

Evaluation of the methacrylamide/ N’N,-methylenebisacrylamide gel binder system for gel-casting of titanium powder

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Abstract. Gel-casting, a near-net-shape manufacturing technique developed for ceramic powder processing, is investigated to produce titanium parts. In this study, the MAM/MBAM gel-binder system is used to develop a suitable slurry formulation and gel-casting procedure for commercially pure titanium powder. The polymeric binder system was evaluated by altering process parameters to produce a stable slurry of uniformly dispersed titanium powder that resists particle settling. Stable slurry formulations are gel-cast into rectangular bars to evaluate the green properties. The suitability of the binder system was studied by evaluating the gelation time and settling behaviour of the slurry for three dispersants at concentrations up to 0.6 wt% of the titanium powder, a range of MAM:MBAM ratios from 3:1 to 15:1 and monomer concentrations from 17 to 40 wt% of the premix solution. The green density and strength were evaluated for bars that were gel-cast from slurries with 37 vol% solids loading, 0.6 wt% Dolapix CE64 dispersant, a MAM:MBAM ratio of 3:1 and a monomer concentration of 23, 29 and 37 wt% in the premix solution. The 37 wt% monomer concentration gel-cast titanium bar produced the highest green density, 2.50 g/cm³ (55% relative density), with density gradients varying less than 4% from this average within the green part. This formulation also produced the highest green strength of 8.92 MPa.

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1 Introduction

Near-net-shape (NNS) manufacturing is an industrial forming technique used to produce parts that closely resemble the final shape of the component. Additive manufacturing (AM) techniques, such as laser powder bed fusion (LPBF), are readily used to produce NNS components with complex geometries on a per-layer basis that reduces raw material wastage [1]. The unique capabilities of AM are well-recognised as a NNS technique; however, it is an expensive process with high capital investment and production costs. Over the past few decades, gel-casting has drawn attention as a potential cost-effective NNS process with the ability to produce complex parts. Gel-casting is a versatile powder forming process that is used to produce net-shaped parts from a powder slurry. It was originally developed for ceramic powder processing, combining traditional slip casting techniques and polymer chemistry for gel formation [2-4]. It has the advantage over melt casting, AM, and other forming techniques in that it relies on sintering to produce a >90 % dense solid material and therefore requires no melting or deformation of raw materials [5-6].

The gel-casting process, shown in Figure 1, starts with the formation of a viscous powder-solvent suspension (slurry) by mixing a powder material with a liquid solvent into which monomers have been dissolved (referred to as the premix solution). Dispersants can be added to the slurry to promote the formation of a stable suspension. Once the slurry has been thoroughly mixed, an initiator and catalyst are added to the mixture to initiate the polymerization reaction of the monomers. The slurry is then cast into a mould while it is still pourable. Once the polymerisation reaction (gelation) is complete, the slurry transforms into a gel with the powder particles evenly dispersed throughout. The gel-cast green part is then removed from the mould and allowed to dry. The gel binder ensures that the dried part retains its shape with adequate green strength for handling; the gel is later removed by thermal debinding. The final step of the process is sintering, a high-temperature heat treatment where the individual powder particles are bonded together by thermally activated solid-state diffusion to form a solid material network. The part densifies during sintering, as interparticle spaces that existed in the slurry become residual porosity in the solid-material network.

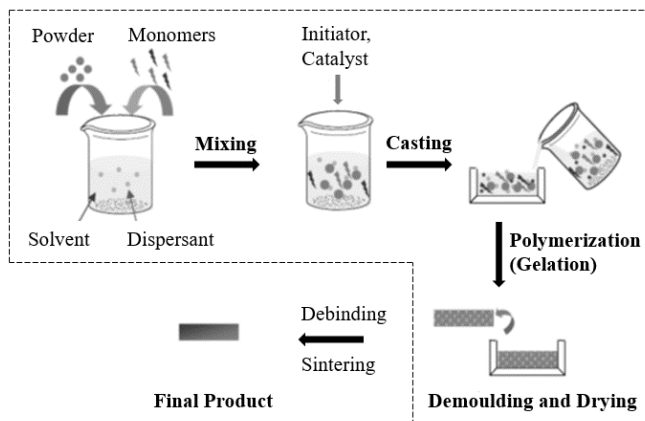


Figure 1. Steps involved in the gel-casting process

To date, there has been limited success when extending gel-casting to metal powders, primarily due to the difficulty in designing a gel slurry that can stably suspend metal powders with a mean particle size > 10 μm [8]. Titanium is a very reactive material with the consequence that very fine (< 10 μm) Ti powders pose a significant threat to health and safety. The typical particle size distribution of spherical Ti powders that is readily available

and is reasonably manageable in a manufacturing environment is in the 30 – 60 μm range, primarily used for powder injection moulding [9]. While the process seems relatively straight-forward to replicate for metal powders, gravity-induced particle settling of the titanium powder out of the slurry occurs with the MAM:MBAM binder system [10]. Unstable slurries where settling occurs are not suitable for gel-casting as the cast part will not have a uniform green density distribution. The consequence is distortion during the sintering step which results in the poor retention of the intended shape, as well as non-uniform mechanical properties [9]. To the authors' knowledge, there are only two previous studies that investigate gel-casting slurry formulations for commercially pure titanium powder [6, 10]. Li *et al.* [6] extended the gel-casting process to titanium powders (produced by the hydride/dihydride process; average particle size = 46.6 μm) with the aim of producing porous parts suitable for biomedical applications using an acrylamide/ N'N,-methylenebisacrylamide (AM/MBAM) binder system. Gel-cast parts with a green strength of 25 MPa was obtained from using a 120:1 AM:MBAM binder ratio with 37 wt% titanium powder in the slurry. Piek [10] investigated the Isobam® binder system, using ammonium hydroxide (NH_4OH) as a dispersant, and found that this binder system does not adequately support Ti powder particles (15 – 45 μm), resulting in powder settling after casting.

In this study, the methacrylamide/ N'N,-methylenebisacrylamide (MAM/MBAM) monomer-crosslinker gel binder system is evaluated in terms of its ability to create a stable suspension of 15 – 45 μm spherical Ti powder as a gel-casting slurry, and prevent settling after casting. Three commercially available dispersants are evaluated in terms of their influence in improving the suspension of powder particles. The scope of this work is illustrated by the dashed lines in Figure 1, which limit the evaluation to stop at the drying step.

2 Experimental procedures

This study continues the evaluation of readily available titanium powder for gel-casting and investigates various aspects of the binder system to develop a stable slurry that prevents particle settling after casting. Two approaches were used in order to promote the formation of a stable suspension of the titanium powder in the slurry: altering the type and concentration of dispersant that is added to the premix solution and adjusting the monomer-crosslinker concentration and ratio in the binder system. The role of the dispersant in the suspension of titanium particles in solvent (distilled water) was evaluated using settling or sedimentation tests. The choice of dispersants was based on commercially available ceramic processing dispersants that have previously been used successfully to cast titanium slip [11]. The influence of the binder composition was evaluated by monitoring the slurry formation and gelation behaviour of different binder solutions and by evaluating the properties of green gel-cast parts.

2.1 Raw materials

In this study, grade 1 commercially pure titanium powder was used (CP-Ti; supplier: Advanced Powder & Coatings, Canada). The powder was produced by the plasma atomization process, resulting in spherical powder particles, screened to a particle size range of 10 – 45 μm with a D_{50} = 33 μm (as reported by the supplier). This study employs the methacrylamide/ N'N,-methylenebisacrylamide (MAM/MBAM) monomer-crosslinker binder system, where MAM is the main monomer and MBAM is the crosslinking monomer. A premix solution is created by dissolving the monomers in a solvent; distilled water was used as the solvent for all experiments.

During polymerization, MAM monomers form linear polymer chains that bind powder particles together, while MBAM links these linear chains to each other, to form a crosslinked polymer network, as shown in Figure 2. The polymerisation of organic monomers is a critical step in the gel-casting process, allowing the formation of a semi-solid gel that suspends the powder particles with an even distribution throughout the gel. Free-radical polymerization (FRP) is initiated by ammonium persulfate (APS) and catalysed by N,N,N',N'-tetramethylethylenediamine (TEMED). Once the slurry has completed the gelation process, it forms a solid green body of bonded powder particles, holding the shape of the gel-cast mould. The chemical names and formulae of gel binder materials used are listed in Table 1.

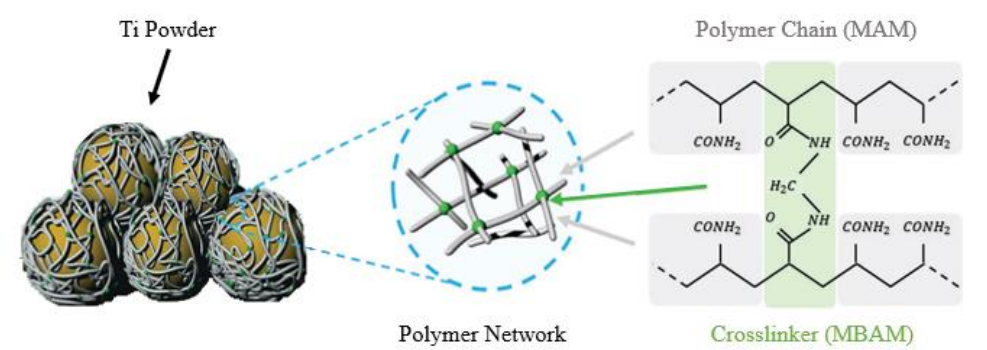


Figure 2. Schematic of the MAM/MBAM polymer network binding Ti powder after gelation (adapted from [12])

Table 1. Materials used for the preparation of Ti gel-casting slurry.

Function	Material Name	Formula	Supplier
Monomer	MAM	$H_2C=C(CH_3)CONH_2$	Sigma Aldrich
	MBAM	$(H_2C=CHCONH)_2CH_2$	
Initiator	APS	$(NH_4)_2S_2O_8$	Chem Lab Supplies
Catalyst	TEMED	$(CH_3)_2NCH_2CH_2N(CH_3)_2$	
Solvent	Distilled water	dH_2O	

The performance of three commercially available dispersants, Dolapix™ A88, Dolapix™ CE64 and Product KV5212 (supplier: Zschimmer & Schwarz, Germany), were evaluated in terms of their effectiveness in creating a stable powder-solvent suspension. All three dispersants are typically used for ceramics manufacturing, for dispersing ceramic powders for spray-drying, slip-casting, and other processes that use ceramic powder suspensions. Dolapix™ CE64 has previously been used to investigate titanium slip casting [11], whereas the other two dispersants were recommended by the supplier.

2.2 Sedimentation tests: dispersants

The influence of varying levels and types of dispersant on the suspension of the CP-Ti powder in distilled water (pH = 7.06 ± 0.1) was studied using sedimentation tests similar to the experimental procedures followed by Piek [10] for gel-casting slurries and Xu *et al.* [11] for slip-casting slurries. Solutions of 24 ml distilled water with dispersant concentrations of 0, 0.3, and 0.6 dry wt%, respectively, were mixed in custom-built glass mixing vessel for

1 hour using an overhead mixer (Dlab OHS40-Pro) fitted with a stainless steel paddle blade. Thereafter 27 g of CP-Ti powder, equivalent to 6 ml of solid titanium (density $\rho = 4.51 \text{ g/cm}^3$), was added to the solution and mixed for 1 hr using the same mixing apparatus, in order to form a 20 vol% solids loading (Φ) CP-Ti powder suspension. Once the suspension was fully mixed, it was poured into a 25 ml graduated cylinder and the settling behaviour of the powder out of the suspension was visually monitored. The sediment height was recorded, to the nearest 0.5 ml, every 5 minutes, until no more settling occurred.

2.3 Gelation tests

The polymeric gel binder system was evaluated in terms of gelation time and gel stiffness for neat gels produced from different MAM:MBAM ratios (1:1; 3:1; 6:1; 9:1; 12:1; 15:1; 30:1; 60:1; 90:1; 120:1), at a monomer concentration of 20 wt% (of the premix solution). Solutions of 32 ml of distilled water and 8 ml of monomers (20 wt%) were mixed using the same mixing apparatus as used for sedimentation tests. The premix solution was mixed for 1 hr at 350 rpm until the monomers were dissolved and the solution became clear. FRP was initiated by APS (1 wt% pf premix solution) and catalyzed by TEMED (1 wt% premix solution). FRP is an exothermic process and therefore the temperature of the different binder ratios was monitored using a glass thermometer. The solution was poured into a 100 ml glass beaker, 1 minute after adding the initiators, and the temperature was measured every minute after pouring for the first 10 minutes and every 5 minutes thereafter. The neat (powderless) gel stiffness was qualitatively characterized by the resistance felt when pressing a rounded plastic rod (1 cm diameter) into the gel during gelation.

2.4 Slurry settling tests

The MAM:MBAM ratio and the monomer concentration in the premix solution were varied in order to determine the most effective parameters for the preparation of stable Ti slurries. The settling behavior of the slurries was evaluated in a manner similar to the sedimentation tests to evaluate the dispersants. The MAM:MBAM ratios that were chosen for evaluation were 3:1, 6:1, 9:1, 12:1, 15:1. These ratios were selected based on the results of gelation tests, where the gelation time was < 15 min. Dolapix CE64 at 0.6 dry wt% of the titanium powder was selected for the dispersant addition, as this produced the best dispersion of titanium powder during the sedimentation tests.

Titanium slurries were prepared using the same apparatus and mixing procedure as indicated for the sedimentation tests, with 20 vol% Φ of titanium powder and monomer concentrations ranging from 17 to 40 wt% of the premix solution. Once the powder was added, the slurry was mixed for 3 hr at 350 rpm under vacuum (KNF NeubergerTM vacuum pump). After this step, the catalyst (1 wt% TEMED) was added to the slurry while mixing, followed by the initiator (1 wt% APS). The slurry was then mixed for 1 additional minute in order to start the polymerization process. Table 1 shows the experimental matrix of the monomer experimental parameter variations for these tests.

Table 2. Monomer ratio and concentration parameters used for * slurry settling and † green property tests

MAM:MBAM	Monomer concentration (wt% premix solution)					
	17	23	29	35	37	40
3:1	*	*, †	*, †	*	*, †	*

6:1	*	*	*
9:1	*	*	*
12:1	*	*	*
15:1	*	*	*

After the initial tests in which all MAM:MBAM ratios indicated in Table 2 were evaluated for monomer concentrations of 17, 23, and 29 wt%, the 3:1 ratio was chosen for further investigation, as it showed the least settling behaviour. The monomer concentration was then systemically increased for the 3:1 monomer ratio, as indicated in Table 2, until no separated gel layer was visible after settling.

2.5 Gel-cast green properties tests

The results of the sedimentation and slurry settling tests were used to select the process parameters to evaluate the green properties of rectangular bars made of gel, 88.7 x 17.6 x 16 mm. The parameters of the slurry formulation were selected on the basis of the formulations that were most likely to produce a uniform distribution of titanium powder particles in the gel-cast shape. Slurries were prepared using the same procedure as indicated for the slurry settling tests, using a monomer ratio of 3:1 and monomer concentrations of 23, 29 and 37 wt%, respectively, as shown in Table 1. Similarly to the gel-casting study of Li et al. [6], which investigated the AM/MBAM binder system for CP-Ti powder with an average size range of 46 µm, a 37 vol% Φ slurry was selected. The gel-cast samples were left to set in the mould and demoulded 10 minutes after casting. The samples were then dried at room temperature for a minimum of 24 hrs. The binder performance was measured in terms of the green density distribution and the green strength of the dried cast parts. The green samples were sectioned into 8 equal blocks, as shown in Figure 6. The density of each block was calculated from the mass and linear dimensions measured. The uncertainty of density measurement is 0.02 g/cm3. The green strength of the samples was calculated using three point bending tests according to the ASTM standard B312 – 20.

3 Results and discussion

3.1 Powder dispersion

Sedimentation tests revealed that Dolapix™ CE64 dispersE titanium powder in distilled water marginally better than Produkt KV5212, while Dolapix™ A88 had no noticeable dispersing effect on the titanium powder. It was observed that the powder settling occurred 5 minutes after casting, regardless of the dispersant and dispersant concentration. Figure 2Error! Reference source not found. shows the sedimentation behaviour of titanium-solvent suspensions with different concentrations (dry wt%) as a function of time for Dolapix™ CE64, the best performing dispersant that was tested. The highest dispersant concentration evaluated, 0.6 dry wt%, produced the best results in terms of powder dispersion with a suspension height that remained constant 20 minutes after casting. These results are consistent with the findings of Xu et al. [11] where sedimentation behaviour for 25 vol% CP-Ti powder (produced by the hydride/dehydride process; D₅₀ = 56 µm) in distilled water with a pH of 7 was evaluated using similar experimental approach. They found that the stable suspension of titanium powder increased with an increase of Dolapix™ CE64 concentration; however, there was marginal difference in this behaviour above 0.3 wt% dispersant. Ultimately, they concluded that a Dolapix™ CE64 concentration of 0.3 wt% was optimal, based on viscosity measurements. Viscosity was not evaluated in this study.

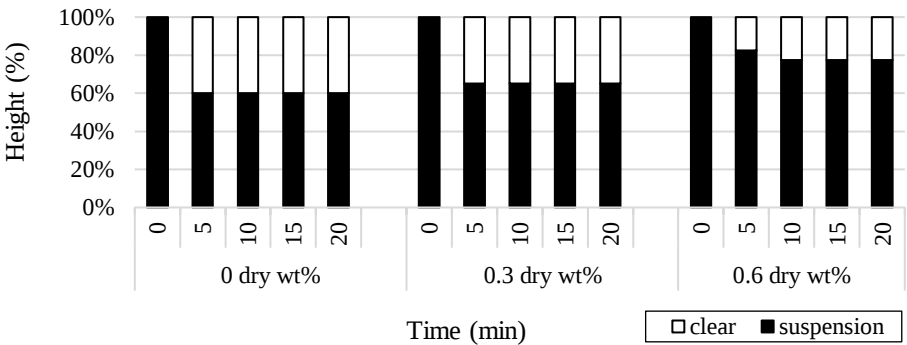


Figure 3. Settling behaviour for a 20 vol% Φ Ti suspension with dispersant concentrations of 0, 0.3, and 0.6 dry wt% Dolapix™ CE64

3.2 Gelation time and gel stiffness

Error! Reference source not found. shows the peak temperatures and gelation times of the polymerization reaction for various MAM:MBAM ratios at 20 wt% monomer concentration. The polymerization temperature was observed to decrease as the MAM:MBAM ratio increases; a 1:1 ratio showed the highest peak temperature (T_{peak}), followed by a decrease in T_{peak} as the binder ratio increases from 1:1 to 60:1. A subjective scale was used to characterize the gel stiffness: a value of 10 is associated with a semisolid, and a system that failed to gel was assigned a value of zero. Based on these results, MAM:MBAM ratios from 1 to 15:1 were selected for further evaluation as they presented reasonable gelation times with gelled premix solutions.

Table 3. Gelation time and gel stiffness values for various binder ratios

Ratio (MAM:MBAM)	T_{peak} (°C)	Time to T_{peak} (min)	Gelation Time (min)	Gel Stiffness	Comment
1:1	48.1	5	± 2	10	Semisolid, not elastic
3:1	47.1	6	± 2	10	Semisolid, not elastic
6:1	43.1	15	6 – 8	8	Slightly elastic
9:1	36.2	15	7 – 8	7	Slightly elastic
12:1	35.8	15	14- 15	7	Elastic, slightly transparent
15:1	36.4	15	24 – 26	6	Elastic, fully transparent
30:1	34.6	20	> 60	1	‘Syrup-like’ viscosity
60:1	31.8	~20	-	0	Failed to gel

3.3 Slurry settling behaviour

Figure 4**Error! Reference source not found.** shows the settling behaviour of Ti slurries (20 vol% Φ) with a monomer concentration of 29 wt% at various MAM:MBAM binder ratios. The 1:1 binder ratio produced gel-cast parts that cracked and disintegrated during drying that may be due to an excessive amount of MBAM. Part disintegration suggests that only short backbone polymer chains formed with inadequate strength to bind powders together. It was found that by increasing the monomer concentration from 17 to 29 wt% in the premix solution, the time to gelation decreased for all binder ratios, and resulted in smaller sediment layer that formed after casting. All the slurries had gelled after 10 min, showing a

denser sediment layer at the bottom of the cylinder and a separated neat gel layer at the top of the dispersion.

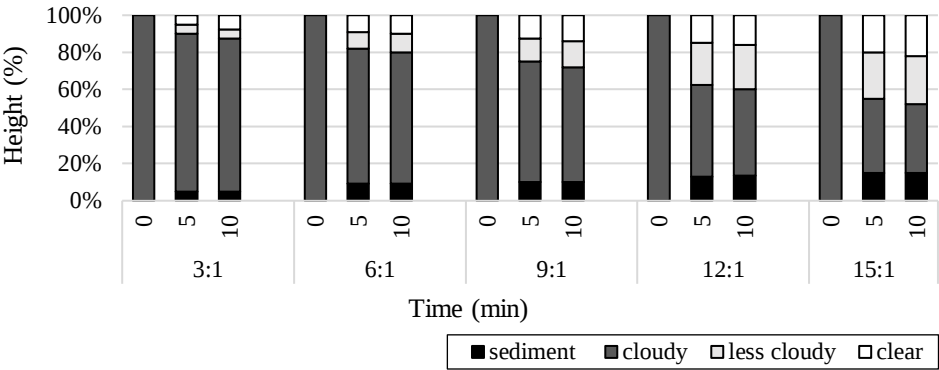


Figure 4. Settling behaviour of 20 vol% Φ titanium slurries with a 29 wt% monomer concentration at various MAM:MBAM ratios (3:1 – 15:1)

Ninciuleanu *et al.* [13] investigated the properties of neat MAA:MBAM (termed BIS in their study) hydrogels and found that when the MAM:MBAM concentration is decreased from 56:1 to 19:1, the crosslinking density increases as more crosslinking bridges are formed in the polymer network. In this study, the 3:1 MAM:MBAM ratio showed the best sedimentation behaviour over all the monomer concentrations that were investigated and is consistent with the work of [13]. The 3:1 MAM:MBAM ratio was used to investigate the settling behaviour of 20 vol% Φ slurries with monomer concentrations above 29 wt% in the premix solution (35, 37, and 40 wt%). Photographs of the gelled slurries for these higher monomer concentration tests, after they were removed from the graduated cylinder, are shown in Figure 5. Although the 40 wt% monomer concentration slurry did not produce sediment or gel layer, it started to gel during casting and is therefore not suitable for further investigation. It was found that a slurry with a monomer concentration of 37 wt% was flowable enough to cast and gel within 1 minute after casting; the system produced a sediment and gel layer of 0.7 % and 1.4 %, respectively, of the starting height of the suspension. Ninciuleanu *et al.* [13] also investigated increased monomer concentrations of

their hydrogels and found that viscosity and crosslinking density increased with monomer concentrations, which is consistent with these results.

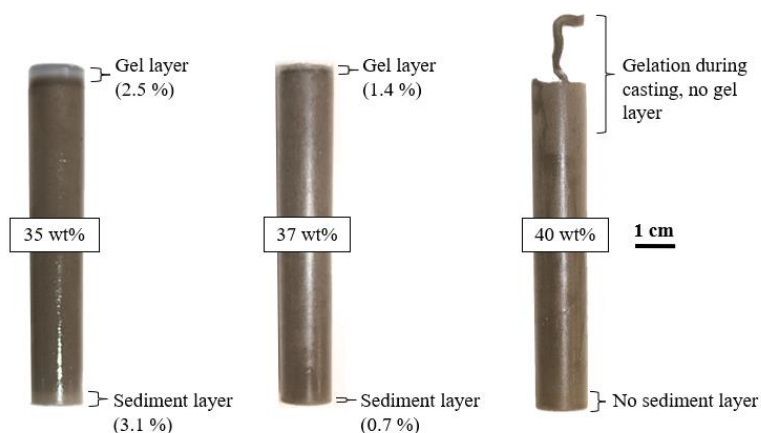


Figure 5. Settling behaviour for a 3:1 MAM:MBAM, 20 vol% Φ titanium slurry, with monomer concentrations of 35, 37, and 40 wt% in the premix solution

The gel-casting study of Piek [10] employed a 6:1 MAM:MBAM binder system (20 wt% monomer concentration) and reported that no settling occurred after 4 minutes of casting. In this study, the 3:1 MAM:MBAM ratio produced the shortest gelation time (± 2 minutes) for slurries with a monomer concentration of 20 wt%. However, by increasing the monomer concentration, the time to gelation decreased to 1 minute and resulted in a smaller sediment and gel layer during polymerization. Thus the 3:1 ratio was selected for further evaluation of the gel-cast material green properties.

3.4 Green properties

While three different levels of monomer concentration were evaluated, 23, 29 and 37 wt%, respectively, the 37 wt% set produced the highest green density, as shown in Table 3. Figure 3Error! Reference source not found. shows the green density distribution of 3 samples cast from a 3:1 MAM:MBAM, 37 vol% Φ slurry, with a monomer concentration of 37 wt% and 0.6 dry wt% Dolapix™ CE64. There was a slightly higher density, 2.53 g/cm³ average, for the bottom layer as compared to the top, 2.48 g/cm³ average. This may be due to powder-binder separation during casting or settling during polymerization. However, the densities of the samples from the bottom half of gel-cast bar were all within 0.1 g/cm³ of their immediate upper counterpart. This represents a density gradient range of 4% from the average, between the bottom and top halves. This trend was similar at lower monomer concentrations.

It should be noted that while the solids loading of the slurry is 37 vol%, this is equivalent to 73 wt% of titanium powder, 10 wt% monomers and 17 wt% solvent, for a 37 wt% monomer concentration slurry. Once the solvent has evaporated, the mass of the sample drops by 17 wt% (absolute). If there was no shrinkage of the gel-cast sample (constant volume), this would result in an increase in the density for the dry part from the wet slurry density of 2.30 g/cm³ to 1.90 g/cm³. The increase in density of the green part to an average of 2.50 g/cm³ is due to the shrinkage of the gel-cast part during polymerization and drying. The rectangular bar maintained its projected area shape, length and width, but reduced in

height by 25%. This indicates that the powder continues to settle during drying, keeping the shape of the sides of the mould, but decreasing in height.

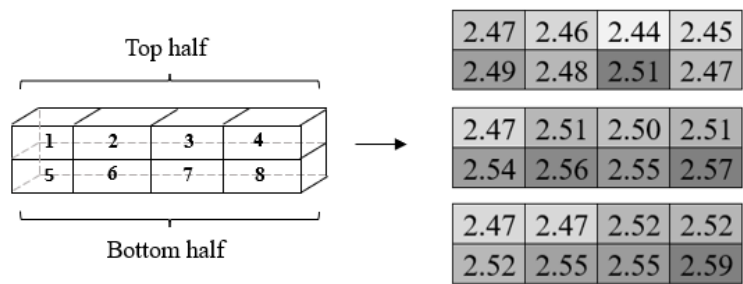


Figure 6. Green density distribution (in g/cm³) for 3 dried gel-cast bars produced from a 3:1 MAM/MBAM, 37 vol% Φ slurry, with a 37 wt% monomer concentration

The strength of gel-cast green bodies was mainly governed by the structure of the polymer network. The green strength and relative densities were found to increase as the binder concentration increased, for the same solid loadings, and are summarised in Table 4. A 3:1 MAM/MBAM, 37 vol% Φ slurry with a 37 wt% monomer concentration, managed to produce gel-cast parts with a green strength of 8.92 MPa (average of 3 tests). There is a significant increase in green strength related to a relatively small increase in green density, which indicates that the effect of the increased monomer concentration in providing a strong, more crosslinked gel was significant. These results are somewhat consistent with the study of Li *et al* [6] who produced gel-cast titanium parts using the AM/MBAM gel-binder system. They found that green strength increased with an increase in monomer concentration, but that it decreased with a decrease in AM:MBAM ratio (more crosslinker). For the same solid loading (37 vol%), they achieved the highest green strength of 25 MPa at a monomer concentration of 30 wt% and a 120:1 AM:MBAM ratio. Decreasing the AM:MBAM ratio decreased their measured green strength. While they provide an explanation for their results, it seems counterintuitive to the increased degree of crosslinking and therefore strength that would be achieved by using a lower AM:MBAM ratio. Additionally, the values obtained in this study are significantly higher than the green strength values they recorded. Li *et al* [6] do not report green density values, so it is not possible to determine whether this is correlated to green density.

Table 4. Strength and density values of green gel-cast samples produced from a 3:1 MAM/MBAM slurry (37 vol% Φ) at different monomer concentrations

Monomer Concentration (wt%)	Green Strength (MPa)	Green Density	
		Absolute (g/cm ³)	Relative (%)
23	0.61 ± 0.23	2.19 ± 0.02	48.61 ± 0.55
29	1.53 ± 0.05	2.32 ± 0.05	51.44 ± 1.01
37	8.92 ± 0.40	2.50 ± 0.03	55.33 ± 0.48

4 Conclusion

In this study, the MAM/MBAM polymer network and three commercially available dispersants were investigated for gel-casting of titanium powder. 0.6 dry wt% Dolapix™ CE64 produced the best results in terms of powder dispersion in distilled water to produce a stable suspension. A MAM:MBAM ratio of 3 to 1 showed the fastest gelation time and gel stiffness for neat gels. A 3:1 MAM:MBAM slurry with a 37 vol% Φ and a 37 wt% monomer concentration gelled within 1 minute after casting and adequately suspended spherical titanium powder particles with a mean size of 33 μm in the mould, preventing powder settling to produce a sediment height of only 0.7 % of the starting suspension height. A 3:1 MAM:MBAM slurry with a 37 vol% Φ and 37 wt% monomer concentration produced cast parts with a homogenous powder distribution with a green density that varied < 4 % within the sample, and produced a very high green strength of 8.92 MPa. Further work will focus on debinding and sintering the samples to evaluate the final properties of titanium material properties.

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