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Research paper

Rheological Behavior of Zirconia Added Alumina Mixture

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Abstract

Zirconia and alumina are one of the materials that is widely used in medical industry. Zirconia Toughened Alumina (ZTA) have great properties to be apply in the ceramic injection molding such as have high hardness and high strength. The powder used in this research are alumina and zirconia while the binder to be used in this research is using 100% single based binder of palm stearin (PS). Behavior of zirconia blended alumina was investigated by rheological testing at temperature 55°C. Two formulations were used which is 60% (alumina/zirconia) plus 40% PS and 64% (alumina/zirconia) plus 36% PS. The ratio of alumina and zirconia used in this research is fixed at (85:15) for both samples. Four basic process involved which is mixing process, injection molding, thermal debinding and sintering process has been implemented to complete ceramic injection molding (CIM). Sample were performed the thermal debinding at a heating rate 0.5°C/min up to 700°C and sintering at heating rate 3°C/min for temperature 1400°C and 1600°C. The hardness was tested using Rockwell hardness test for both AZ60 and AZ64 sample. Highest hardness was obtained from the sample AZ64 at the temperature 1600 °C which is 109HRR compare to the 1400°C that achieved 95.3HRR.

Keywords: *Rheological; Zirconia; Alumina; Ceramic Injection Molding; Sintering*

1. Introduction

Dental implantation is being developed in various application in other to increase the quality of the implantation and give better characteristic for the industries. Zirconia is investigated its characteristic and properties especially in dental implantation because zirconia have received high demand due to good antibacterial response and strengthen the mechanical properties of the element. Zirconia belong to the mineral group of silicates and was discovered by the German chemist which is M.H. Klaproth in year 1789 [1].

Zirconia have a characteristic similar to the titanium that made it being use to replace the titanium in the dental implantation. Zirconia also have a strong, ductile characteristic as well as has been applied as structural material for dental bridges, crowns, insert and implant mostly because of its biocompatibility, high fracture toughness and radiopacity [2].As for the research, the material used are Alumina powder, Zirconia and single binder which is palm stearin. The rheological behavior of zirconia added alumina mixture was investigated to determine its rheological behavior and its mechanical properties through Ceramic Injection Molding (CIM).

Ceramic injection molding (CIM) is being used widely in the industry beside Metal Injection Molding (MIM). In CIM, the process such as mixing, injection molding process, thermal debinding and sintering process are convenient [3]. The green part was obtained by using the CIM in other to determine the morphology of the sample after the mechanical testing via Scanning Electron Microscopic (SEM). In earlier stage of the process CIM, feedstock need to be obtained by following the correct formulation that have been research before going up to the next stage which is injection molding process.

The feedstock was mixed using speed mixer machine and the speed of the mixing process is at the 1200rpm. The materials need to be mixed homogenously so that it can form good sample feedstock to proceed for next stage and takes about 20 minutes mixing period. There is an issue were highlighted regarding to the previous research where the homogenous mixing process was perform with a long period of mixing about 1 to 2 hours using the brabender or internal mixer machine [4, 5]. This is a new invention where the CIM can be performed in just 20 minutes only. The objective of the research is to study the development method of new mixing process by using dual asymmetric centrifuge technique by speed mixer. Next, to investigate the effect of single binder palm stearin towards mechanical properties of alumina sintered part. And lastly, to determine the rheological behaviour of formulating feedstock and its properties for the successful injection moulding process

Before undergo injection molding process, the feedstock was analyzed using rheological test to study the flow behavior of formulated feedstock. A feedstock that have low viscosity, low activation energy and low behavior index, *n* has better rheological properties for effective injection molding.

The next stage is injection molding process where the temperature supply the fluidity properties to melt the feedstock so that it can be well flow through the mold to form a green part. The PS act as temporary vehicle to the feedstock to form a shape. The injection molding process was performed at very low temperature about 55°C-60°C using single based binder palm stearin. As reported by Aziz et al. [4] claim that the use of 100 % palm stearin was promising in providing required pseudoplastic flow for injection molding. The injection molding process can be carried out at relatively low temperature in comparison with the conventional binder systems used.

The binder acts as temporary vehicle to the feedstock. Thus, if the higher temperature used it will evaporate and make the feedstock much more brittle due to lack of binder and not applicable for injection molding requirement. After finished the injection molding process, thermal debinding will take place to remove the binder from the green part so that it will not affect the mechanical testing.

Last stage before mechanical testing is sintering process. Sintering is the process to strengthen the green part in certain temperature. The temperature for sintering process in this alumina zirconia is 1400℃ and 1600℃. Palm stearin is a potential binder system since it is organic and natural sources and widely available in Malaysia. Therefore, low operating temperature is expected during the processing steps, particularly during mixing and injection moulding, thus promoting better economical solution towards high production scale.

2. Method and Procedures

There are three stages to achieve the objectives of this research and the first one is material characterization, secondly is ceramic injection molding and third stages is mechanical testing. The rheological test also will be conducted to determine the rheological behavior of the feedstock.

2.1 Sample Characterization

The material that used in this research are Alumina and Zirconia powder. The morphology of the material Alumina and zirconia was determined using the Scanning Electron Microscopic (SEM). The particle size of the powder also can be determined by using SEM.

2.2 Pycnometer Density, Differential Scanning Calorimetry (DSC) and Thermogravemetric Analysis (TGA)

The pycnometer was used in order to determine the density of the material that used in this research located at the Heat Treatment Laboratory Faculty of Mechanical Engineering. The materials that undergo the test of the pycnometer density are Zirconia, Alumina powder and Palm Stearin. The helium gas was used in the pycnometer density to determine the density of the powder so that it can be easily done to calculate the weight of the sample when it comes the mixing process at the secondary stage. The figure 1 depicted the pycnometer density.

Figure 1: Pycnometer Density

Figure 2: DSC Machine

Figure 3: TGA Machine

The DSC machine was used to determine the melting point of the binder in order to proceed for the rheological behavior and through injection molding depicted in Figure 2. This is an important information where the mixing and injection molding temperature used must not above the melting point of the binder. The binder that used for this research is Palm Stearin as a single binder for this process. The DSC analysis located at the Instrumental Laboratory Faculty Chemical Engineering UITM Shah Alam.

For the test, sample must not be more than 10mg to run DSC analysis and the flow of the gas need to be constant rate which is 50 ml/min to avoid any failure during the process were run. The gas that use for the DSC analysis is Nitrogen gas. The heating temperature need to be set when the DSC analysis were run to test the melting point temperature of the palm stearin is 10℃/min and will stop at the temperature 125℃.

The Thermogravemetric Analysis (TGA) was used to determine the decomposition temperature of the binder that used in ceramic injection molding which is Palm Stearin. TGA also has been conducted at the Instrumental Laboratory Faculty Chemical Engineering UITM Shah Alam as depicted in Figure 3. The parameter such as gas flow rate which is 50 ml/min, heating temperature rate at 20℃/min and maximum weight of the material that can use to get to proceed the TGA analysis is must not exceed 20 mg. The starting temperature before proceed TGA analysis is 25℃ and will stop at the 550℃. The figure 3 showed the TGA machine.

2.3 Feedstock Preparation and Rheology Test

There are two formulations that were used for this project which is 60% (Alumina Zirconia) 40% (Palm Stearin) and 64%(Alumina Zirconia) 36% (Palm Stearin). The composition of the powder and binder can be seen in the Table 1. In other to mix all the powder and binder altogether, the mass of material powders and binder need to be calculated. The machine used to mix the materials and binder was the speedmixer Dual Asymmetric Centrifuge (DAC) 600.1 FVZ. The rotation mixer is 800-1200 rpm and were run until homogenous.

Table 1: show the Formulation of Alumina-Zirconia and Palm Stearin

Formulation	Alumina-Zirconia (%)	Palm Stearin(%)	Total %
1	60: 40	40	100
2	64: 36	36	100

Capillary rheometer was conducted to test the rheological behavior of the material. For CIM it must perform pseudoplastic behavior where the shear viscosity is decreased with the higher shear rate. In this process, the feedstock should be able to flow through the die in the capillary rheometer in order to achieve a successful result in the end of the test. The temperature of the capillary rheometer was set 50-60 °C as the melting temperature of the binder Palm Stearin is low as 55 °C. Previous study showed the relationship between viscosity and shear rate by the equation 1 as shown below.

$$\eta = K\gamma^{n-1} \quad \text{(Eq. 1)}$$

Where the value of K is constant. The Activation Energy also can be defined as equation below:

$$\eta = \eta_0 \exp\left(\frac{E}{RT}\right) \quad \text{(Eq. 2)}$$

Where the value of η_0 is the viscosity at reference temperature. The value of R is constant, 8.314 and the value of T is the melting temperature.

2.4 Injection Molding

For the injection molding process, the temperature was set slightly above from melting point of Palm Stearin and wait for the temperature became constant. It is to ensure the temperature is sufficient for feedstock to flow through the gate and cavity. Then the feedstock was filled with ¾ volume into the chamber with pressure and heat applied to the feedstock. From the previous research, the temperature applied while using the injection molding machine usually 140℃ - 160℃ but in this project, the temperature used is only 55℃. This is because the melting point of the Palm Stearin is low compares to the others binder's melting point.

2.5 Thermal Debinding and Pre-Sintering

The thermal debinding and pre-sintered was begun in a one cycle step. The temperature of the thermal debinding process will go up to 550℃ and the heating rate of the process is 0.5 ℃/min. Then the temperature will rise up until 700℃ with the same heating rate which is 0.5℃/min as for pre-sintering process.

2.6 Sintering

Mold sample were sintered at the different temperature to test the mechanical properties of the mold sample which is 1400℃ and 1600 ℃. The sintering process is the process that strengthen the mold sample at high temperature as the mold sample were sintered at the temperature 3℃/min for both 1400℃ and 1600℃.

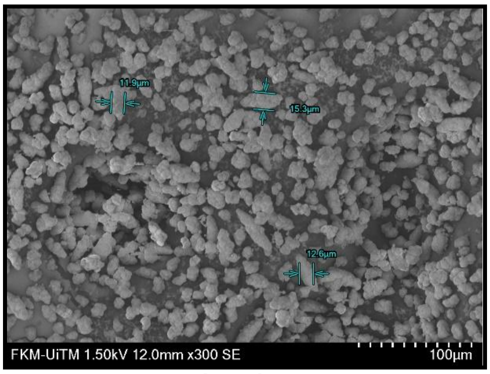
2.7 Mechanical Testing

Hardness test was tested at the Material Science Laboratory Faculty Mechanical Engineering. The machine used for measuring the hardness test is Rockwell hardness test and the scale for the Rockwell hardness test is HRR scale. Each sample will indent about 3 times to get the average of the hardness.

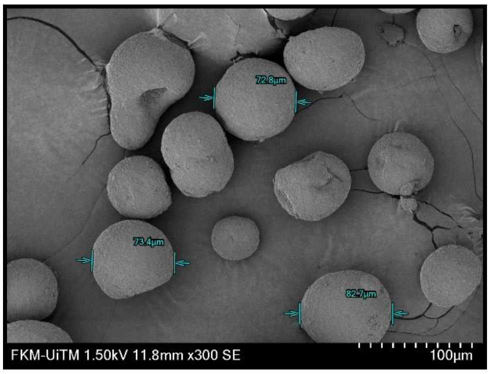
3. Result and Discussion

3.1 Sample Characterization

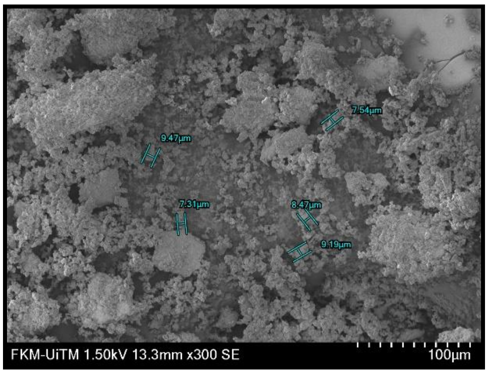
The Scanning Electron Microscopic (SEM) test has been done to determine the characterization of the alumina powder and the zirconia powder. The Zirconia powder showed a good characterization as the size of the powder follow the criteria and give a good rheological behavior. Typical particle sizes in CIM are 1-2 µm, but much finer particles down to submicron or nano region are being used in advanced CIM [3, 7]. As depicted in Figure 3a, the zirconia powder size is comparable for powder injection moulding used. The powder of the Alumina showed that the particle has a big size of powder that will affect the rheological properties of the material and the injection molding process as depicted in Figure 3b. The alumina powder provided in laboratory were performed milling process in order to reduce the size of particle to be used in CIM process as depicted in Figure 3c. The size produce after milling process was below than 10µm and it was comparable with CIM requirement and then was successfully produce the green part.



3a) Zirconia powder with size range 8- 15µm



3b) Alumina powder with size range 70-150 µm



3c) Alumina Powder After using Ball Milling

3.2 Pycnometer Density, TGA and DSC Binder Analysis

The materials were analyzed its properties in order to proceed and calculating the formulation of the feedstock and also for thermal debinding process. The pycnometer density was used to determine its density of the material for each of the component. The Table 2 showed the density after using pycnometer density machine.

Table 2: Density of the Materials

Material	Average Density (g/cm^3)
Alumina	3.6730
Zirconia	5.6627
Palm Stearin	1.0027

TGA and DSC Analysis also were determined in order to determine the suitable temperature that will be used in mixing, rheological test and injection molding process. From the result that has been conducted showed that the binder used which is Palm Stearin fully decomposed is at 358.01°C. DSC machine used to define the melting point of the binder and the result showed that the melting point of the Palm Stearin is 53°C. The mixing and injection molding temperature was set based on the DSC result which is slightly higher at 55-60°C to allow the sufficient temperature to melt the binder.

3.3 Rheological Behavior

Figure 3 show that formulation of (64%Al_2O_3-Zr + 36%PS) and (60%Al_2O_3-Zr + 40%PS) was comparable and exhibit psedoplastic behavior where the shear viscosity obtained was below than 200 Pa.s at very low temperature of 50-60°C. The good pseudoplastic behavior must permit the viscosity in the range of 10 – 1,000 Pa. s and shear rate need to be in range 100 – 10,000 1/s.

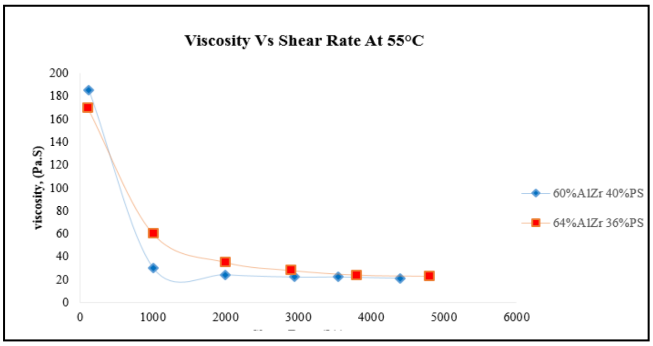


Figure 3: Graph Viscosity Against Shear Rate

Rheological properties are some of the important aspects in determining flowability of the feedstock as a function of shear rate and temperature. The flowability of the feedstock depends on the steady flow and the uniform filling into the mould cavity and subsequently provides important data for the next injection moulding process. The mixture needs to exhibit pseudoplastic behaviour where the viscosity degrades with the rise of shear rate. So it provides data such as the optimum required temperature and pressure to be used for the successful injection moulding process. Temperature used was around plays an important role. If sufficiently high, it will fully melt the binder and provide fluidity to form the desired shape.
Furthermore, Hausnerova et al. [8] reported the rheological behavior of aluminium oxide powder with multicomponent partly water-soluble polymeric binder (Licomont binder) to produce the defect free and non-porous parts. They found that the formulation of 60 vol.% alumina powder with Licoment binder and the surfactant (1 wt. % oleic acid) produce the pseudoplastic behaviour. The shear viscosity obtained was below 1000 Pa.s with increasing of shear rate and the temperatures used for rheology test was 150, 160 and 170 °C.

3.4 The Activation Energy, E

From the previous study, the feedstock is highly sensitive to the temperature fluctuations during injection molding when the activation energy, E is high. As a result, the high activation energy gives a negative feedback because the probability it made the mold sample cracks is high and there is possibility that the feedstock will melt quickly in the mold and affect the structure of the molded part such as a hole and another defect.

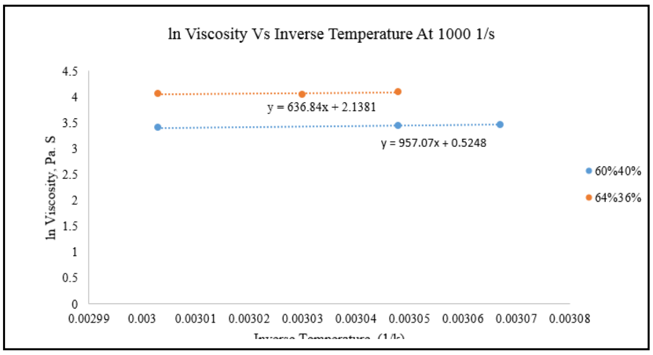


Figure 4: Graph of ln viscosity against inverse temperature

The graph in Figure 4 showed the ln viscosity against the inverse temperature at 1000 1/s where it is one of the step to find the value of the activation energy in order to see is it the formulation inhibits high activation energy or either way. From the figure above, the activation energy can be find where the slope of the graph which is the gradient is equal to (E/R), where R is a gas constant (R = 8.314 J/mol. k) and the result from the calculation to find the activation energy is shown as in table 3.

Table 3: The flow behavior index and activation energy for both formulations

Feedstock	60%AluminaZirconia 40%Palm Stearin	64%AluminaZirconia 36%Palm Stearin
Flow Behavior Index, *n* (At 55°C)	0.94	0.828
Activation Energy, E (KJ/mol. K)	7.95	5.29

Ultimately, for a productive injection moulding process with alumina feedstock, a crucial aspect is the temperature applied, which must definitely be below 70ºC in order to get a better moulded specimen. The viscosity of the powder-binder mixture is the key feature since it is very sensitive to temperature.
It has been proven that at low temperature, the mixture viscosity may be too high for moulding. While at high temperature, the binder may be too thin, resulting in a powder-binder separation during moulding. This study is supported by German [9] who claimed that during injection moulding, cracking may be observed if the binder gradually drops with substantial thermal stress in the moulded specimens.

3.5 Injection Molding Process

Based on the rheological data obtained, the appropriate viscosity can be attained from the selected formulation of alumina feedstock leading to a successful injection moulding process. The good flowability properties exhibited from rheology analysis gave clear evidence of the quality of the moulded parts.
The injection moulding process can be executed very effortlessly since the injection moulding machine is quite simple and uncomplicated for handling. In order to generate uniform molecular orientation throughout the part, it is recommended to maintain a constant velocity at the melt front.
From scrutiny of rheological results, the injection moulding process was continued for 2 formulations of (64%Al_2O_3-Zr + 36%PS) and (60%Al_2O_3-Zr + 40%PS). These two formulations were chosen in order to see the correlation between powder loadings and at the same time the other powder loadings exhibited the same trend during mixing and rheology tests. The injection moulding process was performed at a moulding temperature of 70ºC with the injection pressure applied in the range of 300 kPa to 400 k Pa. The green body which was successfully produced was free from any defects as depicted in Figure 5.

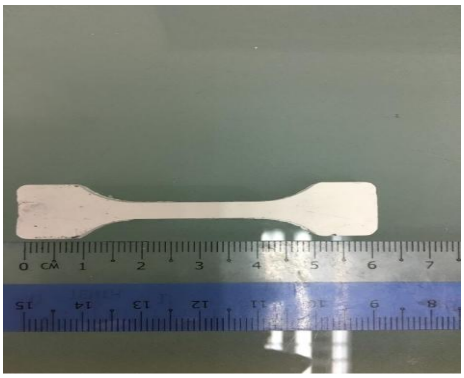


Figure 5: Mold sample after Injection

One of the reason the mold sample being crack as in Figure 6 for the injection molding process is possibly due to the high value of the activation energy. This is because a high activation energy, E lead to the sensitivity of the feedstock towards the temperature. The formulation of the feedstock (60%Al_2O_3-Zr + 40%PS) has higher E than the other formulation that lead it to more hard to get a successful mold without cracks. Other than that, the rheological behavior of the formulation (60%Al_2O_3-Zr + 40%PS) also not a good pseudoplastic as (64%Al_2O_3-Zr + 36%PS) that make it mostly crack after injection molding.

Figure 6: Crack occur after injection molding

3.6 Thermal Debinding and Sintering Process

Alumina wicking powder was used to avoid the mold sample from having any defect or cracks at any part of the mold during the thermal debinding process. Thermal debinding was running at the temperature 550 °C and hold for 3 hours then continued with the heating up to 700 °C at the 0.5 °C/min in order to remove the binder palm stearin from the mold sample.

A slow heating rate was applied based on Gorjan [10] who reported that the successful debinding process is commonly achieved by applying a very low heating rate. As a result, the binder decomposed gradually and the removed binder was eradicated and extracted to the surrounding embedment of alumina powder through the capillary forces. During the thermal debinding stage, the formation of pores grew and subsequently strong adhesion between the adjacent particles began to develop, causing the retraction of the product in which it dimensions are usually reduced between 14% to 20%[11]. The next stage is the sintering process where the process was heated under the different temperature which is 1400 °C and 1600 °C. The heating rate temperature used was 3 °C/min until it reached its temperature of sintering.

3.7 Mechanical Testing

The mechanical properties of the sintered sample, the hardness test was conducted at the Material Science Laboratory and being more specific of the test, Rockwell hardness test was carried. From Figure 8 it show that both formulation exhibit high hardness where the sintering temperature was directly proportional to the hardness value. Result show that the HRR value was about 100-120 HRR for sintering temperature at 1600° C and 85-90 HRR for 1400° C sintering temperature.

This is supported by Ani et al. [12] where they were studied on the ZTA (Zircornia toughened Alumina) of formulation (57%Al2O3-Zr + 43% HDPE/PW/SA). They found that at sintering temperature of 1600°C, the theoretical relative density reached 97.89%, whereas the hardness values reached 1582.40 HV. When at sintering temperature of 1400° C the hardness value obtained was 1220 HV.

3.8 Morphology via SEM

The image of the sintered sample for both formulation was conducted via using Scanning Electron Microscopic (SEM). The result showed that the formulation 60%40% have a pores and cracked after the mechanical testing were conducted. The other formulation which is 64%36% showed less pores and have a good surface with a less crack at the temperature 1600 °C. Table 4 depicted the SEM micrograph of sintered sample of 2 formulation of 60% alumina and 40% zirconia and second formulation of 64% Alumina with 36% zirconia. It shows that for 1400° C sintered temperature, the particle is start to diffuse and bond the particle together. While the 1600°C sintered temperature depicted the alumina and zirconia particle bonding is more strengthen and enhance properties of ZTA.

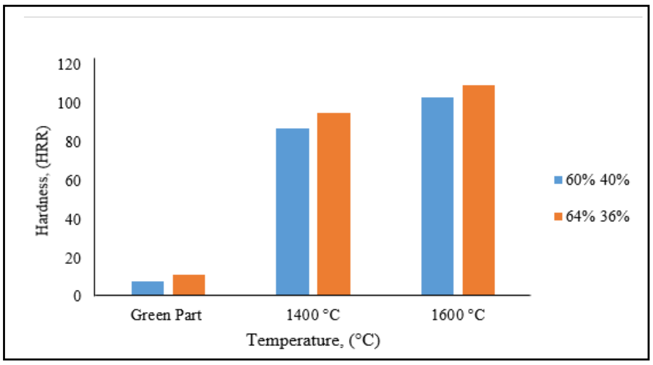
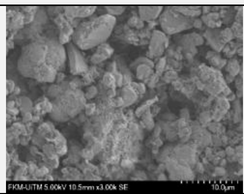
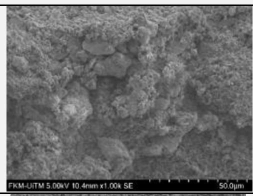
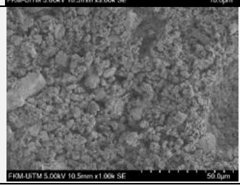
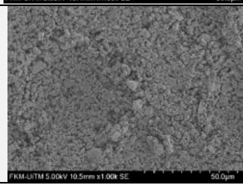


Figure 8: effect of the sintering on the hardness test

Table 4: depicted the SEM micrograph of sintered 2 formulation of 60% Alumina & 64% alumina.

Formulation	60% Al_2O_3-Zr +40% Palm Stearin	64%Al_2O_3-Zr +36% Palm Stearin
1400 °C		
1600 °C		

4. Conclusion and Recommendations

The both formulation of the feedstock (64%Al_2O_3-Zr + 36%PS) and (60%Al_2O_3-Zr + 40%PS) showed the comparable study where effect of additional material of zirconia improve the properties of alumina-zirconia injection molding. The alumina-zirconia (ZTA) was successfully fabricated through powder injection molding by using 100% single based binder of palm stearin by using speed mixer with dual assymetric centrifuge. It shows that even though just using a single binder, it can successfully obtain the pseudo-plastic behavior for rheology test and the processing temperature was used below than 70°C. This can be a great concern for industrial production which can promote green technology and can lower the energy consumption.

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