Biomimetic building of 3D printed tailored structures

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**Summary**
3D printing is changing the whole manufacturing concept of components and products. The freedom of design in 3D printing opens new ways to produce structures with advanced properties. Additive manufacturing is nowadays utilised in some industrial applications, however, there is a need to develop new materials with high quality properties. New tailored materials and optimised 3D printing techniques will make the utilisation of additive manufacturing possible in many new applications.

In this project, the biomimetic multi-scale hierarchical approach was the inspiration for design of materials and structures. In macro to micro-level, the project focused on utilising advanced functional printing technologies in the development of new kinds of ceramic- and cement-based materials with high specific strength. In addition, some organic materials were produced and printed. In micro to nano-level, the formation of cementitious materials was studied, and routes for controlling the crystal growth were examined. The experimental part of the project consisted of production of printable paste-like materials, numerous 3D printing trials and crystal growth manipulation experiments.

Results of the project showed the controlling of crystal growth in some extent possible in nano and micro-level. The development of paste materials made the printing of structures possible and the strength of the cement samples with large volumetric porosity was at the same level than that of the casted samples. The result indicates that a structurally designed material possesses far higher strength than materials with random porosity and 3D printing proved to be a viable method for the manufacturing of such material. The work will be continued in additive manufacturing platform at VTT.

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Preface

The main contents of the MIMECOMP project were the development of printable materials, the 3D printing of biomimetic tailored structures as well as the crystal growth manipulation experiments. This is the final report of the project. The report summarises the main results and conclusions related to different materials developed and used in the trials. The more detailed information can been found from separate papers in references.

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Authors
## Contents

Preface ..................................................................................................................................... 2

Contents ................................................................................................................................... 3

1. Introduction ......................................................................................................................... 4

2. State-of-the-art .................................................................................................................... 5

3. Cement ............................................................................................................................... 7

   3.1 Introduction – Cement ................................................................................................ 7
   3.2 3D printing with cement .............................................................................................. 7
   3.3 Development of printable cement pastes ................................................................... 7
   3.4 Conclusions of the experimental findings on cement paste structure in different size scales .................................................................................................................. 8
       3.4.1 Macro-scale – Cement ................................................................................... 8
       3.4.2 Micro-scale – Cement ................................................................................ 9
       3.4.3 Nano-scale – Cement ................................................................................ 10

4. Titanium dioxide ................................................................................................................ 10

   4.1 Introduction – Titanium dioxide ................................................................................ 10
   4.2 Paste preparations ................................................................................................... 10
       4.2.1 First titanium dioxide pastes ......................................................................... 11
       4.2.2 Complementary titanium hydride and titanium dioxide pastes ..................... 11
   4.3 Printing and sintering ................................................................................................. 11
       4.3.1 About 3D printing and sintering .................................................................... 11
       4.3.2 Printing and sintering results ......................................................................... 11

5. Other materials ................................................................................................................. 13

   5.1 Hybrid materials ........................................................................................................ 13
   5.2 Polycaprolactone ....................................................................................................... 14
   5.3 Nanocellulose and living cells .................................................................................. 14

6. Conclusions ...................................................................................................................... 14

References ............................................................................................................................. 15
1. Introduction

The research in MIMECOMP project focused on utilising advanced functional printing technologies in the development of new kinds of ceramic- and cement-based materials with high specific strength. An increase of 50–100% in specific strength was targeted in this research. In addition, some organic materials were produced and printed to test the viability of the printing system and to get more information on paste preparation. A multi-scale hierarchical approach was used in the development work, as presented in the Figure 1.

New advanced printing technologies open novel routes to build two- or three-dimensional structures and scaffolds for ceramic and cementitious materials. In this project the aim was to utilize the known concepts combined with different biomimetic structures like honeycombs and bone-like structures to increase the specific strength, nano and/or micro porous structures for catalytic and filtering applications and different scaffold structures. By combining biological and synthetic approaches in design, new biomimetic multifunctional materials can be developed (Figure 2).
The objectives of this research were to:

1. understand how a biomimetic approach can be utilised in cementitious and ceramic systems,
2. develop new biomimetically structured materials,
3. learn how to orient the crystal growth of C-S-H in such materials.

2. State-of-the-art

The MIMECOMP project aimed at creating knowledge and preparation readiness of materials to be used as or within printable pastes. In addition, the project was focused on the actual preparation of different bio-inspired structures, especially with gradient porosity in order to envisage biomedical applications or to construct structures with high specific strength. One of the visions of this project was to mimic ultra-strong structures existing in nature and design e.g. strong ceramic and cement-based materials. In tissue engineering, scaffolds are used to construct artificial organs in vitro before implanting them in vivo. These 3D scaffolds mimic nature’s organic components in directing the migration and orientation of the cells in the construct. This field of science was merged into the aims by exploring a wide range of paste materials and scaffold printing as well as conducting nucleation and crystal growth studies of calcium silicate hydrates.

Composites and scaffolds made off various materials for tissue engineering have been introduced by different research groups world-wide (Bose et al. 2013, Srinivasan et al. 2012). In terms of tissue engineering scaffolds, biocompatibility and porous structure with interconnected pores are the necessities for the scaffold material and the structure. The scaffolds must also show mechanical properties equal to those of native tissue, and degradation properties to match the rate of synthesis of a new extracellular matrix.

A wide range of materials such as polymers, proteins, glasses, cements and different hydride materials have been used for implants and scaffolds for tissue engineering. Synthetic polymers such as poly(glycolic acid) (PGA), poly(lactic acid) (PLLA) and polycaprolactone (PCL) are favoured for scaffolds due to their high degree of reproducibility. On the other hand, biological materials are expected to be a more natural choice and more compatible with the human body. Hydrogels, synthetic such as poly(vinyl alcohol) or biological such as chitosan, collagen and hyaluronic acid, are good candidates for scaffolds, since they possess properties similar to human tissues. Inorganic materials have also been used for 3D scaffold structures. Composite materials, on the other hand, are desirable materials, since they have properties distinct from the original single materials.

Besides material science (biomaterials), development of tissue engineering techniques is strongly included in this field. Syringe-based dispensing systems have become popular due to the ability to print porous and complex 2D and 3D objects with controlled chemistry and interconnected porosity to be used in medical devices and in scaffolds for tissue engineering (Bose et al. 2013, Kachurin et al. 2002). Landers at al. (2000) developed a plotting method for 3D objects made off hotmelts, solutions, pastes and dispersions of monomers or polymers. Moisture-curable acetoxysilane was dispensed in a water bath to make 3D objects for biomedical scaffold. Inorganic biodegradable scaffolds ideal for bone tissue engineering have been introduced by several research groups (Bose et al. 2013, Tamimi et al. 2013, Tarefder et al. 2012). These include 3D-printed objects made off calcium phosphates or hydroxyapatite pastes. A physical model of the human external ear has been reconstructed from biodegradable poly(propylene fumarate) by using the direct-write printing technique (Kachurin et al. 2002). Polycaprolactone-hydroxyapatite composite nanofibers have been used to engineer bone by using a precision extruding deposition (PED) technique (Shor et al. 2008).

In addition to medical applications, additive manufacturing and 3D-printed objects have drawn attention also in other fields. Complex 3D components made of rapid-hardening Port-
land cement have been presented by Gibbons et al. (2010). The research group concluded that with further optimisation of powder, liquid and print parameters, the resolution limit of 0.1 mm (i.e. the layer thickness) could be achieved. Engineers and artists have also introduced 3D-printed furniture, art pieces and components made by 3D concrete and cement printers of different scales. Nowadays, there are also on-going projects on large-scale printing of cement/concrete, and the most recent news is dealing with a 3D-printed house project. The DUS Architects has developed its own 6-meter tall 3D printer with the intention of printing a house in the Netherlands by the end of 2013. (http://www.gizmag.com/kamermaker-3d-printed-house/26752/)

Cement is produced in every industrial country and is used mainly for structural concrete, mortar, foundations and roads. New applications for cements outside the construction sector have been identified and documented by Purnell (2009). The established new application areas for cementitious materials include dental and bone reconstruction. The use of bio-cements is based on their compatibility with the human body and their economic and technical benefits. Emerging applications such as rapid prototyping and sculpturing were mentioned as promising new fields. Especially, the quick and cheap 3D printing techniques were seen to have potential. Strong and functional objects can be printed by using cement pastes.

References (State-of-the-art)


6-meter tall KamerMaker to 3D print Amsterdam house by year’s end. http://www.gizmag.com/kamermaker-3d-printed-house/26752/
3. Cement

3.1 Introduction – Cement

One of the MIMECOMP project goals was to adapt biomimetic approach to inorganic materials. The widest definition of biomimetic includes solutions inspired by the nature. In material sciences, a widely used example is nacre shell, where organic materials directs the growth of calcium carbonate to layered structure, by preventing crystal growth of structurally undesired orientations. Living organisms form extremely sophisticated structures having specific features in different size scales. In ordinary wood material the cellulosic fibres constitute the nano-scale, in the micro-scale the cellulosic fibres are composed with lignin and the highly ordered capillary network forms the wood material observed the macro-scale. Finally the trunk and the branches form the observed structure extending to tens of metres. The objective was to mimic nature from the nano-scale up to the macro-scale by applying a selection of different methods. Nature has at least two powerful methods for organizing structure. One is the controlling of crystallization with different surfaces. Multiple protein surfaces are known to favour certain crystallization directions, causing highly organized structures. The other is the alignment of crystal growth with physical barriers or boundaries. Both methods were applied in the present work.

3D printing device nScrypt /10/ was applied for forming the macro-scale specimens in the centimetre size range allowing also for the design of structural details in the 500 µm–2 mm scale /15/. The 3D printing method has impacts also in the micro-scale due to the spatial placement of cement particles particularly in the corners of the printed structural details /15/. The placement of particles was manipulated with sophisticated paste preparation methods /8/. Orientation of crystal growth was studied in order to examine the nano- to micro-scale effects /1,3/ and finally a chemical additive was used for further nano-scale modifications /2,4,5/.

3.2 3D printing with cement

In the 3D paste printing method a ready mixed paste was extruded through a nozzle. The nozzle position and the paste flow were computer controlled and the whole system can be automated. Fully automated 3D printing offers a way to design and manufacture complicated structures. The paste properties were found to be crucial. To be printable the paste should simultaneously be both flowable and attain a fixed 3D structure immediately after printing. From that perspective both Portland cement paste and titanium dioxide paste (presented in Section 4) are suitable materials. Both pastes are known to have flow profile of Bingham liquid and certain yield stress. Development of paste was found to be the key issue of 3D printing.

3.3 Development of printable cement pastes

It was soon discovered that the art of 3D paste printing is a combination of various research areas. Simple relations between paste printability and measurable paste characteristics were not found. It was concluded that following aspects have a large effect on paste printability regarding both cement and titanium dioxide pastes.

- **Paste particle distribution**
  The printing head could be clogged due to different processes. An insignificant number of over-sized particles was able to start a process which eventually clogged the printing head. The problem was solved by milling the paste after mixing. Milling with three roll mill effectively crushed the larger particles enabling improved printability of the paste /8/.
• **Paste bleeding**
Bleeding during printing indicates segregation of water and particles. It leads to inhomogeneity where the more concentrated paste fraction clogs the printing head.

• **Paste rheology**
Paste rheology was also observed to play a key role in printable 3D pastes. First of all, the structure shall maintain its shape immediately after printing through the nozzle. This was only achieved when the paste had a distinguishable yield stress according to Bingham model instead of the Newtonian behaviour with negligible yield stress.

• **3D printer geometry**
3D printer geometry was observed to have a large role in paste printability. Whole route from initial container to printing nozzle should be considered when printability of 3D printer is evaluated. It was observed that any thin corners or edges cause segregation and bleeding in the paste, clogging the printer. Best printer geometry was attained when printing head was straight attached to container syringe.

Portland cement paste was proven applicable to 3D printing (Figure 3) due the hydration reaction which hardens the printed structure without heat treatments. Cement’s tendency to harden without heat treatment is also a drawback from the practical maintenance point of view. The printer must be cleaned carefully after use. Detailed information of printable cement paste is not reported due the patenting considerations.

![Figure 3. Printed cement structures.](image)

### 3.4 Conclusions of the experimental findings on cement paste structure in different size scales

#### 3.4.1 Macro-scale – Cement

The compressive strength of printed specimens was found clearly stronger than could be estimated. The average compressive strength of cast specimens fully filled with the cement paste was 35 MPa while the strength of the strongest printed specimens with large volumetric porosity (~50%) was 31MPa. However, there was a large variation in strength of printed porous specimens. The strength was varied by printing design, the directions of the load and the density of the samples. The reduction of strength of specimens loaded against the print-
ed layers varied only 15–50% even with the highest porosities of ~50% depending on the designed architecture, while such high volume fraction of random porosity is known to reduce the strength by 90% of more /15/.

In general, the compressive strength effect of the designed printed architecture followed the principles of structural mechanics (Figure 4). Placement of the material to the vertical parts (columns) parallel to the direction of compression increased the strength more than the placement in horizontal parts (slabs). More details of the strength effects of the specimen geometry are given elsewhere /15/. The mechanical explanation is probably not the only reason for the high strength of the printed structures. In the micro-scale, the homogeneous spatial placement of cement particles discussed above may play an important role.

![Figure 4. Rössler & Odler, 1985 (Figure 1: Relationship between porosity and compressive strength. Range of experimental data and calculated functions).](image)

3.4.2 Micro-scale – Cement

Because Portland cement hydration largely follows the basic laws of nucleation and crystal growth /5/, the activity and mechanisms of various surfaces play a major role in the control of crystal growth /3/. This principle was applied to the growth of calcium-silicate-hydrate (C-S-H) crystals. As the C-S-H growth is known to propagate from cement grain surfaces outwards, it is reasonable to presume a weaker contact of outside surfaces. The possibility of increasing the contact between silicon carbide whiskers and cement matrix by directing the propagation of C-S-H growth onto the whiskers was studied experimentally. The outcome was successful in sense of showing that the growth was directed into the whisker surfaces, but this was not followed by improved strength of the paste composition compared to pastes with the reference whiskers /1/.

Another micro scale approach was made with the alignment of crystal growth using a physical barrier. Natural organic scaffold (wood) was used to align the growth of calcium-silicate-hydrate. It was observed that the crystal growth of calcium-silicate-hydrate differs significantly from the growth on e.g. calcium carbonate. The external scaffold is able to restrict the growth and the calcium-silicate-hydrate formed a very loose structure and filled the maximum space /16/.
3.4.3 Nano-scale – Cement

In solutions all ions have an impact on the solubility of the ions forming the desired crystal, C-S-H in the cement case. This effect further influences the degree of super solubility and the nucleation of the crystals. Modifying variations of the concentrations over the dissolution period offer means to manipulate the formation of the nano-sized structures. A hydration and strength related hypothesis based on the above facts was formulated and its validity tested theoretically and experimentally indirectly. CaCl₂ was chosen as the model chemical for the solubility manipulation. The result indicates that the underlying mechanism behind the accelerating effect of CaCl₂ stems from enhanced C-S-H nucleation and furthermore the effect can be further enhanced with mineral surfaces /2,4/.

4. Titanium dioxide

4.1 Introduction – Titanium dioxide

Different kinds of pastes were prepared to produce titanium dioxide (TiO₂) structures using nScrypt micro dispenser facilities. The target was to print 3D structures with desired architecture (porous, bone-like, core/shell, honeycombs and scaffolds), mineral form and strength. 3D printed ceramic structures were consolidated by heat treatments at different sintering temperatures /10/. The titanium dioxide paste properties and sintering conditions have an effect on the grain growth and orientation, microstructure as well as the mechanical and surface properties of the 3D structures.

4.2 Paste preparations

Different additives are needed in preparation of ceramic pastes for 3D printing device. Dispersion, homogeneity, softness and drying are adjusted with the additives, solvents and ceramic material selection. Viscosity, flow, drying and shrinkage are the most critical properties which affect the printability and usability of the pastes /6,7/.

In MIMECOMP project the guidelines for paste preparation were able to be drawn and knowhow about the suitable additives was gained. Among other things particle size was found out to affect the solid content which subsequently affects the shrinkage in drying and sintering. Also paste preparation technique, machinery and quality control are important. Effective mixing and dispersing tool is presented in the Figure 5. /8/

![Figure 5. Dispermat mixing system with scraper tool. Pastes with high viscosity can be mixed and dispersed.](image-url)
4.2.1 First titanium dioxide pastes

The development of easy-to-print ceramic pastes for nScrypt printer especially for 3D printing pointed out to be more difficult than it was expected. Lots of experience and knowhow was gained for further work in this field. An acceptable paste receipt containing preselected P25 titania powder and several solvents and additives was found, however, fine tuning of the processing was not finished /7,10/. Suitable tools and machinery are now available at VTT and high demands for the paste compositions are identified in printing with Smart pump™ system of nScrypt dispenser.

4.2.2 Complementary titanium hydride and titanium dioxide pastes

Complementary titanium pastes were prepared by adding TiO₂ or TiH₂ powder to a solvent/plasticizer solution followed by dispersing the resulted mixture with a polyacrylate/solvent solution. During the preparation of the pastes, evaporation of the solvent took place leading to a printable paste with a solid content over 80%. The pastes were used as such for printing, however, in the first trials with the TiH₂ paste, the adjacent strands in the 3D structures fused together. This was partly overcome by increasing the pressure within the printing which lead to more effective evaporation of the solvent and to satisfactory 3D structures. The structures made were subjected to sintering to form TiO₂ scaffolds (Section 0). /9/

4.3 Printing and sintering

4.3.1 About 3D printing and sintering

Two different kinds of pump systems were used in trials of MIMECOMP project. The first ceramic pastes were printed using Smart Pump™ technology. For the complementary ceramic pastes and hybrid pastes (Section 5) simplified pumping system was adapted. Simplified pump system is less demanding for the paste composition, however, it doesn’t allow very fine features.

General requirements for the paste materials are that particles are not (very much) agglomerated, especially regarding micro particles, and they should be distributed evenly in the paste material. It is highly desirable for the printed paste materials to maintain a constant and controllable cross-section or to form a predictable and stable 3D deposition shape. The printing result depends also on the curing process and several printing parameters as speed, pressure, valve opening and printing height /7/.

Too fast evaporation of solvents or too big agglomerates can cause printer head blocking. Perfect ceramic paste should have high ceramic content, low polymer content, slow solvent evaporation rate and nearly high as possible viscosity that is printable. Strong shear thinning rheological behaviour (thixotropic or pseudoplastic) can ease the printing while shear thickening of pastes will make the printing more difficult /7/.

Printed titanium dioxide was sintered at high temperatures in order to harden the structures. With some of the prepared titania pastes, heat treatment caused high shrinkage, which was likely to rupture the printed structure. With organic solvents and engineered heat treatment it was possible to control the shrinkage and prevent the rupture and keep the printed structure in one piece during the sintering.

4.3.2 Printing and sintering results

**First ceramic pastes**

The printing of some titanium dioxide pastes succeeded quite well. Although some difficulties arose concerning the printability of pastes and a lot of knowhow was earned. It was possible to produce few tens of layers high scaffolds with the first ceramic pastes using Smart
Pump™ Figure 6. Scaffolds were sintered carefully at 1000°C and the mineral form pointed out to be rutile. The shrinkage during the sintering was approximately 50% /10/.

Figure 6. Printed and sintered titanium dioxide scaffolds (first pastes).

Complementary ceramic pastes

Scaffold made of the complementary TiO$_2$ pastes

A lattice-like 10-layer cubic object shown in Figure 7 was successfully printed and sintered (the final temperature was 1000 °C) /10,14/. The spacing between the strands in the lattice was ~1.5 mm and they were aligned perpendicular to each other in the adjacent layers. The mineral form of the TiO$_2$ was anatase.

Figure 7. Printed and sintered titanium dioxide scaffolds (the complementary TiO$_2$ paste) shown from the above (left) and from the side (right).

Scaffolds made of the TiH$_2$ pastes

In the first printing trials with the TiH$_2$ paste, the paste strands printed on top of each other fused together. This was overcome by increasing the pressure within the printing which led to more effective evaporation of the solvent. Sintering of the printed structures at 1050 °C resulted TiO$_2$ (rutile) filaments/lattices (Figure 8) which was confirmed by XRD analyses.
Figure 8. Printed and sintered titanium dioxide scaffolds made of the titanium hydride paste. The printing outcome with fused paste filaments (left) and the more satisfactory printing outcome with a more viscous paste (right).

5. Other materials

The main focus in this project was on ceramic and cement materials. However, some other materials were included in the experimental part of the project to test the viability of the printing system. Especially, polymeric pastes without particles were assumed to be very easy-to-print, therefore these pastes gave the opportunity to print using fine nozzles structures with high amount of layers and tailored porosity structures.

5.1 Hybrid materials

The primary objective of the preparation of hybrid pastes was to create material compositions and 3D structures with gradient porosity in view of utilizing the knowledge and the experience gained for tissue engineering purposes. The components in the hybrid paste were polylactic acid (PLA), tri-calcium phosphate (TCP) and dichloromethane (DCM) which were in the weight ratio of 2:1:12, respectively. The excess solvent (DCM) facilitated dissolution of the polymer, however, prior to the printing procedure most of the solvent was evaporated to gain a suitable paste for printing. Homogenous multi-layer (up to 20 layers) lattice structures as well as lattice structures with gradually changing porosity (change in filament spacing) were successfully made (Figure 9). Long-term immersion in water or simulated body fluid (2 and 4 weeks, respectively) resulted in slight weight decreases of the 3D structures indicating dissolution of the calcium phosphate. This implies that additional porosity in the filaments walls of the 3D structures is expected after exposure to wet conditions. /9,10/

Figure 9. Printed hybvide (PLA + TCP) structures.
5.2 Polycaprolactone

Biodegradable polymer paste was prepared by dissolving poly-caprolactone (PCL) in chloroform /11,14/. The paste was used in printability trials and in making of fine demo structures (Figure 10). PCL paste was very easy-to-print using Smart Pump™ and it hardened directly after the printing by solvent evaporation.

![Figure 10. PCL scaffolds (180 layers high and gradient structures and SEM images).](image)

5.3 Nanocellulose and living cells

TEMPO oxidized cellulose nanofibril hydrogel and growth medium containing human adipose stem cells were printed. These materials were potential for biocompatible use in medical applications.

Nanofibrillated cellulose showed extremely high printability making the fabrication of several centimetres high structures possible. In addition, human cells remained alive after the printing and also the cells can be mixed in cellulose gel where they remain unharmed. /12,13/

6. Conclusions

The basic principle of the MIMECOMP project was the utilisation of the biomimetic approach for inorganic materials. This was realised by multi-scale hierarchical approach from nano to macro level in the development of materials and structures.

The inspiration for the computer-designed structures for the printing was found from the fine architectural natural structures such as bone, wood, tooth and nacre. Printable cement, titanium dioxide, hybrid and polymeric paste materials were developed. Different kinds of structures were successfully printed and ceramic materials were also sintered. Valuable knowledge about materials suitable for 3D printing was gathered and potential further development possibilities and applications can be found from several areas e.g. medical scaffolds, filters, membranes, components for machinery, electronics and cell culturing materials.

Three size scales namely nano, micro and macro were studied. In the macro-scale the cement paste specimens were modified with 3D-printing. The compressive strength of the printed specimens was remarkably high in relation to their high porosity. The result indicated that a structurally designed material possesses far higher strength than material with random
porosity and 3D printing proved to be a viable method for the manufacture of such material. Combined with the structural design 3D printing further enabled the design of porosity network form closed pores to continuous and oriented void systems. This finding can be applied to also other materials outside the tested cement and titanium dioxide. These options may prove to be valuable in applications like medical implants or electronic components. The work will be continued in additive manufacturing platform at VTT. A recipe for printable cement paste was developed and the patentability of the recipe is under estimation.

In the micro-scale the material structure was modified by directing crystal growth with modified surfaces and by an external scaffold. Both methods showed impacts to the mode of crystal growth, but neither produced benefits of practical importance regarding strength. However, the findings may prove to be interesting elsewhere. The same applies to the nano-level results. Practical immediate applications were not found, but the increased understanding knowledge will find applications while developing other ionic-based accelerators for blended cements particularly for cold climates. The original project goal of combining the various size-scale modifications into a single high strength structure was not accomplished. However, each separate section was beneficial. In the MIMECOMP project, mechanisms of calcium chloride were revealed and the knowledge will be used to develop other ionic-based accelerators that do not pose corroding properties of chloride.

References


