EFFECT OF BALL CLAY ADDITION IN SLIP CASTING IN MAKING OF GLOVES FORMER

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DECLARATIONS

I hereby declare that I have conducted and compiled the researched work and written the dissertation entitled “Effect of ball clay addition in slip casting in making of gloves former”, I also declare that it has not been previously submitted for the award of any degree or diploma or other similar title of this for any other examining body or University.

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Date 18/08/2022

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LIST OF ABBREVIATION

XRD	X-ray Diffraction
PSA	Particle size analysis
PSD	Particle size distributions
SEM	Scanning Electron Microscope
MOR	Modulus of rupture
BC	Ball clay

LIST OF SYMBOLS

°	Degree
°C	Degree Celsius
µm	micrometre
α	Alpha
%	Percent
mm	Millimetre
g	gram

KESAN TAMBAHAN TANAH LIAT BEBOLA DALAM TUANGAN SLIP DALAM PEMBUATAN ACUAN SARUNG TANGAN

ABSTRAK

Pembentuk sarung tangan adalah bentuk acuan tangan porselin yang digunakan dalam industri sarung tangan dan dibuat dengan menggunakan teknik tuangan slip. Pada mulanya, formulasi bekas sarung tangan mempunyai sekitar 23.10% tanah liat bebola. Dalam kajian ini, kesan penambahan lebih banyak tanah liat bebola ke dalam rumusan telah dijalankan. Selain itu, kesan mengisar tanah liat bebola terhadap sifat bekas badan sarung tangan yang telah dibakar telah dikenalpasti. Penambahan tanah liat bebola masing-masing ditambah daripada 0%, 2%, 4%, 6%, 8% dan 10%. Pembentuk sarung tangan menggunakan proses pengilangan basah sebelum meneruskan pembentukan bekas sarung tangan menggunakan kaedah tuangan berongga. Terdapat beberapa pencirian yang dilakukan terhadap jasad yang divitrifikasikan seperti pengecutan, lenturan, ukuran keliangan, ujian penyerapan air, ujian kakisan asid dan alkali, modulus pecah, dan kejutan haba. Morfologi permukaan bekas sarung tangan diperhatikan dengan menggunakan mikroskop imbasan elektron (SEM). Pada akhir kajian, didapati penambahan tanah liat ke dalam komposisi bekas sarung tangan akan mempengaruhi sifat fizikal dan mekanikal bekas sarung tangan. Peratusan tambahan tanah liat yang lebih tinggi menyebabkan penyerapan air meningkat, ujian kakisan berkurangan manakala peningkatan modulus pecah. Tambahan pula, apabila membandingkan antara tanah liat bebola yang dikisar dan tidak dikisar dengan sifat-sifat badan bekas sarung tangan yang telah dibakar, didapati bahawa, penyerapan air tanah liat bebola yang dikisar adalah lebih rendah berbanding dengan tanah liat bebola yang tidak dikisar. Sementara itu, keputusan ujian kakisan menunjukkan bahawa, set yang tidak dikisar

cenderung mempunyai kadar kakisan yang lebih tinggi terutamanya apabila merendam bekas sarung tangan ke dalam 10% larutan natrium hidroksida. Oleh itu, 4% daripada tanah liat bebola dalam komposisi pembentuk sarung tangan mempunyai sifat terbaik sifat fizikal dan mekanikal. Oleh kerana hasil penyerapan air yang rendah dan kadar kakisan yang rendah, ia membuktikan bahawa penambahan 4% tanah liat bebola untuk memembuktikan mbongkar tanah liat bebola mempunyai sifat yang terbaik. Ini boleh dikaitkan dengan fungsi bekas sarung tangan yang akan melalui proses pembersihan di mana bekas sarung tangan direndam dalam air, asid, dan larutan alkali. Oleh itu, bekas sarung tangan yang berkualiti perlu mempunyai penyerapan air yang rendah, kadar kakisan yang rendah, dan lulus ujian kejutan haba

EFFECT OF BALL CLAY ADDITION IN SLIP CASTING IN MAKING OF GLOVE FORMER

ABSTRACT

Glove formers are a porcelain hand mould shape that used in glove industry and made by using slip casting technique. Initially, the formulation of glove former has around 23.10% of ball clay. In this research, the effect of adding more ball clay into the formulation was carry out. Other than that, the effect of milling the ball clay towards the properties of vitrified body of gloves former was identified. The ball clay addition added from 0%, 2%, 4%, 6%, 8% and 10%, respectively. Glove formers are using wet milling process before proceeding to form the glove former using hollow casting method. There a few characterizations done towards the vitrified body such as shrinkage, warpage, porosity measurement, water absorption testing, acid and alkali corrosion testing, modulus of rupture, and thermal shock. The morphology of the glove former surfaces was observed by using scanning electron microscope (SEM). At the end of the research, it was found that, ball clay addition into the composition of glove former will affect the physical and mechanical properties of glove former. Higher percent of addition of ball clay caused the water absorption increases, the corrosion test decreases while increases of the modulus of rupture. Furthermore, when comparing between milled and unmilled ball clay towards the properties of vitrified body of glove former, it found that, the water absorption of milled ball clay was lower compared to unmilled ball clay. Meanwhile, corrosion test results show that, the unmilled set tend to have higher corrosion rate especially when immersing the glove former into 10% of sodium hydroxide solution. Hence, 4% of ball clay in composition of glove formers have the best properties of physical and mechanical properties. As the results of low water absorption and low corrosion rate, it proved that 4% ball clay addition of unmilling the ball clay has the best properties. This can be related to the function of the glove former that will gone through

cleaning process where the glove formers are immersed in water, acid, and alkali solutions. Therefore, a quality glove former need to be low water absorption, low corrosion rate, and pass the thermal shock test.

CHAPTER 1

INTRODUCTIONS

1.1 Research background

Since the pandemic of Covid-19 strikes in 2019, the glove former industries had encountered a lot of problems with their products due to high demand in glove production in short time. Among the failure faced, warping and cracking are the most common defects that can be found in the whiteware particularly in making glove former. These defects may lead to other types of problems such as if the gloves former does not have of good quality, the quality of the gloves produced will also be affected.

Basically, gloves former is made using slip casting. The structure of the glove former is it has a hollow part. The ceramic slip containing ball clay, kaolin, alumina, calcined alumina and molochite that mixed with water and deflocculant will be poured into mould that is made from plaster of Paris (POP). After a sufficient thickness has been achieved for the solid, the remaining slip is drained off. Then, a solid of the mould cavity is obtained and the solid is taken out from the mould. The solid that was taken out from the mould cavity is called greenware. The process continues by drying the greenware and then it will be fired in a kiln for a certain period of time. In the casting, three ways that will affect the shrinkage of the product are shrinkage due to liquid absorption by the mould, drying shrinkage, and firing shrinkage.

Differential shrinkage of the products during the process can cause warping, cracking, and anisotropic shrinkage. (Rahaman, 2017) reported that, anisotropic shrinkage are occurred when the powder compacts are sintered, there are occasionally significant differences in the linear shrinkage along the different directions. Dimensional control of the finished product is challenging due to this anisotropic shrinkage. This can be related to drying shrinkage and firing shrinkage. A greenware with high thickness that consist of fine particle size of raw materials will affect the drying rate to increase and results in cracking.

1.2 Problem statement

In glove former industries such as MediCeram Sdn Bhd, cracking defects can be found in the finishing goods. This issue may be caused by handling stress on the greenware and cracks that appear after firing. Stresses in the clay cause ceramic cracks. Clays such as ball clay are always under stress because they shrink, expand, and compress during firing. When the stress on the clay becomes too much to handle, it fractures or cracks. Different clays may withstand various levels of stress without cracking. In this study, the composition of ball clay was varied to determine the green strength of the glove former to withstand handling stress and cracks. The amount of ball clay in the body affects key properties such as shrinkage, density, vitrification, and corrosions. The corrosions of the gloves former are due to the glove former in glove industry will go through cleaning process where the gloves former will be immersed in low concentration of acid and alkali solutions. Therefore, the amount of ball clay addition in the body needs to be determined to produce a high green strength without affecting the other key properties of the glove former.

1.3 Objectives

i. To determine the effect of adding different amount of ball clay on the physical and mechanical properties of vitrified gloves former.

ii. To study the effect of using milled and unmilled ball clay on the physical and mechanical properties of vitrified gloves former.

1.4 Thesis outline

Chapter 1: Discusses the research background, problem statement, and the objective of this study. This chapter also briefly outlines the scope of work in this study.

Chapter 2: Discusses the literature review related to whiteware, development of gloves former, type of sintering, problems that occur in ceramic after drying, and the characterization of ceramic surfaces after increasing adding ball clay into the slip casting.

Chapter 3: Covers the raw materials used in the production of glove former as well as the method and characterization method used. Different composition of ball clay is used to produce the glove former and milling of the ball clay together with other raw materials. The characteristic of the raw materials and testing method used also will be discussed in this chapter.

Chapter 4: The outcome of the findings as well as incorporating information on the characterization and testing done in this study such as XRD, XRF, PSA, tabletop SEM, water absorption, acid and alkali corrosion test, porosity measurement, modulus of rupture and thermal shock testing.

Chapter 5: Conclude and provide a clear view of the achieved objectives and justification for this study. Finally, some recommendations for future work have been proposed at the end of this chapter.

1.5 Scope of work

This study will be focusing on the synthesis of gloves former, and the process are divided into 3 stages. Figure 1.1 shows a research flow chart. Stage one involved the synthesis of raw materials by using wet milling. These steps were divided into 2 routes in order to achieve the objectives for this study. The first route is where all the starting raw materials powder such as ball clay, potash feldspar, alumina, calcined alumina, molochite were milled by using raw materials. Meanwhile, for the second route, the raw materials powder except the ball clay were milled. Next, this proceeds by adding kaolin and followed by casting the gloves former. The greenware will be air dried, dried in the oven and lastly the greenware will be sintered. In the second stages, the raw materials powder involved characterizations including X-Ray Diffraction (XRD), X-Ray Fluorescence (XRF), Particle Size Analysis, and tabletop Scanning Electron Microscope (SEM). Stage 3 involved testing and characterization of vitrified body of gloves former including shrinkage, warpage test, acid and alkali corrosion test, water absorption, modulus of rupture (MOR), thermal shock and lastly tabletop Scanning Electron Microscope (SEM).

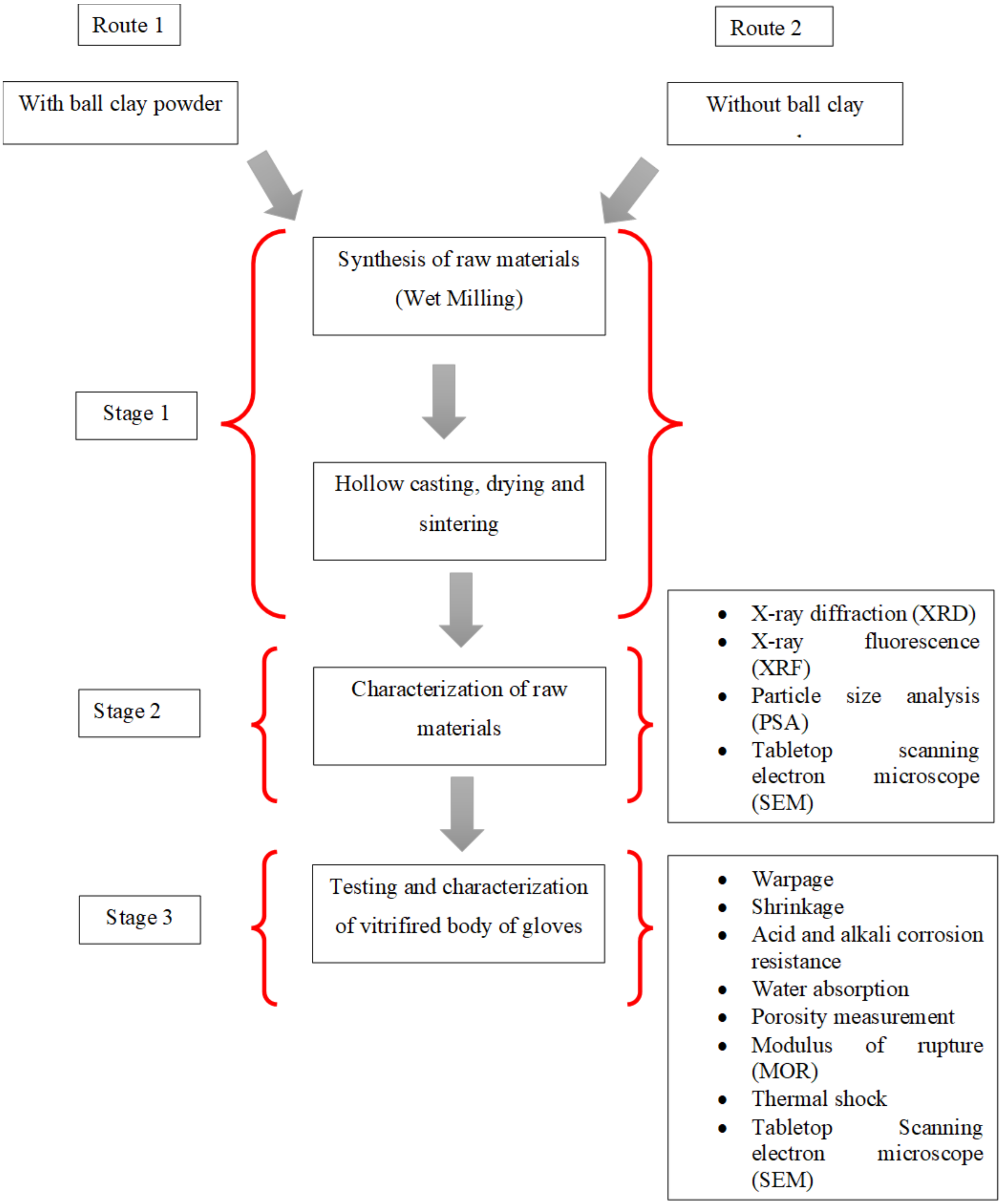

Figure 1.1: Flow chart of research work

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Porcelain is a white-vitrified ceramic ware made from a fine mixture of kaolin, quartz, feldspar, and plastic white-firing clay. It is translucent in thin layers and impermeable to fluids. Common porcelain is used in the most of commercial porcelain hand formers nowadays. In the manufacture of rubber gloves, a hand former is used as a mould (Abdullah, 2006). High hardness, good thermal and chemical resistance, ease of mould preparation, smooth mould surface, and affordable pricing are some of their characteristics. Bone china, in particular, is a type of ceramic hand mould with a high alumina content and excellent thermal resistance (Tharasana et al., 2020).

Drying is an important phase in the production of all-ceramic goods and components, whether it is done separately or as part of the firing process. Ceramics are created from a variety of materials that can be slurry or even more liquid at the start of the production process, as in the case of slip-cast ware. If drying is not done uniformly, problems might arise in a variety of ways. Shrinkage cracking can be a severe problem, especially in product of different thicknesses.

2.2 Whiteware

Whiteware is any of a broad class of ceramic products that are white to off-white in appearance and frequently contain a significant vitreous of glassy component (Wilson, 1996). Moreover, (Sarkar, 2020) states that, whiteware covers a vast field of ceramics, in which clays, quartz and feldspar are the basic raw materials for making whiteware bodies.

2.2.1 Classifications of whiteware

Whiteware encompasses many subcategories such as sanitary ware, earthenware, stoneware, and porcelain (Sarkar, 2020). There are three types of main classes of whiteware product according to their degree of verification and resulting porosity such as porous, semivitreous, and vitreous. Earthenware is non-vitreous, stoneware is a semivitreous with a fine microstructure of solid phase and glass which include tableware, cookware, and sanitary ware. Lastly porcelain is a vitreous whiteware (Oluwagbenga et.al, 2015).

2.2.2 Porcelain

(Carty et al., 2005) said that porcelain is one of the most complex ceramic materials that composed of clay, feldspar, and quartz. The porcelain will be heat treated and form a mixture of glass and crystalline phases. Porcelain also defined as a whiteware component which lack of open porosity in the fired body.

Porcelain also can be defined as white-vitrified ceramic ware made from a fine mixture of kaolin, quartz, feldspar, and plastic white-firing clay. It is translucent in thin layers and impermeable to fluids. Common porcelain is used in the most of commercial porcelain hand formers nowadays. In the manufacture of rubber gloves, a hand former is used as a mould (Abdullah, 2006). High hardness, good thermal and chemical resistance, ease of mould preparation, smooth mould surface, and affordable pricing are some of their characteristics. Bone china is a type of ceramic hand mould with a high alumina content and excellent thermal resistance (Tharasana et al., 2020).

2.2.3 Effect of particle size in whiteware composition

According to (Oluwagbenga et al., 2015), the particle size of a materials is smaller, therefore it will increase the maturation of the body and the firing range also higher. The warpage also can be reduced when the particle size is smaller, thus the translucency and the mechanical strength also will be increase.

The mechanical resistance of semifinished product will depend on clay mineralogy and particles size. The particle size distribution also will affect on particular the plasticity and the size changes during processing. (Dondi et al., 2003).

The particles size ranging from 100 to 300 nm have a low viscosity and have high volume fraction suspensions to produce green bodies of sufficiently high green density to fully densified that will lead to homogenous microstructure (Tallon et al., 2010). The particle sizes of a liquid-based medium, can affect the viscosity of suspensions. The larger particles can increase the flow of the liquid while the smaller particle can increase the suspensions viscosity.

2.3 Raw materials of whiteware powder

2.3.1 Introductions

The ceramics industry offers a wide range of powders. Powders for technical ceramics (alumina, zirconia, nitrides, carbides, titanates, etc.) and powders for traditional ceramics (clay, feldspar, kaolin, silica, talc, etc.) offer a variety of chemical and physical properties that need to be controlled to consistently produce parts with the desired properties. Hence, powder preparation is a crucial step in the shaping processes. The goal is to produce a powder that, when shaping (with issues of particle stacking, dispersion, and rheology of the mixtures), achieves the desired microstructure, generally dense and homogenous, and ensures a proper densification during sintering (problem of powder reactivity). The particles' size and size distribution, shape and state of agglomeration, specific surface area, degree of purity, and chemical composition of their surface all have an impact in this circumstance (Boch et,al., 2007).

2.3.2 Ball Clay

Ball clay are particularly valued for their plasticity as it can act as a binding agent and gives strength in the state before firing process. On the other hand, ball clay also imparts high drying shrinkage which have tendency towards warping and cracking (Loryuenyong, 2009).

Kaolinite (25–80%), illite and mica (10–30%), and fine-grained quartz are the most typical elements in plastic ball clays. Illite/smectite (I/S) mixed-layered minerals can also be found. A low quantity of organic matter—up to 0.5% of the total volume also common (Wilson, 1998). The level of crystallinity of kaolinite and illite, as well as the amount of clay minerals (particularly I/S minerals), influence the ceramic properties of plastic ball clays. The grain size distribution and specific BET surface area of the clays are influenced by these properties. Plastic ball clays contain usually huge amounts of grains 1µm (50–90), and even 0.2µm (25–40%). Clay particle size is inversely proportional to specific BET surface area and plasticity in general. Other elements that influence a clay's plasticity include the crystallinity of kaolinite and illite (Dondi et al., 2003; Stoch, 1964).

2.3.3 Kaolin

Kaolin is a type of clay. Clays are the most important ingredients in traditional ceramic items. Kaolin has a layer silicate with a particle size of less than 2µm. Kaolin is formed through the mechanical and chemical weathering of feldspars in igneous and metamorphic rocks. Kaolin is an important component of China clay. The original rock's location is where primary kaolin deposits are found. Secondary kaolin’s were washed away from the weathering site, spontaneously beneficiated, and redeposited in wide expanses of pure kaolin. Kaolin is white firing clay that composed of kaolinite, which is a type of hydrated aluminium silicate (Surendranathan, 2015).

2.3.4 Potash feldspar

Aluminosilicates of sodium, potassium, and calcium are important feldspars in ceramics (Jones et al, 1993). Fluxes are utilised to help bodies form a glassy phase, which promotes vitrification and translucency. Fluxes also used in glazes as a source of alkalis and alumina. The sodium feldspar is usually used in glasses and glazes, while the high potassium feldspar is used in whiteware bodies. Potassium feldspars ($KAlSi_3O_8$) offers a wide firing range and the best stability of the body against deformation during firing. Sodium feldspar ($NaAlSi_3O_8$) exhibits a lower viscosity compared to potassium feldspar when melted at a given temperature. This allows for lower-temperature vitrification, but it also increases the risk of deformation. (Olupot et al, 2006). Ceramists particularly prefer potassium feldspar because its reaction with silica forms a liquid with a relatively high viscosity that reduces gradually as the temperature rises. This characteristic is believed to protect the pieces from severe deformation during the heat treatment. (Boch et al., 2007).

2.3.5 Aluminium oxide

In the advanced ceramics family, alumina is the most cost-effective and commonly used structural engineering material. The raw materials used to make this high-performance, technical-grade ceramic are easily available and economically priced, resulting in good value for fabricated alumina shape prices (Heimann, 2010). Aluminium oxide or Alumina (Al_2O_3) ceramic has a strong atomic bond in their mechanical and thermal performance which imply to a high hardness, satisfactory mechanical strength, high moduli of elasticity, wear-resistance, and good tribological properties and refractory (Boch et. al, 2007). Aluminium oxide is ground with diamond abrasives due to it has high hardness. Therefore, in slip casting process, the dimensional tolerance is difficult to achieve, and grinding or milling process is adopted (Surendranathan, 2015).

2.4 Milling

The process in which small particles are produced by reducing the size of larger particles by mechanical forces is often referred to as comminution. It involves operations such as crushing, grinding, and milling (Rahaman, 2017). Besides particle size reduction, ball mill is also widely used for mixing, blending, and dispersing, amorphization of materials and mechanical alloying (Vladimir et al., 2012).

In this, the balls constitute the milling media. These balls partially fill a barrel. The material of construction for the barrel and balls is the same. The hardness of the material should be equal or greater than the hardness of the mineral that will be milled in it. The barrel is rotated horizontally during the operation. During the rotation of the barrel, the balls undergo a cascading action. This is shown in Figure 2.1. The cascading action gives rise to shearing and crushing forces on the mineral grains. The size of the balls depends on the final particle size required. The size ranges from 8 cm to 0.6 cm. As the size decreases, finer particles are obtained. Ball milling is a simple and inexpensive process. The media and containers can add impurities to the powder if they are of different materials. Only 2% of the total energy input goes into the reduction of particle size. (Surendranathan, 2015)

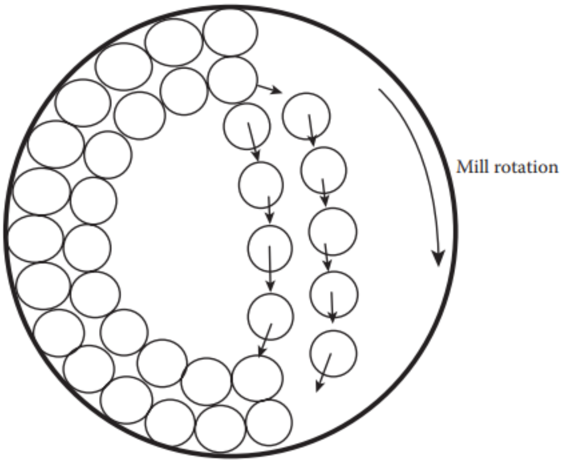

Figure 2.1: Cascading action in ball milling (Surendranathan, 2015)

For mills that incorporate grinding media (balls or rods), comminution occurs by compression, impact, and shear (friction) between the moving grinding media and the particles. Rod mills are not suitable to produce fine powders, whereas ball milling can be used to produce particle sizes from 10 µm to as low as a fraction of a micrometer. Ball milling is suitable for wet or dry milling (Rahaman, 2017). In the milling process, the objective is to have the balls fall onto the particles at the bottom of the mill rather than onto the mill liner itself. For a mill operating at 75% of its critical speed, this occurs for dry milling for a quantity of balls filling 50% of the mill volume and for a charge of particles filling 25% of the mill volume. For wet milling, a useful guide is for the balls occupying 50% of the mill volume and the slurry 40% of the mill volume with the solids content of the slurry equal to 25–40% (Rahaman, 2003).

Wet ball milling has an advantage over dry milling in that its energy utilization is somewhat higher (by 10–20%). A further advantage, as we have mentioned earlier, is the ability to produce a higher fraction of finer particles. Disadvantages of wet milling are the increased wear of the grinding media, the need for drying of the powder after milling, and contamination of the powder by the adsorbed vehicle (Rahaman, 2003)

2.5 Casting

The common casting methods are slip casting, pressure casting, and tape casting. They are based on colloidal systems in which removal of the liquid is used to consolidate particles suspended in a slurry. In slip casting and pressure casting, consolidation of the particles is accomplished as the liquid flows through a porous medium under a pressure gradient. In tape casting, consolidation is accomplished by evaporation of the liquid (Rahaman, 2003).

Slip casting offers a route to produce complex shapes and is widely used in the traditional clay-based industry, for example, for the manufacture of pottery and sanitary ware (Rahaman, 2003). The ceramic stoneware and plaster hand moulds were prepared by slip casting. (Tangboriboon et al., 2020)

2.5.1 Slip casting

Slip casting is the most common method for creating a wide range of items with complicated shapes (culinary, sanitary, refractory materials, technical ceramics). This method involves pouring a suspension (slip) into a porous, plaster-based mould. The formation of a solidified layer of particles on the mould surface is caused by the capillary migration of the liquid into the mould pores. Slip casting is the most common method for creating a wide range of items with complicated shapes (culinary, sanitary, refractory materials, technical ceramics). This method involves pouring a suspension (slip) into a porous, plaster-based mould. The formation of a solidified layer of particles on the mould surface is caused by the capillary migration of the liquid into the mould pores (Boch et al, 2007). When the cast dries, it shrinks away from the mould and can be easily removed. The cast is then heated to burn away the binder and sintered to make the final product once it has dried completely. (Rahaman, 2003).

2.5.2 Slip casting mechanism

A slurry is poured into a permeable mould, usually made of gypsum, in slip casting ($CaSO_4.2H_2O$) (Rahaman, 2017). The liquid in the slip is allowed to absorb completely by the plaster of Paris (POP) mould for the formation of solid parts. As a result, a solid in the shape of the mould cavity is formed. After that, the solid and the mould are both dried. If the design allows for the part to be lifted from the mould, the solid is obtained by cutting the mould open. The dimensions of the solid will be smaller than the dimensions of the mould cavity. It will also be very porous. The next stage, sintering, densifies the material. Sintering shrinks the casting even more. The process can be shown in Figure 2.2. As a result, appropriate adjustments are made in the mould cavity to handle all three shrinkages: shrinkage due to liquid absorption by the mould, drying shrinkage, and sintering shrinkage. After obtaining a proper thickness for the solid, the remaining slip inside the solid is drained off to form hollow sections. This procedure is also known as drain casting due to this stage. (Surendranathan, 2015).

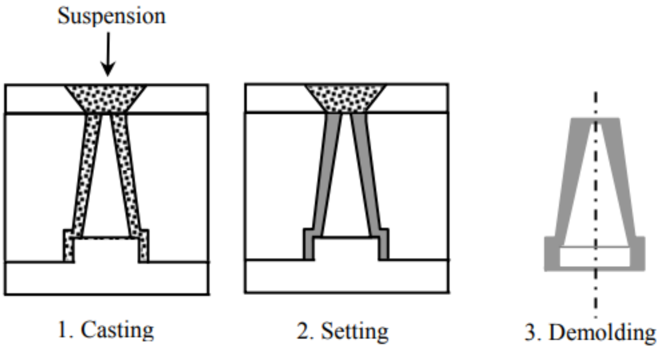

Figure 2.2: Casting between two moulds (Surendranathan, 2015)

2.5.3 Slip slurry parameter`

According to (Gadow et al., 2014), Aqueous suspension, sometimes referred to as slip, slurries, or dispersion, is frequently used in slip casting. A good slip is having the criteria such as high solid content, low viscosity, absence of agglomeration and high homogeneity. This requirement can be achieved by mixing, milling and deairing. Adding a suitable additive such as surfactants, plasticizers, binders, flocculant and deflocculant can help to achieve the desired criteria to produce a good slip. A stable suspension needs to have a small particle to avoid the slips to aggregates (Francis et al., 2016).

There are a few parameters that are important to control while making the slip slurry which are viscosity, density, and thixotropy. The density of slip slurry needs to be in between the defined limit as variations will be affect casting performance. Rapid saturation of plaster moulds and subsequent difficulties with the second cast and mould drying cause by low density value. Meanwhile, when the slip having high density, it can cause a casting and pouring problem due to the particle packing and the fluidity are not well controlled.

Next, thixotropy of slip casting will affect the casting performance. Thixotropy can be define as the tendency of undisturbed slip to thicken with time. Thixotropy also help in newly-cast product to keep their shapes in the mould

Other than that, slip viscosity also need to be control for the slip can be easily poured into the mould and fill in the detailed part (Francis et al., 2016).

2.6 Drying

When the solvent wets the green body, it creates a compressive capillary force that binds it together. When surface tension-driven flows to maintain the surface wet, capillary-induced tension is always present. Due to the liquid evaporates during drying, the capillary force vanishes. The cohesive force of the binder replaces the compressive capillary force when a polymeric binder is present, as shown schematically in Figure 2.3. The cohesive force of the binder is significantly lower than the solvent's original compressive capillary force. If excessive stress is applied on the green body during drying, it may break due to its weakened state.

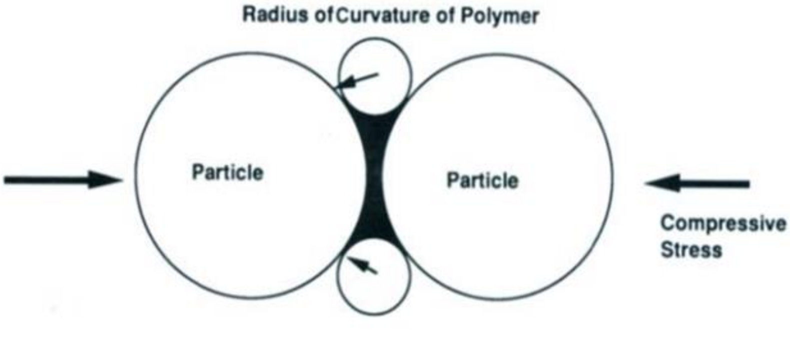

Figure 2.3: Compressive stress inside a ceramic body due to the present of a polymer after it is dried of solvent (Ring, 1996)

Due to (1) the pressure gradient of the flow of liquid during shrinkage in the constant rate period, (2) the macroscopic pressure gradient of the escaping gases during the decreasing rate period, or (3) the differential thermal expansion of the ceramic due to temperature gradients in the green body, the green body is susceptible to nonuniform stresses that may warp or crack it during drying. The drying rate controls the flow of liquid, the macroscopic pressure gradient, and the temperature gradient. The rate at which a green body dries is usually determined by external factors. These external factors must be small enough to prevent excessive stress from building up, which would warp or crack the green body (Ring, 1996)

2.7 Sintering

Connecting the behaviour or changes in behaviour during sintering to controllable variables and processes is one way to develop an understanding of sintering. This can be accomplished either empirically by observing sintering behaviour under controlled conditions or theoretically by modelling the process. Over the last 50 years, theoretical analysis and experimental research have resulted in a superior qualitative understanding of sintering in terms of driving forces, processes, and the impact of key processing variables including particle size, temperature, and applied pressure. (Rahaman, 2007)

Liquid-phase sintering is typically used to improve densification rates, increase grain growth, or provide certain grain boundary characteristics. The distribution of the liquid phase and the following solidified phases created after densification are crucial for producing the sintered material's requisite qualities (Rahaman, 2017). Other than that, liquid-phase sintering offers two significant advantages over solid-state sintering. First, it is much more rapid; second, it results in uniform densification (Barsoum, 2003). However, the formation of a liquid phase is often used in many ceramic systems to aid in sintering and microstructural progress (Rahaman, 2017).

2.7.1 Liquid phase sintering (LPS)

The term liquid-phase sintering (LPS) is used to describe the sintering process when a proportion of the material being sintered is in the liquid state (Barsoum, 2003). Chemical interactions between the particulate solid and the liquid are typically weak in liquid-phase sintering systems, hence interfacial energies have a major effect on the sintering rate. Liquid-phase sintering is widely thought to proceed in a sequence of dominant stages under these conditions, as shown in Figure 2.4. The first stage is redistribution of the liquid and arrangement of the particulate solid under the influence of capillary stress gradient. Next is the densification and grain shape accommodation by solution-precipitation and the final stage is sintering driven by the residual porosity in the liquid (Rahaman, 2003).

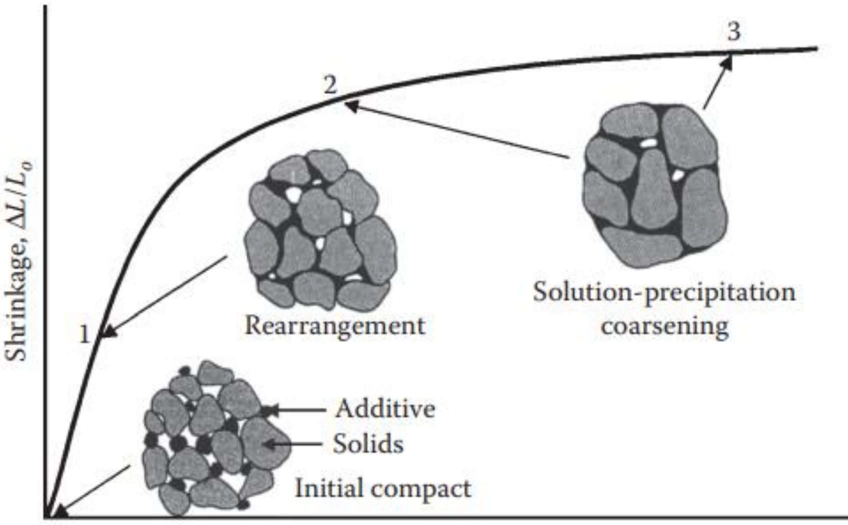

Figure 2.4: Schematic evolution of a powder compact during liquid phase sintering (Rahaman,2003)

Solid-state sintering may occur before the creation of the liquid as the temperature of the green body rises, resulting in significant densification in some systems. Further densification occurs as a result of the capillary force exerted by the liquid on the particles, assuming good wetting between the liquid and the particulate solid. The particles shrink as the solid dissolves in the liquid and rapidly rearranges to produce a higher packing density, releasing liquid to fill pores between the particles. Capillary stresses will cause the liquid to redistribute itself between the particles and into the small pores, leading to further rearrangement. Because of their higher solubility in the liquid, contact points between agglomerates will dissolve, and fragments will rearrange. Throughout the process, sharp edge resolution makes the particle surface smoother, reduces interface areas, and assists in system relocation. Initially, rearrangement occurs rapidly, but as densification occurs, the viscosity of the system increases, and the densification rate continues to decrease.

As the rate of densification through rearrangement slows, effects based on solid solubility in the liquid and diffusivity in the liquid take over, resulting in the solution-precipitation stage. The solid dissolves at a higher chemical potential solid-liquid interface, diffuses through the liquid, and precipitates on the particles at lower chemical potential sites. The wetted contact area between the particles is one sort of dissolution site, where the capillary stress caused by the liquid, or an externally induced stress leads to greater chemical potential. Precipitation occurs at sites apart from the area of contact. Matter can also be moved from small particles to large particles by diffusion through the liquid in systems having a variety of particle sizes, a process known as Ostwald ripening. As a result, the microstructure becomes coarser. The solution-precipitation mechanism causes grain densification, which is followed by changes in grain morphology. When there is a lot of liquid, the grains usually take on a spherical form. To enable more efficient packing, the grains acquire flat faces and assume the shape of a polyhedron for a small amount of liquid, a process known as grain shape accommodation.

The densification of the solid particle skeletal network controls the last step of liquid-phase sintering. Due to the large diffusion distances in the coarsened structure and the strong skeleton of interacting solid grains, the process is slow. The final stage is dominated by Ostwald ripening, and residual holes become larger if trapped gas is present, resulting in compact swelling. Grain shape accommodation occurs in conjunction with coarsening, allowing for more efficient grain packing. Densification can occur when liquid is released from the more closely packed regions and flows into the isolated pores. (Rahaman, 2003)

2.8 Potential defect in whiteware product

When the solvent wets the green body, it creates a compressive capillary force that binds it together. This capillary force disappears during drying. When a polymeric binder is present, the compressive capillary force is replaced by the binder's cohesive force, which is typically lower than the solvent's original compressive capillary force. The green body is prone to stress in its weaker form after drying, which can cause it to distort and shatter. The capillary pressure gradient, the pressure gradient of the escaping solvent, or the differential thermal expansion of the ceramic due to temperature gradients inside the green body all contribute to this stress (Ring, 1996)

Clay is used in ceramics to absorb and store water. It is crucial to remove all physical water before firing so that the component does not crack or rupture when heated. This is frequently done in stages, with firing being the last. The piece gains strength while developing physical surface characteristics as the chemical water is removed during firing. Drying is the process of removing water from the body by evaporation. The water barrier between the clay particles becomes thinner as the ware dries, the solid particles become closer together, and the component shrinks. When the particles ultimately make contact with each other, the shrinkage stops.

Cracking, distorting, and warping are issues that may not be visible until after the component has been fired. They're commonly a result of drying rapidly or unevenly. The pressure from water vapor inside the component might cause cracking if it is heated too fast. Warping and bending of the result if the component is dried only on one side that causing it to shrink more on the other side. When one of the surfaces has dried, the component is too rigid to recover, and the warping is irreversible. This can result in cracking. When component bodies are made of plastic clays or a composition that has a high clay content, it will require uniform and slow drying. Components with thicker walls have a higher tendency to warping or distortion. To eliminate drying issues, ensure that uniform air movement is allowed around all sides of a component. To avoid cracking, drying must be slowed.