearin (PS) and polyethelyne (PE) at 60:40vol%. Internal mixer of Thermo-Haake with roller blade type was used to determine the highest powder loading of the 3mol% YSZ with the addition of oleic acid. 10ml of oleic acid was firstly added followed by 1 ml of oleic acid at every 10 minutes. Based on the highest powder loading which was 61.7vol%, 2-5% range was taken from 61.7 vol% [8]. Thus, 58, 59 and 60 vol% was chosen in this work. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) test were

conducted on the binders to determine their melting and degradation point temperatures (Table 2). These temperatures act as references for the mixing, injecting and thermal debinding processes.

The mixing process was carried out by a Brabender mixer (GmbH & Co.KG) at temperature, time and speed of rotation of 150^{O}C, 90 minutes and 30 rpm, respectively, to produce feedstock. The samples were injected at 170^{O}C in rectangular bars shape having the dimension of 55mm (length) x 5mm (width) x 5mm (thickness). This MPIF 15 standard size was applied accordingly to undergo flexural strength of green part. Thermal pyrolysis (debinding) was performed where the parts were embedded in alumina powder that act as a wicking agent, and heated in a furnace at 550^{O}C. The heating rate was 0.4 C/min and the parts were soaked for 2 hours in order to remove the binders. The pre-sintering was carried out simultaneously after the debinding process at 1100 ^{O}C for 2 hours with a moderate heating rate to initiates the solidification process. The parts were subsequently sintered in the furnace up to 1350 ^{O}C for 2 hours without a wicking agent. The microstructures of as-sintered parts were observed using tabletop microscope (SEM). The, hardness test was performed on the sintered part using the vickers hardness machine

Results and Discussion

Near spherical shape for 3mol% YSZ powder was observed at 1000x magnification, as shown in Figure 1. These particles are clustered due to the agglomeration of powder. Finer particles tend to agglomerate effectively due to higher total surface area. Table 1 shows the particle size distribution and packing density of the 3mol% YSZ powder. The most remarkable feature in the particle size distribution analysis is D_{50} which means the average size of the powders and Sw which means particle size distribution. It was stated that the most appropriate powder size for the PIM process is in the range of 4 to 20 µm although some of the literatures reported that the size of very fine particle powder is 2 to 8 µm [1]. High value of Sw means narrow particle size distribution while low value of Sw indicates the wide distribution of particles. According to Sotomayor et al., (2010), powder with wide powder particle distribution such as Sw = 2 is easier to be injected compared to that of having Sw = 4 or 5. Meanwhile, it would be difficult when the value of Sw is larger than 7 due to wider distributions of powder particles that allow smaller particles to fill in the voids between the larger particles [9].

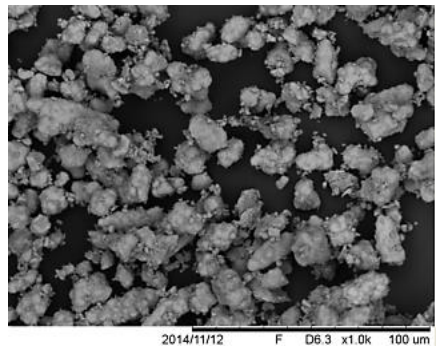

Figure 1: SEM of YSZ powder

Table 1: Results from Particle size analyzer

Powder	D_{10}	D_{50}	D_{90}	S_w	Density (g/cm^3)
YSZ	4μm	13μm	29μm	3	5.60

Table 2: Characteristics of binders component

Binder	Density (g/cm3)	Melting Temperature (ºC)	Decomposition Temperature (ºC)
LDPE	0.95	114.42	446.64
Palm Stearin	0.89	59.93	382.09

Figure 2 (a) shows two curves representing the binder components such as PE and PS. Both of the binders were heated at 500 ^{O}C, which is the maximum temperature for the decomposition of all the binder components. The first endothermic peak for all peaks was observed at nearly 30 – 35 ^{O}C due to a settling effect from the machine. Such effect was caused by the heat transfer from the machine to the samples to achieve equilibrium. The results clearly showed that the single binder component was shown in two different lines had two endothermic peaks respectively. Such peaks indicate different melting temperatures for the respective binder components. For PS, the first onset temperature begins at ~54 ^{O}C and apparently completed just after ~60 ^{O}C. Meanwhile, the melting for PE is approximately 114.42 ^{O}C and and the curve started to deflect at 99 ^{O}C. This finding is quite similar with those reported by Jamaludin et al. (2015) and Subuki, (2010) [10][11]. The second endothermal peaks show the estimation of the decomposition temperature for both binders. Such decomposition temperature is discussed in the TGA section of this paper.

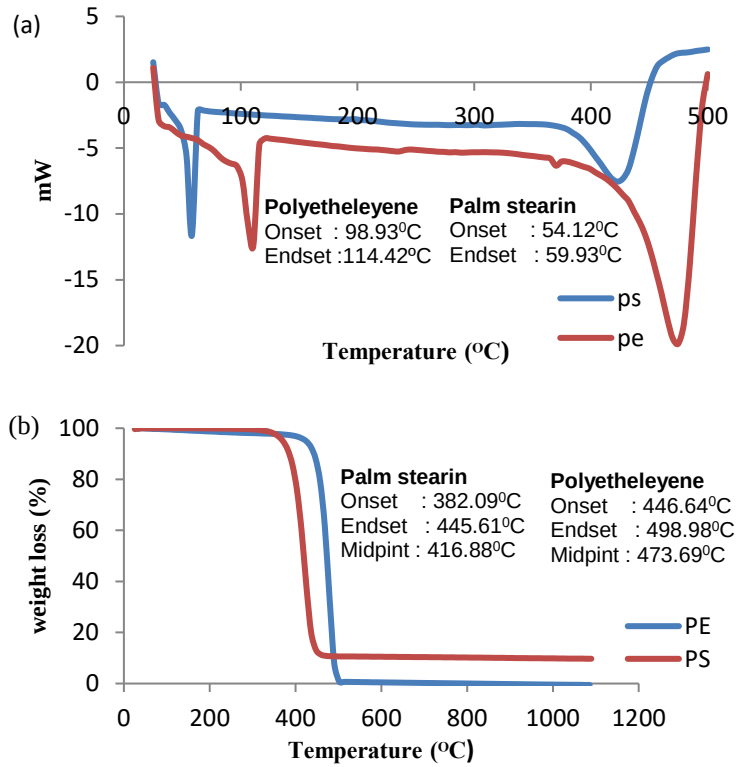

Figure 2: Thermal analysis of the binders (a) DSC (b) TGA

Figure 2 (b) shows the TGA results for the binder components. Different decomposition temperatures and amount of weight losses was observed due to different constituents in the binders. The binders start to decompose at different temperatures, similar to different melting temperatures as shown previously in the DSC results. The first binder material started to decomposed was PS followed by PE where the decomposition temperatures are 382.09 ^{O}C, and 446.64 ^{O}C, respectively. Both binders are completely decomposedat 445.61 ^{O}C and 498.98 ^{O}C for PS and PE respectively. The weight loss percentages for PE components tended to be nearly 0% as the samples was heated up while PS showed to have 10% residue. This residue was assumed to become a carbon content which can affect the mechanical properties. The longer it takes for the decomposition temperature to complete, the higher the temperature to remove the binder is required. This aspect is important, especially during considering the heating cycle in the debinding process.

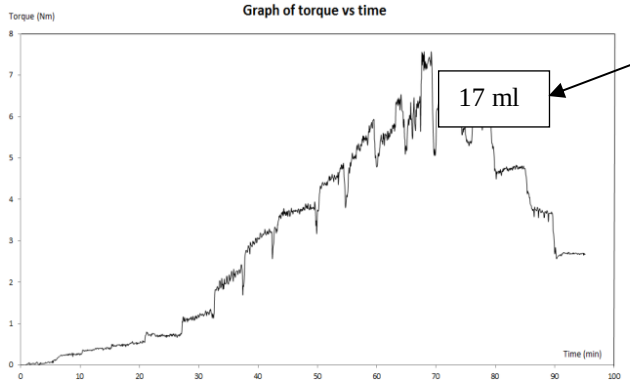

Figure 3: CPVP with critical peak value at 61.7 vol%

Optimal powder loading can be estimated through CPVP where such critical powder loading indicates the maximum powder volume ratio in a defined powder and binder mixture. Oleic acid of 22 ml was added to 154g of YSZ powder in the mixer. The mixing was carried out at room temperature and the speed of rotation was 30 rpm. The critical value of powder loading obtained was 61.7 vol% with 17 ml of oleic acid, as shown by the highest peak in Figure 3. Such value is slightly higher than the range of ceramic injection moulded mentioned by German and Bose, 1997 [8] which is 50~50%. The critical powder loading of this work is also slightly higher than that of as reported by Lee, (2004), [12] and higher compared to other researchers that used nano scale YSZ powder (Zakaria, 2014; Mohd Foudzi et al., 2013; Md Ani et al., 2014) [12]-[14]. This is due to more binder is needed to cover the total surface area of the particle of the smaller size powder. Therefore, the powder content will be smaller.

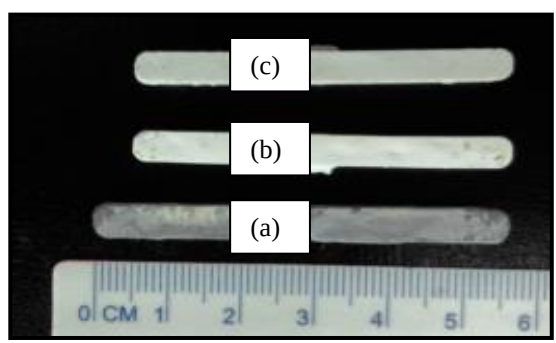

Figure 4: Injected parts (a) Green part (b) Brown part (c) Sintered part

Figure 4 shows the injected moulded parts of 58vol% powder loading at difference stages such as (a) after injection moulding (green part), (b) thermal debinding (brown part) and (c) sintering (sintered part), respectively. All samples were successfully injected without producing any unsatisfying condition such as distortion or cracking. There was a significant dimensional change between green part and the brown part due to removal of the binder. However, There was no substantial dimensional difference can be seen between brown part and sintered part due to necking process and incomplete diffusion process.

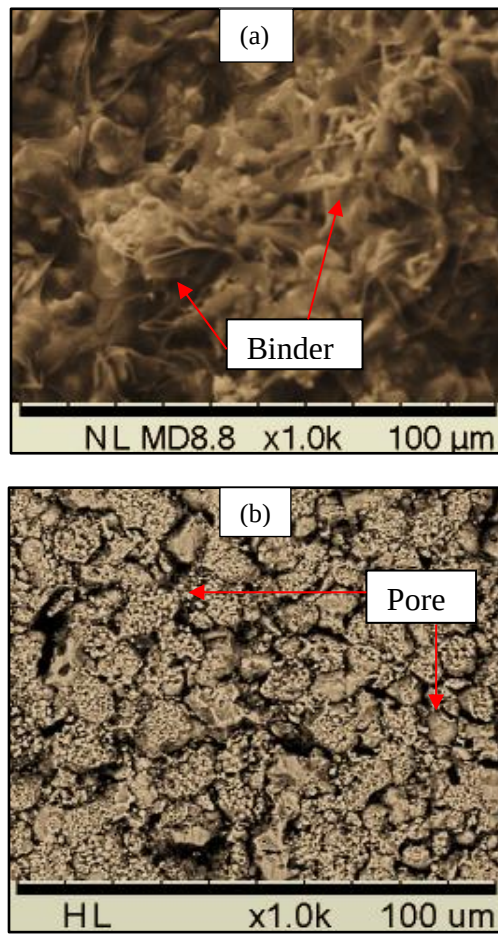

Figure 5: Microstructure of 60vol% powder loading (a)green body (b)sintered part

Figure 5 shows the surface morphology of (a) green part and (b) sintered part for powder loading at 60 vol%. It clearly shows that at the moulded stage, some traces of binder can be seen, indicates that PE and PS covered the powders particles. At the sintered parts as shown by Figure 5(b), all binders were completely removed as proven by porosity appearance and the particles started to diffuse. The grains overlapped with one another and some of the particles did not undergo the necking process or diffuse completely due to lack soaking time during the sintering process. As mention in [8], a higher surface area and higher temperature initially provide faster sintering process. Late in sintering, the motivation forces will be exhausted and result to slower sintering rate. Thus, longer soaking time and higher sintering temperature are required. The mistake occurs in this process affects the mechanical properties of the sintered product. However, the surface of the 60 vol% sintered part had fewer voids than 58 vol%, which resulted in better mechanical properties.

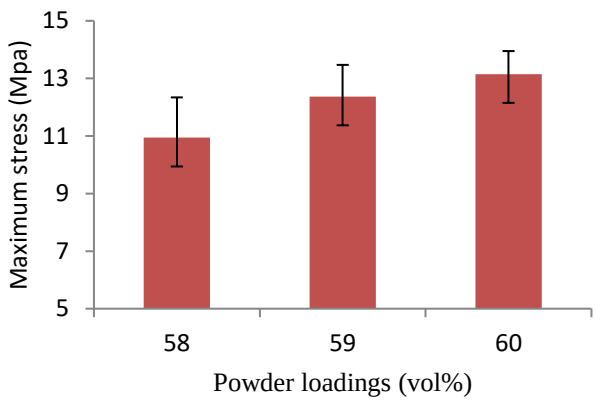

Figure 6: The green strength for different powder loadings

Figure 6 shows the results of flexural strength from 3-point bending test on the green part. The green part of the injected feedstock has the flexural strength ranging from 10 to 13 MPa. The green flexural strength was spotted to increase within the powder loading. The result obtained was slightly lower than Mohd Foudzi et al., [14], in their research on micro ceramic injection moulding using nano powder YSZ which revealed the flexural strength ranging from 13 to 16 MPa with the powder loading ranging from 37 to 43 vol%. As for the reason, the smaller powder particles give an advantage on higher packing densities which results in higher green strength.

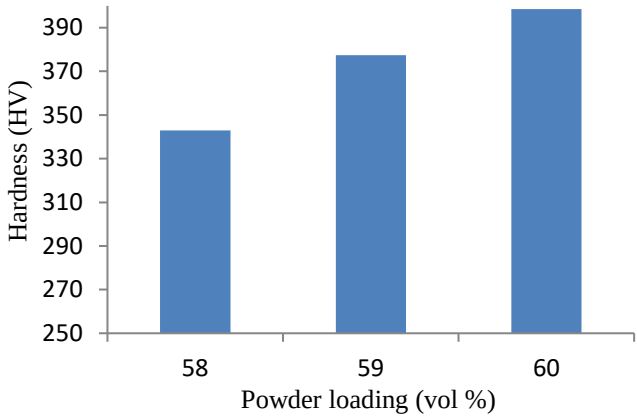

Figure 7: Hardness of sintered parts of various powder loadings

Figure 7 shows the hardness of the sintered parts with increased powder loadings. Powder loading at 60 vol% gave the highest value of hardness, which is 357.42 HV while the lowest value of hardness of 314.72 HV is given by the 58 vol% powder loading. These values were far from the 3 mol% YSZ theoretical value which is 1100HV due to incomplete diffused in the sintered parts, as observed in Figure 5(b), [15] and probably because of high carbon content from PS residue which weakend the ductility properties. P. C. Yu et. al [16] also reported if the sintering process uses temperature at 1350 ^{O}C, the hardness will be below than 1000 HV.

Conclusions

Characterization of the powder material and binders are important to gain success in CIM process. The results from the binders thermal analysis indicate the suitable parameters to be used throughout the process. The powder loading chosen are 58, 59 and 60 vol% based on the CPVP test. YSZ parts were successfully fabricated through powder injection moulding by using PE and PS as the binders with the range of green strenght achieved were 10 to 13 MPa. A hardness of 357.42 HV was exhibited for 60 vol% at 1350^{O}C sintering temperature. This study indicates that the increasing of powder loading will increase the green strength and hardness of the sintered parts. The morphological studies showed that all parts were incompletely diffused where some of the particles retained their near spherical shape. So, study in sintering parameters such as holding time and sintering temperature is recommended for future works to gain better sample properties.

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