FORMULATION OF CERAMICS FEEDSTOCK FOR LOW PRESSURE INJECTION MOULDING

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A project report submitted in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Mechanical Engineering

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DECLARATION

I hereby declare that this project report is based on my original work except for citations and quotations which have been duly acknowledged. I also declare that it has not been previously and concurrently submitted for any other degree or award at UTAR or other institutions.

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APPROVAL FOR SUBMISSION

I certify that this project report entitled **"FORMULATION OF CERAMICS FEEDSTOCK FOR LOW PRESSURE INJECTION MOULDING"** was prepared by **TAN JIA HUI** has met the required standard for submission in partial fulfilment of the requirements for the award of Bachelor of Engineering (Honours) Mechanical Engineering at Universiti Tunku Abdul Rahman.

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ABSTRACT

Injection moulding is a standard manufacturing process in the industry, where it can be categorized into low pressure injection moulding (LPIM) and high pressure injection moulding (HPIM). LPIM is a manufacturing process similar to the additive manufacturing process, direct ink writing (DIW), as both processes, require low pressure to force the feedstock out of the nozzle. The main objective of this study is to formulate a suitable composition of binder-ceramic feedstock for LPIM. The ceramic feedstock applied is kaolin clay with the addition of binders: carboxy methylcellulose (CMC), hydroxypropyl methylcellulose (HPMC), methylcellulose (MC), and a dispersant, polyacrylic acid (PAA). First, the clay and binders ratio was tested multiple times to obtain the suitable output during the LPIM process using a 3D-printed syringe pump extruder, the injection moulding test. Then, the same clay tested in the injection moulding test proceeded for the weight test; it was discovered that the maximum weight to enable a complete extruded sample is 6 kgf (58.86 N). As a result, the optimum mass fraction is 65 wt%, 6 wt%, 3 wt%, and 26 wt% for kaolin, binder, dispersant, and water, respectively; the three sets of clay can be extruded entirely into the mould and still maintains their shape. The samples with the optimum composition have proceeded for debinding and sintering process where Sample A, B and C are using binders CMC, HPMC and MC, respectively. After sintered, the shrinkage of samples was investigated, it was found that Sample A has a shrinkage of 55.80 % and Samples B and C both have a shrinkage of 51.79 %. In the XRD analysis, the spectra of the sintered samples match with the spectra of mullite and coesite.

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LIST OF SYMBOLS / ABBREVIATIONS

% w/v	Percent weight over volume
K	Consistency index (Pa.s^n)
n	Flow index
W/C	Water to clay ratio
σ	Stress (Pa)
σ_y	Yield stress (Pa)
σ_y^{Dyn}	Dynamic yield stress (Pa)
σ_y^{Stat}	Static yield stress (Pa)
τ_y	Shear stress (Pa)
$\dot{\gamma}$	Shear rate (s^{-1})
η	Viscosity of suspension (mPa.s)
3D	Three dimensional
CMC	Carboxy methylcellulose
DIW	Direct Ink Writing
DS	Degree of substation
HPMC	Hydroxypropyl methylcellulose
LPIM	Low Pressure Injection Moulding
MC	Methylcellulose
PAA	Polyacrylic acid
WG	Sodium silicate water glass
XRD	X-ray diffraction

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Injection moulding is a common manufacturing method used in the industry. There are many types of injection moulding, for example, powder injection moulding (PIM), high pressure injection moulding (HPIM) and low pressure injection moulding (LPIM). In this study, the main focus is on formulating a ceramic feedstock for LPIM. The LPIM method applies lower pressure and lowers the injection and mould temperature (Sardarian, Mirzaee and Habibolahzadeh, 2017a).

For the ceramic feedstock, there were various types of ceramic powder that could be applied. The typical ceramic powder applied in the industry for LPIM is Alumina (Al2O3) and Zirconia (ZrO2). Besides that, more examples of ceramic powders such as kaolin and porcelain (contains kaolin content) were uncommon in LPIM but were common in applying Direct Ink Writing (DIW).

DIW is a three-dimensional (3D) printing technology to produce a 3D structure layer-by-layer. The composition for the ink in this method is ceramic or polymer which the powder can be melted in clay-like form. Then, this clay-like colloidal suspension is extruded out from the nozzle forming the desired structure in a stratified sequence (Sun et al., 2019a).

Both LPIM and DIW methods are applications of creating ceramic or polymer products and operates at low pressure. Moreover, the feedstock preparation for both methods was similar, where the clay had to be soft enough to extrude through the nozzle and maintain its structure after removing from the mould (using LPIM) or in open space (using DIW). Therefore, in this study, the investigation of kaolin composition for LPIM is expected to be applicable for DIW in 3D printing.

1.2 Importance of the Study

The importance of this study was to produce a ceramic product with good mechanical properties such as high strength and density from LPIM using an alternative ceramic powder, kaolin. As mentioned in Section 1.1, the common

materials for LPIM were alumina and zirconia; hence, this study will apply the material kaolin. Kaolin is a non-toxic material that can be handled directly by human hands; therefore, it is a good alternative for alumina or zirconia. Moreover, kaolin has a lower melting point than alumina and zirconia; hence, it is more suitable for this study that involves low temperature and low pressure injection moulding. The results of this study may provide insight into formulating an alternative ceramic feedstock that is suitable for LPIM.

1.3 Problem Statement

Most of the material used for LPIM has a high melting temperature, such as alumina and zirconia, which both ceramic materials have a melting point above 2000 ℃. Researchers tend to use these two materials in most journals, which are not suitable for low temperature LPIM. Thus, the problem statement for the current study of formulating ceramic feedstock is to find a suitable ceramic powder for low temperature LPIM.

The rheological properties of the ceramic powders played a significant role in the mechanical strength of the final product. One of the main rheological properties of feedstock in this study is the viscosity of the suspension. When the suspension is extruded or injected out from the nozzle, the structure must be dense enough to avoid slumping caused by gravitational force (M'Barki, Bocquet and Stevenson, 2017). Thus, the viscosity of the suspension is an essential factor to determine the flow speed of the fluid and rigidity of the green product. According to M'Barki, Bocquet and Stevenson (2017), the 45 wt% of boehmite suspension is denser than applying 43 wt% suspensions. Hence, one of the factors that affect the viscosity of the suspension is the weightage of the ceramic powder and binder contents.

The second rheological property is the yield strength of the feedstock. For instance, feedstock 1 with 77 wt% of porcelain powder and feedstock 5 with 84 wt% of porcelain powder had yield stress of 30 kPa and 23 kPa, respectively (Agote et al., 2001). Therefore, the mechanical properties and product quality was further affected after undergoing heat treatment processes such as sintering and debinding.

More research studies used the additive manufacturing technique DIW for kaolin as the ceramic feedstock. Based on the research, some interesting

binders such as methylcellulose (MC) and hydroxypropyl methylcellulose (HPMC) were used in DIW but not explore in LPIM. Furthermore, the manufacturing concept between DIW And LPIM is the same; hence, this study will investigate LPIM as the equipment was more suitable to be carried as a home experiment.

1.4 Aim and Objectives

The main aim of this study is to determine the formulation of ceramic feedstock for LPIM. The specific objectives of this research were:

- To formulate a suitable composition of binder-ceramic feedstock for low pressure injection moulding (LPIM).
- To design and 3D print the mould and the extruder for the injection moulding process.
- To investigate the extrudability of the feedstock with different composition of feedstock and perform sintering process to evaluate its shrinkage.

1.5 Scope and Limitation of the Study

In this study, the mechanical properties and behaviour of the ceramic (kaolin) and binders were vital, affecting the flow and printing qualities. Hence, the mechanical properties of the product will be affected accordingly due to the poor printing qualities. Besides that, the chemical properties of the materials were important as well. The process involves mixing the ceramic powder and binders to create the suspension. Furthermore, one of the essential characteristics of ceramic suspension is viscosity. Therefore, the suspension had to possess a gel-like characteristic so that the printed product would not slump and fail easily.

This study's limitation includes having a better understanding of the suitable ratio of the materials in the suspension. If the amount of the ceramic powder is too high, it will affect the flow of the suspension, causing it harder to flow out of the nozzle. Thus, clogging of the nozzle might occur and destroy the extruder. Besides that, the high amount of ceramic powder will also cause the product to dry rapidly; this is unsuitable for products requiring longer printing time as the printed lines will have difficulty merging.

1.6 Contribution of the Study

This study provides a ceramic feedstock using kaolin as the main ceramic powder for low pressure injection moulding (LPIM). Based on the literature review done in several research journals and articles, the study on ceramic feedstock using kaolin powder were primarily applied in DIW. Hence, this study will provide a better insight that kaolin powder can also be applied as the ceramic feedstock for LPIM due to the similarities between these two manufacturing methods.

The formulation of the ceramic feedstock in this study will maintain its shape after removing the sample from the mould design without stalling for a few minutes to dry the sample. However, please take note that the platform of the mould will still be in contact with the sample as it is still slightly soft and could not withstand pressure from the human hand during the removal of the platform. Hence, the drying time is reduced, and the vacant time of the equipment can be reduced as it can immediately continue the process after removing the product and replace a platform into the mould.

Besides that, the ceramic feedstock formulated is to be able to extrude under low force or pressure. Thus, the cost of power used for the manufacturing process can be reduced as lower power is sufficient to extrude the feedstock from the extruder. Therefore, the ceramic feedstock formulated in this study can aid the industry by reducing the cost and time consumption. Furthermore, when the cost of the product is reduced, the price of the ceramic product can be lower; hence consumers can obtain the products at a lower price. Therefore, creating lower price ceramic markets which are widely used in various sectors.

1.7 Outline of the Report

In Chapter 1, the introduction was written to explain low pressure injection moulding (LPIM) and the ceramic feedstocks that can be applied for this manufacturing method. Then, this study's importance and problem statement were listed to explain the changes brought by this study and the problems to be solved in this study. The aim and objectives of this study were listed, where the main aim was formulating a suitable ceramic composition that is extrudable using low pressure. Furthermore, the scope and limitations of the study cover

the importance and drawbacks face in this study. Lastly, the contribution of this study that can bring to the industry or society.

Chapter 2 focused on the literature review based on the research journals and articles on the materials, method and conditions. First, the research on the ceramic feedstock leaned towards kaolin, and several binders were studied. Then, the rheology tests carried were studied to understand the characteristics of the materials. Moreover, the methodology was studied to understand the clay preparation method and conditions needed to be taken care of during the experiment. Finally, the sintering and testing were investigated to gather information on the clay results after sintering.

Chapter 3 is regarding the methodology of this study. First, the materials chosen for the ceramic powder and binders were specified for choosing the said material. Then, three experiments are to be carried: extrusion test, injection moulding test, and weight test. The experiments carried were elaborated in the respective sections. After the experiment, the debinding and sintering process was elaborated, where only three samples was chosen to carry out the heat treatment. Lastly, the x-ray diffraction (XRD) analysis was mentioned, where this analysis is to check the composition in the materials.

The results and discussion was grouped in Chapter 4. Based on the experiments done, the results and findings were discussed in the respective sections. First, the diagrams were pictures of the sample taken during the experiment. It was observed and discussed based on the quantitative data and composition tabulated in a table. Then, comparisons were made between the clays using different binder systems. After the three sets of the experiment, the best set of clay was chosen for heat treatment to analyze the shrinkage of the samples. Next, the sintered sample and raw kaolin powder will undergo XRD analysis and are discussed in the following section regarding the composition and impurities within the material scanned. Besides that, the design of the equipment being used was discussed. It covers the design and printing process of the extruder and mould to the configurations of the electronic connections.

The last chapter is Chapter 5, regarding the conclusion made in this study. The optimum composition of the ceramic feedstock for this study was concluded. The chapter will end with the recommendations for this study to improve this area of study in the future.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

In this chapter, reviews on various research journals and articles were being evaluated. Firstly, the ceramic powders used by various researchers were discussed. The third subsection, where various types of binders or agents applied were discussed; then, the weightage of the ceramic feedstock and binders were determined, and its rheological characteristics were analysed. In the fifth subsection, the methods used by researchers and the condition (pressure and temperature) of the methods were considered, while the sixth subsection is regarding the sintering process and analysing the mechanical properties. Lastly, all the methods and materials done by the researchers was summarised in the last subsection.

The literature review study was based on the method DIW, due to more research were done on DIW using kaolin as the ceramic feedstock. The concept for DIW and LPIM are the same as mentioned in Chapter 1 Introduction; both methods require low pressure to extrude the product. Hence, the literature review on DIW was applied in this study using another method, LPIM.

2.2 Ceramic Feedstock

There are various ceramic powders used as feedstocks in LPIM and DIW. As mentioned in Chapter 1, the standard ceramic powders used for these two manufacturing processes are alumina, zirconia, porcelain and kaolin. According to Zhang et al. (2020), the ceramic feedstock may compromise more than a single type of ceramic precursor; for instance, mullite, quartz, garnets, steatite, titanium carbide, etc. were chosen according to the function of the final product. Some of the ceramic precursors were more fitted to be manufactured as utensils and tableware, while some were suited to be manufactured as sanitary wares, refractory materials, electrical parts or biomedical implants.

Sun et al. (2019a; 2019b) proposed using kaolin clay to produce a ceramic substrate for semiconductor applications. The particle size prepared for the kaolin clay powder is 3.76 μm, where the surface area and density are 18.78

m2/g and 2.60 g/cm3, respectively. The chemical components of the selected kaolin clay by Sun et al. (2019a; 2019b) are listed in Table 2.1 below.

Table 2.1: Chemical analysis of kaolin clay (wt%) (Sun et al., 2019a; 2019b)

SiO_2	Al_2O_3	TiO_2	Fe_2O_3	CaO	LOI
47.16	37.93	2.18	0.06	0.06	12.61

On the other hand, M'Barki, Bocquet and Stevenson (2017) selected boehmite gels as the ink of the robotic material extrusion. Boehmite is an α-Al2O3 precursor, which has the mechanical properties of high density and fine-grained qualities (results in higher toughness) after undergoing proper processing procedures. The raw ceramic powders were produced by mixing Catapal B with 2.5 wt% nitric acid, seeded with 1.5 wt% 30 nm α-Al2O3 particles to allow a more refined and denser microstructure during sintering at 1300 ℃. Before the suspension has proceeded for printing, a defoaming agent, octan-1-ol, was added to reduce the micro defects caused by air bubbles during the printing process

Besides that, Sardarian, Mirzaee and Habibolahzadeh (2017) proposed using alumina with particle size, 3 μm. The preparation for the feedstock is by mixing alumina powder with 6 wt% of steatite powder (have the same particle size as alumina powder). The proposed alumina powder content is 60 vol% of the overall feedstock; hence, the binder (will be further discussed in Subsection 2.3) will have a total of 40 vol% over the whole feedstock. The characteristics and composition of the feedstock are shown in Table 2.2 below.

Table 2.2: The characteristics of Alumina (Al_2O_3) powder (Sardarian, Mirzaee and Habibolahzadeh, 2017a)

Median particle size, D50 (μm)	Bulk density (g/cm^3)	Specific surface, BET (m^2/g)	Compositions (wt%)			
			Al_2O_3	SiO_2	Na_2O	Fe_2O_3
3	0.8	1.5	99.6	0.03	0.3	0.03

Furthermore, Revelo and Colorado (2018) proposed using kaolinite clay from Columbia as the ceramic feedstock. A few samples were created with the same kaolinite clay but with different water, volumes mixed. Hence, the

outcome of the samples was expected to have different results after undergoing the sintering process. The presence of binder is unavailable in this study; only kaolinite clay and water were involved for the feedstock preparation. The chemical composition of the proposed kaolinite clay is shown in Table 2.3.

Table 2.3: Chemical composition of oxides of La Paz raw clay (Revelo and Colorado, 2018)

SiO_2	61
Al_2O_3	23.2
Fe_2O_3	2.39
TiO_2	2.65
CaO	0.09
MgO	0.17
K_2O	0.29
BaO	0.01
MnO	0.03
P_2O_5	0.02
LOI at 1100 ℃	10.2

2.3 Binders

Binders were also known as binding agents, functioning as glue to hold the materials together. In some conditions, gelling agents were applied instead of binders. Zhang et al. (2020) proposed to use the gelling agent, agarose, mixing it with the ceramic powder, porcelain. The gelling agent was prepared by mixing 1.0 wt% agarose solution and 1.0 wt% fructose solution. The preparation of the gelling agent in mixing the two solutions is noteworthy as the strength of the gel mixture increases compared to a pure agarose gel, as shown in Figure 2.1.

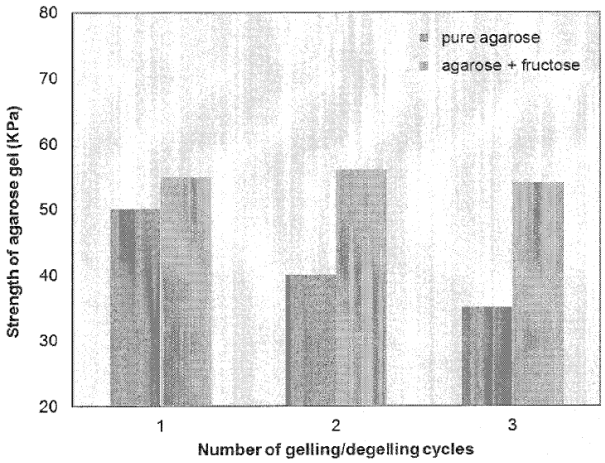


Figure 2.1: Comparison Between the Strength of Pure Agarose Gel and Agarose/Fructose Gel Against Number of Gelling/Degelling Cycles (Zhang et al., 2020)

In the meantime, Sun et al. (2019b) use an alkaline medium, sodium silicate water glass (WG) and a dispersing agent, anionic polyelectrolyte polyacrylic acid (PAA), to create the kaolin suspension. The dispersing agent, PAA, is used to disperse the kaolin particles so that the flow of the kaolin suspension can be improved when extruded from the syringe while also maintaining the sample's shape after extruded (it does not slump easily).

Continuing the research done by Sardarian, Mirzaee and Habibolahzadeh (2017), the binder system used is listed in Table 2.4.

Table 2.4: The characteristics of the binder components (Sardarian, Mirzaee and Habibolahzadeh, 2017a)

Binder components	Components value (wt%)	Chemical structure	Melting point (℃)	Decomposition temperature (℃)	Density (g/cm^3)
Paraffin wax	91	$C_{20}H_{42}$	56	200-400	0.9
Beeswax	6	$C_{15}H_{31}COO_{30}H_{61}$	68	200-400	0.96
Oleic Acid	3	$C_{18}H_{34}O_2$	13	360	0.9

The feedstock possessed shear thinning behaviour as the viscosity decreases while the shear rate increases. The reason is due to the proposed

binder system added into the feedstock. The polymer chains of the binder reduce the frictional force between the alumina powder particles; thus, the feedstock exhibits shear thinning behaviour, which aids the flow during the injection moulding process (Sardarian, Mirzaee and Habibolahzadeh, 2017a).

According to the study by Polamaplly et al. (2019), the binders, hydroxypropyl methylcellulose (HPMC) and methylcellulose (MC) applied on biodegradable support structures using 3D printing was investigated. The binders studied are MC A4M, HPMC E4M and HPMC K4M. The first alphabetic letters (A, E and K) indicate gel strength, gelling temperature and dissolving temperature (lower alphabetic order indicates a higher temperature). Whereas 4M indicates the viscosity of the binders is 4×1000 mPa s in 2 % solution at the temperature 20 ℃. Hence, K4M indicates that the material has the highest dissolving and gelling temperature but the lowest gel strength among the three binders. The properties of binders were summarized in Table 2.5, where DS in the table stands for degrees of the substation.

Table 2.5: The properties and composition of HPMC K4M, HPMC E4M, MC A4M samples (Polamaplly et al., 2019)

Material	Dissolving temperature (℃)	Gelling temperature (℃)	DS (methoxyl group) %	DS (hydroxypropyl group) %
HPMC K4M	25-30	77	19-24	4-12
HPMC E4M	20-25	60	28-30	7-12
MC A4M	0-5	49	27.5-31.5	N/A

The suspensions were prepared by mixing the material powder with deionized water at a temperature of 70 ℃ at different concentrations (8 %, 10 % and 12 % w/v). Then, the samples were cooled to 25 ℃ before centrifuging at high speed of 5000 rpm for 10 mins to create the suspension (gel) for 3D printing. Finally, the green parts have proceeded for testing after dried to investigate the rheological characteristics (Polamaplly et al., 2019).

2.4 Composition of Feedstock and Rheological Characteristics

Different weightage of the ceramic powder and binder will highly affect the mechanical properties and structure of the product; hence, the previous researchers was continued to investigate in this subsection regarding the weightage fraction of the materials and its effects.

The contents of the kaolin suspension proposed by Sun et al. (2019b)is summarized in Table 2.6.

Table 2.6: Compositions of kaolin suspensions with corresponding Herchel-Bulkley equation curve fitting parameters (Sun et al., 2019b)

Kaolin clay (vol%)	WG (vol%)	PAA (vol%)	τ_y (Pa)	K (Pa.s^n)	n	R^2
24	20	5.98	103.35067	3.47148	0.99841	0.99909
26	18	5.98	142.4483	7.28471	0.88994	0.99749
28	16	5.98	780.66108	3.09617	0.99647	0.91622
30	14	5.98	1168.41371	18.32294	0.76627	0.95953
32	12	5.98	1256.70112	163.35793	0.48821	0.91424

From Table 2.6, the 32 vol% suspension has the most significant yield stress, 1256.7 Pa, among the five suspensions. Hence, this suspension needs a higher pressure to enable the flow since it has a higher viscosity. Furthermore, the flow index n for all the suspensions were lower than 1, having a shear-thinning behaviour; hence, benefitting the suspension flow through the nozzle. Besides that, Sun et al. (2019b) prepared an additional 32 vol% kaolin suspension without adding PAA and realised that the yield stress reduces to 808 Pa; thus, PAA also has the function to increase the volume fraction and apparent viscosity. Furthermore, to have a firmer gel (suspension), the yield stress of the suspension is increased by adding PAA to improve the gel strength and maintain its shape from slumping. Consequently, the suspension can withstand more layers with higher strength (Sun et al., 2019b).

On the other hand, two weightage fractions of boehmite suspensions were prepared by M'Barki, Bocquet and Stevenson (2017), 43 wt% and 45 wt%.

The evolution of the elastic modulus, viscosity, stress and yield stress for the two suspensions was plotted as shown in Figures 2.2, 2.3 and 2.4.

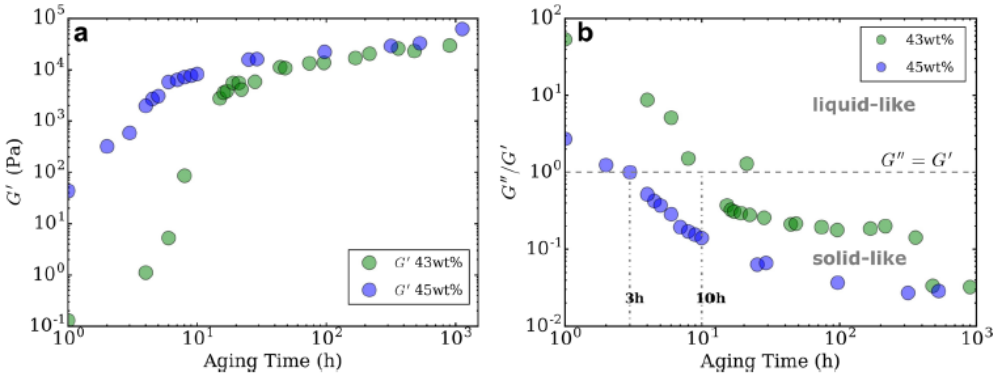


Figure 2.2: (a) Evolution of elastic modulus G' for 43 and 45 wt% suspensions measured at 1 Hz (b) Evolution of G"/G' as a function of aging time for 43 and 45 wt% solids loading (M'Barki, Bocquet and Stevenson, 2017)

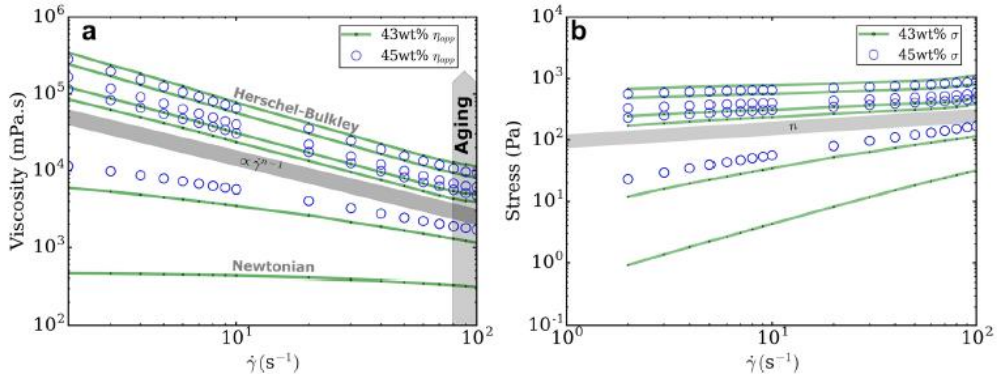


Figure 2.3: Evolution of viscosity η_{app} (a) stress σ (b) as a function of shear rate $\dot{\gamma}$ for 43 and 45 wt% suspension at respectively t_{aging} = 0, 6, 16, 21, 44, 96 h and t_{aging} = 0, 5, 8, 25 h, from bottom to top for both plates (M'Barki, Bocquet and Stevenson, 2017)

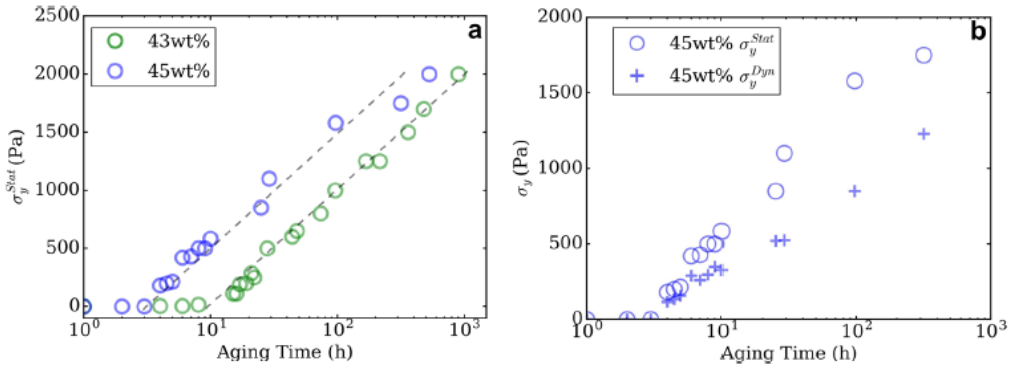


Figure 2.4: (a) Evolution of static yield stress σ_y^{Stat} as a function of aging time for 43 wt% and 45 wt% boehmite suspensions (b) Static and dynamic yield stresses evolution as a function of aging time for 45 wt% suspension (M'Barki, Bocquet and Stevenson, 2017)

From Figure 2.2, the shear modulus being investigated is a complex value which consists of G' (real component) and G" (imaginary component). The ratio G"/G' is a quantifier of viscoelasticity; where the ratio equals 1 indicates the gelation point, ratio smaller than one means the suspension has a solid-like elastic dominant behaviour while ratio larger than 1 is the suspension have liquid-like viscous dominant behaviour. By observing Figure 2.2 (a), initially, 45 wt% suspension has a higher elastic modulus than 43 wt% suspensions, but both elastic moduli are similar at the ageing time between 100 and 1000 hours. Finally, at 1000 hours, the elastic modulus of 43 wt% suspension increases. Figure 2.2 (b) was plotted for further clarification, which involves G"/G'. The two plots in Figure 2.2 conclude that the suspension with lower weightage will have a liquid-like viscous behaviour, 43 wt% suspensions (M'Barki, Bocquet and Stevenson, 2017).

From Figure 2.3, at an ageing time of 0 hours, 45 wt% suspension appears to have shear-thinning behaviour while 43 wt% suspension develops a Newtonian behaviour. After the zero-shear viscosity increases with time to the range 102 to 105 mPa.s, 43 wt% suspension develops a shear-thinning behaviour and increases until it reaches the gelation point. The shear-thinning behaviour of the suspensions became constant after the gelation point. Hence, both suspensions developed shear-thinning behaviour in this finding as well (M'Barki, Bocquet and Stevenson, 2017).

Figure 2.4 (a) shows the increase in static stress for 45 wt% at ageing time 3 hours (after gelation point of 45 wt%) while 43 wt% remains constant and starts to increase after 10 hours (after gelation point of 43 wt%). Figure 2.4 (b) compares the static and dynamic stresses for 45 wt% boehmite suspension. The static stress is higher than the dynamic stress after the ageing time passes its gelation point. The reason is that the static stresses are to destroy the electrostatic bonds of the boehmite compound. Therefore, it concludes that the static stress aids the extrusion process of the suspension from the nozzle; as for the dynamic stress, it is to hold the boehmite particles together so that the structure does not collapse (slump) (M'Barki, Bocquet and Stevenson, 2017).

Besides that, Polamaplly et al. (2019) discovered that the binder's concentration affects the suspension's viscosity. After undergoing the flow ramp test and oscillatory stress sweep test, the results show that the feedstock's yield stress and flow consistency (K) are higher when the concentration of the binder added is higher. The higher the K value indicates that the material becomes more viscous and exhibits shear-thinning behaviour. The test result derived from the Herschel-Bulkley model of the samples is summarized in Table 2.7 below.

Table 2.7: Herschel-Bulkley model parameters for the flow curves of HPMC K4M, HPMC E4M, MC A4M samples (Polamaplly et al., 2019)

Material	Concentration %	Estimated τ_0 (Pa)	K (Pa.s^n)	n
K4M	8	37.09	1910.73	0.16
	10	41.81	4073.80	0.07
	12	45.10	6481.87	0.05
E4M	8	43.26	1060.47	0.27
	10	65.56	2195.33	0.18
	12	39.99	3836.19	0.11
MC	8	29.46	592.38	0.34
	10	43.05	1318.56	0.28
	12	95.69	5222.76	0.05

From Table 2.7, 12 % MC A4M has the highest shear stress (95.69 Pa) among the materials. Hence, higher pressure had to be exerted on the 12 % MC A4M material to enable a better flow during the printing process.

Besides that, a shape fidelity test is carried. It was concluded that HPMC E4M at concentration 12% w/v is unsuitable for undergoing the 3D printing process because the storage modulus is lower than other materials. The low storage modulus will cause a high shape fidelity factor; the higher factor indicates that deformation in the sample layers will be more extensive. 12% w/v HPMC E4M has a shape fidelity factor of 1.39, the highest among the three materials.

2.5 Feedstock Preparation Technique

As mentioned in Table 2.6 (Section 2.4), Sun et al. (2019b) prepared five different volume fractions (ranges from 24 to 32 vol%) of kaolin suspension, WG and PAA mixed with deionized water. Firstly, the kaolin clay was mixed with deionized water and stirred vigorously at 50 rpm for 3 hours using zirconia balls coated with polyethylene. In the second step, WG (silicate modulus = 2.4) was added into the mixture and stirred at 50 rpm for 10 mins. Lastly, 5.98 vol% of PAA was added and agitated using a mechanical agitator for 5 mins. The kaolin suspension prepared is poured into the syringe with a nozzle diameter of 750 μm for DIW. The conditions of the extrusion process took place in the open air at room temperature. The airflow pressure was maintained at 12 to 15 psi (approximately 82.7 to 103.4 kPa) to match the deposition speed at the nozzle.

Besides that, M'Barki, Bocquet and Stevenson (2017) prepared the suspension with deionized water and was sonicated for 1 min; then, the suspensions were mixed under vacuum conditions for 15 mins. Two different mass fractions of the suspensions were produced (43 wt% and 45 wt%) and were allowed to gel by pouring it into the 30 cc syringes. The ceramic samples were produced using the DIW method under the condition of air pressure-driven at the plunger to extrude the kaolin suspension from the nozzle. The starting dispensing time is around 500 ms and ends with a short non-dispensing horizontal line to prevent the printing defect when the printing is in the vertical direction. The printing speed is 3 mm/s, where the expected printed sample is 14 mm long, 5mm high and 500 μm width (nozzle diameter).

The feedstock preparation proposed by Sardarian, Mirzaee and Habibolahzadeh (2017) were mixed and dried for 4 hours at a temperature of 120 ℃ before adding the binder. Then, the alumina feedstock and binders were

mixed using a fast-moving hand mixer at the temperature of 80 ℃ for 30 mins. The homogeneity of the mixture improves when uniform mixing is achieved because the torque will reach a steady state.

The manufacturing method used by Sardarian, Mirzaee and Habibolahzadeh (2017) is LPIM. The feedstock was heated up to 70-100 ℃ in the mould with a pressure increased to 0.1-0.6 MPa during the moulding cycle. Then, the feedstock was injected into a rectangular mould with the dimension $120 \times 4.8 \times 3.5$ mm. The moulded sample manufactured using LPIM is shown in Figure 2.5.

Figure 2.5: Injection Moulded Part (Green Part) (Sardarian, Mirzaee and Habibolahzadeh, 2017a)

Resuming the research done by Revelo and Colorado (2018), the manufacturing technique applied is DIW, which involves using a 3D printer. Firstly, the slurry was prepared by mixing kaolinite clay powder and water according to the water to clay ratio (W/C), ranging from 0.59 to 0.65. The W/C ratio of the samples is listed in Table 2.8 below.

Table 2.8: Fabricated formulations quantified for a typical syringe batch (Revelo and Colorado, 2018)

Sample	1	2	3	4	5	6
Clay (g)	60	60	60	60	60	60
Water (g)	34.2	35.4	36	36.6	37.8	39
Clay (wt%)	63.7	62.9	62.5	62.1	61.3	60.6
Water (wt%)	36.3	37.1	37.5	37.9	38.7	39.4
W/C ratio	0.57	0.59	0.6	0.61	0.63	0.65

During the printing process, different nozzle diameters were used to control the flow of the suspension while the speed of the plunger remained constant. The effect on the flow of the extrusion using different nozzle sizes was summarized in Table 2.9.

Table 2.9: The average mass flow rate and speed of extrusion at different nozzle diameter (Revelo and Colorado, 2018)

Nozzle Diameter (mm)	Average mass flow rate (g/s)	Speed (mm/s)
1.0	0.015	0.0047
1.6	0.025	0.0057
3.0	0.06	0.0096

According to Table 2.9, the result shows that the larger the nozzle diameter, the higher the mass flow rate and speed. Besides that, the printing quality of the samples was also determined based on different printing surfaces. Materials for the printing surface are paper, aluminium, glazed and unglazed ceramic tile. This test's suspension is investigated using Sample 3 (0.6 W/C ratios) for all the surfaces to print the same shape. The results show that printing on unglazed ceramic tile has the best result. The reason was that the surface of the unglazed ceramic tile is rough, enabling the extruded slurry on the surface not to slip and be attached firmly on the tile's surface. For glazed ceramic tile and aluminium, the adhesion force of the printed slurry was weak; hence, it was difficult to control and maintain the shape of the printed sample. For the paper

surface, the sample outcome is good, but since the water content of the slurry deforms the paper, the shape of the final product was affected. This test signifies that the printing process should be done on rough surfaces for better adhesion within the printed product (Revelo and Colorado, 2018).

2.6 Sintering and Testing

For the method proposed by M'Barki, Bocquet and Stevenson (2017), the boehmite ceramic samples were dried for two to three days under room temperature at 90 rh% at ambient humidity. Then, the sintering process was carried out after the sample turned opaque at a low sintering temperature of 1300 ℃ for 1 hour and 5 ℃/min ramp. After sintered, the three-point bending test was carried out on the 22 coarse surfaces finished samples using a Shimadzu SGSX press at a speed of 0.2 mm/s. The distance between the bending points was 12 mm.

After the three-point bending test, surface fracture was found in a sample as shown in Figure 2.6 (a).

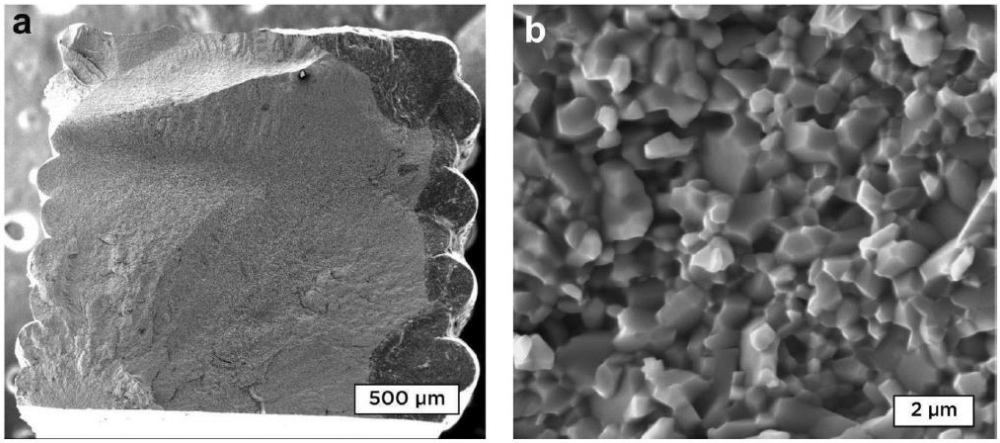


Figure 2.6: (a) SEM image at x120 of fracture surface from Al2O3 bar obtained by sintering boehmite printed with DIW. Fracture resulted from Three-point bending test. Stacked lines are not discernible in the centre of the sample, but clearly visible on the samples surface. (b) SEM image at x10000 of the same fracture surface. The object is dense with a fine grain microstructure, suitable for high strength mechanical properties (M'Barki, Bocquet and Stevenson, 2017).

In typical cases, the 3D printed samples' surface was easily defected due to the DIW technique. When a product is manufactured using DIW, the extruded suspension will leave traces on the boundaries, resulting in an uneven and coarse surface finish. However, this method proposed by M'Barki, Bocquet and Stevenson (2017) shows otherwise as the microstructure in Figure 2.6 does not show the stacked lines (traces from printing). The layers in the inner part of the sample created from the printing were merged, providing a product with a higher density. Therefore, this study is noteworthy as the printed product is denser than the common 3D printed product with higher porosity. However, further improvements were still allowed as the traces at the product's surface are still present.

Moreover, according to the findings from Revelo and Colorado (2018), the samples from Table 2.6 (Subsection 2.5) proceeded for the sintering process. First, the green parts were dried at ambient temperature for 24 hours after being printed. Then, the sintering process is carried in a furnace, heating the samples to 1100 ℃ for 1 hour with a temperature ramp of 5.0 ℃/min.

A compression test was performed on the sintered parts using Shidmadzu AG250KN universal testing machine at the speed of 1 mm/min. The microstructure of the samples was observed under Scanning Electron Microscope (SEM), as shown in Figure 2.7 below.

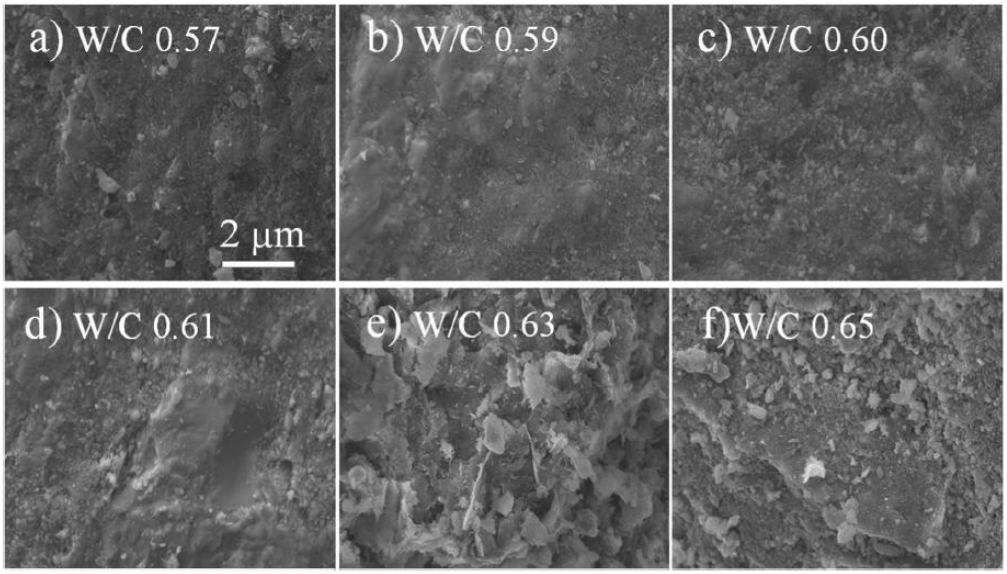


Figure 2.7: SEM images for different W/C ratios of sintered samples fabricated by addictive manufacturing (Revelo and Colorado, 2018)

It was observed that surface fractures were formed on the sintered specimens after the compression test was carried. Furthermore, from SEM images in Figure 2.7, it was observed that the higher the W/C ratio, the higher the porosity within the sample. This is because the water had vaporized rapidly when undergoing the sintering process, leaving the empty spaces behind; hence, voids are formed within the samples. Consequently, the amount of water added to mix the feedstock had to be controlled; the samples with W/C 0.60 and 0.61 show a better result with lower porosity, while the clay is relatively dehydrated during the ignition loss (LOI) (Revelo and Colorado, 2018).

2.7 Summary

In short, the viscosity and shear stress of the prepared suspension affects the flow during manufacturing processes (LPIM and DIW). Hence, a suitable binder had to be chosen for the ceramic powder to prepare the feedstock that could flow well and be injected into the mould (LPIM) or extruded from a syringe (DIW). For DIW, the green product extruded or printed had to withstand the gravitational force and avoid slumping; hence, Sun et al. (2019b) added PAA to the kaolin suspension to improve the gel strength and maintain the shape of the product. Besides that, Polamaplly et al. (2019) proposed some low dissolving temperature binders (HPMC and MC) to improve the gel strength of the suspension so that it exhibits shear-thinning behaviour, which aids the flow of the suspension. Hence, HPMC and MC were suitable for this study due to their low dissolving temperature characteristics.

Besides that, the findings from M'Barki, Bocquet and Stevenson (2017) improved the printed product's density. It was due to octan-1-ol, a deforming agent is added into the feedstock before printing. The defoaming agent reduces the porosity within the printed product; thus, giving a denser product outcome. The mechanical properties, such as the strength of the printed sample, is enhanced. However, the printing trails on the product is not yet solved and will still affect the product's strength.

CHAPTER 3

METHODOLOGY AND WORK PLAN

3.1 Introduction

This experiment was initially planned to be carried out in the university lab as it requires high-temperature procedures such as sintering and 3D printers to print the samples. However, the university was not open to students; therefore, this experiment's mixing and the printing process is carried at home. The X-ray diffraction (XRD) and sintering process was carried in the university laboratory with the help of my supervisor.

Initially, the DIW technique was to be used as the printing test but due to the lack of a 3D printer; a 3D-printed syringe pump extruder was used instead to carry the experiment at home as the feedstock preparation for DIW is also suitable for LPIM. This study will explore LPIM as it is less common to implement kaolin as the ceramic feedstock; moreover, the experiment for LPIM is more suitable to be run at home by using the extruder kit.

The whole set of equipment is divided into two parts, the extruder kit and the mould design. In the extruder kit, the design of the syringe pump extruder was done in a study by Pusch, Hinton and Feinberg (2018) to a low-cost extruder for 3D printing. Hence, the settings behind 3D printing and the electronic connections were studied for the syringe extruder. On the other hand, the mould design was a self-designed mould; therefore, the design process was further elaborated and discussed in Section 3.3.

The first process was started with the preparation of the ceramic powder and binders. The binders were prepared in gel form before mixing them with the clay. Then, some samples of the prepared binder gels and kaolin powder will also be sent to the lab for XRD analysis.

After mixing the feedstock according to the estimated ratio, a few tests were carried to obtain the optimum ratio. The first experiment carried was the extrusion test, following by the injection moulding test and weight test. The extrusion test ensures that the clay cylinders can withstand the gravitational force and maintain their shape. The injection moulding test and weight test check whether the sample is extrudable under a small amount of force. Finally,

the printed sample from the injection moulding test was sent for the debinding and sintering process. The methodology plan is shown in Figure 3.1.

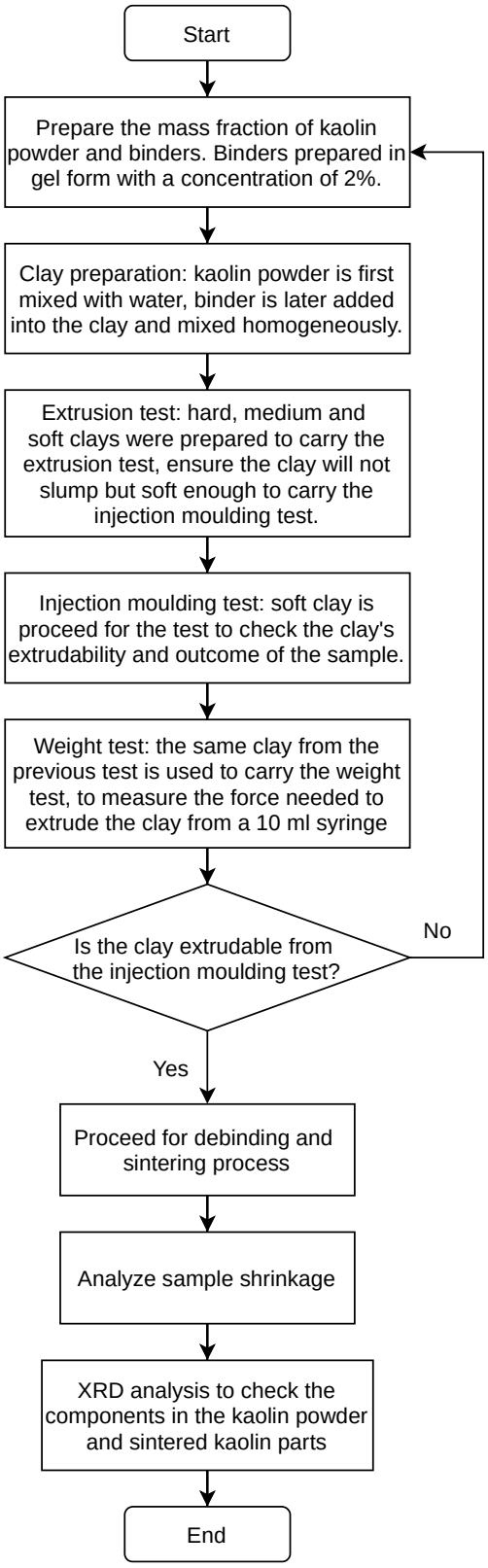


Figure 3.1: Methodology flow chart

3.2 Materials

The materials involved in the experiment is ceramic powder and a few sets of selected binders and dispersant. The ceramic powder chosen for the study is kaolin powder, and the binders involved were HPMC, MC and CMC with the addition of PAA (dispersant). The specific description of the materials is elaborated in the following sections.

3.2.1 Ceramic Powder

The ceramic powder proposed for this study is kaolin clay powder. Kaolin powder was chosen for this study because it is a safe clay material that is nontoxic; hence, it is more suitable for the home experiment. A few samples with different weightage fractions of kaolin clay powder were prepared to investigate the most suitable ratio for the kaolin feedstock. Initially, three sets of samples were prepared with the mass fraction: 65 wt%, 70 wt% and 75 wt% for the extrusion test. These mass fractions of clay prepared are soft, medium and hard clay, respectively (Keep, 2020) Then, the measured kaolin powder was mixed with water, where the mass faction is 17 wt%, 12 wt% and 7 wt%, to prepare soft, medium and hard clay.

After adding the binders, the clay becomes harder than just adding the kaolin powder with water. Hence, for the injection moulding, only the soft clays (65%) were tested with different percentages of binders and dispersant along with the presence of isopropyl alcohol, which is added on the later testings. A full table of the ceramic feedstock contents were constructed and listed along with the observations and results in Chapter 4.

3.2.2 Binders

The primary binders involved in the experiment were carboxy methylcellulose (CMC), hydroxypropyl methylcellulose (HPMC) and methylcellulose (MC). These three binders are also known as thickeners for self-care products and food additives. These three binders are safe chemical products that are suitable for home experiments. All the binders are prepared in gel form beforehand with a concentration of 2% in solution. The viscosity of the HPMC is about 100 000 to 130 000 mPa.s, and the viscosity of the MC is 400 mPa.s. After binder powder with water, the solution was left overnight to enable the powder to dissolve

completely. The HPMC formed two layers where the upper layer is water, and the lower layer is the “jelly” like substrate; hence, the substrate and water had to be mixed homogeneously before adding to the clay.

Besides that, a dispersing agent, polyacrylic acid (PAA), is added to disperse the kaolin particles and provide a better flow of the clay during the extrusion process. PAA is also prepared in gel form at the concentration of 2.5% in solution. The PAA gel needs to be left overnight before the mixing process due to the powder not completely dissolved. The initially planned mass fraction of the binders is 12 wt%, while the dispersant is 6 wt%. A lower amount of PAA is added due to its high viscosity. The mass fraction of the binder system is listed in Table 3.1.

Table 3.1: Mass fraction of the initial binder system

Sets	Binder components	Mass fraction (wt%)
1	CMC	12.0
	PAA	6.0
2	HPMC	12.0
	PAA	6.0
3	MC	12.0
	PAA	6.0

After creating samples from the injection moulding test, it was found that some samples were not extrudable. Therefore, the percentage of binders and dispersants added was reduced by half, as shown in Table 3.2. After reducing the binder system by half, the ceramic feedstock is extrudable in the injection moulding test. The results will be further discussed in Chapter 4.

Table 3.2: Mass fraction of the reduced binder system

Sets	Binder components	Mass fraction (wt%)
1	CMC	6.0
	PAA	3.0
2	HPMC	6.0
	PAA	3.0
3	MC	6.0
	PAA	3.0

3.3 Equipment used for the injection moulding test

In this section, the design of the set of equipment used for the injection moulding test was discussed. The whole equipment set is divided into two parts, the extruder kit and the mould design. The extruder kit comprises the 3D-syringe pump extruder and the electronic configurations. The 3D-syringe pump extruder was adopted from Pusch, Hinton and Feinberg (2018); hence, the settings of the 3D printing process and electronic configurations was discussed in Section 3.3.1.

In Section 3.3.2, the mould design was discussed. The mould is self-designed; therefore, the design process and drawings was discussed along with some 3D printing settings.

3.3.1 Extruder Kit

After designing the models in SolidWorks, the files was saved as STL files to generate G-codes in the software Ultimaker Cura for 3D printing. The syringe pump extruder used in this experiment was adopted from Pusch, Hinton and Feinberg (2018); hence, designing and saving the files in STL format could be skipped. The STL files of the design can be downloaded in an open-source website shared by the authors, where the link is: https://3dprint.nih.gov/discover/3dpx-008366

The material used to print the extruder is polylactic acid (PLA), a common material used for 3D printing. The brand chosen is eSUN, which was specified in the software to auto-generate the printing settings. The printing temperature is set to 210 °C so that the printing material, PLA, can be melted and flow through the nozzle for printing. The printing speed is 60 mm/s, the infill speed is 60 mm/s, and the wall speed is 30 mm/s. The speed settings are

shown in Figure 3.2, where the part being simulated is the big gear. Then, “Slice” is selected to begin the slicing process.

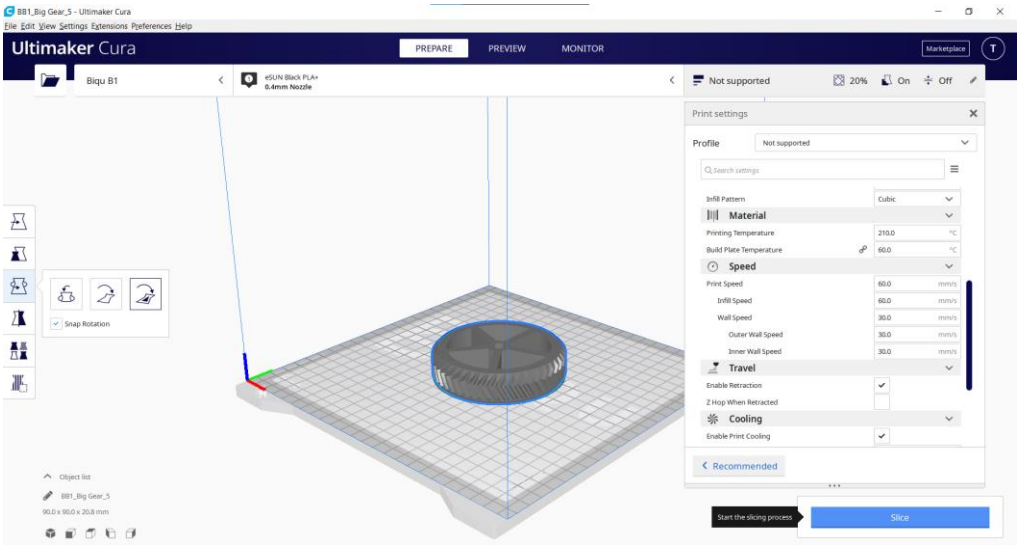


Figure 3.2: Speed settings for printing the big gear

After the slicing process is completed, the duration of printing, amount of material and printing process was calculated and shown in the simulation. The printing takes 8 hours and 5 minutes to complete, where the mass of material needed is 35 g, or in terms of the length, the PLA needed is 11.65 m. The printing process is done layer by layer where the liquid-form PLA is extruded from the nozzle. For example, in Figure 3.3, the printing process can be seen on the last layer, which is 206.

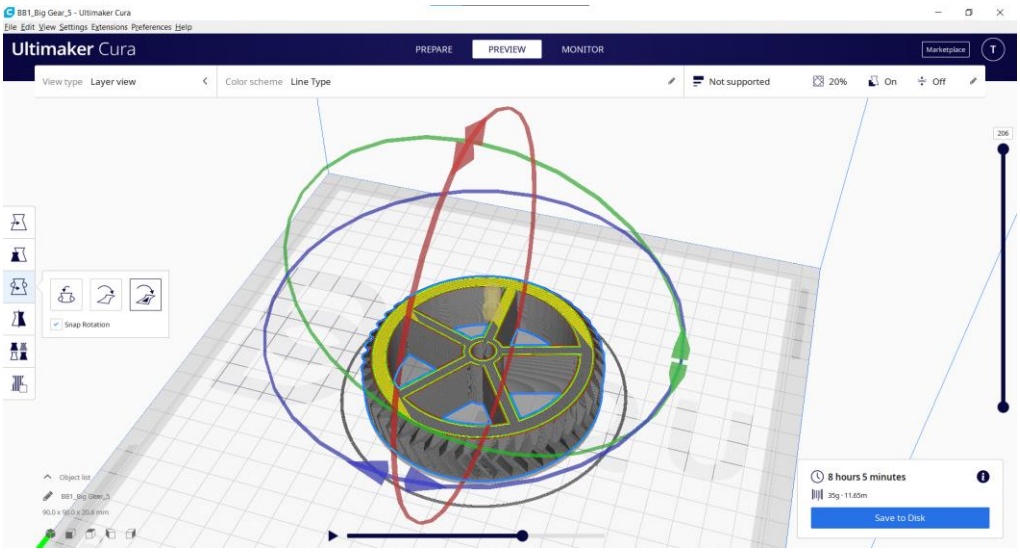


Figure 3.3: Printing the last layer, 206, duration: 8 hrs 5 mins

The infill is the internal filling of the object; the density is set to 20% as the big gear is not used for being subjected to force or loading. As for the wall, the original setting is 0.8 mm, as shown in Figure 3.4. It was observed that the wall thickness of the gear is too thin for rotating and forcing the extruder. The gear will likely fail if the thickness has remained; hence, the thickness is increased to 2 mm to achieve a higher safety factor for the design.

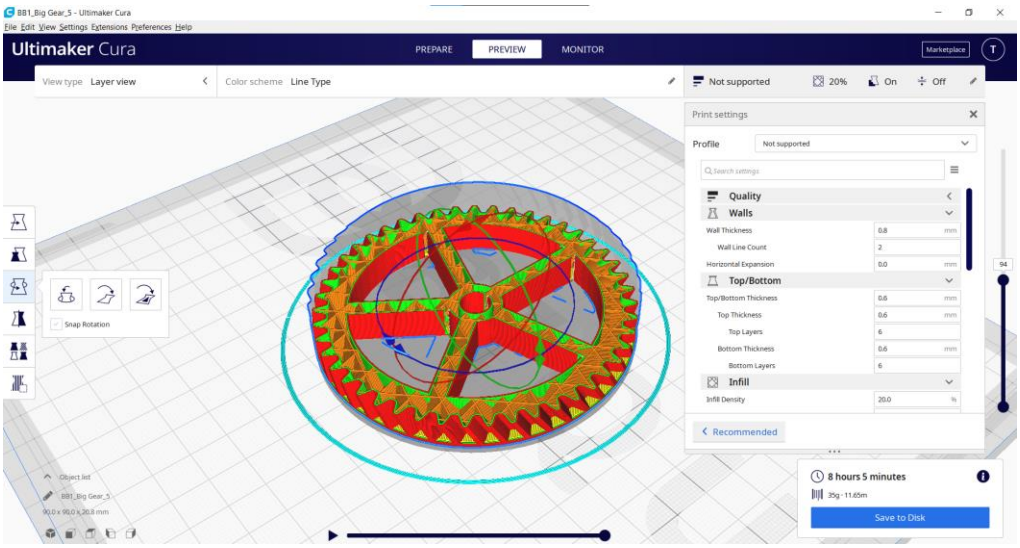


Figure 3.4: Wall thickness and infill settings

Figure 3.5 shows the cross-section of the big gear after increasing the wall thickness to 2 mm. Hence, more material and time is needed for the change. The mass of PLA is 57 g, length 19.21 m, and the completion of the printing is 14 hours and 17 minutes. The time had increased by 6 hours and 12 minutes compared to the previous settings using the wall thickness of 0.8 mm, and an addition of 27 g of material was needed. Therefore, the wall thickness and infill density are adjusted depending on the usage of the printed product so that it saves cost and time.

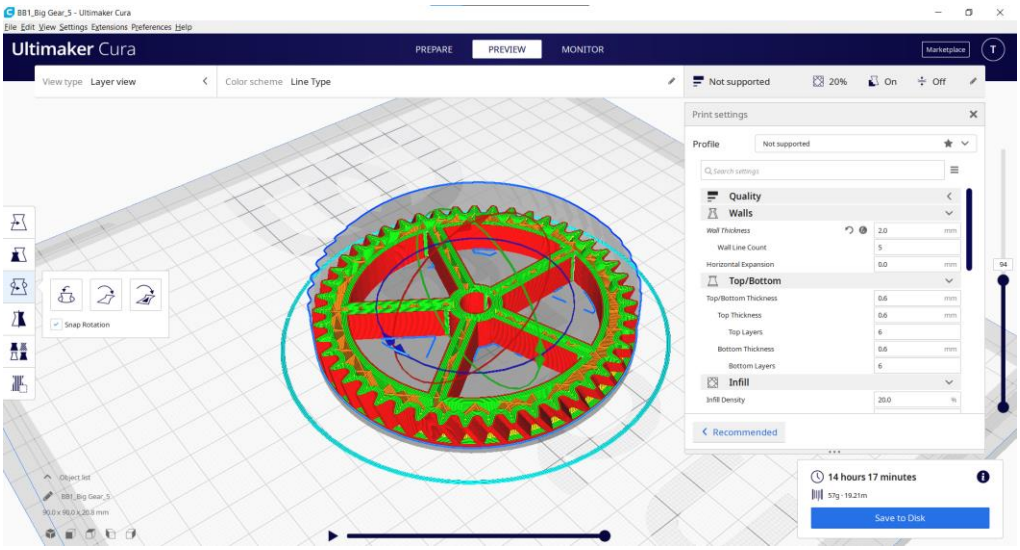


Figure 3.5: Wall thickness changed to 2 mm, duration: 14 hrs 17 mins

After the settings and process in the simulations are confirmed, “Save to Disk” is selected to generate and save the G-codes in the local disk (usually saved in C-drive to print the product through the 3D printer directly). The printing process will occur in the university lab, where there is a 3D printer (shown in Figure 3.6) for students to print samples or design products for their projects. Unfortunately, due to the pandemic, students were not allowed to enter the university; hence, the G-codes were sent to my supervisor to print.

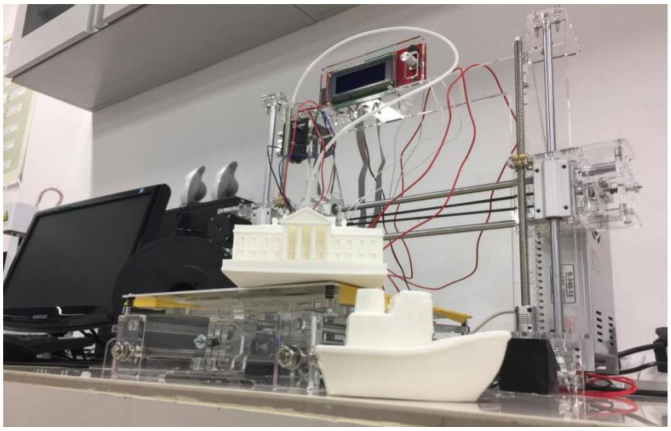


Figure 3.6: 3D Printer Prusa I3 (from Utar lab)

The circuit setup for the extruder kit is shown in Figure 3.7. First, the power supply is connected to the controller board and driver. Then, the driver is connected to the motor, where the motor is attached to the 3D-printed syringe pump extruder. The controller board controls the on and off switch, speed of the motor rotation and direction of rotation. The settings of the microstep driver are

through the six switches at the side, where switches 1,2 and 3 determine the microstep and switch 4, 5 and 6 determine the current. The microstep selection is OFF, OFF, ON for switches 1, 2 and 3; hence, it operates at 16 microstep and 3200 pulse/rev. Likewise, the current selection is OFF, OFF, ON for switches 4, 5, 6; thus, the current is 2.8 A and PK current is 2.9 A.

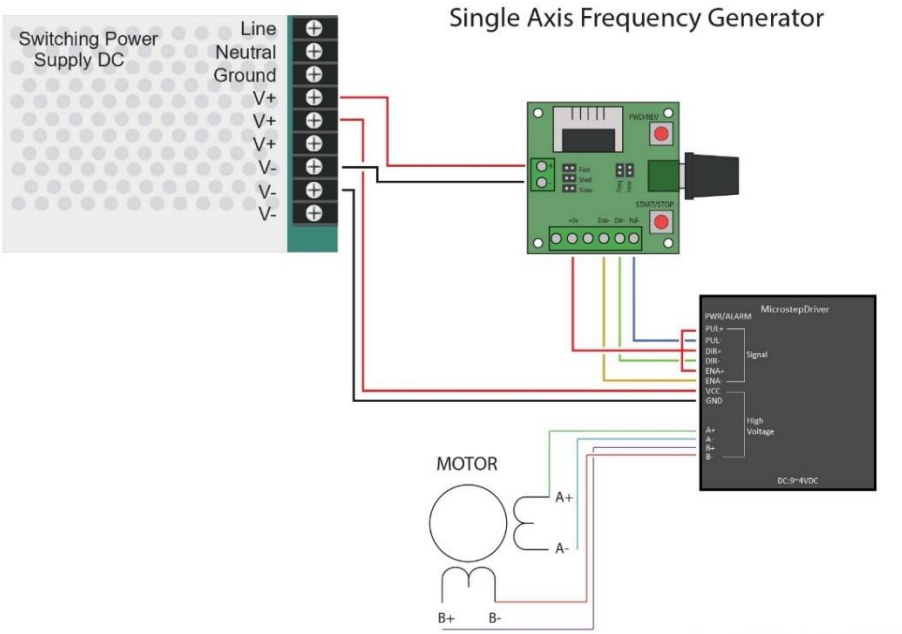


Figure 3.7: Circuit setup for the extruder

The overview of the extruder kit is shown in Figure 3.8. First, the motor is attached to the small gear, where it is force-fit into the motor's shaft and tightened with two sets of bolts and nuts. After securing the small gear, the big gear is inserted into the screw shaft by rotating it. Two M6 hex nuts were used to secure the big gear by using two spanners to counter lock. Thus, when the power is on, and the switch at the controller board is on, the motor will rotate, making the small gear drive the big gear and the screw shaft to rotate. Therefore, the plunger in the syringe can move up and down as it is secured with the nut shuttle.

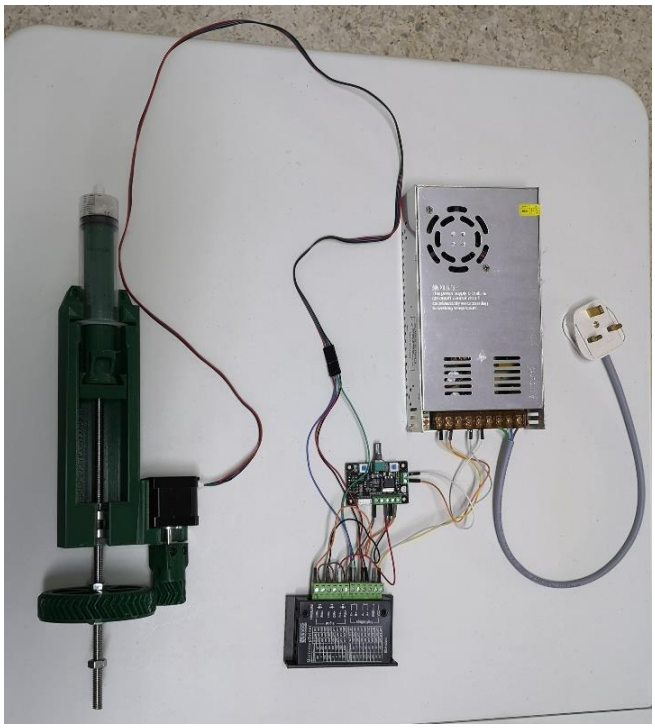


Figure 3.8: Overview of the extruder kit

3.3.2 3D-Printed Mould Design

The mould design drawings are shown in Figures 3.9, 3.10 and 3.11, where it shows the mould's top part, bottom part and the ejector (take note that all the dimensions in the three figures are in millimetres, mm). The top part of the mould has an entrance designed to enable the syringe tip to fit in and extrude the clay into the mould. The diameter of the hole to enable the syringe is 10 mm with a depth of 9 mm. The through-hole with a diameter of 4 mm is a passage that enables the flow of clay into the mould cavity. The passage is designed with a smaller diameter to enable a better flow for the clay to fill up the mould cavity. The four through-holes with a diameter of 3 mm at the top and bottom parts fit the M3 bolts for locking the top and bottom parts tightly with bolts.

The mould cavity has a diameter of 20 mm with a depth of 10 mm. The through-hole with a 10 mm diameter enables the ejector to fit in and push the clay sample out after the injection moulding test. In addition, two thin circular platforms were added so that the samples could be removed and pushed out from the mould cavity altogether to avoid the ejector from destroying the clay sample that is still soft. The dimensions of the circular platforms are 1 mm thick with a diameter of 19.7 mm.

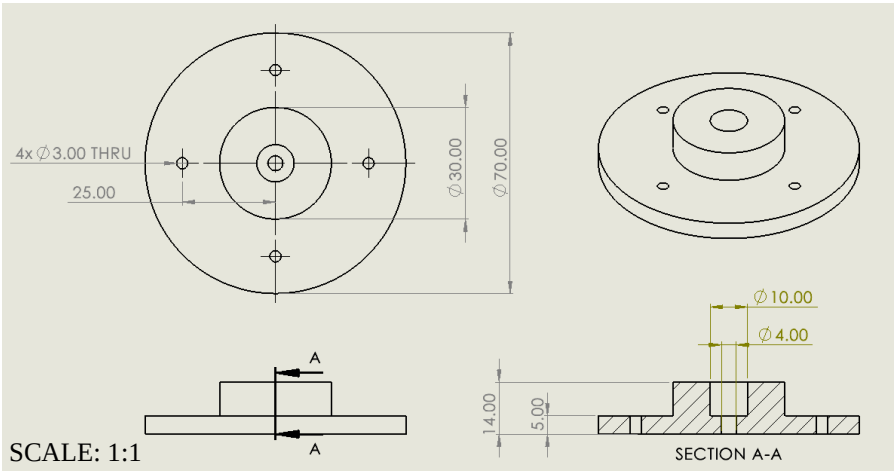


Figure 3.9: Design of the mould top part

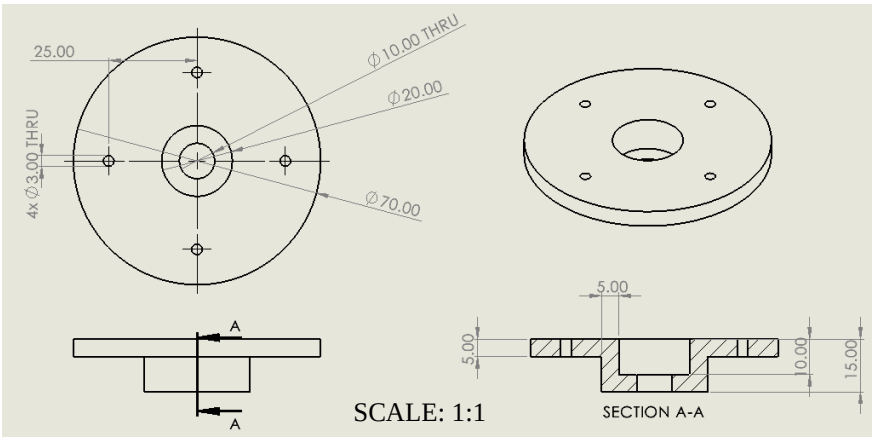


Figure 3.10: Design of mould bottom part

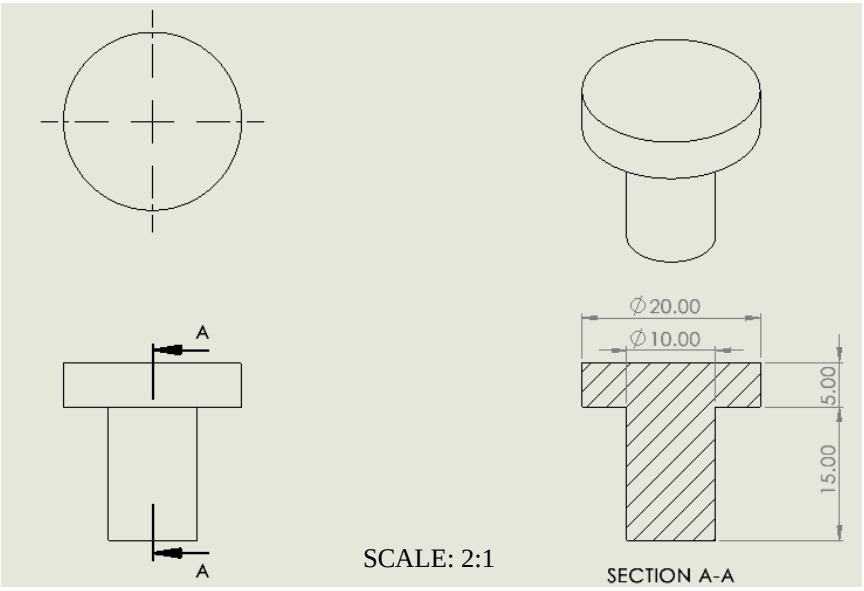
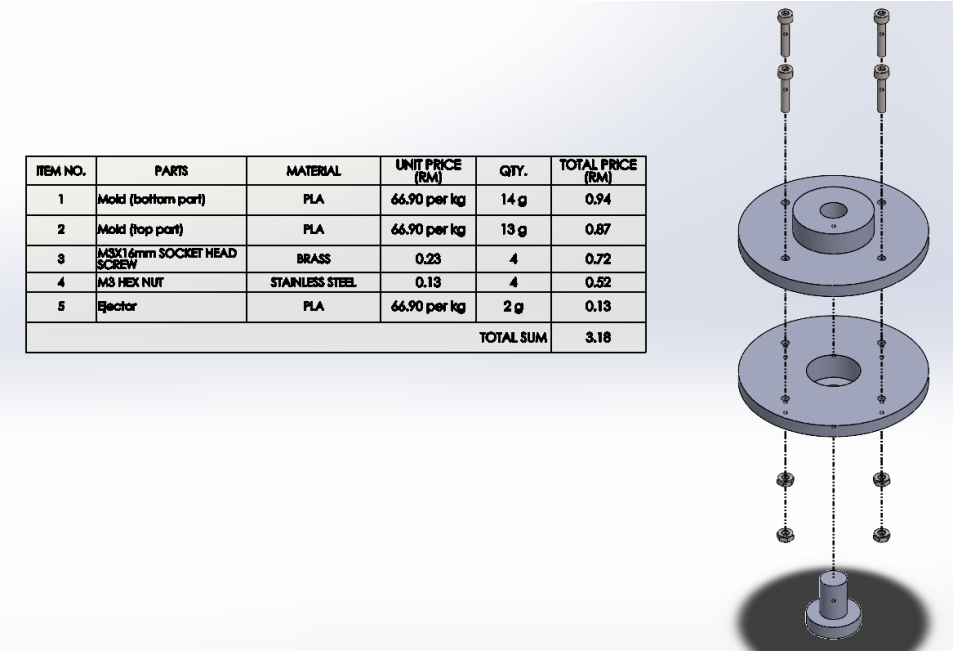


Figure 3.11: Design of ejector

The exploded view and bill of material of the mould design is shown in Figure 3.12. The total price for the mould is approximately RM 3.18.



ITEM NO.	PARTS	MATERIAL	UNIT PRICE (RM)	QTY.	TOTAL PRICE (RM)
1	Mold (bottom part)	PLA	66.90 per kg	14 g	0.94
2	Mold (top part)	PLA	66.90 per kg	13 g	0.87
3	M3X16mm SOCKET HEAD SCREW	BRASS	0.23	4	0.72
4	M3 HEX NUT	STAINLESS STEEL	0.13	4	0.52
5	Ejector	PLA	66.90 per kg	2 g	0.13
				TOTAL SUM	3.18

Figure 3.12: Exploded view of the mould design with the bill of materials

The SLDPRT files for the parts were saved as STL files to generate G-codes in Ultimaker Cura. Figures 3.13, 3.14 and 3.15 presented the printing settings and process of the bottom part of the designed mould. The same material was chosen for printing the extruder and the mould, which is PLA. The printing speed and infill speed was set to 60 mm/s; the wall speed is 30 mm/s. The motion of the nozzle in printing layer 36 is shown in Figure 3.13 below.

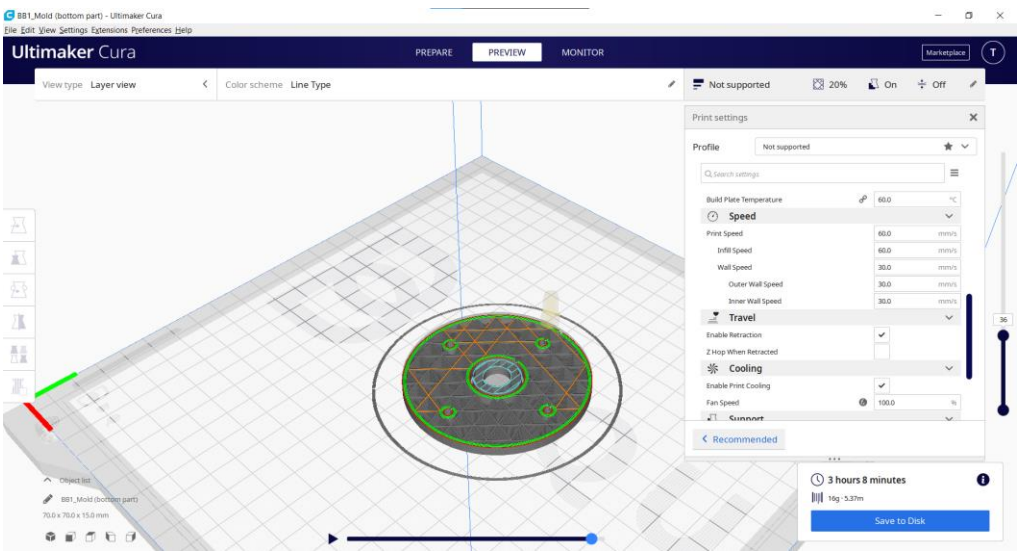


Figure 3.13: Speed settings for printing the bottom mould

The mould was designed to shape the clay when it was extruded into the mould cavity by the extruder. Thus, the wall thickness is set to 1.5 mm (initially set by the simulation) as the mould does not subject to any load or force operations. The infill density will remain the same, 20 %, to save time and material, as shown in Figure 3.14. After slicing, the printing is calculated to be completed in 3 hours and 8 minutes. The mass of PLA needed is 16 g with a length of 5.37 m. There are six layers at the top and bottom, with a thickness of 0.6 mm. Figure 3.15 shows the printing process at the last layer, 148.

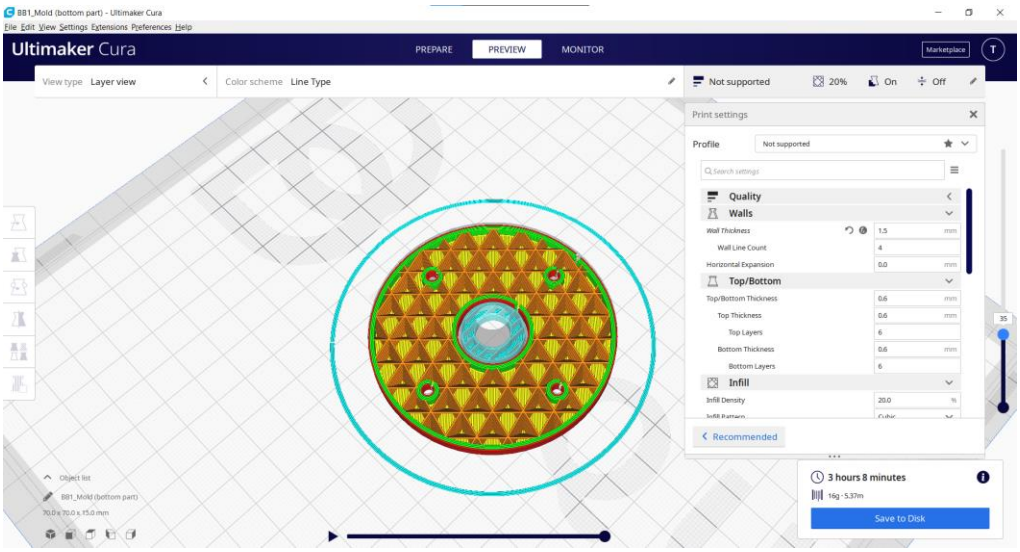


Figure 3.14: Wall thickness and infill settings

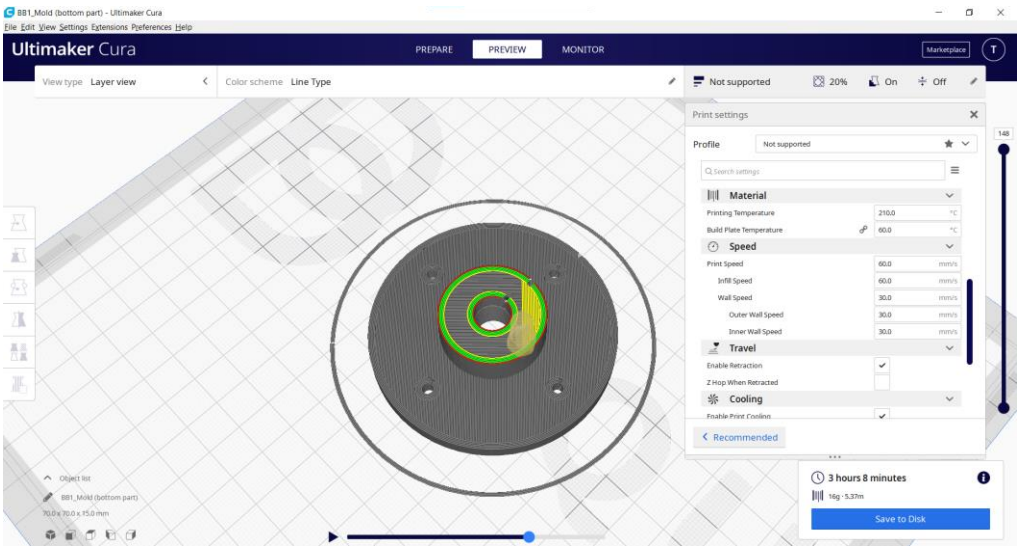


Figure 3.15: Printing process consists of 148 layers

Figure 3.16 shows the overview of the 3D-printed mould design. The arrangement of the parts from left to the right is the bottom part, two platforms,

ejector, and top part. The two platforms were inserted into the bottom part of the mould before enclosing the bottom and top parts together with bolts and nuts. The platforms were ensured to be completely fit into the hollow part of the bottom mould before enclosing it. Initially, the ejector was put aside after the injection moulding test was done; only then the ejector was inserted in the through-hole at the bottom to push the platform and force the sample out.

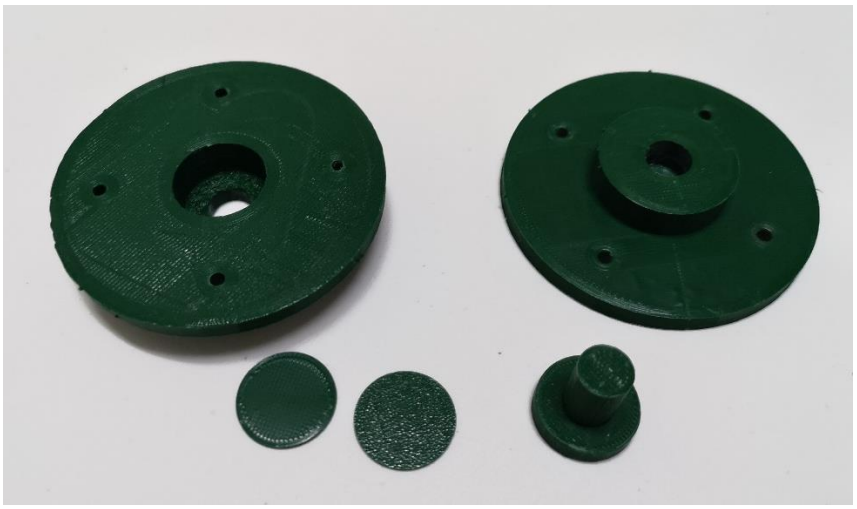


Figure 3.16: 3D-printed mould design

3.4 Clay Preparation

The preparation of the feedstock starts with mixing the kaolin clay powder with water at room temperature. After mixing and kneading the clay homogeneously, the binders were added to the clay. During the kneading process, if the clay has too many cracks, it means that the clay is too dry; thus, additional water is sprayed on the clay before inserting it into the syringe tube. The amount of water sprayed (the amount varies depending on the clay, was further discussed in Chapter 4) on the clay has to be controlled; otherwise, it will become too soft and change the clay's properties. In addition, if the clay sticks to the hand during the kneading process, a drop of cooking oil was added to the clay. The cooking oil is an adhesion-preventing agent where it reduces the adhesion of the clay to the hand. As stated in Section 3.2.2, the binders were added where each type of clay (hard, medium and soft) would be mixed with three sets of binders (Table 3.1). Hence, there will be a total of nine samples for the extrusion test.

Then, three sets of soft clay are mixed for the injection moulding and weight test. The initial test uses the binder system shown in Table 3.1; however,

due to failure in extruding some samples, the binder system was reduced to the mass fraction, as shown in Table 3.2. Softer clay was used for the injection moulding test because this test aims to produce a ceramic feedstock that can be extruded using low pressure. Thus, softer clay was used as the clay became harder with the addition of the binder system than regular clays, kaolin powder mixed with water.

Besides that, additional substance alcohol was used in the clay preparation for the latter test experiment to improve the feedstock. The isopropyl alcohol was used to replace half of the water content so that the clay could dry faster after the injection moulding test. Only the water content is being replaced by alcohol; the kaolin, binder and dispersant content will remain the same as previously proposed.

Moreover, some of the clays were hard during the kneading process, and additional water was added to the clay using a spray. It was measured that 6 sprays of water are equivalent to 1 ml. The type of spray used is shown in Figure 3.17 below, where it is a hair spray. The stiff clays were sprayed up to 15 times of water, while the medium clays required about 8 to 10 times of sprays during the kneading process.

Figure 3.17: Spray used to add additional water into the clay

3.5 Extrusion Test

The purpose of the extrusion test is to test whether the clay can maintain its shape and not slump after being extruded out in a long cylinder form. The extrusion test was tested using a 10 ml syringe, where the tip of the syringe is cut and removed so that when the clay is extruded, it produces a cylinder clay stick. After the clay preparation, the clay is inserted into the syringe tube to reduce the air in the syringe. The clay was inserted from both tops and below the syringe tube to reduce the porosity and cracks. The clay was filled to 10 ml of the syringe; excess clay was removed at the bottom of the cylinder to make the base flat.

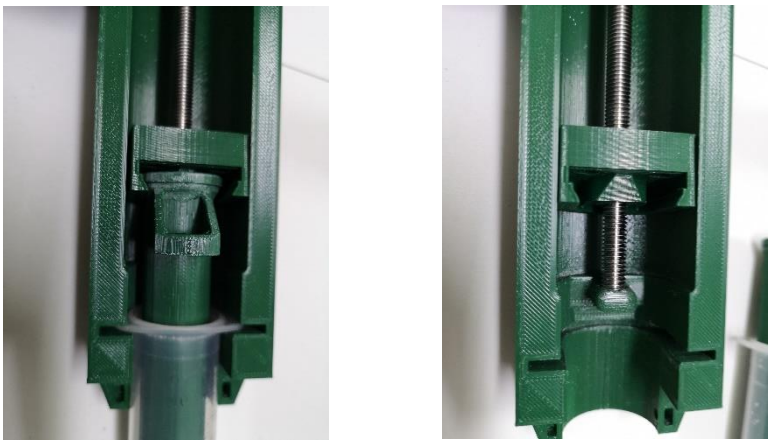
After fully inserted the clay into the syringe, the extrusion test takes place by compressing the syringe and push the clay out, as shown in Figure 3.17. Then, after fully pushing out the clay, the base of the cylinder clay stick will contact the table, where the side will not be supported. The test will end by observing the cylinder clay sticks, whether they will slump or tilt down a lot. If the clay remains in its shape or is slightly tilted, that means the clay is acceptable and suitable for this study. The next step was followed by the injection moulding and weight test to test whether the clay is extrudable using low force or pressure.

Figure 3.18: Extrusion test

3.6 Injection Moulding Test

The injection moulding test uses a 3D-printed syringe pump extruder to extrude the clay into a mould. The clay is inserted into a 50 ml syringe where it is part of the extruder, as shown in Figure 3.18. The extruder kit is connected to a direct current (DC) power supply to start and power the motor. The motor will rotate and triggers the gear train. The output gear that connects directly to the motor shaft will rotate and trigger the compound gear to rotate together. Then, the compound gear which is connected directly to the screw shaft will also rotate. The nut shuttle on the shaft connected with the syringe plunger will then move up or down along the shaft based on the direction of rotation; the close-up is shown in Figure 3.19.

Figure 3.19: 3D-Printed Syringe Pump Extruder



a) b)

Figure 3.20: Close-up view of the extruder a) nut shuttle connected with syringe plunger, b) nut shuttle with syringe plunger removed

The nut shuttle will push the syringe plunger when the motor is triggered to rotate clockwise; hence, the clay will be extruded out. Before connecting the extruder to the mould, some clay is extruded out to remove the air trapped in the syringe and clay. Thus, the shape of the clay injected into the mould will be more uniform and with lower porosity. Besides that, the top and bottom parts of the mould had to be locked with bolts and nuts so that the mould cavity is enclosed tightly to maintain the wanted shape for the injection moulding process.

After removing some of the clay, the syringe tip is connected to the mould to start the injection moulding process. The switch triggers the motor; then, the extruder pushes the clay into the mould. The stop button is pressed when the extruder can no longer push the clay down, and the gears start to slip. The mould was removed from the extruder to lose the screws and bolts. The top part of the mould had to be removed slowly as it may destroy the sample due to it being soft just after the injection moulding test. The ejector for the mould (can be seen in the bottom right of Figure 3.18) will push the platform in the mould, and the platform will push the clay sample out of the bottom part of the mould.

After the sample was removed from the mould and dried with a hairdryer for 1 to 2 minutes, if the clay was too soft to be removed from the platform, it was left to dry for 15 minutes before removal. The remaining clay was used for the weight test.

The function of the extruder is similar to the manufacturing method, LPIM, in the industry. Besides excluding the screw in the injection moulding machine to mix and push the feedstock, it is precisely the same. Therefore, the mixing process is carried manually due to the absence of the screw in the extruder. Finally, both methods will lead to extruding the feedstock into a mould design; hence, the mould's product will follow the mould's design and dimensions.

3.7 Weight Test

The weight test is to estimate the force needed to extrude the clay out from the syringe. In this test, a 10 ml syringe is used to extrude the clay, and body weight estimates the force needed. First, the clay removed from the extruder is kneaded and rolled into a long cylindrical shape before inserting into the syringe. Then, 1 to 3 ml of the clay is extruded out before carrying the test to remove the air trapped within the syringe. After extruding some of the clay, the weight test is carried as shown in Figure 3.20, where the syringe tip faces upwards, and the syringe plunger faces downwards to compress it against the weight.

Figure 3.21: Weight test

The force shown on the weight fluctuates; hence, a video was taken to record the readings on the weight during the test. An average value of the measurements is taken from the recordings. The force range needed to extrude the clay is between 3 to 7 kgf, where this is under the extrudable range; the range between 7 to 11 kgf is under the unextrudable range. The measured weight was converted into Newton (N) by multiplying with 9.81 m/s2. The force was recorded and tabulated in a table.

3.8 Debinding and Sintering Process

The samples (green parts) from the injection moulding test had undergone heat treatment in the lab. The three best samples were heated and kept at 550 ℃ for 2 hours at a ramp of 10 ℃/min for the debinding process. After the debinding process, the brown parts underwent the sintering process, heated and kept at 1300 ℃ for 2 hours at a ramp of 10 ℃/min. The debinding and sintering profile is shown in Figure 3.21. The lab furnace was used in this process, where the model is similar to the furnace shown in Figure 3.22.

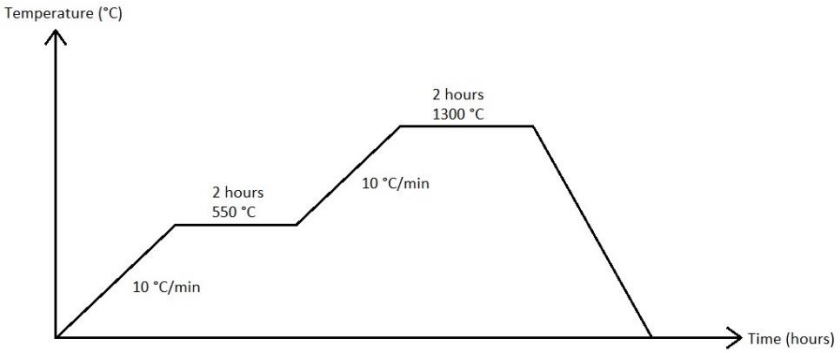


Figure 3.22: Debinding and sintering profile

Figure 3.23: Furnace

The sintered parts were cooled down at room temperature. After cooled, the diameter and thickness of the sintered parts were measured to compare the shrinkage of samples before and after heat treatment. Finally, the sintered samples were sent for XRD analysis in the next step.

3.9 X-Ray Diffraction (XRD) Analysis

X-ray diffraction (XRD) analysis is carried out using the X-ray diffractometer (Shidmazu XRD-6000), as shown in Figure 3.23. The analysis is required to identify whether there are impurities that exist in the sample after homogenization and to identify the compositions within the samples before and after sintering.

Figure 3.24:X-ray diffractometer (Shidmazu XRD-6000)

The materials sent for the XRD analysis in the lab were the raw kaolin powder and the sintered kaolin sample. Then, the generated spectra proceeded for comparison and analysis in software called Highscore Plus, where it is applied to analyze the characteristics of the materials according to the spectra generated from the X-ray diffractometer. First, the raw kaolin powder's generated spectrum was compared with the kaolinite spectrum (found in the database) to check and investigate the impurities within the raw material. As for the sintered kaolin sample, the spectrum was compared with the spectra of the compounds formed under sintering temperature (1300 ℃). The compounds formed from kaolinite above the temperature of 1100 ℃ are mullite and coesite. The more common example for mullite is porcelain, and the examples for coesite are cristobalite and quartz.

3.10 Summary

This experiment involved the feedstock preparation, extrusion test, injection moulding test, weight test, XRD analysis, and heat treatment. The feedstock preparation and the three tests were carried at home, while the XRD analysis and heat treatment will be in the university lab. Hence, the materials chosen are low toxic and not explosive, where safety can be ensured when the experiment is being carried. After the materials (kaolin powder, CMC, HPMC, MC, and PAA) were chosen and binders were prepared in gel form, the ratio and mass fraction of the feedstock composition was determined and tried by mixing kneading the clay. Then, the clay will proceed to carry the extrusion test to estimate whether the clay is hard or soft and can withstand the gravitational force.

After the extrusion test, the soft clay was prepared for the injection moulding and weight test. In this test, the clay was extruded from an extruder into a mould design. The remaining clay proceeded for the weight test to estimate the force needed to extrude the clay. Finally, the home experiment ends here, where the next part had taken place in the university lab. The successful samples from the injection moulding proceeded for the debinding and sintering process. After sintered, the kaolin powder and sintered samples are proceeded for XRD analysis to analyze the impurities in the kaolin raw material and kaolin clay samples.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

In this chapter, the experiment results and various testing conducted will be shown and discussed in section 4.2. The results and discussion will start with comparing the binder, HPMC, where the viscosity decreases after a week—followed by the extrusion test, to discover which type of clay (hard, medium and soft) is more suitable for low pressure extruding operation. Then, all the feedstock compositions tested in the injection moulding and weight tests will be thoroughly discussed, with some comparisons with the different compositions used. The full results of the three test in table form is shown in Appendix A and B.

After the discussion of results from the experiment, it was followed by the debinding and sintering process, where the shrinkage of the samples is studied. Finally, the XRD analysis of the raw kaolin powder and sintered kaolinite samples were studied to understand the characteristics of the kaolin powder and the ceramic feedstock proposed.

4.2 Physical Observation of Binder Solutions

In this section, the physical condition of the primary binders was observed. Figure 4.1 shows the CMC gel binder, which was prepared 2 % in solution. It was observed that CMC has the highest viscosity among the three binders; hence, the clay mixed with CMC is harder and dryer compared to the clays mixed with HPMC and MC. During the clay preparation, the CMC gel on the spatula had to be knocked down to separate with the spatula while other binders were able to be scooped and released from the spatula onto the clay.

Figure 4.1: CMC gel

Besides that, the viscosity and thickness of the HPMC gel were observed. Figure 4.2 shows a more liquid form of HPMC gel (on the left-hand side) prepared a week ago and a thicker HPMC gel (on the right-hand side) prepared a day before the photo was taken.

a) b)

Figure 4.2: Comparison between the old and newly prepared HPMC gel a) old prepared HPMC gel, b) newly prepared HPMC gel

The preparation for the HPMC gel was mentioned in the methodology; the HPMC powder was mixed with tap water that is around 16 to 19 °C in Malaysia. The mixing method is to stir the HPMC powder with water manually where the concentration is 2% in solution. The stirring time is about 10 mins; then, it was left overnight as the HPMC powder is not dissolved. On the next day, the HPMC solution is stirred again to a homogeneous gel form; as

mentioned in the methodology, the HPMC solution formed a substrate in the lower layer and an aqueous solution in the upper layer.

According to Silva et al. (2008), the HPMC in a 2% solution gradually decreases its viscosity when the temperature increases. Hence, the water temperature is not the reason that causes the decrease in viscosity of the HPMC gel. Not much research was done in this area for the effect of time on the viscosity of HPMC; therefore, further improvements can be made for the preparation of HPMC gel binder in the future. The effect of the decreased viscosity of HPMC gel brought to the kaolinite clay can be observed in the injection moulding test and weight test results.

The third binder, MC, is shown in Figure 4.3. The MC solution has the lowest viscosity among the three binders. The MC gel existed in an aqueous form when it was prepared 2 % in solution. In the clay preparation, the MC gel solution could be easy scooped and mixed with the clay due to its low viscosity, which is slightly higher than water.

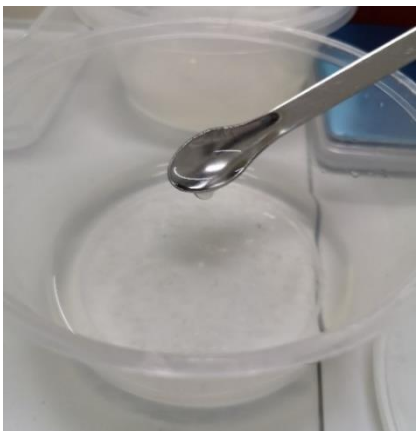


Figure 4.3: MC gel

4.3 Extrusion Test

The extrusion test was carried to ensure that the clay was strong enough to withstand the gravitational force and not slump. According to the results shown in Appendix A, it was observed that all the extruded sample cylinders are strong enough to withstand the gravitational force. The hard clays remain straight for all binder systems, the medium clays are slightly bent, and the soft clays bend a bit more than the medium clays. Overall, the inclination of the bend is within an

acceptable range. The reason was that the binders had thickened the clay, making the clay more rigid and more elastic than clay without binders.

Among the three binders used, the set of samples using CMC as the binder appears to have more cracks. CMC has the highest viscosity among the three binders; meanwhile, MC has the lowest viscosity. Therefore, the clay using CMC is more rigid and dryer, where approximately 20 times of additional water is sprayed on the hard clay and 10 times of water are needed to spray on the medium clay. On the other hand, the soft clay requires adding a drop of cooking oil to reduce the adhesion force of the clay towards the surface of a human hand; where was mentioned in the methodology, the cooking oil acts as the adhesion-preventing agent in the study. Similarly, for the other two sets using HPMC (take note that the HPMC here is newly prepared, so it is highly viscous) and MC, the hard clay requires to spray approximately 15 times of water, and medium clay requires to spray 8 times of water so that the clay does not crack during the kneading process; as for the soft clays, approximately 2 to 3 sprays of water is needed. When the soft clay gets sticky after adding water, a drop of cooking oil is added.

The results and observation is shown in Figures 4.4, 4.5 and 4.6, that all the soft clay shrinks the most as it has more water content in the composition. The samples were all left to dry for one day at room temperature. During the drying process, the soft clay dries the slowest due to the high water content. Nevertheless, soft clay can be considered “medium” clay compared to conventional soft clays that only contain kaolin powder and water. Due to the increase in hardness after adding a binder to the kaolinite clay, the soft clay formulation was chosen to proceed with the injection moulding test, and weight test as the requirement for the ceramic feedstock is to be able to extrude under low pressure.

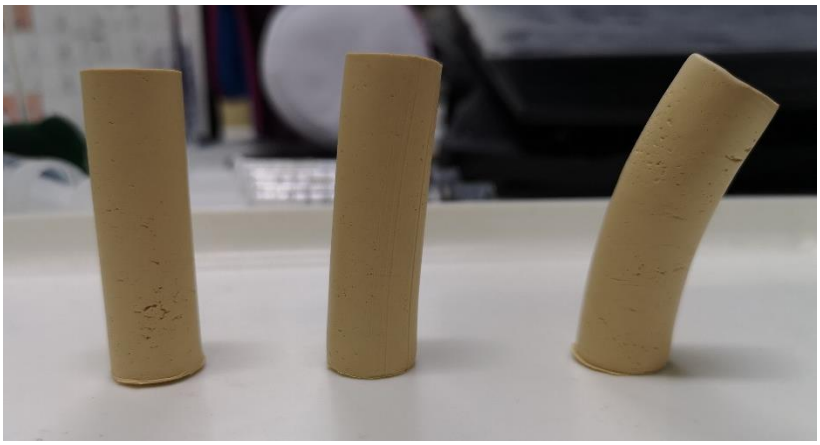


Figure 4.4: Clays using CMC (hard, medium and soft arrangement from left to right)

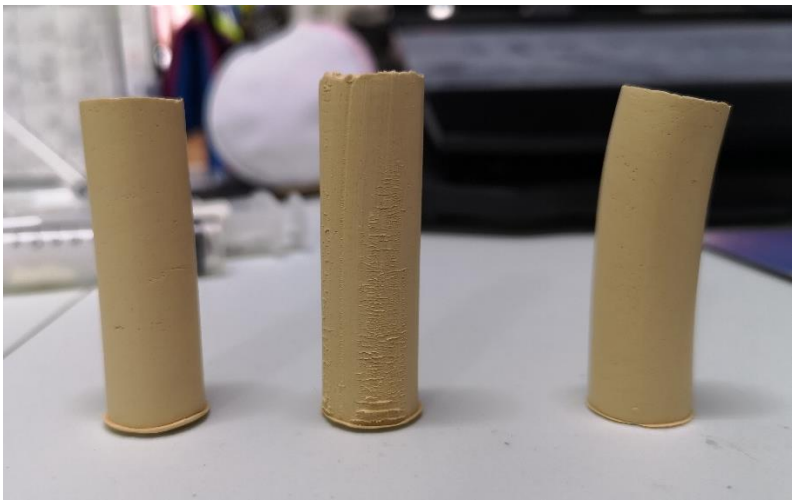


Figure 4.5: Clays using HPMC (hard, medium and soft arrangement from left to right)

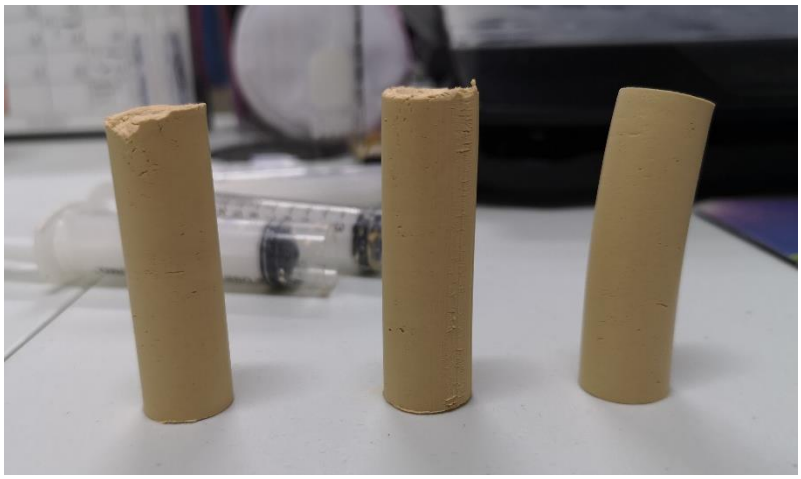


Figure 4.6: Clays using MC (hard, medium and soft arrangement from left to right)

Then, another set of results with a reduced percentage of binders (6%) and dispersant (3%) used is shown in Table 4.1. In the injection moulding test, the clay using CMC as a binder is not extrudable; thus, the binders were reduced for another trial. According to Table 4.1, the cylindrical samples were slightly bent; hence, the composition is not too soft and acceptable in producing a product that will not slump. After dried for a day, the results of the samples can be observed in Figure 4.7. It is estimated that the samples are about 5.0 cm in height; after dried, the samples are approximately 4.5 cm in height. Hence, the shrinkage of the samples in height is approximately 10 %.

Table 4.1: Extruded clay samples using 65 wt% kaolin powder with binder system from Table 3.2

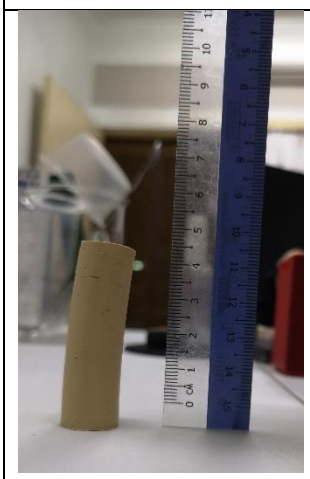
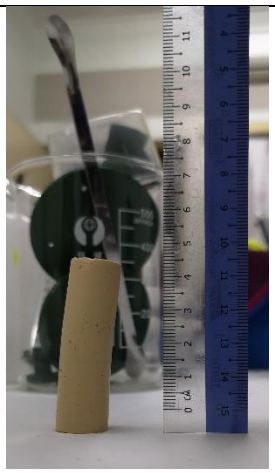
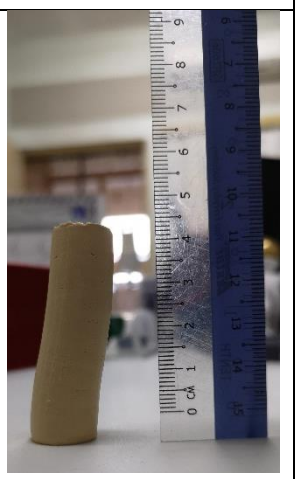
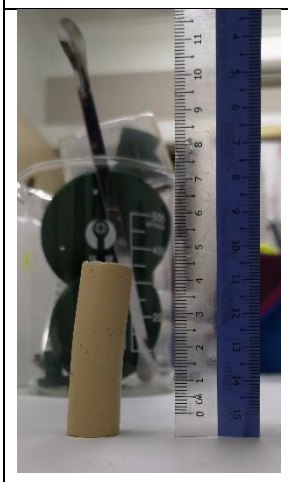
CMC	HPMC	MC
		

Figure 4.7: Same samples from Table 4.1 after dried for one day, binders used from left to right are CMC, HPMC (old) and MC

Then, a comparison was made between samples using the old and new HPMC binders. Besides spraying more water during the clay preparation for using the new HPMC, the outcome of the sample using the new HPMC is preferable as the clay with the new HPMC mixed has a better surface finish than the clay using the old HPMC. The reason is due to the high viscosity of the newly prepared HPMC gel that can act as a thickener for the clay sufficiently; hence, providing a smoother flow when the cylinder clay sample is being extruded from the syringe tube. Unlike the lower viscosity HPMC, which had most likely deteriorated, the clay becomes wet; hence, during the insertion of clay into the syringe tube, air bubbles are more easily trapped in the clay together with the water content than the "thicker" clay. Therefore, the thickening characteristic of the old HPMC has reduced compared to the new HPMC. The shrinkage of the samples using the old and new HPMC are the same as compared to Table 4.2 and Figure 4.8, which is approximately 10 %. Thus, the shrinkage for all samples is approximately identical, which means the binders do not affect the shrinkage before or after the clay samples dried.

Table 4.2: Comparison between the clay using old and new prepared HPMC

HPMC (old)	HPMC (new)
	

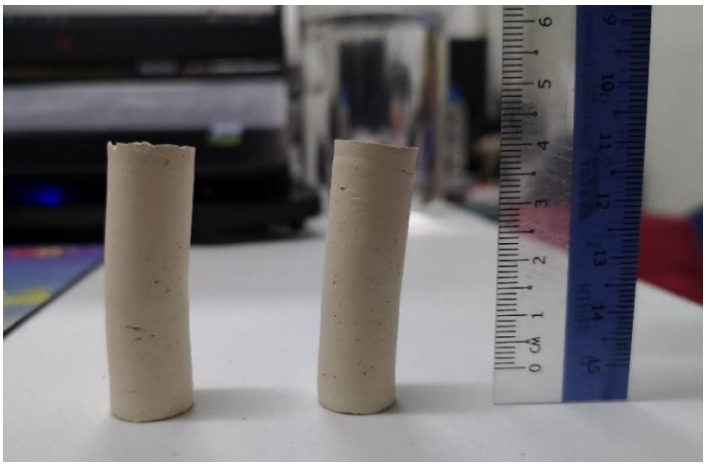
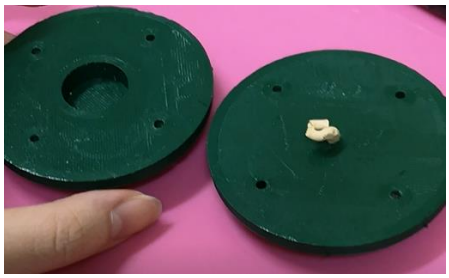


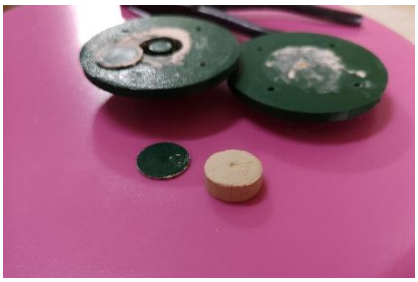
Figure 4.8: Samples from Table 4.2 after dried one day, from left to right are old and new

4.4 Injection Moulding Test and Weight Test

The first set of clays that are being extruded uses 65% kaolin, 12% binders and 6% dispersant with the remaining content, water. The injection moulding test shows that only the clay using CMC is not extrudable; the other two clays using HPMC (take note that the viscosity of HPMC used had reduced) and MC were extrudable. From the weight test, the force to extrude the clay using CMC is 101.04 N, which is the highest force needed among the three clays. As for the clay using HPMC (old) and MC, the force needed were 53.63 N and 32.37 N, respectively. The stated result can be found in Figure 4.9 and Table 4.3.



1A



1B

1C

Figure 4.9: Initial sample set from the injection moulding test with 65 wt% of kaolin powder and 17 wt% of water, the binder system and force for 1A, 1B and 1C were recorded in Table 4.3

Table 4.3: Binder content of 1A, 1B and 1C in Figure 4.5 and the force recorded from the weight test

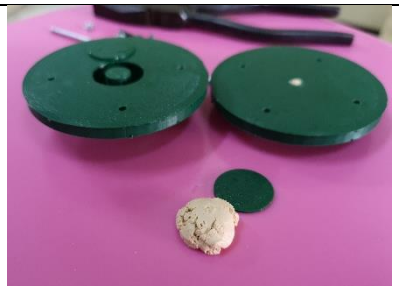
Sets	Binder components	Mass fraction (wt%)	Average force needed to extrude the feedstock from a 10 ml syringe (N)
1A	CMC	12.0	101.04
	PAA	6.0	
1B	HPMC (old)	12.0	53.63
	PAA	6.0	
1C	MC	12.0	32.37
	PAA	6.0	

The surface finish of the clay sample with HPMC is rough, and a lot of small cracks and holes are visible on the surface of the sample. The clay sample with MC has a smooth surface finish with some visible minor cracks on the top and bottom surface of the sample. Hence, the clay using MC has the best result

among the three samples as the cracks on the sample were tiny and minor. The cracks are due to the high strength in the clays; thus, the extruder could not further extrude more clays to fill up the empty spaces in the mould design. Hence, to increase the extrudability of the clay, two new solutions for the ratios of the clay was proposed. The first solution is to reduce the kaolin powder content to 55 wt%, and the second solution is to reduce the binder and dispersant content by half.

Before looking into the results of the two new solutions, the comparison between the old and new HPMC was made on this particular formula (65% kaolin, 12% binder and 6% dispersant). It was found that the sample of clay mixed with the new HPMC has incomplete extrusion, as shown in Table 4.4 with the old HPMC clay sample comparing at the side. The force needed to extrude the clay using the new HPMC from a 10 ml syringe is 102.02 N, about twice the force higher than the clay using the old HPMC. Like the clay using CMC, the new HPMC clay could not be wholly extruded into the mould as it requires a higher force. Hence, the composition of these two clays using CMC and HPMC does not meet the requirement of using low force or pressure to be extruded.

Table 4.4: Comparison of the samples using old and new HPMC

Observation of sample		
	New HPMC	Old HPMC
Force needed	102.02 N	53.63 N

The clay using reduced kaolin powder (55%) is unsuccessful as the clays using HPMC (old) and MC are too soft and slumped after being removed from the mould. Among the three samples, only the clay using CMC is booming as the sample does not slump after being removed from the mould. The surface finish of the clay is smooth with minor visible cracks. The force needed to

extrude the clay are 55.92 N. 8.83 N, and 9.81 N for the binders mixed: CMC, HPMC, and MC, respectively. The results showed that the clay using HPMC and MC as binders are very soft compared to the last results using 65% kaolin powder. The force needed to extrude the clay using HPMC had reduced 83.55%; the force had reduced 69.69% for the clay using MC. The results of the samples are shown in Figure 4.10 and Table 4.5.

2A

2B

2C

Figure 4.10: Sample set from the injection moulding test with 55 wt% of kaolin powder and 27 wt% of water, the binder system and force for 2A, 2B and 2C were recorded in Table 4.5

Table 4.5: Binder content of 2A, 2B and 2C in Figure 4.6 and the force recorded from the weight test

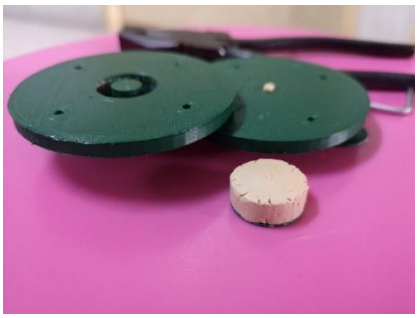
Sets	Binder components	Mass fraction (wt%)	Average force needed to extrude the feedstock from a 10 ml syringe (N)
2A	CMC	12.0	55.92
	PAA	6.0	
2B	HPMC (old)	12.0	8.83
	PAA	6.0	
2C	MC	12.0	9.81
	PAA	6.0	

During the clay preparation, the clays using binders HPMC and MC were too soft and sticky to be kneaded by hand; hence, it was only stirred and mixed using a steel spatula. Hence, the outcome of the sample from the injection moulding test could be foreseen as the clay was too soft for kneading. Compared to the study done by Revelo and Colorado (2018), using clay with a range of mass fraction from 60.6 to 63.7 wt% was all feasible in shape using the DIW technique to print the samples. Hence, using 55 wt% of kaolin powder compared to 60.6 wt% is too soft for producing a clay product using either LPIM or DIW when non or low viscosity binder is used.

Besides that, in the study done by Sun et al. (2019b), the kaolin suspension with 32 vol% of kaolin content was most suitable for printing (DIW technique) into a 3D cavity for the direct plated copper. The reason was that the product's built was able to maintain with a minimal slump compared to the kaolin clay with 24, 26, 28, and 30 vol%. However, similar to this study, 55 wt% of kaolin is too soft, and the extruded clay sample cannot maintain its shape without the mould’s support when low viscosity binders are used. Consequently, reducing the kaolin content to 55 wt% when using HPMC and MC as binders could not achieve the desired result of a well-shaped extruded clay product.

The result of the second solution in reducing the binder and dispersant content had achieved the objective of this study. All the clay were extrudable

and had a better surface finish, given that the sample is a bit soft for the clays using HPMC and MC. The extruded sample of the clay using CMC had many visible cracks on the sample, as shown in Figure 4.11. The shape of the samples using HPMC and MC binders had altered a bit as the samples were not yet dried before removing them from the mould platform. The force needed to extrude the clays using CMC, HPMC, and MC is 39.73 N, 56.90 N and 41.20 N, respectively. Comparing the force from this composition to the previous composition of using 12 wt% binders and 6 wt% dispersant, the force needed for the clay using CMC had drastically decreased while the clay using HPMC and MC were slightly higher. The result of force needed is tabulated in Table 4.6.



3A

3B

3C

Figure 4.11: Successful sample set from the injection moulding test with 65 wt% of kaolin powder and 26 wt% of water, the binder system and force for 3A, 3B and 3C were recorded in Table 4.6

Table 4.6: Binder content of 3A, 3B and 3C in Figure 4.7 and the force recorded from the weight test

Sets	Binder components	Mass fraction (wt%)	Average force needed to extrude the feedstock from a 10 ml syringe (N)
3A	CMC	6.0	39.73
	PAA	3.0	
3B	HPMC (old)	6.0	56.90
	PAA	3.0	
3C	MC	6.0	41.20
	PAA	3.0	

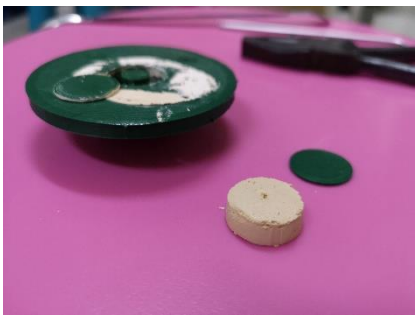
The force for this composition is higher due to the absence of additional water sprayed on the clays using HPMC and MC as the clays were soft enough; therefore, only cooking oil was added to reduce the stickiness of the clays during preparation. As mentioned in the results, indentation was formed on the samples because it was removed immediately from the platform before it was dried and hardened enough to withstand the force during removal. Besides that, a minor accident occurred during the removal of the HPMC sample; therefore, it could be observed that the top surface of the sample inclines. Hence, for future reference, the samples using this clay composition had to be dried and left for at least 15 minutes before removing them from the mould platform. Otherwise, the shape of the samples will be altered, leaving fingerprints on the clay samples.

Another alternative method is to further improvise the clay by replacing half of the water content with isopropyl alcohol. Alcohol is a highly volatile liquid; hence, it will dry faster compared to using water. However, the clay, binders and dispersant composition remained the same; only 26 wt% of water is reduced to 13 wt% of water, the other 13 wt% is replaced with isopropyl alcohol. The result is shown in Figure 4.12, it was observed that the clay using CMC was not completely extruded, and the surface finish of the samples using HPMC and MC were not smooth even though the clay was soft. Although the surface finish of the clay was not smooth, the clay dries faster as the shape of

the sample does not change easily when it is removed from the platform immediately after the injection moulding test.

The sample using HPMC has many small cracks on the top surface, while the sample using MC has many cracks at the curve surface and bottom surface. According to the weight test results in Table 4.7, the force needed to extrude the clays using CMC, HPMC, and MC is 58.86 N, 37.28 N, and 35.32 N, respectively. Comparing to the previous clay composition without adding alcohol, the force needed to extrude the clay with CMC had increased nearly 20 N, while as for the clay using HPMC and MC, the force needed had decreased more than 10 N.

4A



4B

4C

Figure 4.12: Sample set from the injection moulding test with 65 wt% of kaolin powder, 13 wt% of water,and 13 wt% of isopropyl alcohol, the binder system and force for 4A, 4B and 4C were recorded in Table 4.7

Table 4.7: Binder content of 4A, 4B and 4C in Figure 4.8 and the force recorded from the weight test

Sets	Binder components	Mass fraction (wt%)	Average force needed to extrude the feedstock from a 10 ml syringe (N)
4A	CMC	6.0	58.86
	PAA	3.0	
4B	HPMC (old)	6.0	37.28
	PAA	3.0	
4C	MC	6.0	35.32
	PAA	3.0	

The clay using CMC was harder when half of the water content was replaced with alcohol as the sample was incomplete, filling with significant cracks. As the clays using HPMC and MC, the clays were soft, but the outcome of the samples was undesirable due to a lot of visible cracks. Even though the clays were soft, isopropyl alcohol is highly volatile and can quickly evaporate through the air. Hence, some of the moist content within the clay had evaporated during the kneading process before extruding clay into the mould, resulting in clay with uneven moist content. Thus, the uneven clay will affect the flow of extrusion, resulting in a sample that looks “dry” with a lot of visible cracks on the surface. MC had the best outcome among the three binders in most of the testings; therefore, an improvisation test using the reduced alcohol feedstock composition will only try on the clay with MC to save time.

The results from the improvised testing were better as the cracks on the sample had reduced a lot by reducing the alcohol content. The sample result can be observed in Figure 4.13 with the composition of the clay arranged in Table 4.8. The clay dries slower than the previous sample using 13 wt% alcohol as the sample could not be removed from the mould platform immediately after the injection moulding test, but the waiting time was reduced compared to the sample without alcohol added. From the weight test, the force needed to extrude

the clay is 42.35 N, where it requires more force than the clay using 13 wt% of isopropyl alcohol.

Figure 4.13: Improved sample from injection moulding test, composition listed in Table 4.8

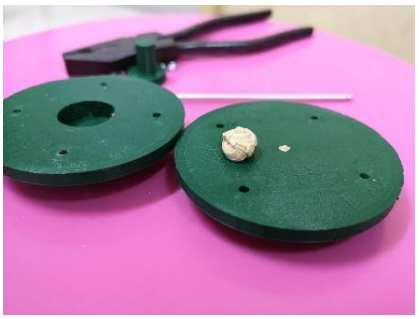
Table 4.8: Feedstock composition of the improvised clay shown in Figure 4.9

Kaolin (wt%)	MC (wt%)	PAA (wt%)	Water (wt%)	Isopropyl alcohol (wt%)
65	6	3	19.5	6.5

The surface finish of the sample is better than the sample using 13 wt% of alcohol but compared to the sample without using any alcohol, the surface finishing is rougher, and there were more minor cracks. Nevertheless, the outcome of the result was satisfactory as the minor cracks can be polished. Furthermore, the clay is still slightly soft after drying it with a hairdryer after 1 to 2 minutes. Then, it was left to be dried at room temperature for about 10 minutes before removing the sample from the platform. Hence, for instant platform removal, the drying duration using a hairdryer can be increased to 5 minutes in future testings.

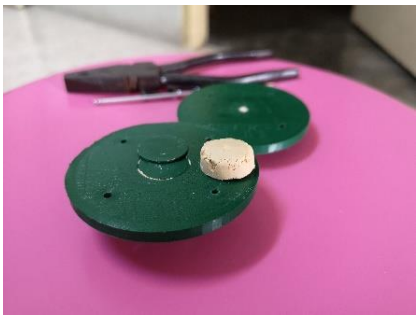
Besides that, an alternative composition for the first binder system was tested to investigate the result in excluding the dispersant and replacing half of the water with isopropyl alcohol, shown in Figure 4.14. Unfortunately, the results showed that without the dispersant, the clay using CMC could not extrude completely. The sample using MC as binder appears to have several significant cracks, leaving the clay using HPMC to be the only successful extruded sample. Although the sample was successfully extruded, two giant

cracks were found between the top and curved surfaces. The force needed to extrude the samples using CMC, HPMC, and MC is 87.31 N, 56.90 N and 66.71 N. Hence, more force is needed to extrude the clay without the dispersant PAA.



a)

b)



c)

Figure 4.14: Sample set from the injection moulding test with 65 wt% of kaolin powder, 11.5 wt% of water,and 11.5 wt% of isopropyl alcohol, the binder system and force for 5A, 5B and 5C were recorded in Table 4.9

Table 4.9: Binder content of 5A, 5B and 5C in Figure 4.10 and the force recorded from the weight test

Sets	Binder components	Mass fraction (wt%)	Average force needed to extrude the feedstock from a 10 ml syringe (N)
5A	CMC	12.0	87.31
5B	HPMC (old)	12.0	56.90
5C	MC	12.0	66.71

A higher force was needed to extrude the clay through the nozzle as the clay flow has reduced due to the absence of dispersant. The dispersant, PAA,

increases the mobility of the clay through the syringe nozzle during the extrusion process (Sun et al., 2019b). The primary function of PAA is to aid the separation of the clay particles; hence, it will enable a better flow when the clay is being extruded from the nozzle into filling the mould cavity. Moreover, due to the high viscosity of PAA prepared, it also had the same functions as the binders to maintain the shape of the extruded clay sample from slumping. Therefore, it is essential to include the dispersant PAA in the feedstock composition.

4.5 Debinding and Sintering

The sample set sent for heat treatment is the feedstock composition: 65 wt% kaolin, 6 wt% binder, 3 wt% dispersant and 26 wt% water. The three samples after sintering are shown in Figure 4.15.

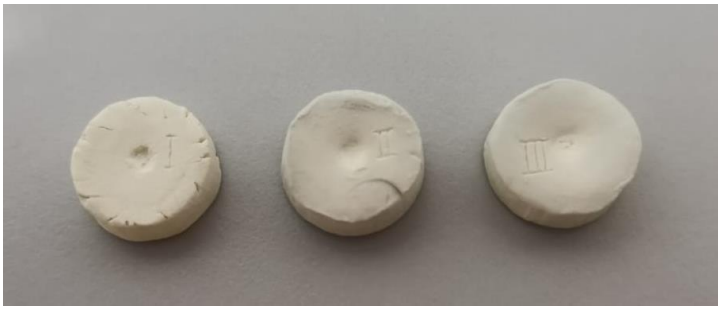


Figure 4.15: Three samples after sintered, binders used for sample I: CMC, II: HPMC, III: MC

The debinding process removes the binders mixed in the clay through evaporation under the temperature of 550 °C. After the debinding process, the brown parts produced were continued for the sintering process to strengthen the sample. In the sintering process, the grain size in the sintered parts will increase, causing the distance between the kaolin particles to decrease; thus, the number of pores between the particles will be reduced. Hence, shrinkage will occur after the sintering process as the distance between particles in samples is reduced to decrease the porosity in the parts.

The shrinkage of the samples before and after sintered was compared. It was measured that samples II and III had the same shrinkage, where both samples had shrunk 51.79 %. The sample I shrunk the most among the three

samples, which is 55.80 %. The volume of the samples before and after sintering, along with the shrinkage, were tabulated in Table 4.10.

Table 4.10: Shrinkage of the sintered samples

Samples	I	II	III
Volume before sintered (mm^3)	2199.11	2199.11	2199.11
Volume after sintered (mm^3)	971.93	1060.29	1060.29
Shrinkage (%)	55.80	51.79	51.79

The sample I had the most shrinkage due to the abundant of cracks formed on the sample. As aforementioned regarding the sintering process, the distance between the kaolin particles will decrease, and pores will reduce. The pores are empty spaces that cause the reduced density within the parts; the cracks are also vacant spaces that reduce the sample's density. Therefore, during the sintering process, the particles will get close to each other to eliminate or reduce the vacancies causing the sample to shrink more for reducing the crack size.

Sample II and III had lesser shrinkage than Sample I due to the absence of significant cracks; hence, the shrinkage is smaller. Thus, the clay for Sample I is not suitable as the density of the sample is low, causing a higher rate of shrinkage.

4.6 X-Ray Diffraction (XRD) Analysis of Kaolinite

The peak lines of the XRD spectra shown in Figure 4.16 corresponds to the raw kaolin powder. The spectra of the kaolin powder are compared with kaolinite ref. Code 96-900-9235 and quartz ref. Code 96-901-0145 from the database COD 2021. Out of the 25 peak lines of the kaolin powder's spectrum, 16 of the peak lines had matched with the peak lines of the spectrum for kaolinite. Therefore, the peak lines were matched with kaolinite and quartz, as shown in Figure 4.16, where it is clearly labelled in the XRD spectrum. Impurities were found at the position of 8.5, 27.5, 29.0 and 55.0 º2θ, where the peaks do not match with the spectra of kaolinite and quartz. The content of the kaolin powder consists of 74 % kaolinite and 26% quartz.

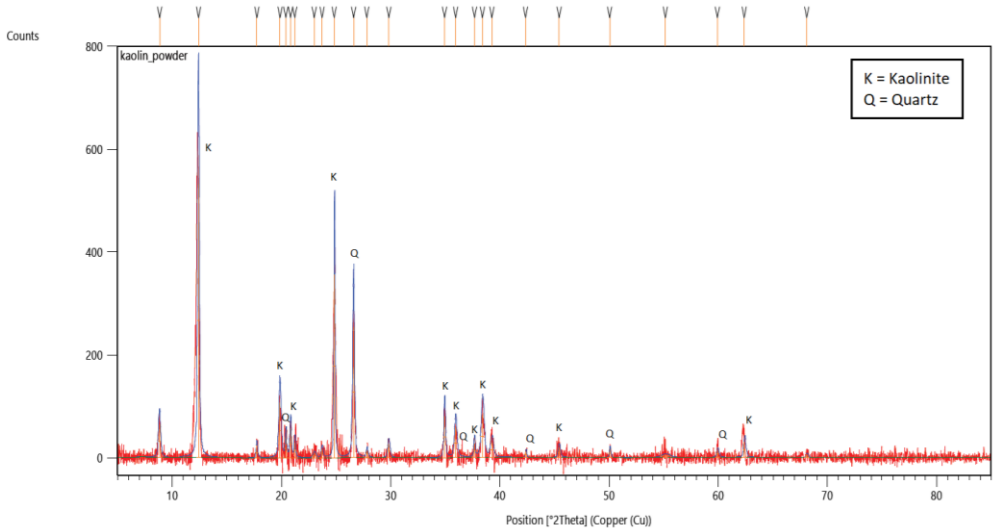


Figure 4.16: XRD of kaolin powder

The spectra analysis shown in Figure 4.17 is the XRD analysis of sintered kaolin. The spectrum of sintered kaolin is compared with mullite ref. Code 96-900-2408 and coesite ref. Code 96-900-0803, which are both taken from the COD 2021 database. By analysing the sintered kaolin using mix and match, the results show that the sintered kaolin consists of 47 % mullite and 53 % coesite. Hence, during the sintering process, mullite and coesite were formed during the phase change of kaolinite under the high sintering temperature of 1300 °C. There were a total of 12 peak lines in the sintered kaolin spectra analysis. It was observed that the peak lines were matched with mullite and coesite, as shown in Figure 4.17, where it is clearly labelled in the XRD

spectrum. An impurity was found at the position of 20.5 º2θ, where the peak does not match with mullite and coesite spectra; hence, the presence of impurity is low.

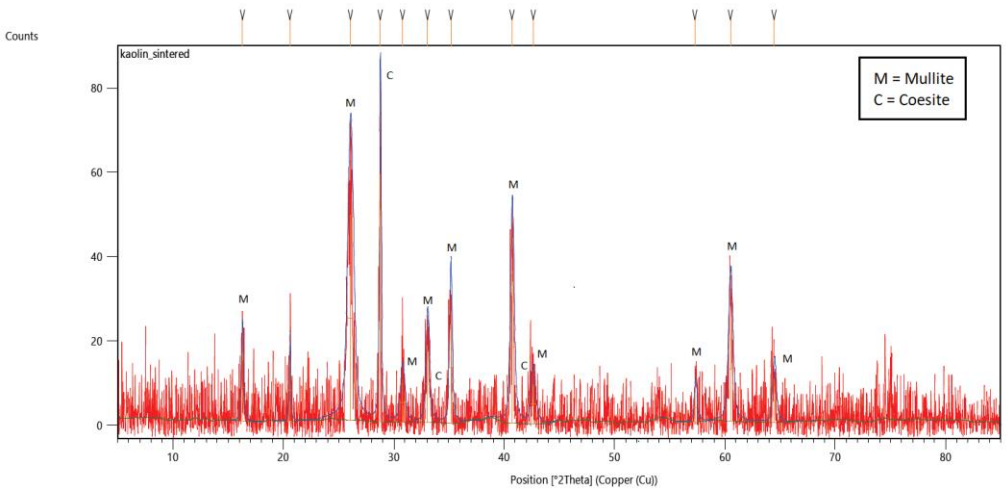


Figure 4.17: XRD of sintered kaolin

Besides that, the XRD analysis of the three samples that undergo the debinding and sintering process is done. Due to the high similarity between the spectra of the three sintered samples, only the spectrum of Sample III will be analyzed in this section. The XRD analysis of Sample III is compared with the spectra of mullite ref. Code 96-900-2408 and coesite ref. Code 96-901-0144 from the COD 2021 database. In the XRD analysis by applying mix and match, Sample III consist of 49 wt% of mullite and 51 wt% of coesite.

The total number of peaks for Sample III is 22, where there are 15 of the lines matched with mullite and 5 matched lines for coesite where it can be observed in Figure 4.18. Impurities were found at the position of 47.0 and 48.0 º2θ, where the peaks do not match with the mullite and coesite spectra. By comparing the spectra of Sample III and sintered kaolin, the difference between the composition is only by 2 %. Thus, it can be justified that the binders mixed into the clay have been removed during the debinding process, where the result shows a low presence of impurities.

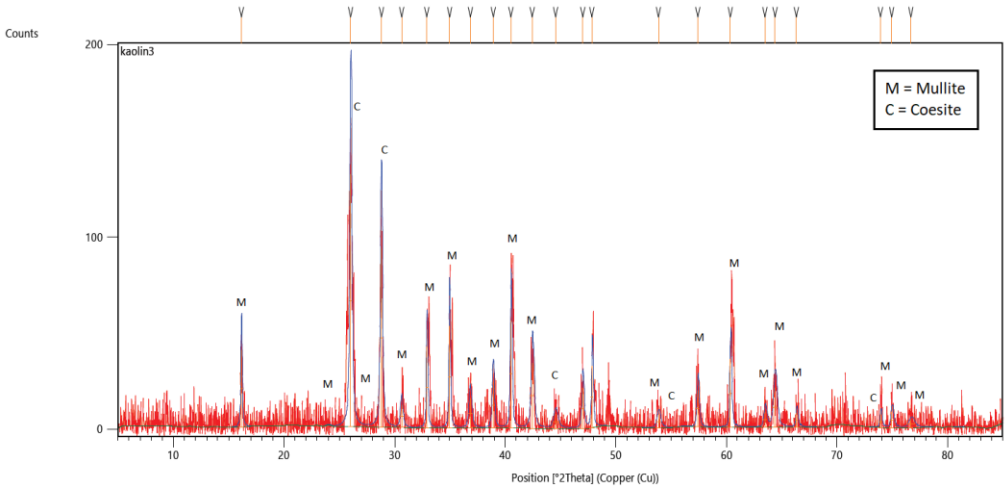


Figure 4.18: XRD of sintered kaolin Sample III

4.7 Summary

After conducting three experiments by testing the different compositions of binder systems, the optimum result is using 65 wt% of kaolin, 6 wt% of binder, 3 wt% of dispersant, and 26 wt% of water. Among the three binders, MC has given the best outcome for all sets of testings done. The clay sample is slightly soft; hence, the shape of the clay will change if the sample is being held. The duration for the sample to hardened is approximately 15 minutes under room temperature. Then only the platform under the sample can be removed.

The clay is later improved by replacing half of the water content with isopropyl alcohol, but the surface finish of the sample is not smooth compared to using only water. For further improvement, only a quarter of water content is replaced by isopropyl alcohol; the surface finish had lesser cracks and is comparable with the original composition that is only using water. However, the clay sample could not be held immediately after the injection moulding test. Therefore, it had to be dried using a hairdryer for more extended periods (about 5 minutes, during the experiment, the hairdryer was only used for 1 to 2 minutes) to remove the platform immediately. The duration for the sample to hardened and able to removed the platform had reduced to 10 minutes.

Then, the three samples with the clay composition of 65 wt% of kaolin, 6 wt% of binder, 3 wt% of dispersant, and 26 wt% of water were taken to the lab to carry heat treatment. The debinding temperature is 550 °C, and the sintering temperature is 1300 °C. The shrinkage for the samples using binders CMC, HPMC and MC is 55.80 %, 51.79 %, and 51.79 %, respectively. Hence,

the shrinkage of the sample using CMC as a binder in the clay has a higher shrinkage, where the other two samples using HPMC and MC in the clay has the same shrinkage. This result is due to the large cracks formed on the sample's surface as the clay using CMC, whereas the other two samples using HPMC and MC have a good surface finish.

In the XRD analysis, the kaolin powder content is 74 % kaolinite and 26 % quartz, where tiny impurities were found according to the spectra. As for the sintered kaolin sample, 47 % of mullite and 53 % of coesite was formed under the sintering temperature, 1300 °C. Compared with the sintered kaolin Sample III, the composition is 49 % of mullite and 51 % of coesite; therefore, the spectrum of Sample III is very similar to the sintered kaolin as the composition difference is only by 2 %. Consequently, the similarity between these two spectra can be proved that the binders have been removed during the debinding process.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In conclusion, the most optimum composition of the ceramic feedstock is 65 wt% kaolin, 6 wt% MC and 3 wt% PAA with 26 wt% water or 19.5 wt% water and 6.5 wt% isopropyl alcohol. The composition using only water gives a better surface finish, while the composition with alcohol added dries faster but with a slightly rougher surface finish than the previous. MC was chosen as the binder in this optimum composition as it was discovered that most of the feedstock composition using MC as the binder has a better result than using HPMC and CMC. This statement is justified by the results in the injection moulding test, as it tests the extrudability of the clay.

The main factor that decides the best composition is the extrudability of the clay during the injection moulding test. It was stated in the methodology, the extruding force below 7 kgf, which is 68.67 N, can only be wholly extruded into the mould by the extruder. The result shows that most of the clay using CMC as binder requires a higher force to extrude in most of the testings conducted compared to the clays using HPMC and MC. Hence, the extruded samples of clay applying CMC were usually not extrudable (incomplete extrusion) or having a poor surface finish. Compared to the clays using MC, the force measured in the weight test usually ranges from 4 to 5 kgf, mostly lower than the clay using CMC.

Besides the high viscosity of CMC that hardens the clay, it was found that HPMC has a significant issue regarding the prepared gel's lifespan. As mentioned at the start of the discussion, the viscosity of the HPMC gel becomes less viscous, from a thicker gel form into a watery-liquid form after a week. Therefore, it was explored in the experiment; the newly prepared HPMC makes the clay harder while the clay mixed with the old HPMC is softer. Therefore, the clays using the HPMC binder might not be accurate as the results fluctuate before and after a week.

Moreover, the shrinkage of the samples with the formulation of 65 wt% kaolin,6 wt% binder, 3 wt% dispersant, and 26 wt% water (best formulation as found in the results) after the sintering process is investigated. The result shows Sample I (using HPMC) has the highest shrinkage, which the sample shrunk 55.80 %, while the other two samples, Sample II and III, had the same shrinkage, 51.79 %. This is due to the poor surface finish of Sample I, as many cracks were found on the sample's surface, whereas Sample II And III have a good surface finish. Thus, the porosity in Sample I is high, affecting a high shrinkage during heat treatment.

Besides the main highlight in this study, suitable formulation of the ceramic feedstock, the design and 3D printing process was also investigated. The mould design was designed to remove the clay sample without destroying the sample by implementing a push mechanism (ejector) and adding the circular platforms to be removed together with the sample. Then, the 3D printing process was studied, where the thickness of the parts had to be controlled based on the applications.

5.2 Recommendations for future work

For further improvements, more binders and different mass fractions of the clay-binder composition can be tested to explore more suitable ceramic feedstock types. Besides that, more testings such as rheology tests, compression tests and SEM analysis can be conducted on the samples to understand the characteristics and mechanical properties better. Unfortunately, there were many restrictions in this study due to the pandemic; hence, these testings could not be conducted.

Furthermore, the extruder kit can be further improvised as the results were not consistent during the experiment. The result of the experiment was inconsistent, were two times of the same sets of clay used ended in three different results. This is highly due to the gears being worn out after conducting the injection moulding test several times. Therefore, it is recommended that the frequent maintenance or replacement of gears be carried in the future to reduce the errors during the experiment.

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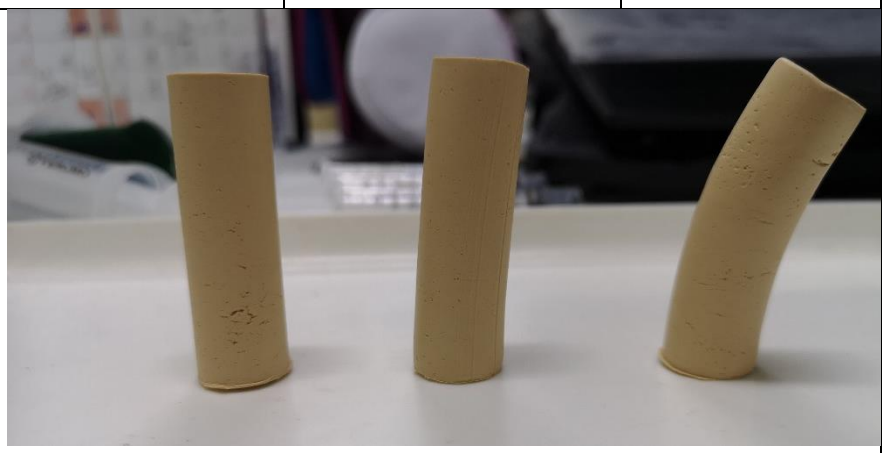
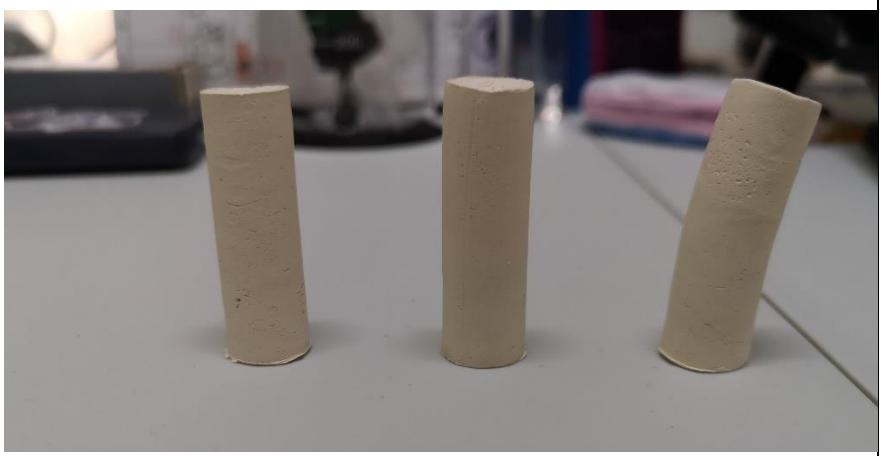
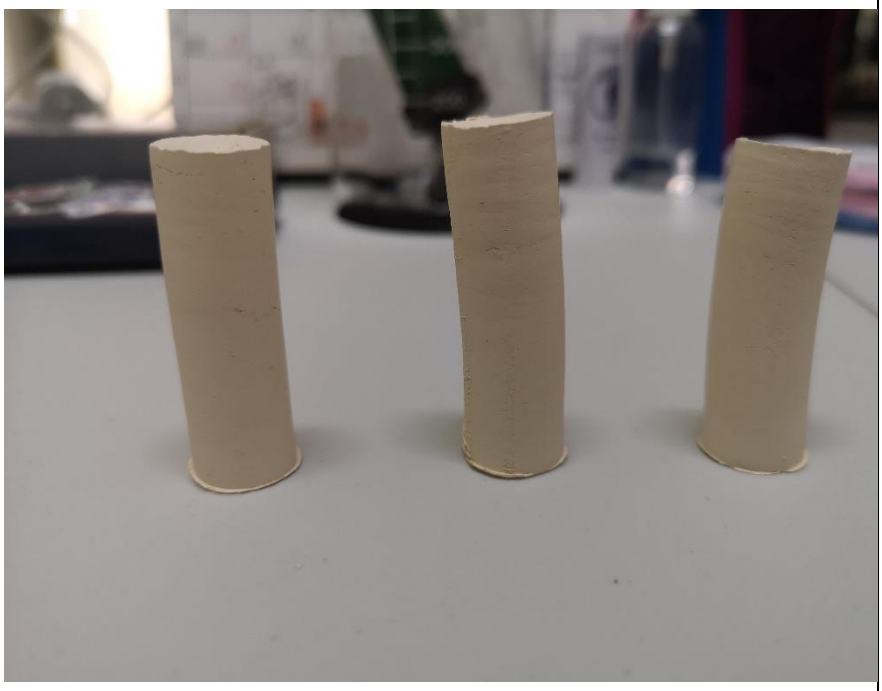
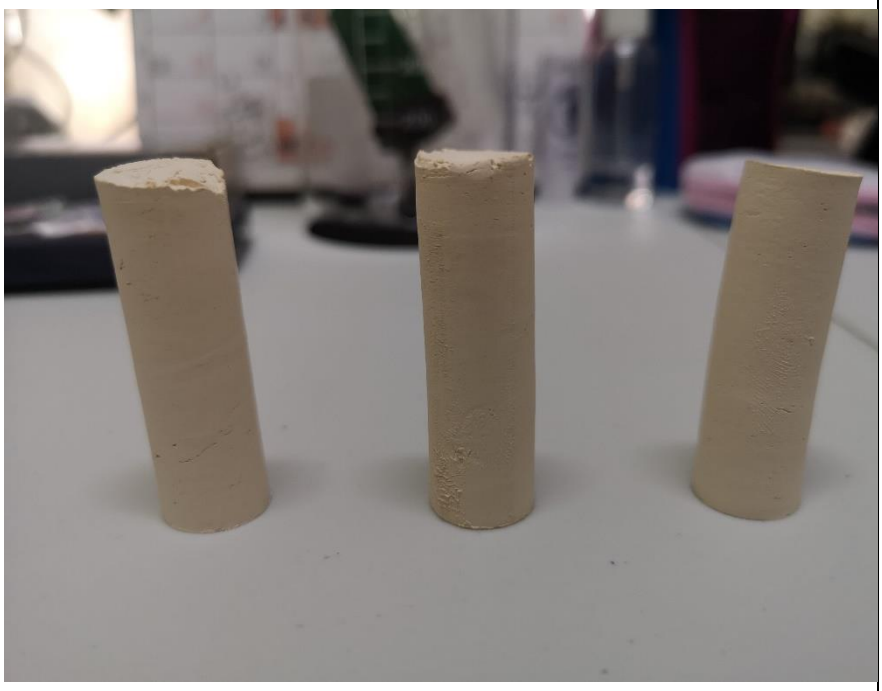
APPENDICES

Appendix A: Results from extrusion test

Table A-1: Results of the extrusion test for hard, medium and soft clays in different binder systems

Binders	Hard Clay (75% kaolin)	Medium Clay (70% kaolin)	Soft Clay (65% kaolin)
12% CMC + 6% PAA	 		

12% HPMC + 6% PAA	 

12% MC + 6% PAA	 

Appendix B: Results from injection moulding and weight test

Table B-1: Clay with 65% kaolin, 12% binder and 6% dispersant

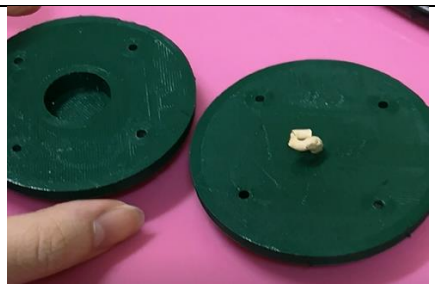
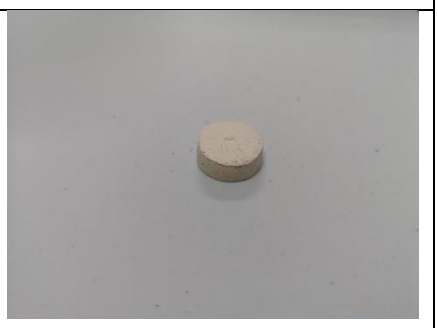
Feedstock content	Force needed to extrude the feedstock from a 10 ml syringe (N)	Observation of the sample from injection moulding	
		After injection moulding	Dried for one day under room temperature
65% kaolin + 12% CMC + 6% PAA + 17% water	101.04	 Incomplete extrusion	-
65% kaolin + 12% HPMC + 6% PAA + 17% water	53.63		
65% kaolin + 12% MC + 6% PAA + 17% water	32.37		

Table B-2: Clay with 55% kaolin, 12% binder and 6% dispersant

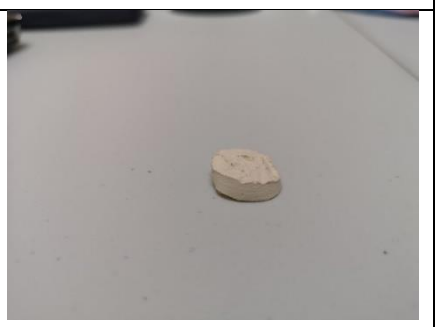
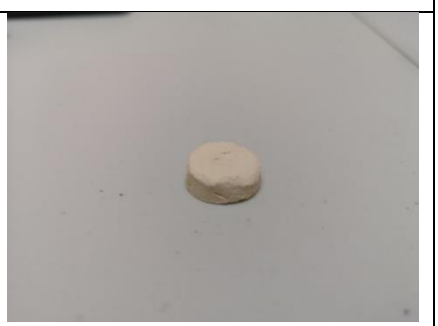
Feedstock content	Force needed to extrude the feedstock from a 10 ml syringe (N)	Observation of the sample from injection moulding	
		After injection moulding	Dried for one day under room temperature
55% kaolin + 12% CMC + 6% PAA + 27% water	62.78		
55% kaolin + 12% HPMC + 6% PAA + 27% water	8.83		
55% kaolin + 12% MC + 6% PAA + 27% water	9.81		

Table B-3: Clay with 65% kaolin, 6% binder and 3% dispersant

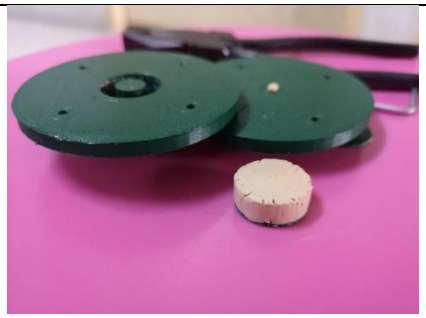
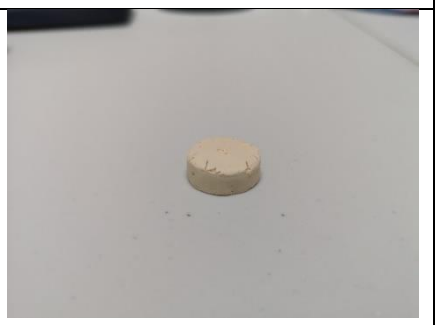
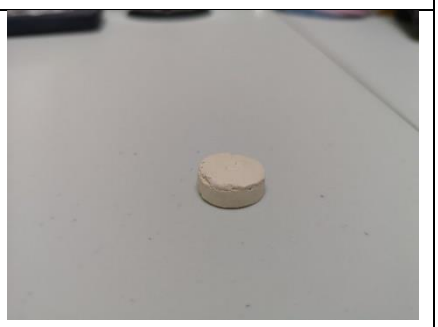
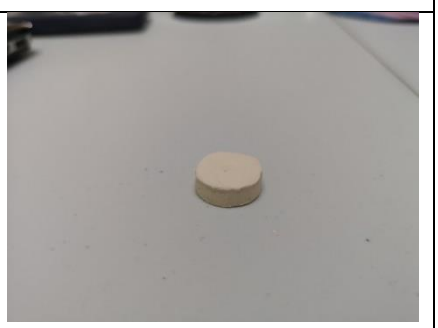
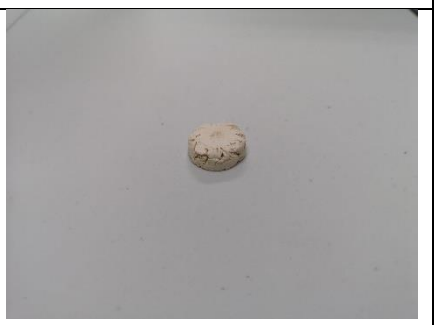
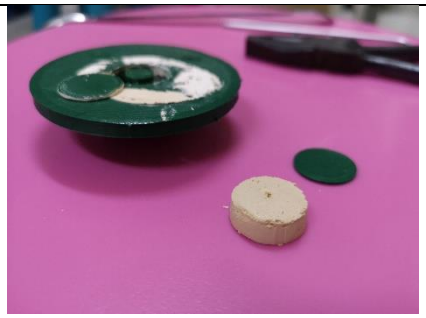
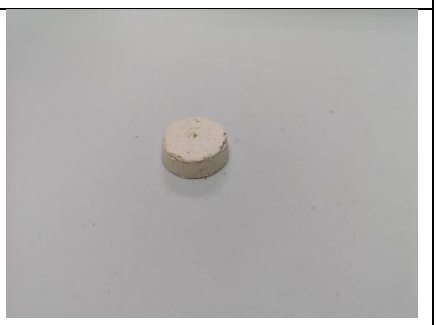
Feedstock content	Force needed to extrude the feedstock from a 10 ml syringe (N)	Observation of the sample from injection moulding	
		After injection moulding	Dried for one day under room temperature
65% kaolin + 6% CMC + 3% PAA + 26% water	39.24		
65% kaolin + 6% HPMC + 3% PAA + 26% water	56.90		
65% kaolin + 6% MC + 3% PAA + 26% water	41.20		

Table B-4: Clay with 65% kaolin, 6% binder and 3% dispersant with alcohol

Feedstock content	Force needed to extrude the feedstock from a 10 ml syringe (N)	Observation of the sample from injection moulding	
		After injection moulding	Dried for one day under room temperature
65% kaolin + 6% CMC + 3% PAA + 13% water + 13% isopropyl alcohol	58.86		
65% kaolin + 6% HPMC + 3% PAA + 13% water + 13% isopropyl alcohol	37.28		

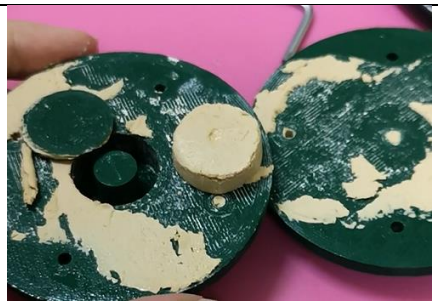
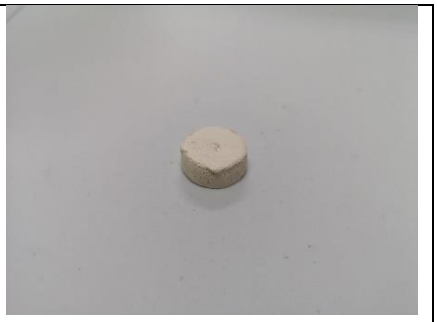
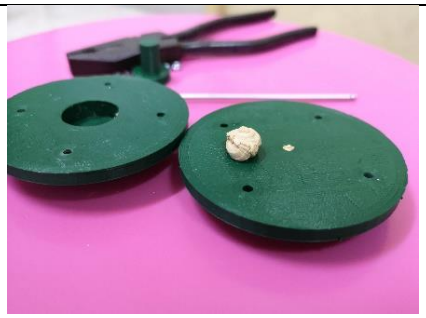
65% kaolin + 6% MC + 3% PAA + 13% water + 13% isopropyl alcohol	35.32		

Table B-5: Clay with 65% kaolin, 12% binder with alcohol

Feedstock content	Force needed to extrude the feedstock from a 10 ml syringe (N)	Observation of the sample from injection moulding	
		After injection moulding	Dried for one day under room temperature
65% kaolin + 12% CMC + 11.5% water + 11.5% isopropyl alcohol	87.31	 Incomplete extrusion	-

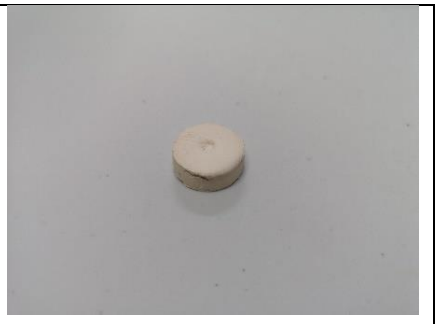
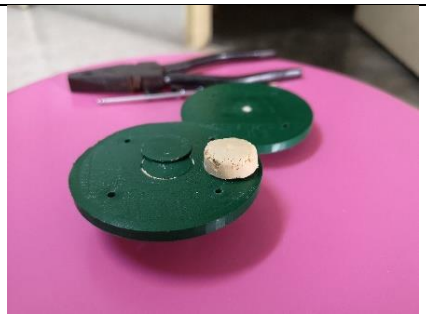
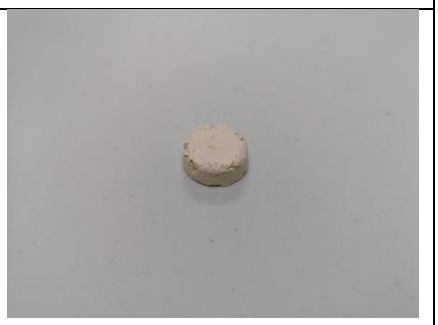
65% kaolin + 12% HPMC + 11.5% water + 11.5% isopropyl alcohol	56.90		
65% kaolin + 12% MC + 11.5% water + 11.5% isopropyl alcohol	66.71		

Table B-6: Improvement for MC (65% kaolin, 6% binder and 3% dispersant with alcohol)

Feedstock content	Force needed to extrude the feedstock from a 10 ml syringe (N)	Observation of the sample from injection moulding	
		After injection moulding	Dried for one day under room temperature
65% kaolin + 6% MC + 3% PAA + 19.5% water + 6.5% isopropyl alcohol	42.35