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# Mechanism of Bonding in Seashell Powder Based Ceramic Composites Used for Binder-Jet 3D Printing

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#### Abstract

Binder-jet 3D printing responses of sea-shell powder based ceramic composites have been evaluated considering the material consolidation mechanisms and mechanical characterisations. Initial experimental printing trials are done manually, varying the composition of the composite powders from 5% to 50% of the seashell powder and the rest plaster. Overall, the seashell and plaster combinations worked well in terms of achieving the necessary green strengths within the binder-jet process conditions. Scanning electron microscopy and 3-point bending results indicated no significant loss of properties at lower levels of the seashell component, but the strength decreased beyond the 25% mark. The optimum levels of seashell powder are found to be within 15-20% by weight in terms of the best compression strengths. Neat sea-shell powder however goes too sticky immediately after the interaction with the binder liquid and does not show evidence of any binding mechanism that can be accelerated.

**Keywords:** Seashell powder; Plaster; Binder-jet; 3D Printing; Bioceramics; Sustainability

#### Introduction

Additive manufacturing is a set of technologies allowing build three dimensional forms direct from computer generated files through the layer-by-layer processing methods [1,2]. Selective Laser Sintering [3], Selective Laser Melting [4], and three dimensional printing [5] are the most important of these technologies. Seashell powder is a natural bioceramic and has been used as an abrasive aggregate auxiliary ingredient in the production of low strength and lightweight concrete, suitable for applications such as concrete pavers [6]. Considering the abundant availability of seashells and the powder-based processing options, it is interesting to evaluate the feasibility of additively processing seashell powders. The most promising additive processing route for ceramics being the binder-jet approach, the current research addresses this, evaluating the responses of specific seashell powder compositions for processing by the binder-jet 3D printing method.

Seashell powders are not used for 3D printing so far, but earlier attempts using them as additional ingredient in cement and concrete mixtures are evident as already noted. Cuadrado-Rica et al. [7] observed that the use of crushed shells as the aggregate replacement could decrease the mechanical properties and increase the porosity of the concrete, possibly due to entrapped air. Replacing the aggregate with uncrushed shells up to a maximum of 20% by weight was proposed to increase the strength of the concrete. However, it was observed that the aggregate attains low workability due to the size, shape, and the texture of the seashells [8].

Further, the conversion of the seashells into the powder form is very intensive as the burning and subsequent grinding into fine powder are quite energy-consuming. In spite of this, there have been many attempts using seashell powders as essential ingredients of normal concrete, considering the abundant supply as well as the mechanical attributes. Othman et al. partially replaced cement with ground cockle, from 5-50% by weight [9]. The ground cockle shells constitute of 95-99% by weight of Calcium Carbonate (CaCO<sub>3</sub>), which is suitable as a filler material in concrete. It was observed that replacements above 15% by weight of cement could lead to decreased strengths and higher permeability and porosity within a setting time of 28 days [9]. PMMA-

seashell powder composites were evaluated for dental applications and the micro hardness values were noted to increase beyond 2% of the seashell powder. More significant gains in micro hardness values were noted beyond 4% seashell powder, while the values achieved were the highest at 12% seashell powder [10].

However, there are quite drastic differences in the setting mechanisms between concrete used for civil construction and the means of generating complex 3D forms out of the binder jet 3D printing process. While the traditional cement setting takes longer times running into days, the 3D printing requires instantaneous setting as a certain amount of green strength is essential to be acquired within the short time, the powder sweeping arm comes with the next stroke. It is essential that an accelerated particle consolidation mechanism is at play, achieving the rapid green strength required to keep the previously consolidated layers intact, while the sweep spreads the next layer of the powder. The focus of this paper is to establish how seashell powders perform under these conditions.

The binder-jet 3D printing process was originally developed at the Massachusetts Institute of Technology based on the work by Sachs et al. [11]. A further enhancement in terms of an additional compression step after printing each layer of the ceramic was introduced by researchers at Bowling Green State University, targeting higher densities of consolidation [12]. While the focus of any manufacturing process is normally to build fully dense parts, the main drawback of most additive processing solutions is porosity. However, the mechanism of achieving controlled porosity also draws attention to specific applications, particularly in the medical field.

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Further, the ability to fabricate porous parts with complicated geometries could also have wider applications in energy management and lightweight structures [13]. Biocompatible metals, and biodegradable polymer and ceramic materials have attained considerable research attention in the recent past in the context of medical applications [14]. There has also been a lot of interest in applying 3D printing to process the bio-compatible and degradable materials targeting patientspecific solutions. Reports have been found on porous scaffolding structures, printed to suit to specific locations of implants [15]. The porous structures possible from 3D printing have also been exploited to achieve metal-ceramic composite structures. Essentially, a porous ceramic matrix is first 3D printed using one or the other common techniques and then the metal component is developed by infiltration [16]. The binder jet process in particular is very effective in processing ceramic materials allowing build complex shapes with minimal waste. The method is currently employed to fabricate biodegradable implants, ceramic composites, casting patterns, moulds and cores, etc.

Seashells are natural materials and the powder is a bio-ceramic. There has been no past literature on the processing of seashell powders based on 3D printing. In particular, the binder-jet method is specifically suited to process ceramic materials. However, the absence of any a priori data is indicative of the research gap. The current research aims at filling this gap through 3D printing trials based on seashell powder composites processed by the binder-jet method. Initial trials are based on neat seashell powder and based on the responses, the plaster-seashell ceramic composite material with varying compositions has been identified as the material suitable for processing by the binder jet route. The post-process responses are evaluated based on microstructural and mechanical characterisations.

# **Materials and Processes**

Oyster grit supplied by Lifestyle Animal and Pet Supplies Ltd (Auckland, New Zealand), was ground using a ceramic ball miller (Star Machinery Manufacturing Co. Ltd, Australia) for 2 hours. The powder was subsequently sieved using an H-4330, 5F motorised sieve shaker (Humboldt, USA) to recover the fraction between 125 and 250 microns. Initial 3D printing trials are conducted based on pure seashell powder at the Additive Manufacturing Research Centre, Auckland University of Technology, New Zealand. However, the powder was found to be inert to the presence of moisture, which is the basic triggering mechanism in plaster-based 3D printing materials options. As a result, plaster-seashell powder composites are developed mixing the two powders in different weight constituencies. Photographs of the two ingredients in the raw powder forms are shown in Figure 1.

The binder-jet 3D printing method is employed for all the 3D printing trials undertaken as part of the current research. The commercial Z-Corp systems are usually the platforms for conducting such research. These systems are currently replaced by the 3D systems project versions, but the working principles are the same and in particular, the binder





Figure 1(b): Raw powder forms: plaster (CaSO<sub>4</sub>. ½ H<sub>2</sub>O).

solution remains more or less the same. Considering the complications in altering the binder solutions, we have employed the same solution as is commercially available, which is equivalent to the Zb60 of the erstwhile Z-Corp materials options. All the specimens built as part of this research are based on the same Zb60 binder fluid. Considering the need to produce large quantities of materials in order to employ the actual printer, all the trials are done in a simulated binder-jet printing approach, where the powder is dispersed manually layer after layer in a plastic container, while the binder is jetted through a syringe. It may be noted that all the specimens are prepared based on make-shift printing arrangements and manually dispersing the binder. This is difficult to be calibrated, and the experiments are mainly intended to evaluate the preliminary responses of the new powder composites to processing by the binder jet method.

# Basic characterisation of seashell powder for 3D printing

In binder-jet 3D printing, the powder substrate has to be spread into a flat layer. The aqueous glue selectively ejected from the print head should react in a timely fashion so that the layer attains a green strength sufficient to withstand the sweeping action of the formation of the next layer. The spreading characteristics, the reaction rates, and the wetting angles are essential attributes any new powder should have in order to qualify for 3D printing. The seashell powders produced at Scion, New Zealand are first evaluated for both the spreads, reaction rates, and the wetting angles. The first is a simple test where the powder is spread on a glass plate, using a flat ruler. It was noted that the seashell powder absorbs moisture quickly and goes lumpy and will not allow to be spread into a thin layer. Ideally, each individual particle is expected to move individually, in order to achieve a uniform spread and a smooth surface for the powder substrate. With rapid moisturisation, however, the seashell powder appears to be building inter-particle adhesion, leading to an unfavourable distribution of the powder.

The reaction rates are observed by taking the powder samples in small plastic containers and treating with calculated amounts of the glue liquid delivered through a syringe. Ceramic powders treated with the ejected glue usually attain the green strength in a short time, either by the electrolytic bonding forces or by the formation of crystals and the subsequent interlocking of the same. The strengthening process is studied over a period of time, observing several droplets of the glue placed on multiple powder specimens. In the case of neat seashell powder, it was noted that the wet areas remained wet and sticky even after many hours of waiting, indicating that the glue-powder combination has no reaction mechanisms at play, allowing the substrate to attain the green strength necessary.

Further, the wetting angle of the glue over the surface also depends on the interactions between the glue and the powder. It was noted that the seashell powder does not allow the droplet of the glue to remain as a bubble and instead instantaneously swallows it to seep through the surface. This means that the flow of the glue on the surface of the

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powder cannot be contained and the printed form will not be sharp and confined to the actual dimensions. Based on all these results, it was clear that seashell powder on its own cannot be a candidate material for 3D printing by the binder-jet method.

Evidently, all three fundamental aspects required of a material candidate for 3D printing are not naturally available with the seashell powder and need to be fixed by means of adding other ingredients. After trying several alternatives, the plaster powder was identified as a good combination to form the seashell powder-ceramic composite that qualifies through all these three tests. The plaster powder can remain dry and allows break the moisture-related bonds between the CaCO<sub>3</sub> particles and helps achieve the uniform spreading into smooth layers. Further, the hydration processes of the plaster when treated with the moisture of the binder fluid would allow the gypsum crystallisation and the achievement of the green strength subsequently. It is also observed that the combination of seashell powder with the plaster powder will increase the contact angle of the liquid droplet and as a result allow the control of the spreading of the binder and the dimensions of the printed part. Further experimentation characterising the seashell powder for 3D printing is done based on the combinations with plaster in varying weight proportions as discussed next.

# Experimental conditions and trials

The range of the amount of the seashell powder in the plaster is selected to be from 15% to 50% by weight. Accordingly, powder composites of varying compositions as listed in Table 1 are prepared by thoroughly mixing the two powders together for a few minutes in

Specimen No.	Composites	
	Seashell powder (S) (% weight)	Plaster (Ceramic) (C) (% weight)
1	15	85
2	20	80
3	25	75
4	30	70
5	35	65
6	40	60
7	45	55
8	50	50

Table 1: Compositions of the seashell powder-plaster composites tested.



each case. Once the seashell powder is ensured to be uniformly mixed with the plaster, the powder composite is transferred to a clean and dry beaker. The binder glue is taken in a syringe and deposited on to the layers manually. Rectangular samples are prepared for 3-point bending tests with the overall dimensions as shown in Figure 2. For each layer, the required amount of powder deposited on to the substrate and then spread uniformly using a wooden spatula, maintaining the layer thickness to be around 1mm. Then a calculated amount of the binder fluid is added to the layer moving the syringe in a zig-zag raster path pattern. The process is repeated to build ten layers and once all the layers are printed, the specimens are left to cure for at least 6 hours before taking them out. Photographs of the printed and cured specimens once taken out of the print tray are presented in Figure 3 along with the powder compositions used.

Once taken out of the plastic tray, each sample is cleaned to remove unbound powder particles if any, and then heated in an oven for further drying. Primarily, the residual moisture is driven off by heating at around 250°C for 3 hours. Further, the gypsum crystals are also to be dehydrated, resulting in anhydrous gypsum. Further heating is likely to result in friability and loss of dry strength and so the samples are removed from the furnace and subjected to mechanical testing.

# **Results and Discussion**

# Microstructures

The SEM image of the specimen printed based on pure plaster is shown in Figure 4. It may be noted that the plaster hydration mechanism is effective in developing the needle like gypsum crystals. The dendritic growth of the crystals led to an intricate network, resulting in an overall strengthening mechanism based on mechanical interlocking. The postprinting backing does not disturb the gypsum crystal network, as is evident form Fig. 4, though excessive heat may lead to rounding of the crystals. Pure seashell samples could not be evaluated as the samples remained wet all through and with no green strength achieved. It is clearly evident that there is no bonding mechanism between the binder solution and the seashell powder particles. However, it remains interesting to evaluate how the combination of the two powders will affect the bonding mechanisms within the moisturised powder substrate.

SEM photomicrographs of specimens printed with varying compositions of the composite powders are presented in Figures 5a-5f. It is clearly evident from Figures 5a and 5b that the lower amounts of the seashell powder at 15% and 20% respectively do not alter the plaster hydration process to any significant levels. The gypsum crystal growth has been quite profuse in both these cases, while the seashell powder particles are accommodated within the inter-crystal spaces. However, crystal formation and growth conditions have gradually deteriorated with further increase in the weight content of the seashell powder. Figure 5c clearly shows patches of grey and blank areas, where



the gypsum crystal growth is restricted due to the excessive amounts of seashell powder at 25%.

The lack of free space and congestion are probably the mechanical aspects leading to the restricted crystal growth at higher levels of seashell powder. Further, the seashell powder might be absorbing significant amounts of the moisture made available from the binder-jet solution. This deprives the plaster of the moisture needed to hydrate and consequently, the gypsum crystal growth diminishes. This trend continues as the seashell powder content is increased further, as is evident from the photomicrographs of Figures 5d-5f. While there is some evidence of the presence of the gypsum crystals in Figure 5d, at



Figure 4: SEM image of the printed pure plaster specimen.



Figure 5(a): SEM images of the specimens printed with varying compositions.



Figure 5(b): SEM images of the specimens printed with varying compositions.







Figure 5(d): SEM images of the specimens printed with varying compositions.



Figure 5(e): SEM images of the specimens printed with varying compositions.



Figure 5(f): SEM images of the specimens printed with varying compositions.



30% by weight of the seashell powder, the crystal growth is severely diminished with the seashell content raised to 35% and 40%, as evident from the photomicrographs of Figures 5e and 5f. The excessive seashell powder content is spread widely between the sparsely developed gypsum crystals, probably leading to a loss of mechanical strength. The specimens at still higher contents of the seashell powder did not attain sufficient green strengths to be handled and so no further testing could be done on them.

#### **EDS** analysis

EDS analysis is done to substantiate the observations noted above on the formation and growth of the gypsum crystals and the dispersion of the seashell powder in the interstitial spaces. The results of the pure

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plaster sample presented in Figure 6 confirm the chemical composition of the plaster. Further, the EDS analysis results of the seashell- plaster composites with varying compositions as shown in Figure 7 conform to the chemical compositions of the printed samples. Further, point analysis is done in order to ascertain the predictions around the dispersion of the seashell powder within the gypsum crystal network.



Figure 7(a): EDS analysis of the samples printed using seashell composite powders of varying compositions.



Figure 7(b): EDS analysis of the samples printed using seashell composite powders of varying compositions.



Figure 7(c): EDS analysis of the samples printed using seashell composite powders of varying compositions.



Figure 7(d): EDS analysis of the samples printed using seashell composite powders of varying compositions.



Figure 7(e): EDS analysis of the samples printed using seashell composite powders of varying compositions.







Figure 8(a): Point analysis of printed samples based on composites at higher contents of seashell powder.



Figure 8(b): Point analysis of printed samples based on composites at higher contents of seashell powder.

The results of the point analysis done on printed samples of varying compositions, particularly at the higher levels of the seashell powder are presented in Fig. 8. The increasing of the weight percentage seashell powder increased the size of accumulation showed in the Figures 8a-8c. To confirm the accumulation material examined the point analysis at the different position on the specimen as shown in the Figure 8. The results are clearly in support of the arguments presented above on the mechanisms of crystal growth and the dispersion of the non-reactive seashell powder within the inter-dendritic spaces. For example, in Figure 8a, the peaks of graphs at points 1, 4, and 5, show the composition of the plaster. These are locations on the needle like gypsum (CaSO<sub>4</sub>) crystals that grew out of the plaster hydration reaction. Points 2 and 3 indicate the chemical composition of CaCO<sub>3</sub> which is the seashell powder residing in the inter-dendritic spaces. Similar observations are also noted based on the point analyses presented in Figures 8b and 8c for other samples with still higher contents of the seashell powder.

# Three-point bending resistance

The rectangular blocks printed with varying compositions of the powder composites are then subjected to three-point bending tests in order to ascertain the mechanical properties. The specimens are simply supported on a fixture with end supports and loaded under compression using a Tinius Olsen H50KS (Tinius Olsen Material Testing Machine Co., US) system. The maximum compressive loads the specimens can bear before breaking are recorded in each case. The

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Figure 8(c): Point analysis of printed samples based on composites at higher contents of seashell powder.



results are plotted in the form of the bar chart as shown in Figure 9. Evidently, the pure plaster printed specimen gave the best maximum compressive resistance, bearing up to a maximum of around 420 N. However, the addition of the seashell powder in general only led to the deterioration of the maximum compressive resistance. The more the seashell powder, the lesser the maximum compressive loads the specimens can bear before breaking. These results will allow further insight into the bonding mechanisms and correlations between process, structure and property attributes.

At lower levels, such as the addition of up to 15% by weight of the seashell powder appears to have a negligible influence on the loss of the compressive strength. The bar graph corresponding to this composition in Figure 9 shows a compressive load almost close to 400 N. Further, the compressive load is still reasonably at around 300 N, even with 20% by weight of seashell powder in the plaster matrix. However, the compressive strength of the printed composite specimens almost linearly reduced to zero with further increase in the amount of the seashell powder to about 50% by weight. The SEM images of the printed samples, the EDS and the point analyses discussed above indicated the coexistence of the gypsum crystals and the seashell powder within the printed samples. The three point bending results further elucidate that there are no further bonding mechanisms between the two phases.

The seashell powder remains neutral and gets pushed into the gaps between the dendritic gypsum crystals growing out of the plaster hydration reaction at relatively low contents such as up to 20% by weight. With further increase in its quantities, the seashell powder becomes the dominant as the gypsum crystal growth is restricted both due to a lack of moisture as well as the space to grow within the seashell powder matrix. The excessive presence of the unbound seashell powder leaves wide areas of fragile powder subsequent to the baking of the printed samples. In the absence of either the electromotive forces or the mechanical interlocking of the intricately evolved gypsum crystals, the specimens break easily, resulting in linearly diminishing compressive resistances.

# Conclusion

Overall, seashell powder and plaster combinations are proved to

be suitable for 3D printing by the binder-jet process. However, the seashell powder has no inherent reactivity or mechanism to enhance the bonding strength. It will remain in the crystal network of the gypsum phase and will not deteriorate the mechanical properties up to 15-20% by weight. Beyond this, the compressive strengths will be too low and the printed samples will be too fragile. The ability to include up to 20% by weight of the seashell powder in itself is an interesting finding as the powder composite brings biological flair into the material system and also ticking the boxes with sustainability. The following are specific conclusions:

• Seashell and plaster based composites are suitable for 3D printing by the binder-jet method.

• The maximum limit of seashell powder in plaster based composites for 3D printing is 20%, with no significant loss of mechanical properties.

• For the dimensions of the specimens used within this research, the maximum compressive load from the three-point bending test is around 400N for the pure plaster powder.

• The compressive resistance of the printed samples almost reduces to zero when the seashell powder and plaster contents are 50:50% by weight.

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#### References

- Gao W, Zhang Y, Ramanujan D, Ramani K, Chen Y, et al. (2015) Reduction in the corrosion rate of magnesium and magnesium alloy specimens and implications for plain fully bioresorbable coronary artery stents: A review. CAD 69: 65-89.
- Huang SH, Liu P, Mokasdar A, Hou L (2013) Additive manufacturing and its societal impact: A literature review. Int J Adv Manuf Tech 67: 1191-1203.
- Tan KH, Chua CK, Leong KF, Cheah CM, Cheang P, et al. (2003) Scaffold development using selective laser sintering of polyetheretherketonehydroxyapatite biocomposite blends. Biomater 24: 3115- 3123
- Wiria FE, Leong KF, Chua CK, Liu Y (2007) Poly-epsilon-caprolactone/ hydroxyapatite for tissue engineering scaffold fabrication via selective laser sintering. Acta Biomater 3: 1-12
- Wong KV, Hernandez A (2012) A review of additive manufacturing. ISRN Mech Engg 2012
- Olivia M, Mifshella AA, Darmayanti L (2015) Mechanical properties of seashell concrete. Procedia Eng 125: 760-764.
- Cuadrado-Rica H, Sebaibi N, Boutouil M, Boudart B (2016) Properties of ordinary concretes incorporating crushedqueen scallop shells. Mater Struct 49: 1805-1816.
- Muthusamy K, Sabri NA (2012) Cockle shell: A potential partial coarse aggregate replacement in concrete. IJS, Environ & Tech 1: 260-267.
- Othman NH, Bakar BHA, Don MM, Johari MAM (2013) Mechanical properties of seashell concrete. MJCE 25: 201-211.
- Karthick R, Sirisha P, Sankar MR (2014) Mechanical and tribological properties of PMMA-sea shell based biocomposite for dental application. Procedia Mater Sci 6: 1989-2000.
- Sachs E, Cima M, Cornie J (1990) Three dimensional printing: rapid tooling and prototypes directly from a CAD model CIRP. Annals-Manufg Tech 39: 201.
- 12. Balistreri J, Dion S (2013) US. Patent No. 8,568,649. Washington, DC: U.S. Patent and Trademark Office.
- Ziaee M, Tridas EM, Crane NB (2017) Inkjet based 3D additive manufacturing of metals. JOM 69: 592-596.
- Zheng YF, Gu XN, Witte F (2014) Progress of biodegradable metals. Mater Sci and Engg R Reports 77, 1-34.

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 Karageorgiou V, Kaplan D (2005) Porosity of 3D biomaterial scaffolds and osteogenesis. Biomater 26: 5474-5491.  Myers K, Cortes P, Conner B, Wagner T, Hetzel B, et al. (2015) Structure property relationship of metal matrix syntactic foams manufactured by a binder jet printing process. Add Manuf 5: 54-59.