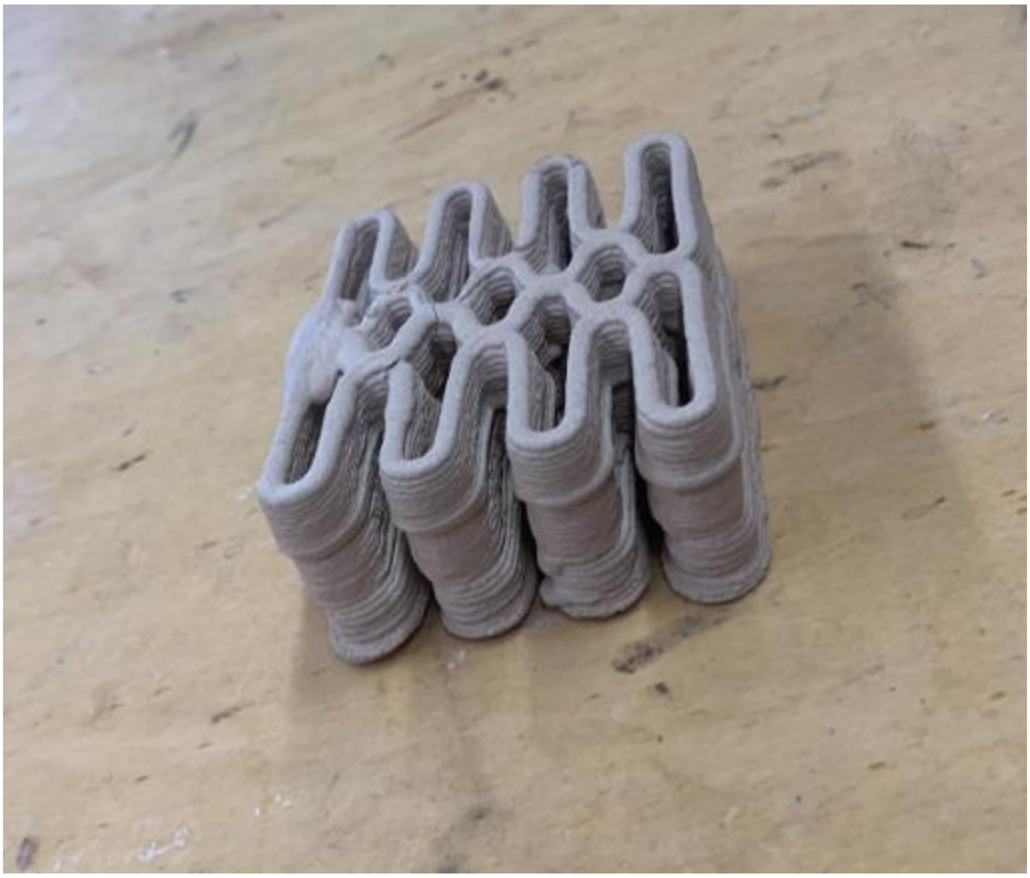

EXPLORATIVE RESEARCH FOR NEW BIOBASED BINDERS IN 3D PRINTING

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Abstract

Currently, there is a shift toward using more biobased materials in 3D printing, which presents an eco-friendly alternative to traditional plastics due to their potential for benefits such as waste reduction, biodegradability, and reduced toxicity. However, challenges such as mechanical strength, structural integrity, and water resistance still pose hurdles to their widespread adoption. Therefore, this study aimed to develop methods to find and optimize novel natural binder formulations that enhance the structural integrity, water resistance, and durability of biobased 3D-printed objects. The focus of this research was to use natural binders and combine them with fillers derived from biobased waste streams. Initial research identified Latex, Linseed Oil, Pine Resin, Lignin, and Casein glue as promising binders. Tests resulted in casein glue, a milk protein derived from cows, mixed with calcium carbonate (CaCO3) from oyster seashells as the best-performing combination. Further exploration revealed that adding cork as an additional filler significantly improved the viscosity, workability, and performance of the paste. From there, two successful formulations emerged: a cork-dominant paste and a CaCO3-dominant paste. Water absorption tests were conducted and resulted in the CaCO3-dominant paste being more water-resistant and structurally sound, despite absorbing more water, compared to the cork-dominant paste, which exhibits increased rigidity at the cost of being prone to cracking and deformation when drying. In collaboration with BESE and Biobased Creations, prototypes were developed that demonstrated their potential application in the biobased building sector. Through a set of experiments, this study highlights the impact of external factors such as environmental conditions, printer settings, and lab equipment on the performance of the paste. Future research should focus on optimizing cork and calcium carbonate ratios, experimenting with the casein glue mixture, testing other fillers, conducting mechanical and biodegradability tests, and exploring crosslinking and biobased waterproofing coatings to enhance material properties. These findings aim to set a framework for investigating new potential binders and creating binder formulations for biobased 3D printing.

Layman's summary

The current trend of using more biobased materials in 3D printing is a promising step toward making the technology eco-friendlier. Traditional plastics that are currently used in 3D printing are often not biodegradable, can often be toxic when produced and disposed of, and thereby lead to serious environmental consequences. On the other hand, biobased materials, which come from plants or waste biomass, offer the benefit of being less harmful to the environment. However, they bring their own challenges, such as often lacking strength, structural integrity, and water resistance. These traits are necessary for real-world applications, especially in the construction sector.

This study aimed to tackle these challenges by finding, developing, and testing new binders and creating mixtures (called "pastes") for 3D printing. The natural binders are substances that hold all the materials together. They are combined with fillers that come from biobased waste, for example, calcium carbonate from oyster seashells or olive pit powder. The focus was to find combinations of binders and fillers that would allow strong, water-resistant, and durable objects to be 3D printed.

Initially, research was conducted to identify potential binders for testing, resulting in the selection of Latex, Linseed Oil, Pine Resin, Lignin, and Casein. After testing all of them, casein glue, when mixed with calcium carbonate (from old oyster seashells), turned out to be the best-performing binder in terms of workability and maintaining the printed shape. During these experiments, cork was added to see its effect, and it significantly improved the performance and the paste's ability to maintain its shape. Further experimentation with these two fillers resulted in two pastes: one with relatively less cork and one with more calcium carbonate. However, each had its strengths and weaknesses. On the one hand, the cork paste was very strong and hard to break but would often crack and deform during drying. On the other hand, the calcium carbonate paste was better at resisting water and maintaining its shape and structure.

This study also showed that not only the paste itself influences the final performance, but also external factors like room temperature, the speed of the 3D printer, and whether the used equipment was properly cleaned can affect the final outcome. Together with two companies from the biobased construction sector, prototypes were developed to explore their potential applications in real-life settings.

In the future, the different ratios of cork and calcium carbonate should be explored further, and other fillers should be added to see their effects on the final performance. The casein glue itself can also be modified by adjusting the amount of its components and investigated to see how its properties change. Additionally, other biobased materials could be used as coatings to increase water resistance. All these aspects could be studied to improve the paste formulations and make the objects even more durable and water-resistant. This could bring the goal of creating sustainable and durable materials for the 3D printing sector one step closer.

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Introduction

In recent times biobased materials have emerged as a promising alternative to conventional plastics, gaining attention in various industries among which one is 3D printing. These materials can be sourced from renewable organic streams such as algae, plants, and waste biomass. They can offer notable environmental benefits such as reduced toxicity, waste reduction and biodegradability (Wijk, 2015). Compared to traditional petrochemical-based plastics, which are often non-biodegradable and contribute to pollution and greenhouse gas emissions during their production and disposal, biobased materials and plastics can offer a more sustainable solution (Saleem et al., 2023; Wijk, 2015). However, biobased does not simply mean biodegradable under natural conditions. Some bio plastics, like the in 3D printing commonly used polylactic acid (PLA), sourced from fermentation of sugar cane starch, is only degradable under industrial conditions posing challenges regarding disposal and environmental impact (Ali et al., 2023).

The technology of 3D printing, or also known as additive manufacturing, has revolutionized manufacturing processes by enabling efficient and precise creation of complex structures, composed of a variety of materials. Compared to conventional subtractive methods, which remove material from building blocks through milling or cutting to create a part, 3D printing generates less waste through the tailored production of adding material layer by layer. Furthermore, 3D printing has the capacity of local production reducing emissions that are otherwise associated with traditional supply chains and logistics that mainly depend on fossil fuels (Jandyal et al., 2022).

Among the various 3D printing techniques, Extrusion-based 3D printing is widely used as it is accessible and affordable. It involves depositing material layer by layer to construct a 3D object. Within this method a range of approaches are covered each defined by the specific extrusion mechanism and type of material used. One commonly used method is the Fused Deposition Modelling (FDM), in which thermoplastic filament is molten through a heated nozzle and deposited layer by layer onto a heated print bed to create a 3D part. As the material cools and solidifies the 3D object is created, layer by layer. The dominant plastics currently in use are the biobased PLA and fossil-based, non-biodegradable acrylonitrile butadiene styrene (ABS) (Wijk, 2015).

Other extrusion-based 3D-printing techniques are Direct Ink Writing (DIW) or Liquid Deposition Modelling (LDM). These methods do not rely on extruding molten plastics but instead use a syringe/- or air pressure-based extrusion technique, making the need for a heated nozzle and heated print bed obsolete thereby saving energy, while opening a range of other (biobased) materials that can be used (Faludi et al., 2019). The materials are extruded as a semi-liquid paste-like suspension, which harden through drying and can consist of anything that can be liquid enough to be extruded but rigid enough to maintain shape once deposited. The bio based pastes are made up of a binder (e.g. sodium alginate, potato starch etc.), a filler (e.g. oyster shell powder, cacao husk etc.) and a solvent (e.g. water, ethanol etc.) (Vette, 2018).

Switching from synthetic polymers to biobased materials and stepping away from external heat sources can impose an even further positive environmental impact in 3D printing technology, but it also has its own developmental challenges.

A complicated hurdle lies in the discovery and formulation of effective bio-based binders that fulfil the demands of the biobased building sector such as providing mechanical and structural integrity, adhesion properties, durability, and biodegradability of printed structures (Imam et al., 2013). Furthermore, many biobased materials derived from nature are inherently hydrophilic, making water resistance and the premature biodegradability a challenging yet critical requirement for expanding their application potential as well as ensuring the performance of the final product (Andrew & Dhakal, 2022).

Historically, natural binders such as collagen, blood, and casein have been used for centuries, with fish glues and soy glues having emerged in the 1800s and 1900s, respectively. Other natural adhesives include starch, tree gum, clays, cellulose, lignin, tannin, pitch, and dextrines (Dhawale et al., 2022; Langejans et al., 2022). Casein, for instance, a protein derived from cows' milk is available as a powder that, when solubilized in water and mixed with an alkali, has been used since ancient Egyptian times as a mortar and through Middle Ages as a and wood glue and bookbinding agent (U.S. Department of Agriculture, 1961).

Therefore, in this study, the objective is to address the challenges of water resistance in 3D-printed objects made from biobased materials. This will be achieved by investigating and exploring various natural binder formulations, with the goal of developing binders that are not only waterproof and structurally robust but also suitable for printing. Specifically, these water-resistant binders will be combined with fillers sourced from bio-based waste streams, aiming to create new printing pastes with potential applications in the biobased building sector.

Through collaborations between AMS Institute, Biobased creations and BESE, prototypes will be developed and tested that aim to explore the possibilities of using the newly created 3D printing pastes in the context of material development and form studies. Additionally, this study seeks to establish a framework of different methods for effectively finding and exploring new paste formulations, paving the way for future research in this field.

The research questions are thereby:

1. How can natural binder formulations be developed to enhance the water resistance, structural integrity, and printability of 3D-printed objects made from biobased materials?
2. What are the most effective combinations of natural binders and fillers derived from biobased waste streams for creating durable, water-resistant 3D printing pastes suitable for the biobased building sector?
3. What methods can be established for systematically discovering and optimizing new biobased paste formulations for 3D printing?
4. How can the newly developed 3D printing pastes be applied in real-world prototypes to explore their potential use in material development and form studies within the biobased building sector?

These questions aim to address the core objectives of developing effective biobased pastes for 3D printing, enhancing their performance, and applying them in practical contexts.

Research Methodology

Selection of Binders and Method of Evaluations

In the process of extrusion-based 3D printing using biobased materials, a paste is extruded layer by layer and then left to dry. This paste is made up of three main components: a binder, a filler, and a solvent.

1. **Binder:** The binder, such as gelatine, alginate, or starch, holds the particles together. It ensures cohesion and adhesion between the filler particles, providing overall structural integrity.
2. **Filler**: The filler provides structural strength and modifies the material's properties. It can be organic, like hemp fibres, or inorganic, like calcium carbonate (CaCO3), or a combination of both. The filler acts as the "body" of the material.
3. **Solvent**: The solvent is the liquid component used to dissolve or disperse the other materials (binders and fillers), creating a homogenous mixture that is suitable for printing. Common solvents include water, alcohol, and acetone.

At the beginning of this research, an initial assessment of potential binders was conducted to identify the most suitable options for the 3D printing process. The evaluation was guided by several key criteria, including:

1. **State at Room Temperature**: The binders were assessed based on their physical state at room temperature—solid, liquid, or semi-solid—to determine their ease of handling and processing.
2. **Water Resistance**: The ability of the binders to resist water was evaluated, as this characteristic is crucial for ensuring the durability of the final printed products and key point of this research.
3. **Cross-Linking Ability**: The potential for the binders to form cross-linked networks was considered, which can enhance the waterproofing capability of the printed material.
4. **Solvent Compatibility**: The compatibility of each binder with various solvents was examined, as this affects the homogeneity and printability of the paste.
5. **Flammability**: The safety of the binders was assessed by examining their flammability, an important factor for safe handling and processing and later application.
6. **Applications and Prior Use in 3D Printing**: The past applications of these binders, particularly in 3D printing, were reviewed to check for existing knowledge and ensure their potential in 3D printing.
7. **Price per Kilogram**: A comparison of the cost-effectiveness of each binder was made by considering their price per kilogram, which is important for the begin of a research project.
8. **Combinability with Other Materials**: The ability of each binder to combine with different fillers and solvents and other binders was assessed to see cross working would be possible.
9. **Attributes and Workability**: The physical and chemical attributes of the binders, such as viscosity and drying time, were examined to ensure they would perform well during the printing process.
10. **Workplace Safety and Waste Stream Considerations**: Safety risks associated with handling each binder and the implications for waste management were considered, aiming to minimize hazards and environmental impact.

11. **Shrinkage and Drying**: The extent to which the binders shrink upon drying was evaluated, as excessive shrinkage could compromise the accuracy of the printed objects.
12. **Origin and Availability**: The source and availability of the binders were considered, with a preference for sustainable and readily available options to align with the project's goals.

This thorough evaluation helped to identify the most promising binders that meet the necessary criteria for successful 3D printing with biobased materials. Detailed findings from this assessment are documented in Appendix List 1.

A meeting with material scientist Stephen Picken and archaeological adhesive scientist Geeske Langejans was done to gain professional insight and advise. This has resulted in an expanded list and but also complemented with a variety of practical and feasible ideas (see app. List 2). However, due to time constraints and the need to narrow the focus, more concrete boundaries were set for the commence of actual binder testing.

In the case of this research, the final selection criteria of the material traits for binder choice were:

- it should be workable at room temperature,
- no heat or pressure treatments should be necessary for handling the paste,
- material had to be readily available.

Furthermore, the final paste should have these traits:

- be highly water resistant,
- possess strong structural integrity,
- be printable and biobased.

After consideration of all these criteria the final biobased binder candidates were latex milk, cooked flaxseed oil (together with pine resin, cork), lignin and casein protein.

The evaluation criteria the binder exploration try-outs were:

- Workability while making the paste,
- Hand extrudability,
- Shape fidelity.

Pre-Testing and Binder Exploration

To get an initial understanding of which binders might work well in 3D printing pastes, a focused approach was taken. Calcium carbonate ($CaCO3$), derived from ground-up oyster shells, was used as a standard filler. This allowed for a consistent baseline, making it easier to identify binders with the most potential for further exploration and development.

Each binder was gradually mixed with its solvent and weighed until a homogeneous, liquid, or gooey, gel-like substance is created. From this moment on calcium carbonate was gradually added to the binder/solvent mixture and weighed until it seemed like the created paste had the viscosity and texture of being able to maintain its shape when untouched but also still be freely movable when touched or pressure being applied. Water was added and weighed when mixture seemed to dry or hard. Every recipe was conducted as trial and error and worked with weight percentage (%w). The desired texture was like wet clay or toothpaste.

When the consistency is considered ready it was tested with hand printing. The created paste is put into a syringe and extruded by hand. In this extrusion process the material is examined by the guidelines of:

- extrudability and shape fidelity.

The performance of extrudability entails how easily and smoothly the paste comes out of the syringe and how much applied pressure is needed to get a running extrusion. Lines are drawn from the paste and these lines are stacked on top of one another.

Then the shape fidelity is examined. If the stacked lines completely merge into each other and form into a big ‘’blob’’ the is no fidelity. A slight merging of lines is desired in which the paste maintains its extruded shape well but is still able to merge with the other layers to form a strong adhering bond (see Fig. 1).

Based on the performance the material was tweaked; when it seemed to dry water was added, when it seemed to wet or runny more filler or binder was added. Every addition is weighed, and the changes are protocolled.

Once hand extrudability and shape fidelity were of satisfaction and proved potential, the materials were tested in a 3D Printer (Creality 3D Ender-5, modified through Junai DIY-extrusion kit). A standard shape of a triangle with 15 layers, (height: 20 mm, 30 mm triangular contour), with the same printer settings of extrusion flow and movement speed was used to assess the performance of each paste (see Fig. 1). Again, based on these outcomes, the recipes were tweaked and retried.

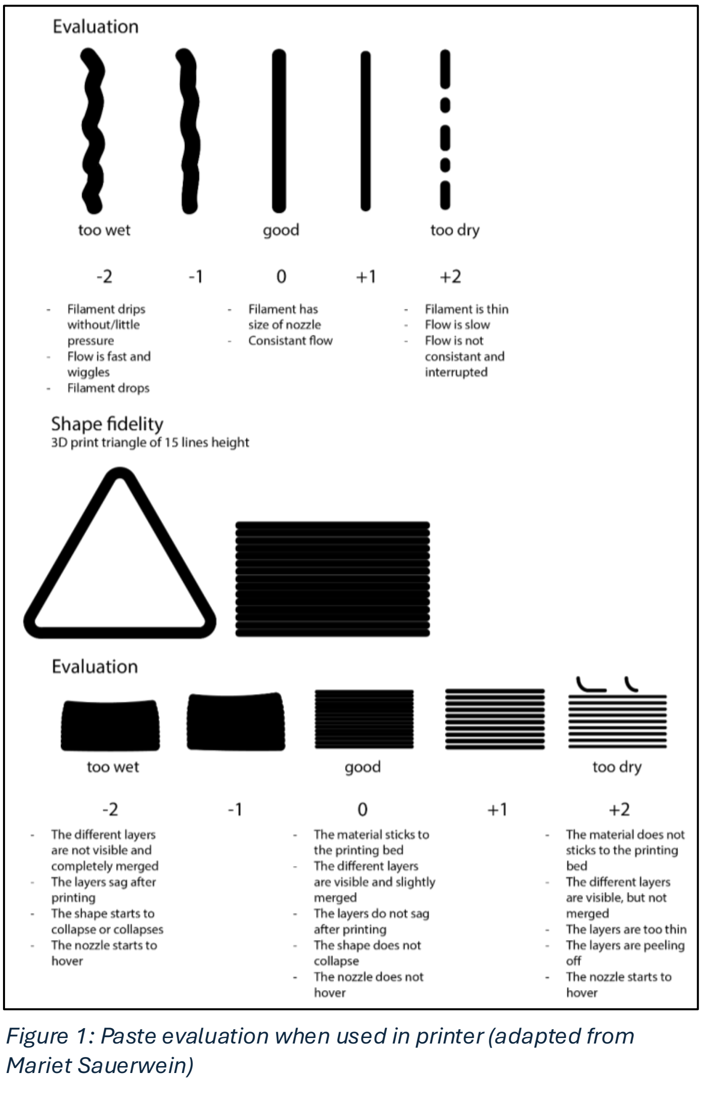


Figure 1: Paste evaluation when used in printer (adapted from Mariet Sauerwein)

Testing of successful Binders with different fillers

The binders that identified to be most promising from the binder exploration will be tested with a variety of fillers. A standard amount of binder mix is created and gradually X g amount of filler is added and assessed as described in Chapter: “Pre-Testing and Binder Exploration”.

Further Exploration of Casein Glue as Binder

Exploration of fillers for Casein Glue

To explore the different amount and combinations of fillers using casein glue as a binder, different methods were used as an approach. As a starting reference base for every method, the same standard recipe of casein was used (see Chapter: “Casein glue recipe”). This always resulted in 11.2 grams of made casein glue.

Casein glue recipe

The recipe of casein glue has been taken and adapted from pigment reseller: Sehestedter Naturfarben (https://www.sehestedter-naturfarben.de/blog/rezepte/rezept-kaseinleim). All materials were bought at the chemical reseller Labshop.nl

Materials:

- Casein powder (O6320-1000 Caseïne 1 KG, Labshop)
- $CaOH_2$ (P433-500 Calciumhydroxide - gebluste kalk - 500 gram, Labshop)
- Ground cork (O59792-500 Gemalen Kurk 0.5 - 1 MM, Labshop)
- Potassium silicate (O77750-1000 Kaliwaterglas 28/30 - 1 L, Labshop)
- H_2O (tab water)

Recipe for around 11.2 g of casein glue:

- 2 grams of casein powder are mixed with 5 grams of water in a beaker, stirred and left to swell for 2 minutes.
- In the meantime, 0.8g $CaOH_2$ is dissolved into 2g of water in a separate beaker.
- After the 2 minutes, the swelled casein is added into the dissolved $CaOH_2$ and stirred until a gooey homogenous paste is created.
- Then 1.4g of sodium silicate is added and stirred.
- The result is 11.2 grams of casein glue that can be used as a binding agent.

Every component used as a filler is ground up to the smallest scale with the Mockmill 200

Explorative Feel

The first method is to go by feel as described in Chapter: “Pre-Testing and Binder Exploration”.

Systematic Approach (extrusion saturation test)

To eliminate the influence of added water and rely solely on the water content present in the casein glue, 11.2 g of casein glue was used as the starting point. This approach isolates the number of fillers as the only variables in the paste-making process. Gradually, X g of filler was added, and the behaviour of the paste was tested and evaluated.

First the fillers were independently added until saturated (until hand extrusion was not possible anymore). This resulted in saturation limits of cork and $CaCO_3$ with the given 11.2g of Casein glue as starting point.

Secondly this test was done in combination, to assess cross workings between Cork and Calcium carbonate. In the second approach cork saturation steps / ranges were used as starting point to add calcium carbonate until saturation is reached because cork proved to be essential for shape fidelity from prior testing.

Method:

- 10g Casein mix + gradually add X g Filler

Testing of Water absorption

The experiment aimed to evaluate the water absorption properties and material behaviour of three different pastes—Cork, Reef, and Oyster Shell—by analysing their water content at various stages, their percentage of water absorption, and physical changes observed before, during and after exposure to water.

$Wa = \frac{m_{2-}m_1}{m_1} * 100$, where:

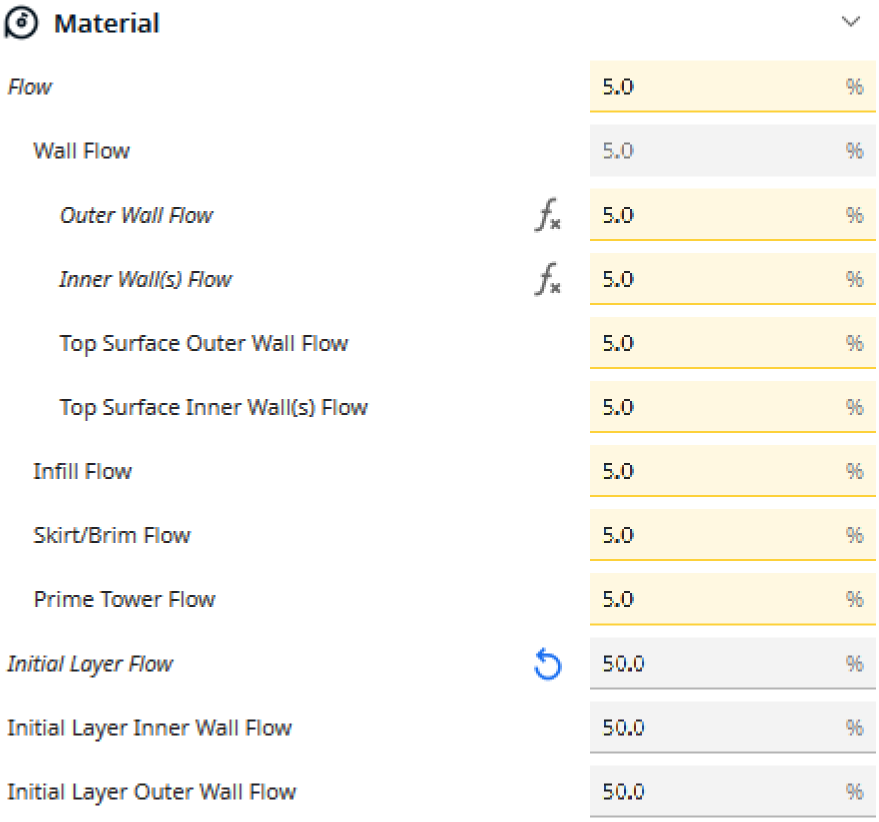
Wa= Water absorbing capacity (%)
m_2= mass of material saturated with water (g)
m_1= mass of dry material (g)

To test the water absorption capability of each paste, at least 5 standard triangles (see Testing of binder exploration) of each paste were printed and the fresh weight right after printing was recorded. 24h, 5 days and 6 days after the print, the weight was recorded to ensure the paste being fully dry before proceeding with submerging. Then samples were submerged in glasses filled with water for 24 hours, taken out, damp dried and the soaked weighed was recorded. After 24 hours the samples were weighed again for their final dry weight and water loss and reuptake are calculated from the averages.

Print Settings

Models were first designed in Rhino8 or Fusion Autodesk and imported into Cura as an .stl file to create the necessary GCode for the Creality 3D Ender-5 Printer. After a lot of printing and tweaking the final print setting used are the ‘’PasteExtruder_Ender3’’ setting available at (XY) but modified to:

- Initial layer Height: 0.7 mm
- Flow: 5 % (for all associated flow settings)
- Initial Layer flow: 50% (for all associated initial layer flow settings)



Material

Flow	5.0 %
Wall Flow	5.0 %
Outer Wall Flow	5.0 %
Inner Wall(s) Flow	5.0 %
Top Surface Outer Wall Flow	5.0 %
Top Surface Inner Wall(s) Flow	5.0 %
Infill Flow	5.0 %
Skirt/Brim Flow	5.0 %
Prime Tower Flow	5.0 %
Initial Layer Flow	50.0 %
Initial Layer Inner Wall Flow	50.0 %
Initial Layer Outer Wall Flow	50.0 %

Figure 2: Print settings in Cura Software

Results and Discussion

The results and discussion section are written in one chapter as this creates a more coherent story line and presentation of the process. It also shows the decision making that has taken place in the exploration of paste making.

Selection of Binders and testing their potential / Testing of Binder Exploration

For all exact recipes see Appendix (Binder trials)

Cooked Linseed Oil / Pine rosin

Cooked Linseed Oil has been chosen as a potential binder due to it being the binder in conventional Linoleum flooring and being renewable, non-toxic, long lasting and biodegradable (Gorrée et al., 2002). In process of linoleum making, it is combined with calcium carbonate, pine resin, jute backing and cork. That also gave way to the opportunity to combine these materials with the other potential binders.

Testing of binder:

The cooked linseed oil has been progressively mixed with calcium carbonate until a homogenous paste has been reached and tested with the hand syringe. The hand extrusion has posed some difficulties as sometimes the extrusion went well and at random times, strong blockages inhibited the further extrusion. The resulting extruded material was quite elastic, oily, and rubber-like, did not possess great fidelity and did not seem to harden after the first day and nor after two weeks. (See Appendix binder trials Exp No.:3)

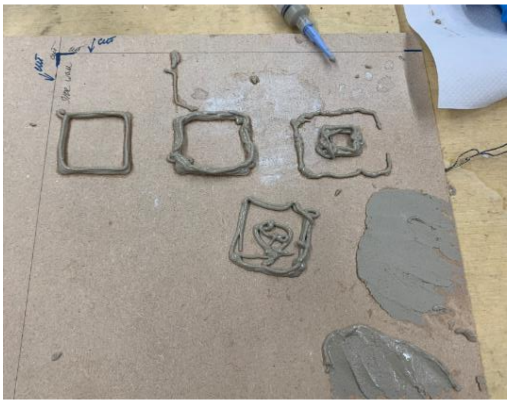


Figure 3: Handprints linseed oil test

A second approach was attempted which is similar to the recipe of linoleum flooring. Therefore, cooked linseed oil, pine resin, ethanol, calcium carbonate and wood flower were combined. Is has resulted in a somewhat printable paste which however posed similar challenges to the prior try-out: the extrusion was unreliable and clogged at times, the paste seemed to not be completely homogenous and seemed like a non-Newtonian fluid in which solid and liquid phase seemed to separate at times. Therefore, cooked linseed oil was discarded as a potential binder but there was still the pine resin to be tested. (See Appendix binder trials Exp No.:4)

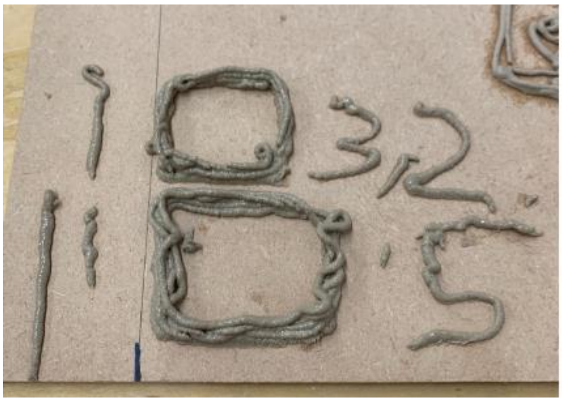


Figure 4: Handprints linseed oil test.

Pine resin:

Pine resin is a natural and waterproof product that was already available through the attempt of creating linoleum (see "Cooked Linseed Oil / Pine Resin). It can also be used to create a natural glue (https://www.instructables.com/How-to-Make-and-Use-Glue-From-Pine-Resin/) and has found application as a binder in novel biobased composite materials (https://designwanted.com/composite-materials-arrosia/) . Therefore, it was worth trying it out as a potential binder.

The solid pine resin was first dissolved with ethanol in a liquid. The calcium carbonate was progressively added. The final paste was unable to homogenize into a paste but rather stayed separated in a liquid and solid phase, like wet beach on a sand. Furthermore, the extrusion was near impossible, as only the resin/ethanol was extruded but the solid calcium carbonate stayed in the syringe. Furthermore, a mess was created while working with it and all used materials were near impossible to be cleaned. The next day the material was very hard but also brittle and therefore it was concluded to discard pine resin as a potential binder (See Appendix binder trials Exp No.:2).

Figure 5: Dissolved pine resin in ethanol

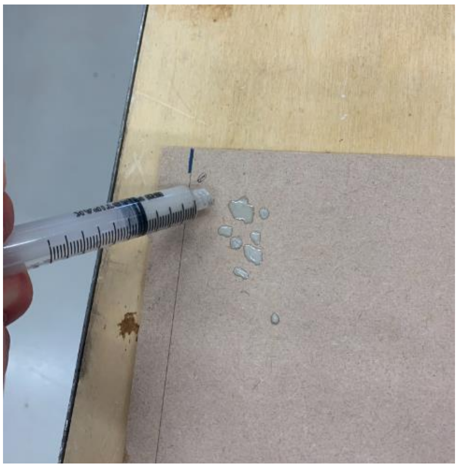


Figure 6: Intent to extrude dissolved pine resin mixed with oyster shell powder

Lignin

Lignin works as a natural binder in plants holding the cellulose fibres together and thereby providing rigidity and strength. (Mili et al., 2022). It is inherently hydrophobic, and it currently is a huge waste stream from the paper industry. Several studies have highlighted the versatile uses ranging from applications as wood adhesives, 3D printing, epoxy asphalts, coatings, plywood. (Bierach et al., 2023; Liebrand, 2018)

<u>Testing of binder:</u>

Organosolve Lignin was mixed with calcium carbonate and ethanol as an organic solvent. The resulting paste had a very similar consistency to a sort of liquid tar. It extruded well but possessed no fidelity at all. The drying process was very rapid, probably to ethanol evaporating quickly. The workability was extremely messy, and the used utensils were not able to be cleaned (See Appendix binder trials Exp No.:14).

Figure 7: Handprints from lignin/ethanol test.

The second approach was to combine organosolve lignin with acetic acid as an organic solvent. A tar like substance was created, which had no fidelity and left an absolute mess. As no immediate potential was seen considering the available time for further paste development, lignin had been discarded from further research (See Appendix binder trials Exp No.:16).

Figure 8: Handprints from lignin/acetone test

Latex

Latex has natural adhesive properties and flexibility. It is derived from natural sources, mainly from the sap of rubber trees (*Hevea brasiliensis*). It consists mainly of polyisoprene unit giving it its elastic properties. Another characteristic is its natural water resistance which can potentially be used either as a binder or perhaps as a coating (Nakanishi et al., 2019).

Testing of Binder:

The acquired Latex milk was already in a liquid state and thereby no water needed to be added in the beginning. 5.5 g of Calcium carbonate (from ground of oyster seashells) were added to 5.1 g of liquid latex milk. This mixture has quickly turned into a semi solid, semi-jelly chewing-gum like state, which could not be further mixed or shaped. After the addition of 2g of Latex no mixing between the Latex/$CaCO_3$ clump and additional Latex happened. To see whether, it could be made soluble 2g of ethanol were added but still no mixing or change of the clump state were apparent. Due to these very apparent difficulties in workability this binder had been eliminated from further research (See Appendix binder trials Exp No.:1).

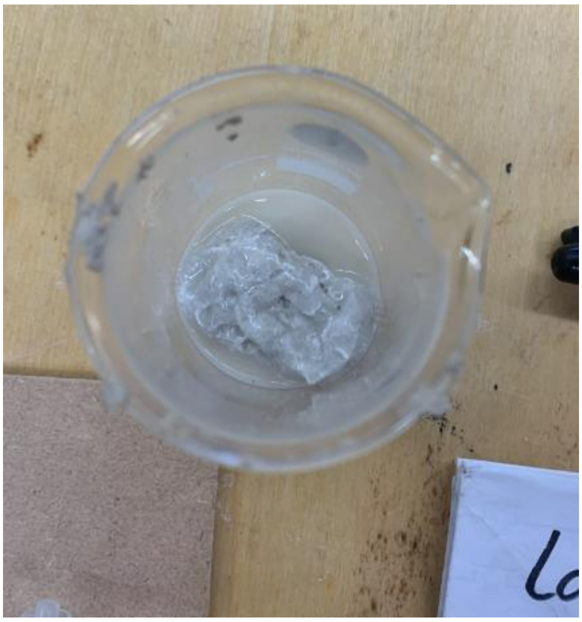


Figure 9: Mixing latex with oyster shell powder

Casein

Casein is a family of phosphoproteins predominantly found in mammalian milk. They make up around 80% of the proteins in cows' milk and about 20-45% in human milk. Their structure is unique in such a way that it can be formed into a gel or network of protein fibres when coagulating which can be leveraged for binding purposes (Guo & Wang, 2016). Historically, casein has been used a natural adhesive due to is waterproof and heat resistant binding properties. When mixed with an alkaline medium (like lime water) casein glue is formed and has found application in ancient Egyptian times as mortar and later in the Middle Ages in wood working, instrument construction, later in bookbinding and even aircraft construction in the first world war before the rise of synthetic adhesives (Guo & Wang, 2016; U.S. Department of Agriculture, 1961; Vienna et al., 2014). The oldest detailed recipe for making a glue from curd and lime comes from a manuscript from the High Middle Age. Casein obtained from curd or cheese produces a glue by reacting with slaked lime or other alkaline substances. The major disadvantage of such a glue is its short pot life (workability time). This period can be increased by reducing the lime content, but only at the expense of the glue's strength and water resistance or by adding Potassium silicate. The advantage in this glue lies in being water soluble during production stage, while being water resistant and water insoluble after curing (U.S. Department of Agriculture, 1961). Furthermore, it is long lasting, durable, waterproof, heat resistant, biodegradable, and environmentally-safe (Strube et al., 2015; Udic et al., 2003).

Testing of binder:

The prepared casein glue was mixed with calcium carbonate and water and resulted in a mediocre paste form, with once again a bit of a separation between liquid and solid state, being like wet sand. It had very good extrudability but and a mediocre fidelity but not yet the desired state. It showed potential so it was decided to experiment with an array of other fillers to see how it would perform and especially because of its use as wood glue, cellulose rich compounds were of interest (See Appendix binder trials Exp No.:5-6).

Figure 10: Handprints from casein glue and oyster shell powder

Testing of casein binder and cellulose based fillers

Combining the casein glue with **wood saw dust powder** has resulted in gooey, extrudable paste, which maintained fidelity to a certain extent. However, in the drying process the shape has changed immensely, presumably due to high water content, which evaporates in the process. Therefore, it was concluded to discard it (See Appendix binder trials Exp No.:9).

Figure 12: Mixing casein glue with wood saw dust.

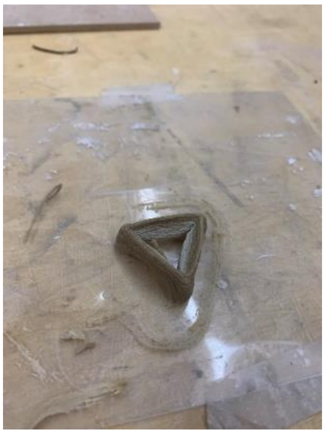


Figure 11: Resulting triangle print

Olive pit powder in combination with casein glue turned into a very gooey, jelly chewing gum like paste which was very hard to work with and changed shape a lot in the drying process. There it was excluded from further research (See Appendix binder trials Exp No.:10).

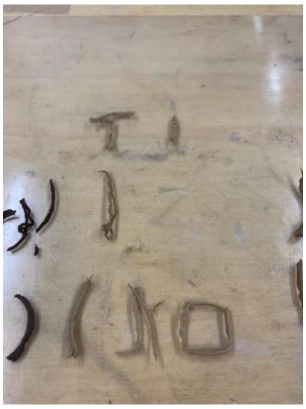


Figure 13: Casein glue with olive pit powder handprints

When working with casein glue and **cork** and added water the result was a paste with very good workability, extrudability and a fidelity that enabled to print the first triangle in the 3d printer (See Appendix binder trials Exp No.:8).

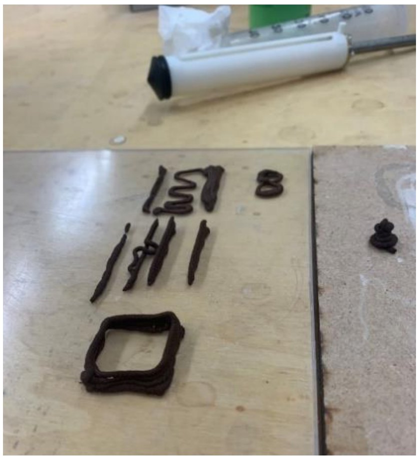


Figure 14: Handprints of first casein glue / cork/ oyster shell powder recipe


Figure 15: Print with printer of first casein glue / cork/ oyster shell powder recipe (semi-dry)

However, during the drying process, it has changed in shape quite a bit and it was not a very strong material and so the idea arose to combat that by reducing the percentual water content by adding calcium carbonate and thereby also increasing the strength and shape fidelity of the paste. From several try outs of "explorative feeling", two well working Cork:CaCO3 ratios were discovered. The addition of cork gave the paste a great workability and fidelity, changing it from being like wet sand into a strong, shape maintaining homogeneous paste with good extrudability (See App. Exp: 18)

Around 1:3 and 1:13 ratio:

Table 1: Material contents of discovered cork and oyster shell pastes

Paste Type	Casein Mix (g)	CaCO3 (g)	Cork (g)	added H20 (g)	Total (g)
Cork (1:3)	11.2	4	1.5	0.8	17.5
Mass %	64.00	22.86	8.57	4.57	100
Oyster shell (1:13)	11.2	18.75	1.45	5.05-5.5	36.85
Mass %	30.39	50.88	3.93	14.79	100

The 1:3 ratio will be referred to ''Cork'' Paste and the 1:13 as Oyster shell.


Figure 17: Fresh print of 1:3 ratio sample.

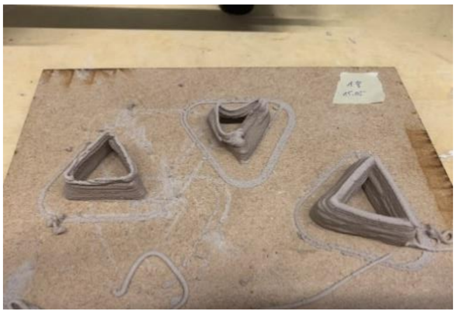


Figure 16: Fresh print of 1:13 ratio samples.

Explorative Feel

In the collaborative process with BESE, we were provided with a sample of their reef paste which mainly consist of ground up oyster seashells ($CaCO_3$), an unknown confidential but mainly water-resistant binder, and certain chemical cues that facilitate the settlement of oyster larvae.

This ground up "reef powder" has been used equivalently as the oyster seashell powder in testing and experiments.

1:3 Ratio and 1:13

Table 2 displays the final discovered material contents of the cork, reef and oyster seashell paste that have resulted from the explorative feel method.

Table 2: Material contents of cork, reef, and oyster shell paste

Paste Type	Cork	Reef Paste	Oyster shell
Binder (Casein) content of initial paste (mass %)	16	7.6	7.6
Filler ($CaCO_3$) content (mass %)	22.86	50.88 (+- unknown binder)	50.88
Filler (Cork) content (mass%)	8.57	3.93	3.93
Water content (mass %)	52.57	37.58	37.58

Systematic Approach

Extrusion Saturation Test

To test different ratios of cork to calcium carbonate without the extra variable of added water content an initial saturation test was for cork and calcium carbonate in casein glue was done. Starting with the 10g of casein glue, cork was progressively added and assessed for good extrudability and fidelity until extrusion was not possible anymore becoming unworkable and saturation being reached. The same has been done for casein glue and calcium carbonate. This resulted in a range of 1.5g of cork for 10 grams of casein glue and 15g of $CaCO_3$ for 10g of casein glue. Knowing both saturation limits it was possible to systematically try different ratios and assess their performance.

The 1.5g of cork were divided into 10 steps to be individually assessed with added $CaCO_3$ until saturation is reached. This resulted in:

Figure 18: Saturation testing: assessment of fidelity in handprints

Table 3: Table of Cork and $CaCO_3$ saturation experiment

Cork (g)	$CaCO_3$ (g) (add until saturation)	Fidelity	Printable	Ratio Cork:$CaCO_3$
0	15	🟥	🟥	
0.15	14.09	🟥	🟥	1 : 93.9
0.45	12	🟥	🟥	1 : 26.7
0.6	9	🟥	🟥	1 : 15.0
0.75	7.5	🟥	🟥	1 : 10.0
0.9	5	🟥	🟥	1 : 5.6
1.05	2.75	🟩	🟧	1 : 2.6
1.2	1.25	🟩	🟧	1 : 1.0
1.35	0.75	🟩	🟧	1 : 0.6
1.5	0	🟥	🟥	1 :0

This resulted in only pastes with a cork content between 1.05g and 1.35g per 10g of casein glue being workable, extrudable, and able to maintain fidelity. Once these initial ratios were established, the goal was to refine them further and determine more precise ratios.

However, during this process, the previously successful recipes and ratios became inconsistent and unreproducible (therefore printability indicated in orange in table 3). All pastes within the 1.05g to 1.35g cork range became excessively fluid and unable to maintain their shape. To understand the cause of this unreliability, a series of experiments was conducted and will be discussed in the next chapter (see Paste Inconsistency and other challenges).

Due to time constraints and the success of prints based on the “exploratory feel" method, it was decided not to continue with the saturation method experiments. However, this approach could be revisited and adapted in the future. The idea behind the saturation method was to find a systematic and simplified way of determining effective ratios between cork and calcium carbonate by minimizing the variable of extra water. A key limitation of this method was the restricted water content available in the casein mixture, which limited the range of ratios that could be tested. As a result, the successful ratios found through exploratory methods might not have been identified using this approach. Therefore, while the saturation method could be useful for fine-tuning once a working ratio is established, the exploratory method may be more effective for initial discovery.

Paste Inconsistency and other challenges.

A variety of assumptions have been proposed to explain the inconsistent and unreliable behaviour of the paste that occurred during the saturation testing. The two main factors considered were:

1. The importance of using clean beakers.
2. The swelling time of casein.

In some instances, cloudy residues were observed in beakers containing calcium hydroxide residues. Even after washing, slight films were still visible once the beakers dried. Additionally, casein is not water-soluble but can swell to a certain extent when exposed to water. During the saturation testing, time constraints may have led to insufficient swelling time, which could have been overlooked.

To investigate this, two experiments were conducted to assess the impact of:

1. Different calcium hydroxide ($Ca(OH)_2$) conditions in beakers.
2. Swelling time on casein's consistency and printability.

and its effect on consistency and printability.

Experiment on the Importance of Clean Beakers and Casein Swelling Time

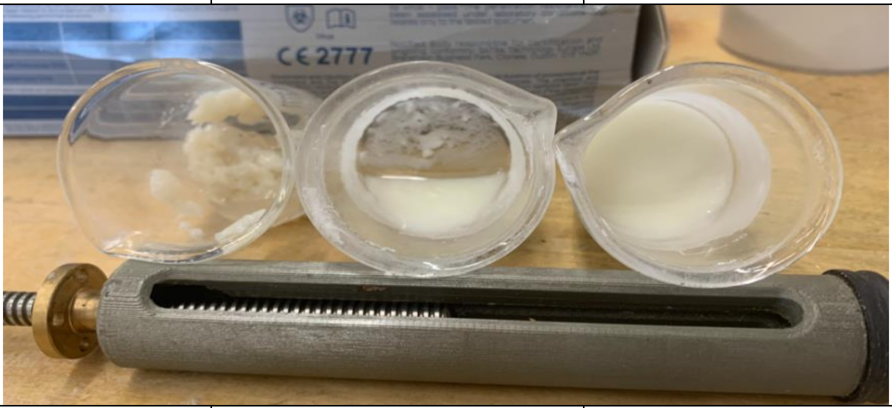
Three beakers with different conditions were used in the experiment. First, 2g of casein and 5g of water were allowed to swell in each beaker. Then, glue was created, followed by the addition of filler to form the paste, which was subsequently tested for printing behaviour. A working recipe from a previous test, with no additional water, was used to ensure consistency.

Used Recipe: Casein glue: 11.2g, Cork: 1.5g, $CaCO_3$: 4g

- The first beaker contained 10g of calcium hydroxide ($Ca(OH)_2$).
- The second beaker had slight residues of calcium hydroxide due to inadequate washing.
- The third beaker was thoroughly washed, leaving no visible film.

The experiment was conducted three times, varying the swelling time at 30 seconds, 2 minutes, and 10 minutes.

Table 4: Testing of influence of clean beakers and swelling time

	10g Ca(OH)2	**Slight Ca(OH)2 residue**	**No Residue**
Beaker before			
Addition of Casein and Water (2 minutes)			
Swelling	**2 minutes:** Clump formation right away, clump and water clearly separated and cannot mix, no swelling occurring. **10 minutes:** not performed **30 seconds:** not performed	**2 minutes:** High water phase with clumps, swelling occurring slightly **10 minutes:** Less swollen, more free water **30 seconds:** Less swollen, more free water	**2 minutes:** Swelling happens very well, no free moving water **10 minutes:** More swollen almost no free water **30 seconds:** More swollen, a little free water
Creation of casein Glue	**2 minutes:** Not possible to create glue **10 minutes:** not performed **30 seconds:** not performed	**2 minutes:** Very liquid casein glue **10 minutes:** worked fine **30 seconds:** worked fine	**2 minutes:** Much gooier **10 minutes:** worked fine **30 seconds:** worked fine
Creation of paste (adding of filler of filler)	**2 minutes:** Not possible to create paste **10 minutes:** not performed **30 seconds:** not performed	**2 minutes:** Very movable and low viscosity **10 minutes:** Good texture but slightly dry **30 seconds:** quite gooey	**2 minutes:** Paste has much higher viscosity and fidelity **10 minutes:** Good texture but slightly dry **30 seconds:** Very gooey (very
Print attempt	**2 minutes:** not attempted **10 minutes:** not performed **30 seconds:** not performed	**2 minutes:** not attempted **10 minutes:** somewhat worked **30 seconds:** Way too dry to print	**2 minutes:** not attempted. **10 minutes:** too dry and too gooey **30 seconds:** Way too dry to print

The experiment demonstrated several factors which can be attributed to inconsistencies in the paste's behaviour. Both the assumed cleanliness of the beakers and the swelling time of the casein showed to influence the consistency, viscosity, and printability of the paste.

The thoroughly cleaned beakers allowed for optimal swelling of the casein with better fidelity and more printability. This goes to show the importance of using strictly clean equipment in the paste making process to avoid contaminations from the CaOH2 that might disrupt chemical processes, are essential for creating a reliable paste.

Furthermore, the swelling time of the casein also influenced the result of the final paste. A longer swelling time resulted in a thicker and more viscous paste. However, this also notably effects the workability of the paste as being too viscous results in unprintability. Additionally, it must be noted, that the recipe used to make the pastes for this experiment were based on prior successful prints, which were conducted some months before in spring during cooler room temperature conditions compared to the time of this set up in summer.

Therefore, there were difficulties achieving good prints with the same recipe as almost all the pastes resulted in being too dry, despite varying conditions. This leads to the assumption that the air temperature either causes water to evaporate faster from the paste or it reduces the setting time of the casein glue through which is starts to polymerize faster. However, in the continuation of the research the used recipe also proved to be suboptimal, and therefore this experiment could be redone with a recipe that works with certainty in the future.

Other factors that emerged in the discovery process of paste making that played out to be crucial were the flow extrusion speed of the printer, the movement speed of the nozzle, the diameter size of the nozzle, initial layer height of the first line, the individual layer height between printed lines and room temperature.

This underlines that the same recipe can behave differently under varying external circumstances (e.g. When room temperature rises, more water must be added, or a smaller nozzle diameter is wished to be used and the paste must be liquified etc.) and must be adapted adequately to conditions or always be performed under strictly the same conditions. This makes it difficult to provide a very clear framework to work in and always requires independent adaptive measures.

To understand the binder even better it is recommended to alternate compositions of all constituents that make up the casein glue. Higher CaCOH2 content is suggested to improve the water resistance but would also cause the glue to gel faster and shorten the working time (Hadert, 1937). Additionally, potassium silicate increases workability but could also increase the water resistance of the binder. Varying these components might lead to an array of binder compositions that are applicable to different conditions and possess a variety of traits (U.S. Department of Agriculture, 1961). Furthermore, finding a balance for great printability within these traits could pose a future challenge as well.

Testing of Water absorption and comparison of pastes

Table 5: Percentual contents of binder, filler, and water for used pastes in water absorption experiment.

Paste Type	Cork	Reef Paste	Oyster shell
Binder (Casein) content of initial paste (mass %)	16	7.6	7.6
Filler (CaCO3) content (mass %)	22.86	50.88 (+- unknown binder)	50.88
Filler (Cork) content (mass%)	8.57	3.93	3.93
Water content (mass %)	52.57	37.58	37.58

The composition of each paste used in the water absorption experiment is outlined in Table 2. The Cork paste has a higher binder (casein) content at 16% compared to the Reef and Oyster Shell pastes, both of which contain 7.6%. The filler content, primarily calcium carbonate ($CaCO_3$), is significantly higher in the Reef and Oyster Shell pastes (50.88%) compared to the Cork paste (22.86%). The Cork paste also contains a notable proportion of cork (8.57%), which is more than double that in the other two pastes (3.93%).

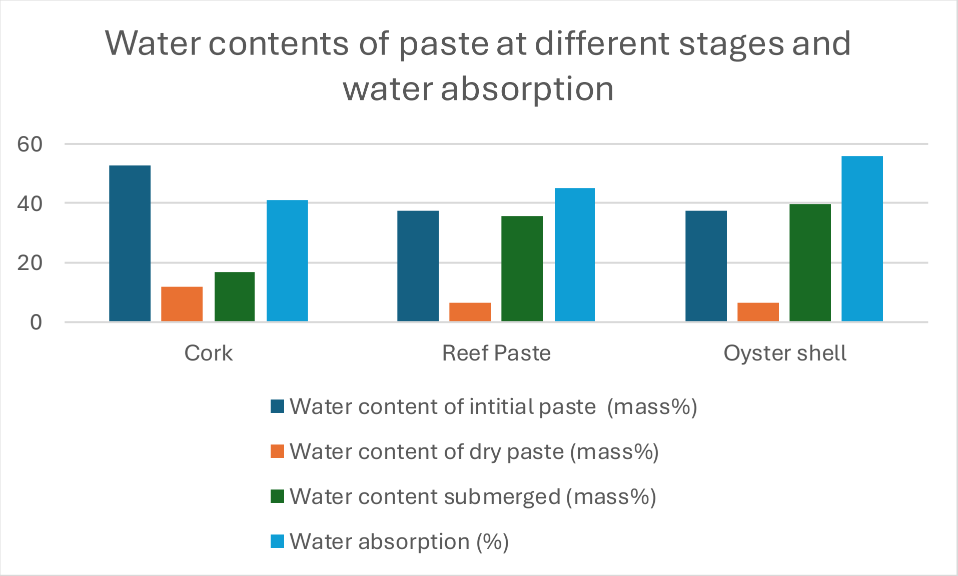


Figure 19: Water content of the pastes at various stages: initial wet state, after drying, submerged state, and re-dried state and water absorption

Figure 19 presents the water content of the pastes at various stages: initial wet state, after drying, submerged state, and the percentual water absorption capacity.

Table 6: Water contents of pastes at different stages and water absorption

Paste Type	**Cork**	**Reef Paste**	**Oyster shell**
Water content of initial wet paste (mass%)	52.57	37.58	37.58
Water content of dry paste (mass%)	11.82	6.69	6.64
Water content submerged (mass%)	16.99	35.85	39.89
Water absorption (%)	41.26	45.07	55.79
Fresh weight (g)	6.59	11.22	10.39
1st dry weight (g)	3.54	7.53	6.94
Wet weight (g)	5.0	10.92	10.83
2nd dry (g)	3.48	7.4	6.73

The experiment tested the water absorption for three different pastes: Cork, Reef and Oyster shell and changes within of samples were observed.

The Cork paste showed the lowest water absorption with 41.26% even though it's the paste initially containing the highest water content (52.57%). It is followed by the reef paste absorbing 45.07% and lastly the oyster shell paste (55.79%). This could be due to a couple of reasons.

Cork is naturally hydrophobic and water repellent (Engel et al., 2022) and its relative content in the cork paste is more than double of that than in the oyster and reef paste, which could explain the lower water absorption compared to the other two pastes. Furthermore, as seen in table 2, the percentual content of the water-resistant casein glue binder is 16%, twofold of what is contained in reef and oyster seashell paste (7.6% respectively), adding to its lowered absorption. This proportionally higher binder content could also explain why the cork paste is more rigid and harder when dry. However, the initially higher water content (52.57%), and thereby higher loss of water during the drying process leads to the formation of cracks and shrinkage, which cannot be seen with the oyster shell and reef paste. The reef paste has a slightly lower water absorption than the oyster shell paste even though being made up of almost the same components besides, the reef paste containing an additional unknown binder, which is mostly water insoluble (BESE), potentially contributing to its lowered water absorption.

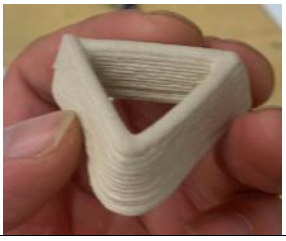
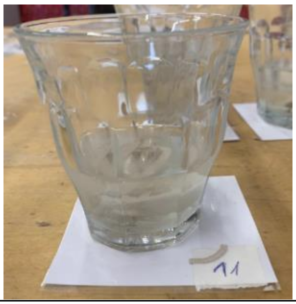
Calcium carbonate is known for its hygroscopic properties, the capability to absorb moisture from the atmosphere, further potentially explaining the higher absorption of water. (Barletta & Puopolo, 2020). Furthermore, the higher content of calcium carbonate in the oyster shell and reef paste could lead to a higher the porosity and allowing more water to penetrate and be retained. The proportionally higher binder content in the cork paste could lead to a higher density, further explaining its lower water absorption.

Despite the higher water absorption of reef and oyster shell paste, the display a balance of water resistance, durability, and structural integrity, making them suitable for environments with sporadic wet-dry cycles. Cork paste on the other hand, is a very tough and rigid material when dry, but cracks during drying, which decreases its applicability.

Interestingly, all pastes exhibited a reduction in mass from the first to the second dry state, possibly due to the leaching of water-soluble components during submersion, which might explain the yellow and in transparent water changes in submerged reef and oyster shell samples (see table 7). Additionally, the Oyster Shell paste weighed more after submersion than in its fresh state, indicating significant water uptake. It has to be noted that the samples were only submerged for 24 hours and redry weighed was recorded after 24 hours. The samples might have not reached the fully saturated nor completely dry state after that time and further tests should consider these aspects and consider longer periods of exposure.

For future research, additional mechanical tests such as compression and bending tests are recommended to comprehensively evaluate the material properties of these pastes. Investigating the biodegradability and susceptibility to bacterial and fungal mold growth will provide insights into their environmental stability. Furthermore, crosslinking experiments could be explored to enhance the biodegradability and water resistance of these pastes, making them more suitable for a wider range of applications. Ideas for future research could be to use biobased latex as a water proofing coating or a coat of potassium silicate, which is already used in the casein mix as a prolonger of workability agent. Potassium silicate is used as a sealant of plaster, masonry, and natural stones from weather influences through the occurring silification. Furthermore, it is used for sealing the surface layers of concrete, increasing wear resistance and decreasing capillary water absorption by 80% (S. A. Wyrzgol, 1999).

Table 7: Observation of samples during water absorption testing

Stages	Cork	Reef Paste	Oyster Shell
1st dry state	dark brown colouring, mostly deformed shape high shrinkage triangles started to show cracks at corners, yet very rigid and hard to break 	Very smooth surface once dry, smoother than oyster shell paste Comparable to oyster shell in terms of strength and durability No crack formation visible 	Once dried, no cracks visible, very strong and stable, durable Rougher surface texture than reef paste No crack formation visible 
Submerged state	No dissolving to be seen	when submerged a film accumulated on water surface and water became cloudy/intransparent 	When submerged water turned yellow but stayed clear 
Saturated state	Got very flexible but not brittle, however still easily breakable when pressure applied.	still very hard but breakable when pressure applied, material can be scratched off a little bit	still very hard but breakable when pressure applied, material can be scratched off a little bit
2nd dry state	Majority of cracks have increased in size and a white layer formed (perhaps CaCO3) and totally changed appearance 	When dried again it returns to being very stable and durable material, no crack formation visible, soft texture vanished 	When dried again it returns to being very stable and durable material, no crack formation 

	Cork	**Reef Paste**	**Oyster Shell**
Advantages	Once dry very hard to break Lower water absorption	Less to no shrinkage Great fidelity More stability and strength when wet (even though more water absorption) Little to no crack formation during drying	Less to no shrinkage Great fidelity More stability and strength when wet (even though more water absorption) Little to no crack formation during drying
Disadvantages	Prone to cracking, deformation and shrinkage during drying, significant deterioration after water exposure.	Breaks easier than cork. Higher water absorption May release material into water	Breaks easier than cork Higher water absorption May release material into water
Possible applications	Applications where high rigidity when dry is needed but where water exposure is minimal, or where the material will be kept dry consistently	Applications requiring a balance of water resistance, durability, and structural integrity, especially in environments where exposure to moisture is frequent, but drying is expected afterward.	Applications requiring a balance of water resistance, durability, and structural integrity, especially in environments where exposure to moisture is frequent, but drying is expected afterward.

Collaboration with Biobased Creation and BESE

The collaboration between AMS and Biobased creations and BESE aims to explore the possibilities of using the newly created 3D printing pastes in the context of material development and form studies.

Collaboration with Biobased Creations

Together with Biobased Creations the aim is to potentially create planter pot façade modules for their living pavilion which will be exposed at Dutch Design Week 2024.

The desired material properties are supposed to be a rigid, waterproof structure that can withstand frequent exposure to humidity through rain and thereby wet-dry-cycles in an outside environment and the weight and dynamic growth of contained plants.

Figure 21: Sample that cracked during drying

Figure 22: Well dried sample

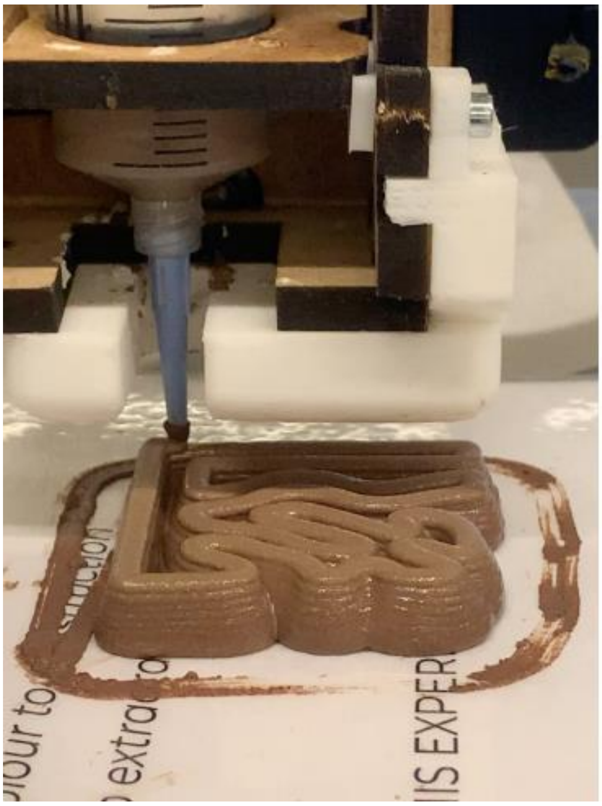


Figure 20: Sample from figure 22 in the printing process.

The cork paste has dried into an extremely hard material, but it is susceptible to cracking and shape deformation during the curing process, creating potential breaking points. Understanding how different shapes dry, identifying areas within the printed body where varying drying rates occur, and recognizing the forces at play could enhance the design and thereby create improved shapes broadening the paste's applicability. Furthermore, the water absorption tests showed the poor submerged performance of the cork paste, making it unsuitable for the application of an outside façade in which constantly wet soil and plants will be contained, making Indoor applications rather suitable.

Collaboration with BESE (Reef paste)

The collaboration between AMS Institute and BESE is centred around the innovative application of a newly developed reef paste material, designed specifically for creating sustainable and ecologically beneficial oyster reefs. Oyster reefs take up an important role in coastal marine ecosystems and coastal protection as well as acting as natural water filters and providing habitat for a variety of marine life.

In this partnership we tried to explore their reef paste together with the developed casein binder regarding possible 3D printed structures and if it can be used to enhance oyster reef restoration efforts, particularly in urban and coastal environments. Through 3D printing, we can produce intricate designs that enhance the functionality of these reefs, particularly in urban waters where visibility and integration with man-made urban structures are important.

Figure 24: High triangle sample from reef paste.

Figure 23: High sample made from reef paste, oyster reef prototype.

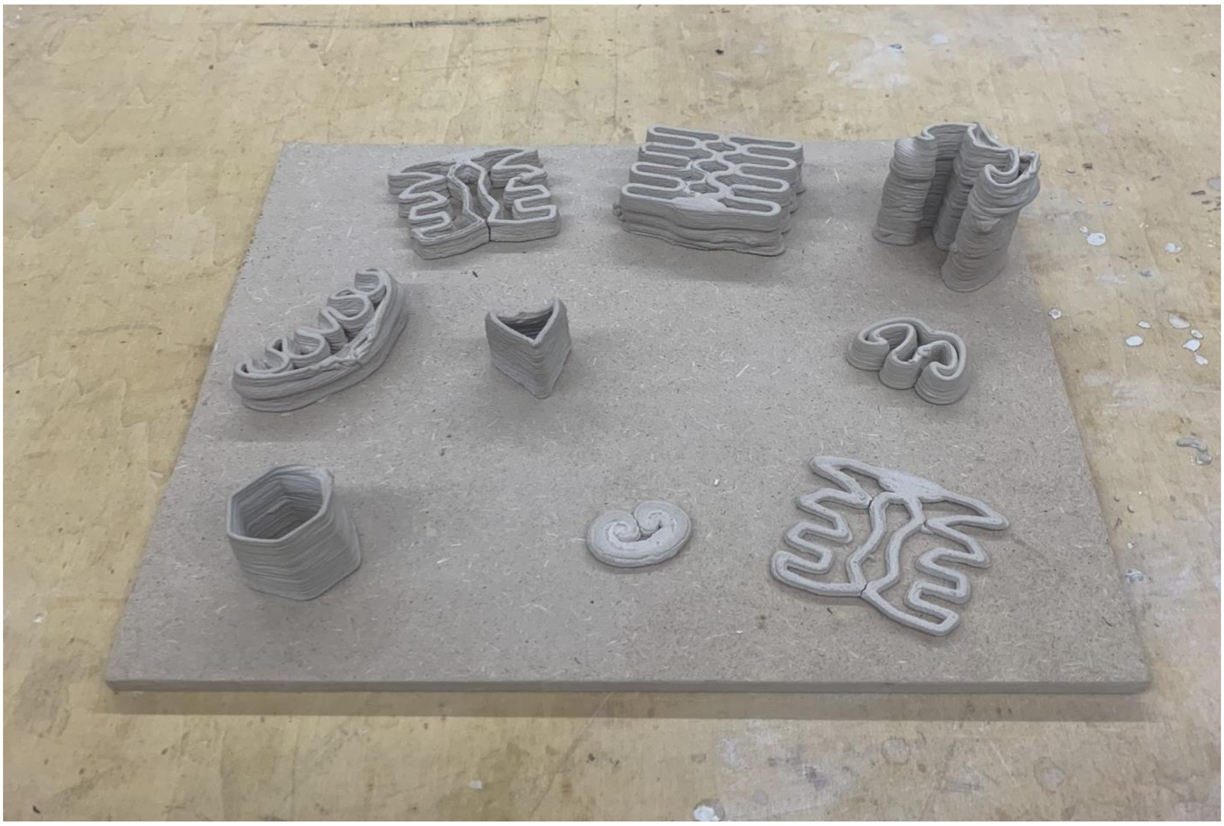


Figure 25: Collection of reef paste prototypes

Figure 27: Oyster reef protype

Figure 26: Oyster reef prototype

With the reef paste it was possible to achieve print heights of almost 10 centimetres as well as spanning of several centimetres across the X and Y plane. Unfortunately, it is not possible to print with an overhang and thereby create extra dimensions to the shape. However, a great variety of shapes is printable and thereby this paste has great potential for further exploration of different habitat restoration concepts. In the context of underwater structures, there might be challenges however, as the paste regains rigidity after drying again, but while being submerged it loses a lot of its integrity and tensile and compressive strength. Therefore, it would be recommended to apply this paste more in the context of the Biobased Creations as wet-dry cycles would be the determining environmental conditions rather than constant submersion and currents impacting he structure.

Ecological footprint of paste

The developed casein paste consists of Casein, water, calcium carbonate (from oyster seashells), cork, and potassium water glass. To bring the industry, change from petroleum based to biobased materials a step further it also important to be aware and informed of the origins and production steps from the used materials and to consider origin and production, energy intensity, environmental impact, and biodegradability.

Casein is a milk protein, which is won through enzymatic or acid-based precipitation. Its production is energy intensive as it requires the production milk which in turn requires the energy and recourse intensive dairy production (water, feed, and land). This further extends into the contribution of greenhouse emissions, soil and water pollution (Thomassen, 2008). However, casein is biodegradable making it more environmentally friendly than synthetic polymers and if for example only overdue milk used for production, it could be considered a waste stream and thereby significantly lower its ecological footprint. Another way to reduce the footprint would be to try and experiment with casein won through microbial fermentation, thereby stepping away from the dairy industry. Possible collaborations with “Vegan Cowboys” and “FORMO” (vegan cheese producers) are currently in discussion.

Calcium carbonate from old oyster seashells is waste recourse and a byproduct from the fishing industry, making it a form of recycling and upcycling. The collection and crushing of seashells require minimal energy compared to the industrial production of calcium carbonate from limestone. Furthermore, it is biodegradable and environmentally friendly (Owen, 2024).

Cork is harvested from the bark of cork oak trees and can regularly be harvested without the need of felling the tree. The cork extraction is relatively low in energy consumption. Additionally, the environmental impact is minimal as cork oak forest are vital for biodiversity and help preserve ecosystems. Cork is also biodegradable and can easily be recycled making it an eco-friendly material. The paste could be made even more sustainable if only cork from a waste stream is used for example from old wine corks. (Knapic et al., 2016)

Calcium hydroxide is won through slacking (controlled addition of water) to quicklime (calcium oxide). Quicklime is created by heating limestone (calcium carbonate) at high temperature at around 900 °C for longer periods and is also an essential part of energy intensive the cement industry. Furthermore, an environmental burden arises from the CO2 emissions that arise during the calcination of limestone. $Ca(OH)_2$ self however, is relatively harmless and often used in environmental protection applications, such as water treatment and soil improvement. Calcium hydroxide reacts with CO2 from the atmosphere and reverts back to CaCO3 which is biologically and chemically sable and poses no environmental issue (Mikulčić et al., 2016).

Potassium silicate is an aqueous solution of quartz and potash, using a calcination process that combines silica sand (SiO2) and potassium carbonate (K2CO3) at 593°C to 1260°C for up to 15 minutes, basically making it glass dissolved in water. It is an energy intensive melting process which further releases CO2 in the chemical reaction, both from energy consumption and in the chemical reactions. It is not biologically degradable however, chemically stable, being relatively inert in the environment and thereby not posing toxic effects and according to US Environmental Protection Agency Office of Pesticide Programs the environmental/ecological effects from potassium silicate are likely to be negligible (US Environmental Protection Agency Office of

Pesticide Programs, 2007). Furthermore, if potassium silicate solution dries out it turns into silica which is an element widely spread in nature (Summary, 2007; US Environmental Protection Agency Office of Pesticide Programs, 2007).

The development of the casein of the biobased casein paste shows the potential to reduce the environmental Impact by using biodegradable and recycled waste streams materials like oyster shell calcium carbonate and cork. Furthermore, all the other essential components are biologically degradable as well. However, the dairy industry contributes highly to greenhouse gas emissions and the production of calcium hydroxide and potassium silicate involve significant CO2 emission. Therefore, the search of new biobased materials requires careful consideration of their origins, production process and overall environmental impact. The materials have the potential to offer biodegradability and recyclability, but their production might still have a recourse-intensive and environmentally taxing background. There the dilemma lies in balancing energy and recourse demands with the ecological advantages of biodegradability.

Education

As part of this internship, I assisted in delivering courses on 3D printing biobased habitats. Two courses were conducted between February and May. The first course was a collaboration with students from AHK, Codam, and MADE, where the goal was to create birdhouses. The second course involved architecture students from AHK, who were tasked with designing habitats for aquatic insects.

The primary aim was to teach students the process of making biobased pastes, encouraging them to discover and bring their own materials, and to put themselves in the position of their assigned organism. They conducted biological research on their organisms' habitats, which informed their design of a shelter tailored to support the organism's life cycle. Additionally, students learned how to create a 3D computer model, use the relevant software, and operate the hardware to ultimately 3D print their designs.

My role involved providing biological advice and offering context on the criteria that are important or negligible for the animals' lives. Furthermore, I assisted in teaching how to create pastes, guiding students on what to look out for in that process, and helping with laser cutting, assembling, and printing structures to ensure successful final products could be presented.

This was a highly enjoyable experience, as observing how ideas and concepts are developed and turned into reality is, in my opinion, a very valuable process for humans, one that I deeply appreciate. Being able to assist in that process, helping to shape ideas and bringing them to life, was a rewarding experience, and I believe the students felt the same. Moreover, embedding early innovative concepts into education, even if those concepts are not yet fully developed, sparks ideas and ways of thinking in students, which can hopefully inspire them to invest in their own innovative ideas. To make novel concepts, such as using biobased materials in 3D printing, a widespread application, it requires the contributions of many people, ideas, and different approaches to build a solid foundation. By showing students the potential of this technology, we can ignite that mental spark and contribute to the wider adoption of currently emerging ideas.

Figure 28: Meeting during course with AHK, Codam and MADE students

Conclusion

Biobased materials offer a promising and eco-friendly alternative to conventional plastics in 3D printing. However, certain challenges—such as insufficient strength and water resistance—still hinder their effective utilization. Developing biobased pastes and identifying binders that ensure printability, mechanical strength, structural integrity, water resistance, and durability is crucial for their adoption and advancement in various applications. The goal of this investigation was to address these challenges by exploring natural binders that are waterproof, strong, and compatible with biobased fillers derived from waste streams. Additionally, the aim was to create methods that facilitate the development of biobased pastes for 3D printing and to collaborate with BESE and Biobased Creations to create prototypes from these pastes.

Initial binder research identified Latex, Linseed Oil, Pine Resin, Lignin, and casein glue as potential candidates. Through the “explorative feel” method, casein glue mixed with CaCO3 from oyster seashells emerged as the most promising binder. To explore alternative fillers to CaCO3, cellulose-based materials were screened, leading to the discovery that cork significantly enhances paste viscosity and workability. This improvement enabled successful prints that maintained their shape when wet—something that CaCO3 alone could not achieve. The trial-and-error process, or “explorative feel” method, led to the development of two well-functioning pastes with different cork-to-calcium carbonate ratios: a "high cork" paste (1:3) and a "high CaCO3" paste (1:13). Through collaboration with BESE, a "reef paste" was developed (1:13), in which oyster seashells were substituted with a reef restoration paste consisting of oyster shells, an additional binder, and chemical cues for oyster larvae settlement.

Additionally, the study aimed to develop a more systematic method for paste formulation. The "extrusion saturation method" was designed to exclude the variable of added water content and effectively explore the ratios between cork and CaCO3. However, the limited water available in the casein glue restricted the range of ratios that could be tested. Due to time constraints, this method was set aside in favour of the explorative feel method, which may be better suited for initial formulation discovery, while the saturation method could be valuable for fine-tuning established pastes.

Water absorption tests on the pastes revealed that the cork paste absorbed less water than the oyster shell and reef pastes. Despite being rigid and tough, the cork paste was more prone to cracking and shape deformation during drying. In contrast, the oyster and reef pastes demonstrated better water resistance, overall durability, and structural integrity, making them more suitable for environments with sporadic wet-dry cycles. Prototypes developed in collaboration with BESE and Biobased Creations showcased the first attempts at creating intricate designs with the oyster shell and reef pastes, highlighting their potential applications in oyster reef restoration.

The paste-making process also demonstrated that, even with a reliable and replicable casein glue paste formulation—which is inherently influenced by the binder, filler, and solvent formulation—various external factors can significantly influence the performance and print behavior of the paste. Factors such as equipment cleanliness, paste setting time, printer extrusion speed, nozzle movement speed, nozzle diameter, initial layer height, individual layer height between printed lines, and room temperature all need to be carefully considered, as they can each alter the performance of the paste.

Future investigation should focus on further exploring the range of cork and CaCO3 ratios through saturation testing to determine their effects on water resistance, printability, and durability. More filler materials can be tested with the casein glue, and a broader array of combinations could be investigated. The binder composition of the casein glue itself could also be experimented with to assess its effects on binding properties, as altering individual components of the glue could lead to improved water resistance, strength, and durability. Additionally, adding mechanical tests, such as compression and bending, as well as biodegradability tests, will provide deeper insights into material properties and help define further formulations for specific applications. Furthermore, research should explore ways to improve water resistance through crosslinking or the use of biobased waterproofing coatings such as latex or potassium silicate. Both the reef paste and cork paste lost structural integrity to a great extent under continuous wet conditions, indicating the need for further research to advance underwater restoration applications. For the cork paste, understanding the drying dynamics during the curing process is key to improving structural integrity and could extend the range of printable pastes. This could involve studying the drying process of different geometries and developing strategies to control moisture loss evenly across printed objects. Lastly, while the biobased casein paste shows potential for reducing environmental impact, it is important to critically assess the entire life cycle and production process of its components. Identifying binders that minimize greenhouse gas emissions and resource consumption while offering biodegradability and recyclability is crucial for achieving truly sustainable solutions for the future of 3D printing technology with biobased materials.

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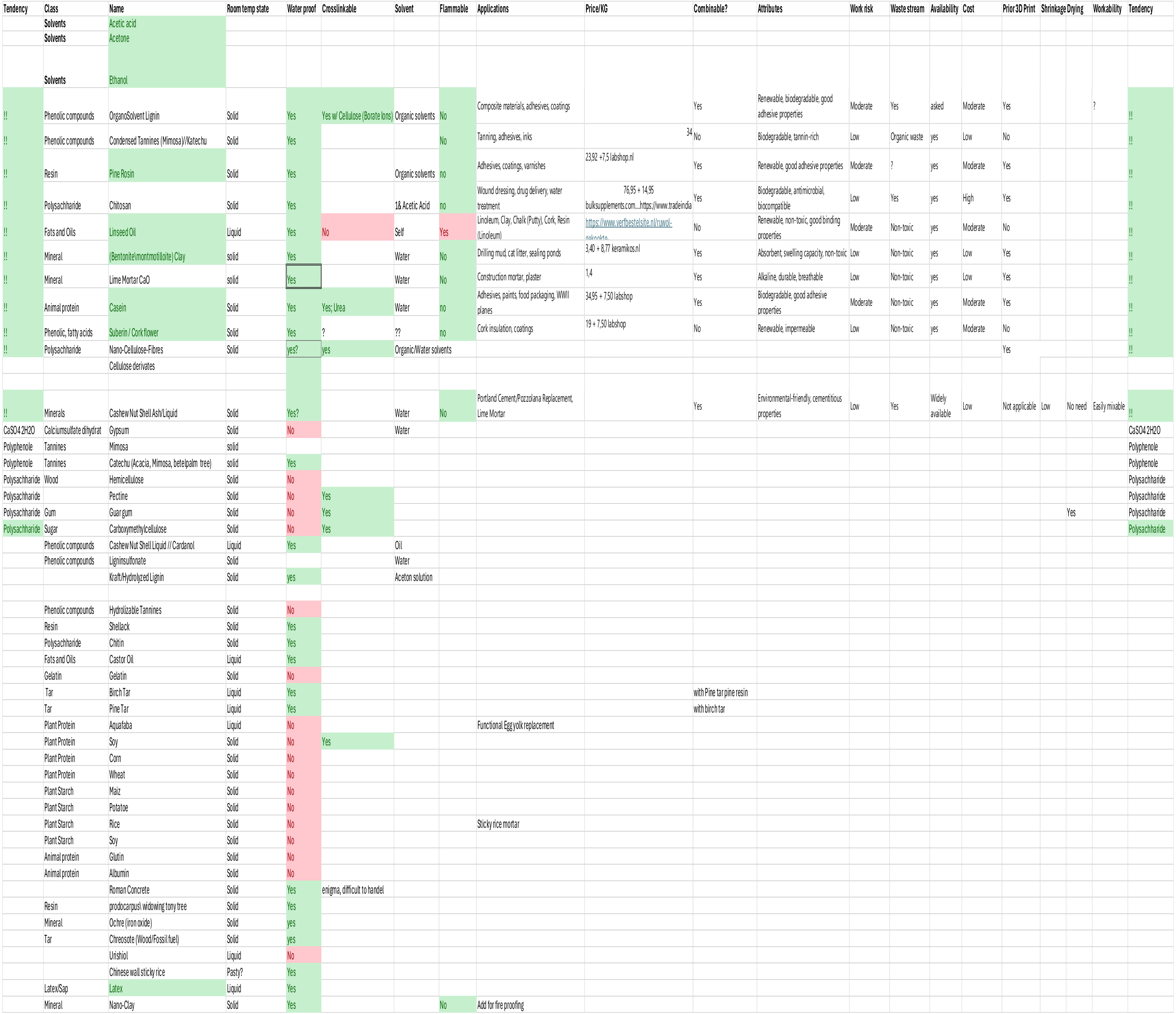
Appendix

Binder research



Tendency	Class	Name	Room temp state	Water proof	Crosslinkable	Solvent	Flammable	Applications	Price/KG	Combinable?	Attributes	Work risk	Waste stream	Availability	Cost	Prior 3D Print	Shrinkage	Drying	Workability	Tendency
	Solvents	Acetic acid																		
	Solvents	Acetone																		
	Solvents	Ethanol																		
!!	Phenolic compounds	OrganoSolvent Lignin	Solid	Yes	Yes w/ Cellulose (Borate Ions)	Organic solvents	No	Composite materials, adhesives, coatings		Yes	Renewable, biodegradable, good adhesive properties	Moderate	Yes	asked	Moderate	Yes			?	!!
!!	Phenolic compounds	Condensed Tannines (Mimosa)//Katechu	Solid	Yes			No	Tanning, adhesives, inks	34	No	Biodegradable, tannin-rich	Low	Organic waste	yes	Low	No				!!
!!	Resin	Pine Rosin	Solid	Yes		Organic solvents	no	Adhesives, coatings, varnishes	23,92 +7,5 labshop.nl	Yes	Renewable, good adhesive properties	Moderate	?	yes	Moderate	Yes				!!
!!	Polysachharide	Chitosan	Solid	Yes		1& Acetic Acid	no	Wound dressing, drug delivery, water treatment	76,95 + 14,95 bulksupplements.com....https://www.tradeindia	Yes	Biodegradable, antimicrobial, biocompatible	Low	Yes	yes	High	Yes				!!
!!	Fats and Oils	Linseed Oil	Liquid	Yes	No	Self	Yes	Linoleum, Clay, Chalk (Putty), Cork, Resin (Linoleum)	https://www.verfbestelsite.nl/ruwol-gekookte-	No	Renewable, non-toxic, good binding properties	Moderate	Non-toxic	yes	Moderate	No				!!
!!	Mineral	(Bentonite\montmotilloite) Clay	solid	Yes		Water	No	Drilling mud, cat litter, sealing ponds	3,40 + 8,77 keramikos.nl	Yes	Absorbent, swelling capacity, non-toxic	Low	Non-toxic	yes	Low	Yes				!!
!!	Mineral	Lime Mortar CaO	solid	Yes		Water	No	Construction mortar, plaster	1,4	Yes	Alkaline, durable, breathable	Low	Non-toxic	yes	Low	Yes				!!
!!	Animal protein	Casein	Solid	Yes	Yes; Urea	Water	no	Adhesives, paints, food packaging, WWII planes	34,95 + 7,50 labshop	Yes	Biodegradable, good adhesive properties	Moderate	Non-toxic	yes	Moderate	Yes				!!
!!	Phenolic, fatty acids	Suberin / Cork flower	Solid	Yes	?	??	no	Cork insulation, coatings	19 + 7,50 labshop	No	Renewable, impermeable	Low	Non-toxic	yes	Moderate	No				!!
!!	Polysachharide	Nano-Cellulose-Fibres	Solid	yes?	yes	Organic/Water solvents										Yes				!!
		Cellulose derivates																		
!!	Minerals	Cashew Nut Shell Ash/Liquid	Solid	Yes?		Water	No	Portland Cement/Pozzolana Replacement, Lime Mortar		Yes	Environmental-friendly, cementitious properties	Low	Yes	Widely available	Low	Not applicable	Low	No need	Easily mixable	!!
CaSO4 2H2O	Calciumsulfate dihydrat	Gypsum	Solid	No		Water														CaSO4 2H2O
Polyphenole	Tannines	Mimosa	solid																	Polyphenole
Polyphenole	Tannines	Catechu (Acacia, Mimosa, betelpalm tree)	solid	Yes																Polyphenole
Polysachharide	Wood	Hemicellulose	Solid	No																Polysachharide
Polysachharide		Pectine	Solid	No	Yes															Polysachharide
Polysachharide	Gum	Guar gum	Solid	No	Yes													Yes		Polysachharide
Polysachharide	Sugar	Carboxymethylcellulose	Solid	No	Yes															Polysachharide
	Phenolic compounds	Cashew Nut Shell Liquid // Cardanol	Liquid	Yes		Oil														
	Phenolic compounds	Ligninsulfonate	Solid			Water														
		Kraft/Hydrolyzed Lignin	Solid	yes		Aceton solution														
	Phenolic compounds	Hydrolizable Tannines	Solid	No																
	Resin	Shellack	Solid	Yes																
	Polysachharide	Chitin	Solid	Yes																
	Fats and Oils	Castor Oil	Liquid	Yes																
	Gelatin	Gelatin	Solid	No																
	Tar	Birch Tar	Liquid	Yes						with Pine tar pine resin										
	Tar	Pine Tar	Liquid	Yes						with birch tar										
	Plant Protein	Aquafaba	Liquid	No				Functional Egg yolk replacement												
	Plant Protein	Soy	Solid	No	Yes															
	Plant Protein	Corn	Solid	No																
	Plant Protein	Wheat	Solid	No																
	Plant Starch	Maiz	Solid	No																
	Plant Starch	Potatoe	Solid	No																
	Plant Starch	Rice	Solid	No				Sticky rice mortar												
	Plant Starch	Soy	Solid	No																
	Animal protein	Glutin	Solid	No																
	Animal protein	Albumin	Solid	No																
		Roman Concrete	Solid	Yes	enigma, difficult to handel															
	Resin	prodocarpus\ widowing tony tree	Solid	Yes																
	Mineral	Ochre (iron oxide)	Solid	yes																
	Tar	Chreosote (Wood/Fossil fuel)	Solid	yes																
		Urishiol	Liquid	No																
		Chinese wall sticky rice	Pasty?	Yes																
	Latex/Sap	Latex	Liquid	Yes																
	Mineral	Nano-Clay	Solid	Yes			No	Add for fire proofing												

Figure 29: Potential Binder list

Binder trials

Tested Binder: Latex **Experiment No.:** 1

Date: 04.04.2024

Weight of Glass: Final Weight: Amount Paste: 14,6g

	Ingredients (Amount in Grams)		
Addition Steps	Latex	CaCO3	EtOH
1	5,1	5,5	
2	+2		
3			+2
Final Weight / Percentage	7,1 48,6%	5,5g 37,7%	2 13,7%

Tested Binder: Pine Resin **Experiment No.:** 2

Date: 04.04.2024

Weight of Glass: 33,03 g Final Weight: 57,43g Amount Paste: 24,4

	Ingredients (Amount in Grams)		
Addition Steps	Pine Resin	EtOH	CaCO3
1	2,0	2,0	
2		2,0	
3			2,54
4			2,48
5			5,16
6			5,13
7			2,08
8			1
9			
Final Weight / Percentage			

Tested Binder: Cooked Linseed Oil **Experiment No.: 3**

Date: 05.04.2024

Weight of Glass: 33,29 Final Weight: Amount Paste:

	Ingredients (Amount in Grams)		
Addition Steps	Cooked Linseed Oil	CaCO3	
1	8,82	4	
2		3,82	
3		5,23	
4		8,74	
5		5,59	
6		1,72	-2ml
7		2,18	-2,7ml
8			-1ml
9			-3ml
Final Weight / Percentage			

Tested Binder: Cooked Linseed Oil **Experiment No.: 4**

Date: 09.04.2024

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)				
Addition Steps	Linseed	Pine Resin	EtOH	CaCO3	Cellulose
1	6,4	2,2	0,5		
2				5	
3					0,3
4					0,75
5				3,44	
6				12,8	
7			HE 3,2		
8				2,75	
9			HE -5 ml		
Final Weight / Percentage					

Tested Binder: Caseine Experiment No.: 5

Date: 09.04.2024

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)							Total
Addition Steps	Caseine Mix	H2O	Ca(OH)2	Wasserglas	CaCO3	H2O	Extruded	
1	4	14	1,8	2,8				22,6
2	22,6				7,66			30,26
3	60,25%				+7,25(39,72 %)			37,51
4	-1,875g				-1,19g		-3ml	34,51
5	20,725 (53,8%)				+4,14 (T:17,86; 46,2%))			38,65
6	(T18,842) -1,883				-1,16		-3,5 ml	35,15
7		0,5						
8		0,5 (79,6 %)						36,15
9					2,05			38,2
10							-2,5 ml	35,7
Final Weight / Percentage	19,842	(15)						

Caseine Recipe used:

20g; mix (4g Caseine, 10g H2O), mix (1,2-1,8g Ca(OH)2 + 4g H2O) add 2,8 Wasserglas

Only 10g used for first experiment

Tested Binder: Caseine Experiment No.: 6

Date: 09.04.2024

Weight of Glass: Final Weight: Amount Paste: with rest from experiment 5

	Ingredients (Amount in Grams)					
Addition Steps	Caseine Mix	H2O	Ca(OH)2	Wasserglas	CaCO3	total
1	11,2 (43,83%)				14,35 (56,15%)	25,55
2	-1,25g			-2,85	-1,6g	22,7

3					4,54	
4		0,2				27,24
5		0,35				
6		0,5				
Final Weight / Percentage	9,95 (35,2%)	1,05(3,7%)			17,29 (61,1%)	28,29

Tested Binder: Caseine / Cork **Experiment No.: 8**

Date: 06.05

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)			
Addition Steps	Casein	Cork	H2O	Extrusion
1	10			
2		1,02		
3				-1,85
4		0,43		
5				-1,15
6			0,5	
Final Weight / Percentage				

Tested Binder: Caseine / Saw Dust **Experiment No.: 9**

Date: 06.05.24

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)			
Addition Steps	Casein	Saw Dust	H2O	Extrusion
1	10			
2		1		
3		0,5		
4				1,1
5			0,5	
6			08	
7			1	
8		0,12		
9		0,2		
10			1	

Final Weight / Percentage				

Tested Binder: Caseine / Olive **Experiment No.: 10**

Date: 06.05

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)			
Addition Steps	Casein	Olive	H2O	Extrusion
1	10			
2		2,5		
3			1	
4				1
5			1	
6		0,3		
7		0,2		
8			2	
9				-0,5
10			0,3	
Final Weight / Percentage				

Tested Binder: Caseine / Cork / CaCO3 **Experiment No.: 11**

Date: 08.05

Weight of Glass: Final Weight: Amount Paste:

		Ingredients (Amount in Grams)				
Addition Steps	Casein	Cork	CaCO3	H2O	Extrusion	
1	10,10					
2		1				
3			4,06			
4		0,31				
5					-1,53	
6				0,4		
7				0,6		
8					PE	
Final Weight / Percentage	10.10g / 67.6%	1.31g /8.8%	4.06 g / 27.18%	1g / 6.7 %		14.94

Tested Binder: Caseine / Saw Dust / CaCO3 **Experiment No.: 12**

Date: 08.05

Weight of Glass: Final Weight: Amount Paste:

		Ingredients (Amount in Grams)				
Addition Steps	Casein	Saw Dust	CaCO3	H2O	Extrusion	Total
1	10,3					
2		1,5				
3			2			
4				0,5		
5					-1,37	
6		0,33				
7				0,5		
8		0,1				
					PE	
Final Weight / Percentage	10.3 g/ 74.32	1.93 g/ 13.92%	2g / 14.43 %	1 g / 7,22 %		13,86

Tested Binder: Caseine / Olive pit / CaCO3 **Experiment No.: 13**

Date: 08.05

Weight of Glass: Final Weight: Amount Paste:

		Ingredients (Amount in Grams)			
Addition Steps	Casein	Olive pit	CaCO3	H2O	Extrusion
1	10				
2		1,56			
3			2,07		
4		0,5			
5			2,07		
6			1,75		
7					1,5
8				0,5	
9				0,5	
Final Weight / Percentage					

Tested Binder: OrganoSolv Lignin / EtOH /CaCO3 **Experiment No.: 14**

Date: 14.05.24

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)				
Addition Steps		OrganoSolv Lignin	EtOH	CaCO3	Extrusion
1		2,4			
2			1,41		
3					-1
4		1,6			
5				4,2	
6			0,5		
7		1			
8		0,5			
9					
Final Weight / Percentage					

Tested Binder: OrganoSolv Lignin / H2O **Experiment No.: 15**

Date: 14.05.24

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)				
Addition Steps		OrganoSolv Lignin	H2O		Extrusion
1		0,8	1,2		
Final Weight / Percentage					

Most hydrophobic material ive ever witnessed, like cinnamon, lignoin coated droplets rolled over water, no chance of mixing

Tested Binder: OS Lignin/Acetic Acid/ CaCO3 **Experiment No.: 16**

Date: 14.05.24

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)				
Addition Steps	OS Lignin	Acetic Acid	CaCO3	E	
1	1				
2		0,53			

3	1,12				
4		0,3			
5			1,44		
6	0,17				
Final Weight / Percentage					

-

- **Tested Binder:** Caseine/Cork **Experiment No.: 17**
- Date: 15.05.24
  - Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)				
Addition Steps	Caseine mix	Cork	H2O	E	
1	10				
2		1.53			
3		0.26			
4			0.6		
5				HE/PE	
6					
Final Weight / Percentage					

-

- **Tested Binder:** Casein/ CaCO3 **Experiment No.: 18**
- Date: 15.05.24
  - Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)				
Addition Steps	Caseine	CaCO3	H2O	E	Cork
1	13,8				
2		18,75			
3				1	
4			2,4		
5					0,45
6					1
7				1	
8			2,64		
9					
10					
Final Weight / Percentage					

Tested Binder: Caseine /Cork / CaCO3 **Experiment No.: 19**

Date: 15.05.2024

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)				
Addition Steps	Caseine	Cork	CaCO3	H2O	E
1	10,27				
2		1,53			
3			5		
4				0.5	
5				0.5	
6				0.5	
7				0.3	
8				1	
9				0.55	
10					
Final Weight / Percentage					

➔ Tested Binder: Experiment No.: 20

➔ Date: 15.05.2024

➔ Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)				
Addition Steps					
1					
2					
3					
4					
5					
6					
Final Weight / Percentage					

➔

Tested Binder:Caseine/Cork/CaCO3 Experiment No.: 21

Date: 15.05.2024

Weight of Glass: Final Weight: Amount Paste:

	Ingredients (Amount in Grams)					
Addition Steps	Caseine	Cork	CaCO3	H2O	E	Total
1	11,54					

2		1				
3			4,2			
4		0,5				
5				0.3		
6				0.25		
				0.55		
Final Weight / Percentage	62,9%	1,5 / 8,2%	4,2 / 22,9%	1,1g / 6%		18,34