Gel casting of high strength ceramics

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Summary

Gelcasting is a new ceramic forming technology for making complex-shaped ceramic products with high performance. The processes used in gelcasting are similar to processes often used in conventional ceramic forming process. However, when new high performance materials are introduced with the aim to improve the strength, defects such as air bubbles or agglomerates that can be found in many traditional ceramic materials are no longer be allowed since this would reduce the performance and reliability of the final ceramic products. The aim of this thesis project was to find an appropriate recipe of the ceramic suspension meanwhile improving the process of gelcasting and obtaining ceramic products with excellent mechanical behavior.

To achieve this specified target, alumina and zirconia powders were studied in the following experiments which included rheological measurement of viscosity and storage modulus measurement for ceramic suspensions and drying shrinkage measurement of cast materials. The binder was burned out and the density was measured for ceramic materials sintered at different temperatures. The mechanical strength of sintered materials with high density was evaluated and the microstructure of fracture surfaces of ceramic samples was studied.

Through rheological measurement, a good balance between fluidity and solid content of ceramic suspension was found. For alumina suspensions a solid content of 55vol% was selected and for zirconia solid contents of 46, 48 and 50vol% were studied. A monomer was dissolved in the suspension and an initiator was added to facilitate the polymerization of the monomer when the temperature was increased to around 70° C. The failure analysis of the fractured bending bars showed that the defects that caused the failure were not air bubbles but agglomerates.

As a result, in future research for ceramic gelcasting with the intention to improve the mechanical strength, the suggestion is to use an appropriate recipe for the ceramic suspension and focus on elimination of granules and agglomerates from the suspension

Key words: gelcasting, ceramic suspension, alumina, zirconia, solid loading

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List of symbols

MAM	Methacrylamide	
MBAM	Methylene bisacrylamide	
vol%	Volume procent	
wt%	Weight procent	
HMAM	Hydroxymethylacrylamide	
NVP	N-vinylpyrrolidone	
MPEGMA	Methoxy poly(ethyleneglycol) monomethacrylate	
PEGDMA	Poly(ethylene glycol) dimethacrylate	
APS	Ammonium persulfate	
TEMED	Tetramethyl-ethylene diamine	
AZAP	Azobis (2-amidinopropane) HCl	
AZIP	Azobis[2-(2-imidazolin-w-yl)propane]HCl	
°C	Celsius	
°C/min	Celsius per minute	
SEM	Scanning electron microscopy	
μl	Microliter	
ml	Milliliter	
s	Second	
ROM	Rule of mixtures	
g	Gram	
TGA	Thermogravimetric analysis	
TG	Thermogravimetry	

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1. Introduction

Engineering ceramics have replaced metals in many applications and fields in the last decades. Nevertheless the requirement of both the properties and shapes of ceramic products used are continuously increasing with technology development. A component with a high material performance is not easily combined with a complex shape ^[1]. Consequently, to solve this issue a new forming process would be required. At the Oak Ridge National Laboratory (ORNL), the researchers initiated the work to develop a new shaping method called gelcasting, which allows high performance ceramic materials with a complex shape to be produced ^[2]. This new forming technique has the potential to improve the microstructure of ceramics such as less agglomerates and higher homogeneity ^[3]. Gelcasting is a process where a monomer is added to a water-based ceramic suspension. The monomers are polymerized and the suspension is consolidated which allows the cast part to be removed from the mould to dry and finally densified^[4].

However, in spite that ceramic products from gelcasting have high quality and good performance, some drawbacks of the processes are still to be solved. Some problems that lower the strength of the ceramic material still exist such as air bubbles that are preserved during de-airing or large powder particles are not crushed into smaller particles in ceramic slurry, which thus produce strength limiting defects in the final products.

The aim of this project was to investigate the most appropriate amount of initiator which can assist alumina and zirconia suspension respectively with MAM-MBAM monomer system to form high-quality ceramic products under the most appropriate temperature and gelling time. The rheological behavior of alumina and zirconia suspensions as well as pure monomer solutions has been evaluated. Meanwhile, for these two kinds of ceramic materials, the shrinkage, weight change during sintering, density under different sintering temperatures, mechanical properties and reason of failure have been studied.

2. Literature review

2.1 Gelcasting

Gelcasting is a new ceramic forming process developed by the Oak Ridge National Laboratory (ORNL) about a decade ago. Advanced ceramics display some superior properties compared to metal such as lower environmental impact, higher strength and better reliability in some applications^[4]. Nevertheless, higher cost and shape limitation hinder further development and wider application of ceramics^[5]. Therefore, developing a new process for making complex-shaped ceramics with lower cost is urgent.

In gelcasting, a concentrated ceramic slurry is created by mixing a ceramic powder and a monomer solution. After this ceramic suspension is poured into a mold to get desired shape and during heating the monomers will polymerize in-situ to form a green body with network structure. Then, to obtain pure ceramic part, solvent from ceramic suspension should be removed by drying in air followed by burnout for binder removal. Finally, sintering ceramic materials to get full density^[1].

In gelcasting, higher solid content of ceramic suspension can provide much more possibility to get higher density of the final ceramic products. Also the solid loading can be controlled at a desired level. Therefore, the method to obtain ceramic products with good performance is producing a ceramic slurry with low viscosity so that slurry is flowable and with as high solid loading as possible. Higher solid loading can reduce the shrinkage of ceramic green body during drying and sintering. Lower shrinkage will decrease the possibility of problems with cracking and warping of the component^[4]. In all, high solid loading is desired in gelcasting.

However, ceramic slurry with too high solid loading usually leads to higher viscosity which causes difficulties to cast the slurry into the mold. As mentioned above, ceramic suspension with at least 50vol% solid loading should have a good fluidity. For attaining flowable ceramic slurry with high solid loading, an appropriate dispersant system is required. The monomer systems that was used in this work did not affect the function of the dispersants that are used for on other forming processes with zirconia and alumina powder such as slip casting^[4].

As mentioned before, there are some different points between gelcasting and other traditional forming processes. These unique positions will give several advantages following in production. Firstly, gelcasting will not cost more. As gelcasting is not far away the traditional ceramic manufacturing, it means the required equipment for gelcasting do not need new one. The equipments for conventional forming technique

can be used in gelcasting^[6]. Secondly, gelcasting can eliminate the dimension constraints in making complex-shaped like arc tube^[7]. Thirdly, high green strength and good green machinability give a strong point in competition with other forming processes^[8].

2.2 Monomer systems

Gelcasting is a process based on combination of traditional ceramic forming and polymer chemistry. Therefore, for improvement of ceramic forming process, the key element of gel casting process is addition of monomers, thus the selection and ratio of monomers play an important role.

The monomer solution should consist of monomers which are responsible for forming chain and cross-linked structure respectively. A single double bond in monomers is required to form linear polymer chain while at least two double bond in monomers are required to form cross-linking polymer molecules. As a result, during searching for water-soluble monomers, acrylamide gel system was found and some good results came from the acrylamide system^[1]. However, after toxicity research, acrylamide monomer was found to be neurotoxic^[1], could cause cancer for animals in laboratory experiments and some information showed that acrylamide could give a cancer risk in humans^[9].

In addition, from newest research, less toxic monomers were found. Take a example, if the health hazard rating which is most important factor for chemistry application are divided into 4 levels(extreme=4, high=3, moderate=2 and low=1), acrylamide is 4 and methacrylamide is 2^[1]. Thus instead of acrylamide, methacrylamide (MAM) and methylene bisacrylamide (MBAM) are used as a new standard system because of their relatively low toxicity. In this new system, MAM is the preferred chain former and MBAM is the preferred branching former. In MAM-MBAM system, it is typically that there are 12-20wt% monomers in solution and ratio of MAM and MBAM is $6:1^{[4]}$. to Besides. between 2:1 other common monomers such as hydroxymethylacrylamide (HMAM), N-vinylpyrrolidone (NVP) and methoxy poly(ethyleneglycol) monomethacrylate (MPEGMA) are used as chain forming monomers and poly(ethylene glycol) dimethacrylate (PEGDMA) is used as crosslinker^[4]. Thus, the two common monomer systems which are used in practical experiment are MAM-MBAM and MAM-PEGDMA. In fact, besides consideration of monomers' toxicity, the selection of monomer system depends on strength, stiffness, toughness of gel, wet and dry material strength, green machinability, reactivity and price. Generally speaking, if the monomer concentration or ratio between crosslinker and chain monomer is higher, the gel strength will be higher and ceramic final materials will be stronger and stiffer with gelcasting process^[4].

In gelcasting, the free radical initiator system also plays an important role. The initiator can make monomers to react each other to form polymer molecules. As fig. 2-1 presented, the chain forming monomer is depicted as "M" and the crosslinker is depicted as "X". Under free radical initiator activation, chain forming monomers form a longer polymer chain with reaction and crosslinker reacts with chain monomer to form branch polymer molecules. The formation of high molecular weight polymer fill space between particles in ceramic slurry and thus cause the ceramic powder to form near network structure together with the polymer. This kind gelation usually takes place at elevated ambient temperature such as 40-80°C.



Fig. 2-1 The sketch of process that monomers polymerize to form a polymer-solvent gel in gelcasting

The commonly used initiators are ammonium persulfate (APS), tetramethyl-ethylene diamine (TEMED), azobis (2-amidinopropane) HCl (AZAP) and azobis[2-(2-imidazolin-w-yl)propane]HCl (AZIP)^[4]. However, toxicity data indicate that APS and TEMED cause skin irritation in humans.

2.3 Comparison between gelcasting and other ceramic

processes

In gelcasting, the key technology is using organic monomers which can be polymerized to form a kind of crosslinked polymer-solvent gel^[4]. This is the main difference between gelcasting process and traditional ceramic process. In fact, using monomers solution is because the aqueous solution can provide a low-viscosity environment where ceramic powder is combined with monomers and appropriate dispersants to form a highly fluid ceramic slurry^[4]. Besides, formed polymer-solvent gel can fill space between ceramic particles and be removed before sintering. What is more, shrinkage of this gel during drying is less than it of components from other processes such as slip casting because of less monomers used.

Table. 2-1 gives a comparison between gelcasting and other ceramic processes such as slip casting, injection molding and pressure casting. From comparison for some parameters of these processes, gelcasting is desired forming process in many categories^[4].

As shown in table 2-1^[4], gelcasting can give a rapid forming cycle and the strength of ceramic products is higher than materials from other processes. Meanwhile, the limitation of mold materials is less. The time of binder removal is short because the amount of binder is lower. Less molding defects and warpage can provide high-quality final ceramic products. The dimension range including thick or thin sections of products are larger leading to wider application on gelcasting.

Property	Gelcating	Slip casting	Injection molding	Pressure casting	
Molding time	5-60 minutes	1-10 hours	10-60 seconds	10 minutes-5 hours	
Strength (dried)	Very high	Low	N/A	Low	
Mold	Metal, glass,		Matal	Porque plastic	
materials	polymer, wax	Flaster	Wietai	Polous plastic	
Binder burnout	2-3 hours	2-3 hours	7 days	2-3 hours	
Molding defects	Minimal	Minimal	Significant	Minimal	
Maximum part dimension	> 1 meter	> 1 meter	About 30 cm, 1 dimension must =< 1cm	About 1 meter	
Warpage during drying/binder burnout	Minimal	Minimal	Possibly be severe	Minimal	
Thick/thin sections	Both are OK	Thick section needs longer casting time	Problem with binder removal for thick section	Thick section needs longer casting time	

Table 2-1 comparison between gelcasting and slip casting, injection molding, pressure casting on process parameters

For other traditional processes, injection molding can produce complex shaped ceramic products but long binder removal time, size limitation and defects appearance are big problems which are hopefully solved. Slip casting can provide large size products but long forming time limits the practical applications for high performance materials. Pressure casting have improved the rate of casting and needs less molding time^[1].

2.4 Applications of gelcasting

Gelcasting is a ceramic forming process which is close to traditional slurry processing. As a result, there is no significant change in equipment which are required conventionally for gelcasting. Therefore, it can be said that it is possible many ceramic components from other forming processes can be produced with gelcasting. Meanwhile, a large difference between gelcasting and other processes is that solid loading is higher in gelcasting. Generally speaking, the solid loading needs up to at least 50vol% while in slip casting and spray drying, the solid loading is about from 25 to 55vol%^[4].

Gelcasting provides an efficient method to manufacture complex-shaped component such as turbine rotors which need highly uniform properties. Also, gelcasting can be used in manufacturing for large components with simple shape such as a ceramic ring^[4]. In addition, gelcasting can be used in metal powder forming as well such as tool steel, a nickel-based superalloy and so on^[4].

About decade ago, it was researched if gel casting could be used in industrial production. For example, in fig. 2-2 bottom right picture was a silicon nitride turbine wheel which was manufactured for commercial aircraft and use in on-board engines in military. This kind turbine was usually manufactured by injection molding and slip casting. Compared to these two forming process, gel casting can provide higher percentage of defect-free products. Besides, silicon nitride was used as the materials for the blade and vane of turbine rotor as shown in fig. 2-2 top left picture. The density of blade with gel casting was uniform while the density of blade slip casting was varied. In rest pictures, the top right was silicon nitride tensile test bars and the bottom left was alumina gears^[19].



Fig.2-2 Ceramic products with gel casting

3. Experimental

3.1 Materials

In this project, two kinds ceramic powders---- alumina and zirconia were used. Dispersant solution contained 25wt% Dolapix PC 21 (composition is polyacrylic acid with aminomethyl propanol). As monomers, methacrylamide (MAM) and methyenebisacrylamide (MBAM) was used. What is more, 20wt% monomer solution and 4:1 ratio of MAM to MBAM were selected for the experiments. Initiator solution contained 10wt% Azobis (2-amidinopropane) HCl (AZAP).

As an example, the table 3-1 shows a recipe for preparing alumina with 55vol% solid loading slurry. The density of alumina powder was 3.99g/cm³ which was used for recipe calculation. The top table showed the recipe for 150ml ceramic slurry and the bottom table shown the amount ratio between suspension and monomers which should be added into ceramic slurry. The amount of pure dispersant is 0.3wt% of the ceramic powder. Meanwhile dispersant was dissolved in water as usual for use in ceramic slurry. Therefore, the concentration of dispersant was considered and eventually the amount of dispersant solution was calculated.

Recipe for suspension	weight	Weight percent	Volume
Unit	g	%	cm ³
Ceramic powder	328.35	82.95	82.5
Dispersant solution	3.94		2.96
Water	64.54	17.05	64.54
Total	395.85	100	150

monomer(20% MAM-MBAM 4-1)			
	100ml suspension	100g suspension	
monomer	16.875	4.26	
MAM	13.5	3.41	
MBAM	3.375	0.85	

Table 3-1 Recipe of alumina suspension with 55% solid loading

3.2 Procedure

The gelcasting flow chart below shows the process to make the final products from the ceramic powder.

At the beginning, as demonstrated in fig. 3-1, the alumina and zirconia powder with dispersant and water following recipe, for example as table 3-1, used for preparation of ceramic suspension with varied solid loading which were ball milled by milling media. After the powder was milled for one and half hours, the organic monomers should be added into the slurry. Then these monomers and slurry were mixed completely and the organic monomers should be solved thoroughly. Before filtration of the suspension, the initiator should be added into it. Then the suspension was de-aired for 20 minutes with mechanical vacuum pump to remove air. Otherwise, air bubbles as a kind defect could form and gave a negative effect on the properties of final products.

After the ceramic suspension was prepared, the suspension was pumped into the molds with a vacuum pump which prevents air to come into the suspension when casting. Then, the suspension was heated in the molds at the appropriate temperature. At this temperature, the initiator would cause the monomers to form polymer with cross-linked molecules. After molds were heated for an appropriate time at the appropriate temperature, unmold was necessary. The ceramic part would be removed from the molds. Then the ceramic parts were put in room temperature and room humidity to be dry thoroughly. To avoid cracking or warping, the pattern to place samples was important. The minimum area of contact surface was preferred. In this way, the primary ceramic parts were obtained. Then, they needed to be machined and heat-treated.

Before materials were heat-treated, the ceramic parts were machined with grinding and polishing for different shapes. Then, the binder should be burned out and ceramic was sintered. At the beginning of sintering, samples were baked from 20°C to 500°C at 1°C/min. The polymers in the ceramic needed to be removed carefully to minimize the possibility of forming defects as cracks or pores. Therefore, ceramic were heated at low temperature rate. Then, the temperature was raised up to 1600°C for alumina and 1500°C for zirconia to sinter ceramic and get products with high density. This process was sintering which was used to consolidate the product. During consolidation, shrinkage and densification occurred ^[10].



Fig. 3-1 Gel casting process flow chart

After the ceramic suspensions were prepared, the rheological measurement was required because this kind measurement can give some details such as viscosity and storage modulus of suspension. The rheological behavior of the ceramic suspension was related to the interaction between the ceramic particles in the suspension. This interaction depended further on the distance between the particles which decreases as the solids loading of the ceramic suspension increases. This influence could be studied by measuring the rheological properties such as viscosity of the suspension and the storage modulus during consolidation. The consolidation occur when the added monomers were polymerized during the temperature increased, which created a gel net-work structure^[10]. From the storage modulus, the temperature where the gelation was initiated and speed of gelation would be obtained. Finally, a good balance between viscosity and temperature where polymerization of the monomers was initiated could be obtained.

After binder was burned out, the ceramic green bodies were obtained. Some of them were used to measure density after sintering from 900°C to 1600°C for alumina or 1500°C for zirconia. Meanwhile, density of ceramic from die-pressing as a comparison was measured after sintering at same temperature as casting samples. Then, after fully sintered ceramic materials were obtained, bending tests were performed for evaluation of the mechanical properties. The bending strength of the samples was measured by four-point bending shown in fig. 3-2. As illustrated in fig. 3-3, this was the typical fracture of ceramic materials that there was no plastic

deformation under short-term loading at ambient temperature^[18]. Finally, the kind of defects that caused fracture was investigated by scanning electron microscopy (SEM) of fracture surfaces.



Fig. 3-2 4-Point bending Fig. 3-3 Stress-strain behaviour of typical ceramic fracture

3.3 Composition of suspension

In this project, two kinds of ceramic powder were selected. They are alumina powder and zirconia powder. In alumina suspension, 55vol% alumina powder was used and the amount of added dispersant was followed by 0.3wt% alumina powder. While in zirconia suspension, 46vol%, 48vol% and 50vol% zirconia powder were used and the amount of added dispersant was followed by 0.35wt% zirconia powder. Besides, in these four kinds of ceramic suspension, the amount of monomers kept 20wt% of ceramic powders respectively.

Therefore, in series experiments, the only varied factor which could cause different results was varied AZAP solution contents in monomer solution or ceramic suspension. In this project, there were five kinds of the amount ratio between initiator and ceramic powder using in rheological measurement of monomer solution. They were 0.25%, 0.5%, 1%, 2% and 4%. In addition, there were four kinds of the amount ratio between initiator and ceramic powder using in rheological measurement of solution. They were 0.25%, 0.5%, 1%, 2% and 4%. In addition, there were four kinds of the amount ratio between initiator and ceramic powder using in rheological measurement of ceramic suspension. They were 0.25%, 0.5%, 1% and 2%. In other words, these ratios showed varied AZAP solution contents in ceramic suspension.

4. Results and discussion

This part demonstrated some results from rheological measurements for ceramic suspension, drying shrinkage of four kind materials, ceramic sintered process and density measurement of ceramic materials from die-pressing and gelcasting. It was found out that there was a good balance between fluidity and solid content with rheology study. This result figured out that not only suspension was casted easily, but also kept the storage modulus of ceramic materials in a high level. Besides, relative low shrinkage was obtained from alumina and zirconia. In addition, the green density of alumina and zirconia were obtained through density measurement. Finally, the results from bending tests of ceramic bars were shown and failure analysis was illustrated.

4.1 Rheology study

The rheological behaviours such as viscosity and storage modulus of ceramic suspension were studied by rheological measurements in order to find out a good balance between fluidity and solid loading of ceramic suspension. The suspension with low viscosity would provide better fluidity which gave a convenience in various processes. Besides, the temperature where the gelation was initiated, the speed of gelation and an estimation of the stiffness of the consolidated ceramic parts were obtained.

There were several rheological measurements of monomer solution with varied initiator contents, alumina suspension with varied initiator contents and zirconia suspension with varied solid loading. Next, the results from these experiments would be discussed in detail.

4.1.1 Monomer solution

The amount of initiator that was added to the monomer solution determines the temperature where the polymerization of the monomer was initiated. In order to control the gel formation and the consolidation of the suspension, a suitable ratio between the initiator and the monomer solution was thus necessary. A series of monomer solutions with various amount of initiator was prepared and used to study the gel formation by storage modulus measurements as shown in figure 4-1 before the measurements were made with ceramic suspensions.

From fig. 4-1, it was easy to figure out that much more the amount of initiator, the gelation occurs more quickly at lower temperature. However the monomer solution with 0.25% AZAP shown a different behaviour that it would not occur gelation during

6000s. This result gave a indication that in this monomer solution, monomers would not react and form a polymer. There was no gel. In fact, in order to start a reaction between monomers, the amount of initiator played a key role. In addition, if the amount of initiator enough was determined by monomers including chain former and cross-linker, initiator and reaction temperature^[4]. In this series experiment, the only variable parameter was the amount of AZAP solution. Consequently, the main reason for this result would be considered as too small an amount of initiator which caused the cross-linked network structure not being formed by monomers.

As shown in fig. 4-1, there are 4 kinds of monomer solution with varied AZAP solution contents left. When the concentration of AZAP solution was 0.5% and 1%, the polymerization of the monomers was initiated over 70°C. While when the concentration of AZAP solution was 2% and 4%, the polymerization of monomers was initiated below 70°C. This result demonstrated monomers required higher temperature to react with less initiator solution.

Once polymerization started, the speed of reaction was almost the same for these 4 kinds monomer solution as the slope of curves were similar as shown in fig. 4-1. It was a fact that the amount of initiator would not influence the speed of gelation once polymerization started. Meanwhile, increased storage modulus meant rigidity of monomer solution was increased because the polymer molecules contacted each other closer.

In addition, the peak of the storage modulus did not give a significant effect. When storage modulus was increased up to peak, it would be reduced later. The reason was some extra water from gelatin came out and made a small gap between gelatin and inductor. In this case, the data relating to storage modulus as measured by the testing equipment to computer was smaller but in fact, there was no change for the degree of rigidity of gelatin. Therefore, the peak part of storage modulus from fig.4-1 was not useful to identify the precise storage modulus of ceramic suspension.



Fig.4-1 The storage modulus of monomer solution with varied AZAP solution contents.

According to results above, when monomers reacted each other under initiator activity to form gel, it was essential to consider two factors during gelation. One was the temperature required to initiate gelation and the other was the temperature gradient to be reduced as possible. Based on two above consideration, an ambient temperature between 60°C-70°C should be applied for monomer solution with this initiator content range. And this temperature range as a reference could be selected for ceramic suspension. Besides, a most appropriate temperature selection for ceramic suspension with different amounts of initiator would decrease the possibility of temperature gradient.

4.1.2. Alumina suspension with 55% solid loading

1. Suspension with varied initiator contents

A good balance between fluidity and solid content could easily be obtained with the alumina powder used. The powder was used to prepare suspensions with 55% solid loading to study the influence on viscosity and storage modulus during consolidation for various amounts of additives used in gelcasting.

A series of suspension with different amount of AZAP solution were tested for rheological behaviors. They were 0.25%, 0.5%, 1% and 2%. The measurements showed a normal sheer thing behavior of the suspension where the viscosity decreased with increasing shear rate (fig. 4-2). The addition of AZAP solution used as initiator was further found to increase the viscosity of the suspension. With concentrations up to around 0.5% of AZAP, a small increase in viscosity was obtained while a significant increase occurred when the concentrations were around 1% or above. To facilitate the casting procedure, a low viscosity would be preferred and thus a low concentration of AZAP.



Fig. 4-2 The viscosity of alumina suspension with 55% solid loading and varied AZAP solution contents

The polymerization of the monomers was initiated earlier when the concentration of AZAP in the ceramic suspension was increased (fig. 4-3). For concentrations of 1% and 2%, the polymerization was initiated before the top temperature of 70°C was reached, while a short period of time at the top temperature was required in order to initiate the polymerization when 0.25% and 0.5% of AZAP was used. It was further found that the rate with which the storage modulus was increased also was dependent on the concentration of AZAP used, which was in contrast to the behavior when the

pure monomer solutions were studied (fig. 4-1). When the polymerization proceeded and a high storage modulus was reached, the values begun to fluctuate a lot and seemed not to be very stable. The reason for this was that the stiffer sample formed during the consolidation slipped against the sample holder. This influenced the measured stress and the storage modulus.

It was generally desired to have a balance between the viscosity of the suspension and the storage modulus obtained during consolidation. A low viscosity would give a better fluidity of the ceramic suspension, which would facilitate various processes such as sieving, elimination of air bubbles and casting. On the other hands, it was also desired that the cast suspension obtained a high storage modulus during consolidation in order to allow de-molding and handling without deformation of the cast material.

Gelcasting was generally assumed to be a method which produces green bodies without any internal stresses ^[11]. However, if the consolidation in the suspension was initiated before the top temperature was reached, thermal stresses were likely to be formed in the cast material. The reason was that the density of water changes with the temperature and the volume of the suspension would then also be changed. It could then be assumed that a suspension with a homogeneous temperature would be preferred before the consolidation is initiated. To achieve such a situation, a suitable combination of initiator and temperature for the consolidation process can be selected based on the rheological measurements.



Fig. 4-3 The storage modulus of alumina suspension with 55% solid loading and varied AZAP solution contents

2. Comparison between suspension and monomer solution

When the measured storage modulus of the monomer solution was compared to the alumina suspension, it was found that the polymerization was initiated at the same temperature which indicated that no interactions between the alumina and the monomer or initiator occurred (fig. 4-4). The significantly increased storage modulus of the consolidated alumina suspension compared to the monomer solution can be explained by the presence of the alumina powder. The material obtained from the ceramic suspension can then be seen as a composite consisting of ceramic powder and a water filled polymer gel, which contributed to an increased stiffness compared to the pure monomer solution which only consist of water filled gel.

According rule of mixtures (ROM) which was simplest model for predicting composite properties, a property of a composite can be calculated according to the equation below^[12].

$$P = \sum_{i=1}^{n} f_i P_i \tag{2-1}$$

Where P was some property and f_i was the volume fraction. Here, the property was represented as storage modulus and f_i was the volume fraction of solid content if the total amount of monomer and powder as unit one. Therefore, from the trend of these two curves in fig. 4-4, it was easy to understand why the storage modulus of ceramic suspension was larger than it of monomer solution.



Fig. 4-4 The storage modulus of alumina suspension with 55% solid loading with 2% initiator and monomer solution with 2% initiator

3. Suspension with 2% initiator at varied temperature ranges

The alumina suspension with 55% solid loading with 2% AZAP solution was selected in a series of experiments which tested the storage modulus of the suspensions in three kinds of varied temperature ranges. These were positioned at 60° C, 70° C and 80° C.

As observed in fig. 4-5, the different gelling behaviors of the suspensions were shown when the consolidation temperatures were changed. As seen in table 4-1, when the top temperature was 80°C, ceramic suspension started to form gel rapidly and at almost 62° C (below 80° C). It was said that in this temperature range, the gel formed with increased temperature not constant temperature. If using this mode to heat molds, there would be temperature gradient which caused problems with the quality of final ceramic products. When the top temperature was 70° C, the polymerization of monomers was initiated at almost 65° C (below 70° C). In this temperature range, the temperature gradient would occur as well, however, the influence of temperature gradient was less than it at 80° C as the top temperature because the duration of temperature gradient was longer in ceramic materials at temperature up to 80° C.

When the top temperature was 60°C, it can be seen clearly that gel forming did not start until the temperature was stable. This situation almost avoided generation of temperature gradient during gel forming. But a period of time and energy was required to initiate the polymerization of monomers after environment came up to constant temperature. As a result, when the alumina suspension with 55% solid loading with 2% AZAP solution was casted into the molds, molds should be heated at not more than 60°C for reducing temperature gradient as possible.



Fig. 4-5 The storage modulus of alumina suspension with 2% AZAP solution at varied temperature ranges

Temperature range	Temperature of polymerization initiated	Final temperature
20°C to 60°C	60°C	60°C
20°C to 70°C	65°C	70°C
20°C to 80°C	62°C	80°C

Table 4-1 Temperature of starting and ending gelation for alumina suspension at three kinds of temperature ranges respectively

The liquid in suspension was only pure water, therefore, the variation of density of water with increasing temperature is a concern. At 4°C, the density of pure water reached up to a maximum of 1 g/cm³. As shown in table 4-2 ^[13], it was easy to figure out with raised temperature, the density of pure water was decreased and volume per 1 g pure water was increased.

When ceramic suspension was heated, pure water was heated as well. The water molecules got energy and had more kinetic energy to make them further apart slightly. It meant the density went down and the volume increased. In other words, the expansion of suspension was related to increased volume of water when suspension was heated. Therefore, higher temperature caused larger expansion of ceramic suspension. This was the reason why when suspension was heated, the volume was increased a little.

Pure water at temperature	Density (g/cm ³)	Volume per 1 g (cm ³)
20°C	0.9982	1.0018
60°C	0.9832	1.0171
70°C	0.9778	1.0227
80°C	0.9718	1.0290

Table 4-2 Density and volume of pure water at different temperatures

Consequently, besides temperature gradient problem, the issue of varied volume of suspension which probably produced stress in ceramic parts should be concerned. To sum up, 60°C was suitable temperature as final temperature to heat mold for alumina suspension with 55% solid loading with 2% AZAP solution.

4. Suspension with 2% initiator at varied time ranges

The alumina suspension with 55% solid loading with 2% AZAP solution was selected in a series of experiments which tested the storage modulus of the suspensions in three kinds of varied time ranges. There were set at one day, one week, two weeks and three weeks. Fig. 4-6 represented the viscosity of alumina suspension with added initiator at varied time ranges. It was clear to see the viscosity was not significantly influenced by time.



Fig. 4-6 The viscosity of alumina suspension with 55% solid loading with 2% AZAP solution at varied time ranges

However, as shown in fig. 4-7, the storage modulus of suspension which was measured up to 60°C as final temperature was affected obviously by time. From fig. 4-7, when the alumina suspension which was kept in bottle for one day was measured by rheological measuring instrument, a short period of time at 60°C was required in order to initiate the polymerization of monomers and highest storage modulus was reached during a reasonable period of time. With increased keeping time for alumina suspension, longer time was required to initiate polymerization of monomers. Moreover, for these suspensions, the peak of storage modulus could not be reached during 8000s. Especially when the alumina suspension was kept in bottle for three weeks, the initiator almost expired. This could be that initiator was oxidized by oxygen in bottle. Therefore, monomers could not react and form cross-linked polymer molecules with initiator which lost activity. Thus macroscopic result was no gel forming.



Fig. 4-7 The storage modulus of alumina suspension with 55% solid loading with 2% AZAP solution at varied time ranges

When the top temperature was raised up to 70°C and 80°C, curves of storage modulus gave a similar trend as curves in 60°C. A slight difference was that in the alumina suspension, polymerization was initiated quicker and gelation was more complete with higher ultimate temperature. The most important point was that the influence of the activity of initiator was similar. In summary, the activity of initiator controlled the level and rate of gel forming.

4.1.3. Zirconia suspension with 46%, 48% and 50% solid loading

The rheological behaviour of zirconia suspensions was measured with 50%, 48%, 46% solid loading. An alumina suspension with 55% solid loading was used as a reference for comparison. The AZAP solution as initiator was added into the ceramic suspension with same proportion, 2% the weight of ceramic powder for zirconia suspension with different solid loading and the alumina suspension.

As the viscosity of zirconia suspension with different solid loading were presented in fig. 4-8, the trend of curves was expected as theoretical law that the viscosity of ceramic suspension with higher solid loading was higher. The Krieger-Dougherty equation (equation 4-1 below) gave a relation between the relative viscosity and solid loading of ceramic suspension.

$$\eta_r = \left(1 - \frac{\phi}{\phi_m}\right)^{-[\eta]\phi_m} \tag{4-1}$$

Where, ϕ is the volume fraction of solids, ϕ_m is the maximum solids loading, $[\eta]_r$ is the intrinsic viscosity and η_r is the relative viscosity.

For zirconia suspension with varied solid loading, there still was same ceramic powder used. Therefore, the maximum solids loading and the intrinsic viscosity were same for these three suspensions. According the Krieger-Dougherty equation, the only variable factor which influenced the relative viscosity of suspension was the volume fraction. Also, the relative viscosity of suspension was increased with raised solid loading of suspension. This law shown by this equation was consistent with the trend of curves shown in fig. 4-8. The viscosity of zirconia suspension with 50% solid loading was highest in this three kinds suspension while 50% was also highest solid loading applied in this experiment.

The Krieger-Dougherty equation can be used to evaluate the colloidal quality of the ceramic slurries. The viscosity of the ceramic slurry depended on the solid loading of ceramic suspension. When the volume fraction of solids reached up to highest, the distance between ceramic particles in slurry was so closed that their average separation distance was nearly zero. It meant the slurry flow hardly. In other words, the viscosity of this slurry was too high. In conclusion, the solid loading was higher, the viscosity of the same ceramic suspension was higher^[14].



Fig. 4-8 The viscosity of zirconia with varied solid loading and alumina with 55% solid loading

For zirconia suspension with 46%, 48% and 50% solid loading and alumina suspension with 55% solid loading, the mass ratio between initiator and ceramic powder kept in 0.2%. Meanwhile, the mass ratio between monomer and ceramic powder was same that it kept in 20% for this four kind suspension. Therefore, it could be assumed that the polymerization of monomers was initiated at the same time as shown in fig. 4-9 because when the polymerization for suspension with same ceramic powder was initiated depended on the amount of monomer and initiator.

For zirconia suspension with higher solid loading, an earlier increase of the storage modulus was obtained. When monomers started to react under activity of initiator to form crosslinked structure, the distance between the ceramic particles in the gel structure would be reduced as the solids loading was increased. When the polymerization was initiated, a material with short distances between the stiff particles would thus give a higher storage modulus compared to a material with a longer particle distance. In other words, in suspension with higher solid loading, the particles would need less gel to be stiffer. The difference in storage modulus would thus not necessarily correspond to how the polymerization proceeds but rather to the difference in composition of the suspension.

Meanwhile, for different material powder, alumina suspension with 55vol% solid loading presented almost same curve as zirconia suspension with 50vol%. The temperature for alumina suspension initiating to form gel was closed to zirconia suspension's. This was because when volume percent of ceramic powder was increased, the distance between powder particles would be decreased meanwhile.



Fig. 4-9 The Storage modulus of zirconia with varied solid loading and alumina with 55% solid loading

4.2 Drying shrinkage measurement

Shrinkage occurred during drying ceramic materials. In that case, water was removed and the distance between particles was decreased^[10]. In this experiment, the shrinkage was assumed to be isotropic and the linear shrinkage was expressed by ($\Delta L/L$) where ΔL was length loss and L was length of sample.

4.2.1 Alumina with 55% solid loading

The final shrinkage of alumina material with 55% solid loading was 3.55%. From fig. 4-10, the shrinkage of alumina decreased rapidly with weight loss. After almost 10 hours, the shrinkage curve became flatter. At the beginning of drying, the evaporation of water occurred. In that period, the ceramic inter-particle spacing was proportional to the linear shrinkage^[14]. Particles were not so closed and water existed between particles. Therefore, the shrinkage occurred fast. While, when particles came to be closed up to a certain level with water loss, the distance between particles hardly be decreased. It meant length loss was small. As a result, the change of shrinkage percentage was small in the end of testing. In summary, shrinkage was decreased rapidly at the early drying process while shrinkage only had a little bit change after materials was drying for a longer time and particle-to-particle contact had been established^[1].



Fig. 4-10 The drying shrinkage and weight loss of materials cast from alumina suspension with 55% solid loading

4.2.2 Zirconia with varied solid loading

Drying shrinkage for zirconia components with 46%, 48% and 50% solid loading with same weight proportion initiator (0.4% AZAP solution) were measured. For zirconia with 46% solid loading, the final shrinkage was 4.14%. For zirconia with 48% solid loading, the final shrinkage was 3.31%. And for zirconia with 50% solid loading, the final shrinkage was 2.51%.

The trend of shrinkage curves were expected that final linear shrinkage was decreased with higher solid loading of ceramic suspension. Because ceramic suspension with higher solid loading meant less water would be removed during drying measurement. This smaller shrinkage would decreased the possibility of defect appearance during drying.



Fig. 4-11 The drying shrinkage and weight loss of materials cast from zirconia suspension with varied solid loading

At the beginning of drying, the shrinkage was increased fast with weight loss. While after 15 hours later, the shrinkage of all three groups was increased slowly, but the weight was still lost during this period. To explain this phenomenon, it was necessary to figure out what was going on in these materials during the drying process.

As shown in fig. 4-12 (A), at the beginning of drying, liquid was removed by the evaporation from the external surface of ceramic particles. In this stage, water was evaporated with weight loss, meanwhile, the particles moved to each other closer. Thus, the distance between particles was decreased which meant materials shrinked obviously. This was why there was a noticeable change of shrinkage at the beginning from fig. 4-11. While, when internal liquid transport between the particles or in pores

of materials was lower than evaporation of surface, the drying rate would be decreased. Materials needed longer exposures in a dry environment to remove inter particle water. As in the end of first stage of drying, ceramic particles had been contacted each other as shown fig. 4-12 (B). Therefore, although water was removed and weight loss did not stop, the shrinkage just changed slightly^[10].



Fig. 4-12 Distribution of liquid among ceramic particles during the drying. (A) Beginning of drying, liquid is saturated in materials, (B) liquid is only left in between the particles.

4.3 Burn out and sintering

To obtain a green body without the organic additives used in gelcasting, it was required that materials were heat-treated in a furnace. As an example, alumina materials with 55% solid loading were heated to burn out binder and organic composition. The procedure that was used consisted of keeping a constant weight loss with varied heating rate. TGA (thermogravimetric analysis) can be used to characterize the thermal stability and decomposition of materials under varied conditions such as time or temperature^[4]. The method was however mainly used to find decomposition temperatures when the sample was heated with a constant heating rate, which would result a large mass loss when the additives were burnt out. To avoid a rapid mass losses that may cause the green body to fracture, a weight loss controlled burn out process would be preferred.

As illustrated in fig. 4-13, the heating rate was varied in order to obtain a constant weigh loss during the burn out process where remaining moister and all binder were combusted and only ceramic part left. From room temperature to 500°C, the mass loss was a lot. In order to keep a slow constant weight loss, a small heating rate was required. In this experiment, 1°C/min was used as heating rate in this period. In this case, lower temperature rate can reduce the possibility to produce defects such as crack in materials during the decomposition gases escaping from the ceramic materials and network structure left ^[16]. Above 500°C, there was a sharp change on temperature as the raised rate of temperature was up to 5°C/min because the mass loss was very slowly in this period. When temperature reaches up to 900°C, the green body of ceramic materials was obtained.



Fig. 4-13 The tendency for weight of materials cast from alumina suspension with 55% solid loading.

After burning out binder, ceramic part was worked in firing process to develop the desired structures and properties. Thus sintering ceramic parts was necessary. Sintering was a complex process that mass transfer via parallel mechanisms which included lattice, surface and grain boundary diffusion, meanwhile, vapor transport and viscous flow. Uniform sintering would be based on uniform powder dispersion and one of the advantages with gelcasting was the possibility to obtain homogeneous ceramic materials. Hence, ceramic with higher solid loading would be easier to reach high relative density after the uniform sintering^[16]. During the sintering, the densification rate depended on many factors including environmental conditions and intrinsic factors such as temperature, initial particle size, surface energy, diffusion constants and viscosity for transport mechanisms mentioned above^[17].

4.4 Density measurement

Density is a very important property of ceramic materials. There are several factors which give some effects on density of ceramic materials. They are size of particles, atomic weight of the elements, the packing arrangement of the atoms in crystal structure and the amount of open porosity which is concerned in this project^[18].

In this project, two kind ceramic materials were selected. They were alumina and zirconia. Meanwhile two processes were selected. They were gelcasting and die-pressing. As seen from fig. 4-14, the final relative density for both alumina and zirconia, both with casting and die-pressing, were almost same. In addition, the relative density of ceramic materials was increased with raised sintering temperature.



Fig. 4-14 The relative density for materials cast from alumina suspension with 55% solid loading and die-pressed from alumina powder and for materials cast from ziconia suspension with varied solid loading and die-pressed from ziconia powder

In this experiment, pressing was used as a comparison process. With this method, ceramic part can be compacted and shaped simultaneously in a rigid die as fig. 4-15 shown ^[10]. During this process, ceramic parts would not have any drying shrinkage and can be produced with a wide range of particle size or shape^[10]. Besides, the quality of ceramic materials with pressing was stable. From fig. 4-14, the density of ceramic materials from both casting and pressing were almost same. It figured out the trend of density of ceramic materials with casting with casting was similar as it from pressing at different sintering temperature.



Fig. 4-15 change in granule shape during pressing

In all, as usual, the green density was obtained at 900°C. The sintered density can be obtained at 1500°C for zirconia and 1600°C for alumina. The green density almost reached 50% relative density for zirconia and 60% relative density for alumina. And when temperature was raised to sintered temperature, the sintered density almost can reach 100% relative density for both zirconia and alumina.

4.5 Mechanical behaviour

In mechanical testing, the ceramic bars of zirconia with 46%, 48% and 50% solid loading respectively were used as samples in 4-point bending. The size of the surface area under the load was around 3mm*4mm.

The average bending stress of zirconia with 46% solid loading was highest which reaches about 800 MPa, while the average bending stress of zirconia with 48% and 50% solid loading were about 610 MPa and 500 MPa respectively. However, the average value could not describe a comprehensive mechanical behaviour of these ceramics. As shown in fig. 16, for zirconia with 46% solid loading, there was a small spread in fracture stress while for both of zirconia with 48% and 50% solid loading, a wider spread with some low-strength samples reduced the average stress. For same stress range such as around 800 MPa, the stress was almost same for these three kinds materials. Thus, there could be a speculation that in this stress range, there similar types of defects causing material fracture while those low-strength samples of zirconia with 48% and 50% solid loading were caused possibly by other defects.



Fig. 4-16 The bending stress of zirconia with varied solid loading

As fig. 4-16 shown, zirconia with 46% solid loading presented a good and stable mechanical behaviour. Then a comparison experiment between zirconia materials with 46% solid loading from casting and pressing was done to find out if there are same defects leading to the samples from both processes fracture. Unfortunately, during cutting casting samples to specimen bars, many cracks appeared on surface of ceramic bars due to operational errors. Those cracks gave a significant influence on the bending strength of cast bars. Therefore, it did not make sense to search for whether defects were same for ceramic parts from casting and pressing. The values of

Zirconia with 46% solid loading	casting	Pressing
	45.0	800.4
	57.3	753.2
	81.1	843.4
	215.0	565.1
	112.6	832.9
	226.0	738.4
Bending stress (MPa)	94.5	943.1
	59.2	703.4
	155.5	636.2
	169.7	
	192.1	
	90.3	
	119.9	
	138.8	
Average bending stress (MPa)	125.5	757.3

bending stress from casting and pressing of zirconia with 46% solid loading are shown in Table 4-3.

Table 4-3 Bending strength of zirconia with 46% solid loading from casting and pressing

4.6 Failure analysis

Failure analysis is important in ceramic engineering to find out the failure-causing problems and then to solve them. Especially, failure analysis can provide many clues to help determine which kind of defect that causes fracture^[18].

To obtain further information about materials fracture, it is essential to find out the position and type of the fracture origin. In this project, the fracture surfaces of test ceramic bars were investigated by scanning electron microscope (SEM).

Generally speaking, there were some most important features on fracture surface such as shown in fig. 4-17. The defect which caused material fracture at around 800MPa was investigated. As the zirconia bars with 46% solid loading gave a stable performance around 800MPa, several zirconia bars were selected to be investigated by SEM. The fracture surface of zirconia bars with 46% solid loading which were broken were magnified up to 300 times for searching these features easily. The image below (fig. 4-17) was one of them had illustrated the position of features such as fracture origin, fracture mirror, mist and hackle^[18]. It was clear to see there was a granule as flaw to form fracture origin. The flat and smooth surface was called fracture mirror. The faint ridges which were close to fracture mirror were called mist while larger ridges were called hackle.



Fig. 4-17 Scanning electron photomicrographs of fracture surfaces of ziconia with 46% solid loading.

As mentioned before, several ceramic bars which were broken at around 800MPa were chose for SEM investigation. The same flaw, granule at the fracture origin position, was observed on fracture surface of these ceramic bars. Fig. 4-18 gave a clearer image that fracture surface was magnified up to 1000 times using same sample as shown in fig. 4-17. It was clear to see a granule in fracture origin position as flaw which caused stress concentration in fig. 4-18. While when the concentrated stress reached up to high enough, crack would be initiated and fracture would occur. Therefore, it can be said that in this project, through a series of experiments, the limitation of materials bending strength was from granule in ceramic component. It meant the materials failure problem came from agglomerates from ceramic suspension.



Fig. 4-18 Scanning electron photomicrographs of fracture surfaces of ziconia with 46% solid loading (*1000)

To solve this problem, a suggestion for research in the future is that ceramic suspension could be mixed or rotated with milling media to break up soft agglomerates in slurry. High-strength ceramic products required fine particles typically less 1µm to form a fine-grained microstructure with less and smaller flaws^[18]. In this project, ceramic powder which was only 100nm was used. It was said that the final ceramic materials should be with high quality. However through images of fracture surface from SEM, granule was found out as main factor for material damage. On one hand it was not difficult to figure out that granules which were 100µm consist of ceramic powders which were 100nm. On the other hand during milling, these agglomerates would be crushed to be smaller particles. In the other

words, by increased the milling time, the chance to crush the granules will increase. In this case, the possibility of granules appearance will be decreased. As a result, materials with fewer defects can afford higher load and will be with higher strength and better quality.

5. Conclusion

This thesis report has presented the processes of gelcasting and some results from a series of experiments.

Alumina powder and zirconia powder were selected as ceramic powder using in experiments. Meanwhile, MAM and MBAM were selected as monomers, and AZAP solution was selected as initiator for ceramic slurry. To find out a good balance between fluidity and solid loading of ceramic suspension, through rheological measurement, different ratios of ceramic suspension to the initiator solution were evaluated. Integration of the following factors such as viscosity, the storage modulus of ceramic suspension at different temperatures, by comparing all kinds of recipe for ceramic suspension, the best ratio can be obtained for alumina suspension and zirconia suspension respectively. For alumina suspension with 55% solid loading, 2wt% AZAP solution was selected. As same as alumina suspension, for zirconia suspension with 46%, 48% and 50% solid loading, 2wt% AZAP solution was preferred. Meanwhile, ceramic suspension should be fresh and be heated up to 60oC for high gelling efficiency without residual stress.

In drying shrinkage measurement, the final shrinkage of alumina material with 55% solid loading was 3.55%. For zirconia material with 46%, 48% and 50% solid loading, the final shrinkage was 4.14%, 3.31% and 2.51% respectively. It was easy to figure out the final shrinkage decreased with solid loading of ceramic suspension increasing. Lower final shrinkage was good for ceramic products away from warping and cracking. Therefore, higher solid loading would give a good influence on the strength of final ceramic materials.

In the period that binder was burned out and materials were sintered, there was the most important operation which was mass loss controlling during decomposition temperatures. In fact, lower heating rate like 1°C/min should be applied when wight loss of materials was quick in order to obtain a constant weight loss for reducing the possibility of defects appearance. Otherwise, during the decomposition gases, the network structure in materials would not be close enough causing emerge cracks or pores. In that case, these defects would give some adverse impact on the quality of final ceramics.

Through density measurement, the sintered density of alumina and zirconia were obtained at 1600°C and 1500°C respectively. And the green density almost reached 50% and 60% relative density for zirconia and alumina respectively. Besides, the density of materials from die-pressing had a similar tendency as from casting at different sintering temperature.

After bending test, zirconia with 46% solid loading was found as stable highest-strength materials comparing with zirconia with 48% and 50% solid loading. From failure analysis, images of SEM have shown that granule in materials was a main problem for materials damage. To break up these agglomerates, longer milling for ceramic suspension might be a good approach.

6. Future work

By considering the previous and current research which are mentioned above, there are some recommendations for the future work.

Increase the milling time to crush agglomerates as much as possible during the milling step of experimental procedure. Or use someone additive when mixing to disperse ceramic particles and prevent fine particles to form larger granules.

Comprehensive study on all procedure of gelcasting process to find out whether there is any better way or more appropriate test equipment to improve someone step in this procedure. Thus the possibility of defects forming during ceramic production could be reduced.

Focus in-depth research on the recipe of ceramic suspension. Through rheologcial measurement, find out ceramic suspension with better balance between viscosity and the storage modulus to decrease the chance of air bubble into slurry as low as possible. Meanwhile, the strength of ceramics could reach higher.

Much test on ceramic suspension with different kinds of ceramic and with different solid loading.

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