

Exploring Polycaprolactone (PCL) as a Material for Design

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ABSTRACT

Demand for sustainable materials, manufacturing and design has been increasing over the past years. Polycaprolactone (PCL) is a biodegradable polymer with a melting temperature around 60 °C, that has widely been used in the biomedical industry. This study takes an explorative and iterative approach in studying this material and how it could be used for design. After initial experimental iterations, the gained tacit knowledge has been applied to a case study within the context of aerial seeding, an agricultural method of delivering seeds by aircraft. The main findings are that PCL's malleability, blend compatibility (by which we refer to the material's ability to form material composites with various other materials with ease), biodegradability, and biocompatibility provide opportunities for the material to be used in design prototyping, origami or folded structures, and applications in nature, agriculture, or living organisms. We discuss these advantages and provide design implications. Finally, opportunities for further research are identified.

Author Keywords

Material Research; Biodegradable polymers; Polycaprolactone; Sustainability; Material-Driven Design.



INTRODUCTION

In recent years, the need for sustainable manufacturing has become increasingly evident, due to the environmental impact of synthetic materials and their production [11]. To slow down the growth of this problem, the use of biomaterials has increased within the industries, offering a valid alternative. Therefore, the purpose of this research study is to identify the potential of Polycaprolactone (PCL) as a versatile material for design applications. The primary intention is to investigate different types of processing techniques through an iterative design process, which involves material tinkering, literature review and benchmarking, and designing material vision manifestations. The practice and processing methods of PCL advanced in this pictorial, aim to extend its application beyond the biomedical field, where it is currently widely applied.

In order to refine the vision of the material in design applications, PCL was placed in a hypothetical context, which exploited the findings enlightened during the design research.

For this purpose, the context of aerial seeding offered an optimal case study. The importance of this study relates to the consistent increase in the importance of sustainability and the demand for biodegradable materials over the past years [11]. Although growing fast, the market share of biodegradable polymers was still less than 0.1% in 2019 [17]. Therefore, this research can contribute to the transition towards biodegradable polymers by thoroughly exploring these materials for further use in the fields of design, engineering, and material sciences. This pictorial shares the design exploration of polycaprolactone and provides suggestions for the design implications of this polymer.

Polycaprolactone

Over the last decade, the biopolymer Polycaprolactone (PCL) has been mostly studied concerning biomedical applications. Its chemical and mechanical properties, such as biocompatibility, biodegradation, and hydrophobicity [5] qualify it as an efficient material for drug delivery systems, tissue engineering and repair, bone engineering, wound healing, scaffolds, sutures, and implants [10]. PCL is a semicrystalline biopolymer usually synthesized through Ring Opening Polymerization of the cyclic monomer ϵ -caprolactone. It is one of the few synthesized polymers that biodegrade in nature in a period of 2 to 4 years [3]. PCL can be degraded without polluting the environment by hydrolysis of ester bonds or by microorganisms. The biodegradation depends on the amount of crystallinity, polymer molecular mass, and other degradation parameters, such as environment, temperature, pH, and salinity [9]. Modifying these parameters can result in a change of degradation time. In natural soil, PCL's breakdown can range from a few months to several years, influenced by factors such as soil composition, microbial activity, and environmental conditions [13]. Additionally, the degradation can be reduced to a shorter time if combined with other materials, some of which are TPS, starch, and coffee husk [4, 14, 3].

Related Work

Several related works should be highlighted. Firstly, the paper *Polycaprolactone: synthesis, properties, and applications* by Guarino et al. [5] provided the foundation for understanding the material polycaprolactone, including its material properties and current key applications. This is further supported by the paper *Degradation mechanisms of polycaprolactone in the context of chemistry, geometry, and environment* [2] which delves deeper into the biodegradability property of PCL by elaborating on its specific degradation mechanisms and timelines. Secondly, *Meaning Driven Materials Selection in Design Education* [7] describes a similar approach we have integrated to evaluate the meaning of material samples used in this study. This is further supported by *Shape-Changing Interfaces: A Review of the Design Space and Open Research Questions* [15] by Rasmussen et al. who offer a framework for describing shape-changing interfaces – a crucial practice for discussing the different shapes and processing methods presented in this paper. Closely related is the paper *Shape-Changing Particles: From Materials Design and Mechanisms to Implementation* [19] which discusses the mechanisms of shape-change within polymer networks. In addition, *New Tree Tech: Cutting-edge drones give reforestation a helping hand* [1] should be mentioned as it provides the context in which our case study about aerial seeding is positioned. Finally, the paper *Biodegradation Study of a Novel Poly-Caprolactone-Coffee Husk Composite Film* [3] was promising, highlighting that the combination of coffee husks with polycaprolactone increases the materials' polymeric biodegradation rate.

METHOD

The research method within Research through Design has been an iterative process (which was documented in a process workbook (see Figure 2 and Appendix) that was in some ways inspired by *Flipping Pages* by Rutten et al. [16]) that was similar to the *Reflective, Transformative, Design Process* [8] involving material tinkering, literature review and benchmarking, and designing material vision manifestations. The material tinkering, as part of the proposed step of understanding the material by Karana et al. [2015] in *Material Driven Design* involved using various material processing techniques, including blowing; rolling; pressing, and folding, to gain (tacit) knowledge of material properties and character, as proposed by Wiberg [2013] in *Method for Materiality* [8, 22]. Examples illustrating this are experiments of adding powders and fibers to the material to change the strength, flexibility, character, and sensorial feeling, as well as trying manual molding (Figure 1), blowing, folding, and pressing to achieve different physical forms. These ways of gaining tacit knowledge are supported by a literature review and benchmark, which took the form of an ever-evolving (partly visual) document. In addition to these ways of understanding the material and design space, two other steps that stem from *Material Driven Design* [8] have iteratively been taken: envisioning design intentions and manifesting design concepts. These are important actions for finding a context for design as well as generating design implications for further use. Examples of such vision manifestations are creating origami shapes that are compressible, strong, or 'pop' at pressure; or incorporating nichrome wires in the material for location-based heating to automate and control shape change. By utilizing material understanding, exploration, and visions for design, new insights for designing with polycaprolactone have been identified.



Figure 1. Molding heated PCL

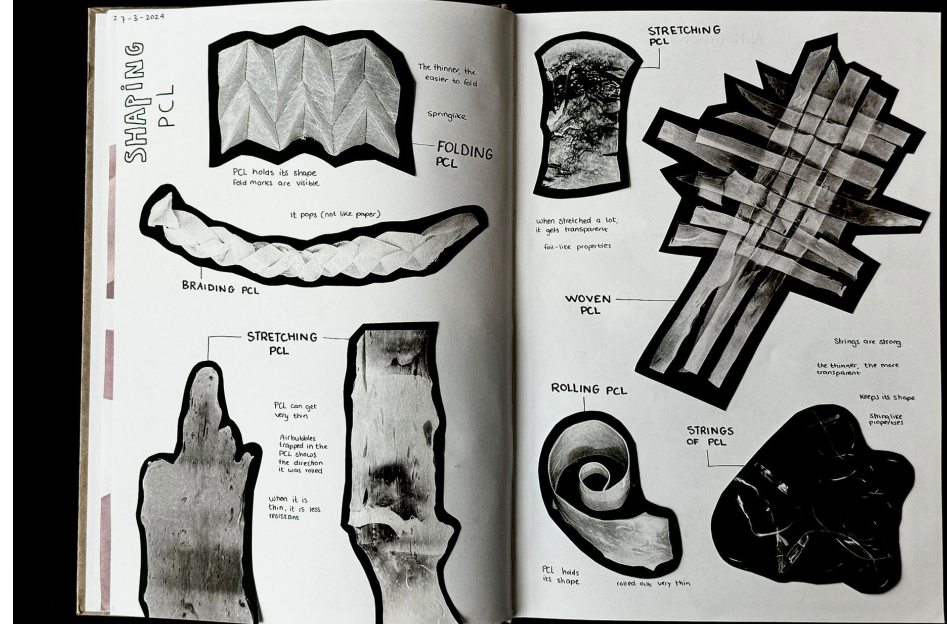


Figure 2. Process Book

In order to gain deepened design knowledge of the material, a case study was conducted in which different properties of PCL were applied to the context of aerial seeding, as this context was one where the different properties of PCL (such as biodegradability, strength, blend-ability, and malleability) could well be applied. In this iterative process, criteria for these containers were constantly updated based on tests evaluating their performance. Three different tests have been completed at different times in the process. The first type measured soil penetration success rate when dropping containers from a 50 centimeters and one-meter height. The second type placed radish seeds in PCL containers and evaluated their growth. Here, seeds were pressed within molten PCL, or placed in capsules with open top, open bottom, or open top and bottom to compare differences in growth. Finally, thin and folded pieces of PCL were placed in natural soil to evaluate their degradation. Here, different PCL samples have been tested, but also a composite sample containing 30% used coffee grounds. After these tests and iterations, the gained knowledge about PCL as a material for design has been evaluated and described, noting design knowledge, and suggesting design implication

Highlighting the limitations of the study, it should be noted that the study was conducted within a relatively short timeframe, with a low budget, and without access to scientific measuring equipment. As a result, doing accurate and reliable tests as well as evaluating change over longer periods of time was not possible. In addition, because material evaluations were done based on experienced qualities, a certain degree of research bias should be accounted for.

RESULTS

The findings from the iterative design process revealed several significant insights about the characteristics of PCL and its potential design applications.



Figure 3. PCL blends with natural powders, liquids, and pastes

Figure 4. PCL blends with textile



Figure 6. PCL and different amounts of paper pulp blends

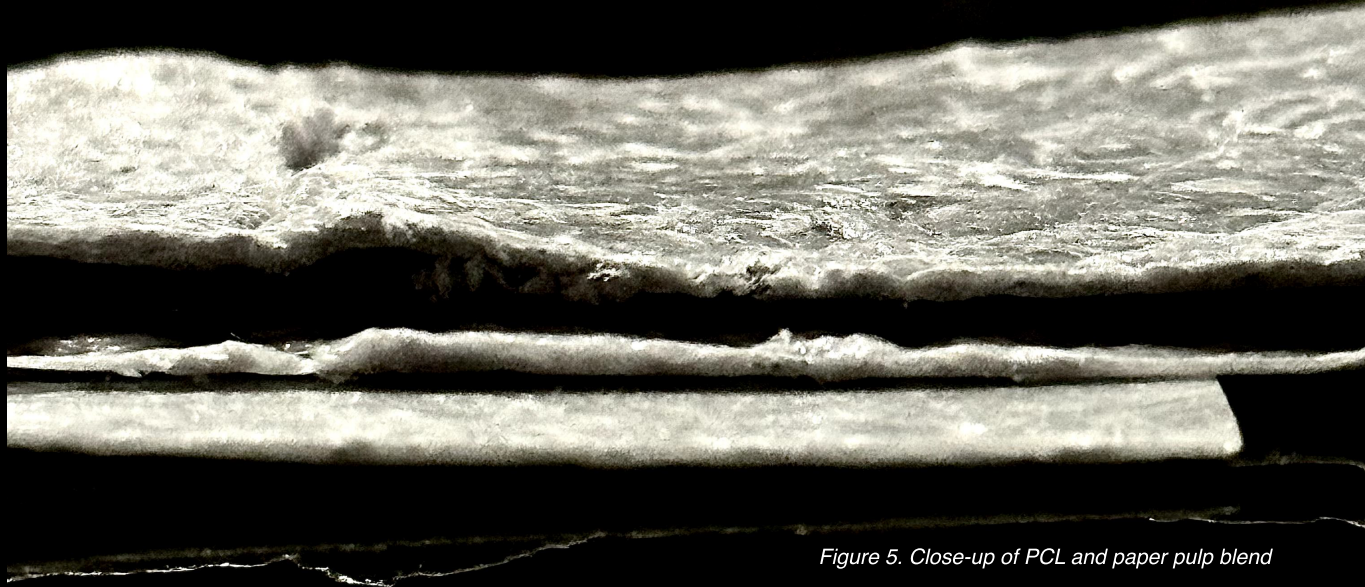


Figure 5. Close-up of PCL and paper pulp blend

Primary Findings

Blend Compatibility

After incorporating various materials into PCL, we discovered that PCL exhibits a high degree of blend compatibility, readily accepting and integrating with other substances. Adding natural powders, liquids, and pastes (e.g. curry, bamboo fiber, smashes berries) mainly changed the PCL's aesthetic and sensorial qualities: the PCL samples gained a new color, smell, or texture (Figure 3). We also experimented with combining PCL with textiles to explore its potential (Figure 4).

While we were able to partially incorporate the textile into the PCL, we encountered difficulties in achieving a proper blend. This resulted in large chunks of textiles becoming embedded in the PCL rather than integrating smoothly. By blending PCL with various amounts of paper pulp (Figure 5, 6), its texture got rougher the more paper pulp was added. Furthermore, the composite could be easily torn like paper, unlike pure PCL.

Shape-change

Through various material processing techniques, such as pressing, rolling, folding, and blowing the material, we observed that PCL showed great malleability and flexibility. The low melting point allows for it to be easily molded and reshaped into various forms. This was particularly evident when folding PCL into origami structures (Figure 9). The material retained its form, even after compression (Figure 8), and showed no signs of wear after up to 100 folds, as evidenced by our repetitive folding tests.

Through more experimenting, we found that PCL sheets with a thickness below 0.7mm can fold well with a limited decrease in strength. The thicker the sheets, the more rigid the origami structure will be, making it able to 'pop' out of place and remain its new shape until 'popped' back, resembling a bistable system: the sample has two stable equilibrium states (Figure 10).

In order to try and control the one-way shape change of PCL, we conducted an additional experiment by incorporating nichrome wires into the folds of a PCL origami shape for location-based heating (Figure 7). Although our concept of creating a mechanism for automated shape-change was successful, the heating proved difficult to control. This resulted in inconsistent and imprecise shape changes that were only one-directional. Furthermore, incorporating a nichrome wire into the PCL would compromise its inherent biodegradability, negating one of its most significant properties.

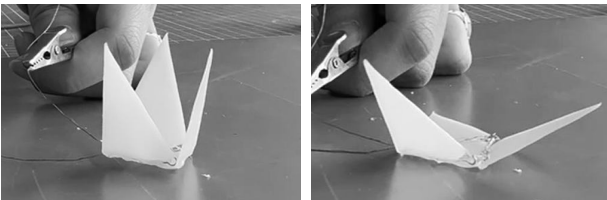


Figure 7. Activated nichrome wire integrated into PCL shape

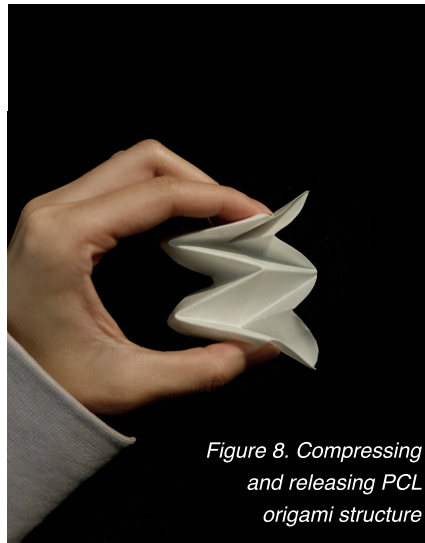
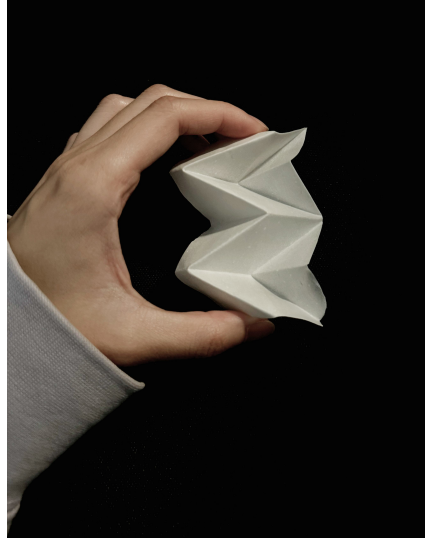


Figure 8. Compressing and releasing PCL origami structure

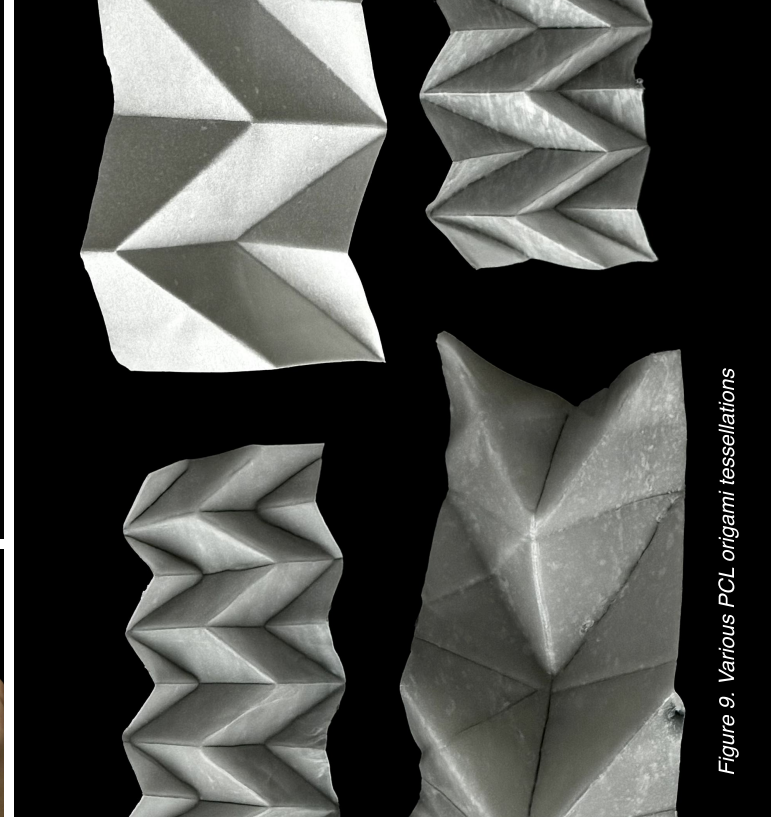


Figure 9. Various PCL origami tessellations

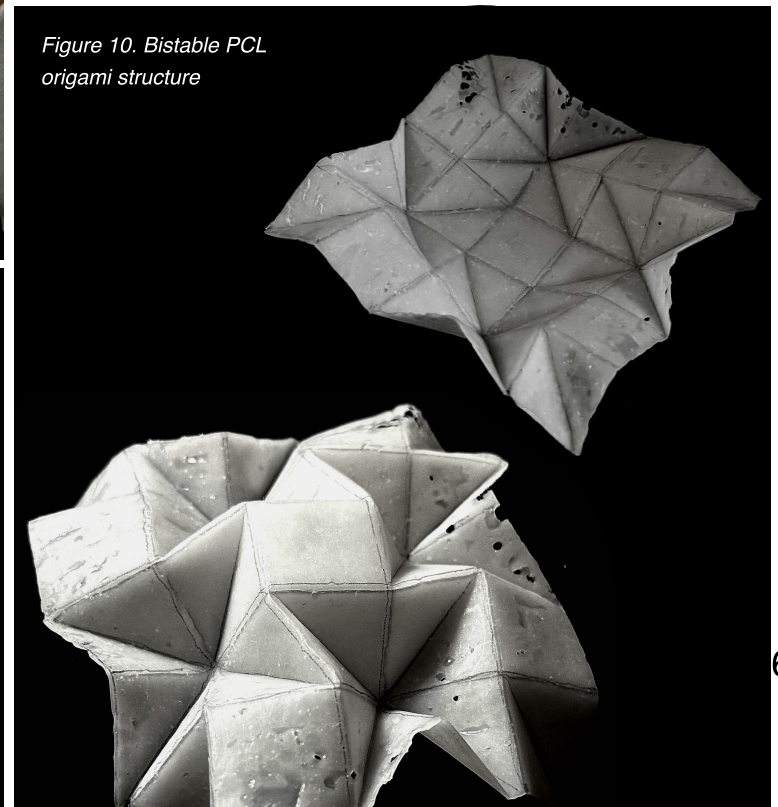


Figure 10. Bistable PCL origami structure

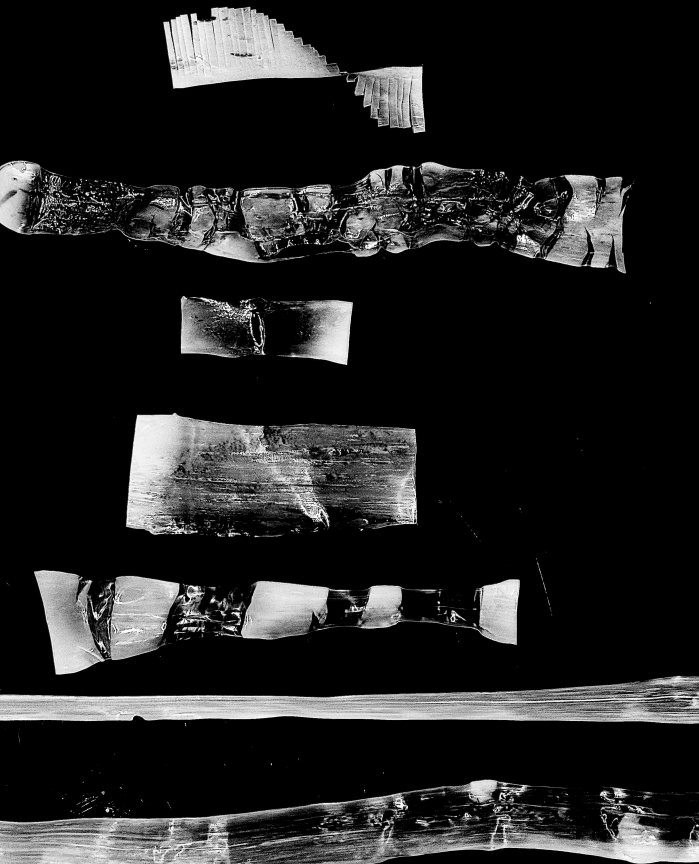


Figure 11. Stretched PCL into thin foil

Stretchability

PCL's ability to be stretched into thin, yet strong forms presents another noteworthy quality. The material maintained its structural integrity even when reduced to very thin sheets.

When rolling the PCL extremely flat right after heating, it could be reduced to translucent or even transparent foil-like sheets (Figure 11). Stretching the PCL at room temperature right after heating would showcase transparent areas in the material (Figure 11). When a thin sample got stretched after cooling down, it would result in wire-like formations (Figure 12).

When blowing the PCL, it was also able to stretch thin and form organic shapes. However, blowing was an inconsistent method and resulted in different sizes and thicknesses (Figure 13).

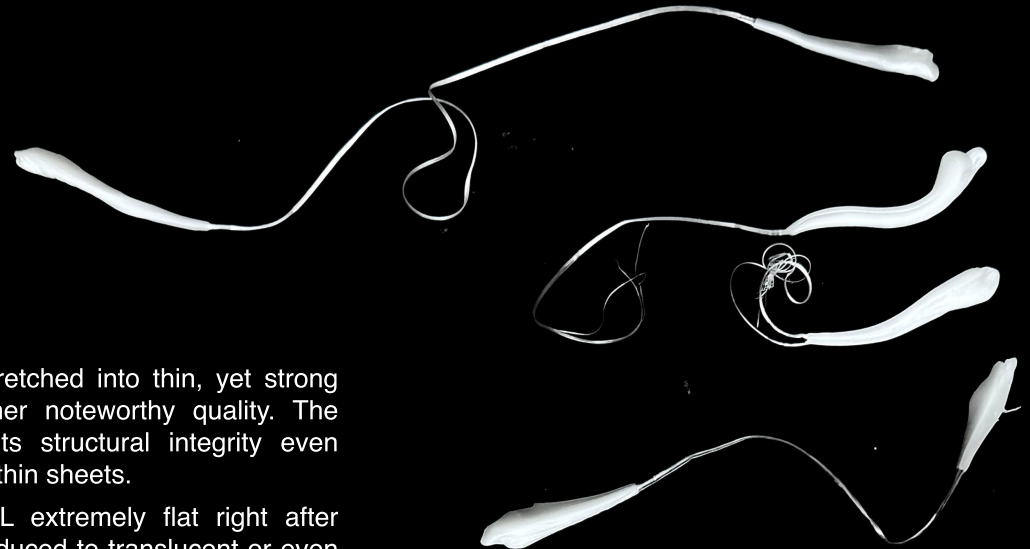


Figure 12. Stretched PCL into wires

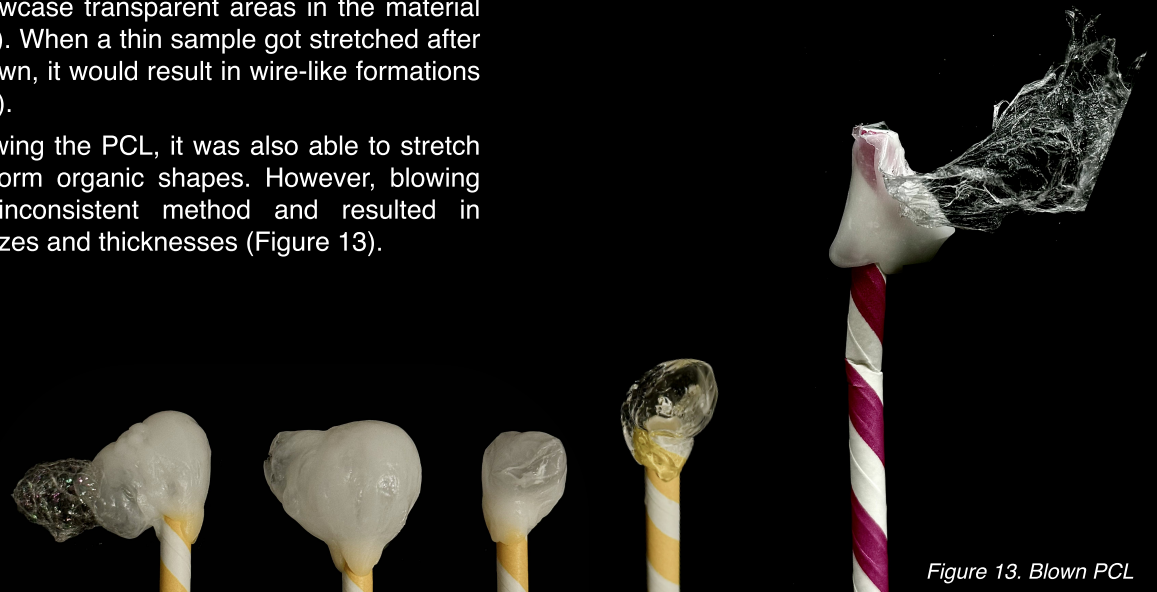


Figure 13. Blown PCL

Secondary Findings: Case Study

In the context of aerial seeding, we explored various shapes for PCL containers through iterative testing and evaluated their performance. The containers were created with the following main criteria in mind:

- It needs to be able to hold seeds and nutrients
- It needs to be able to penetrate the soil
- It needs to be able to support the growth and germination of the seeds.

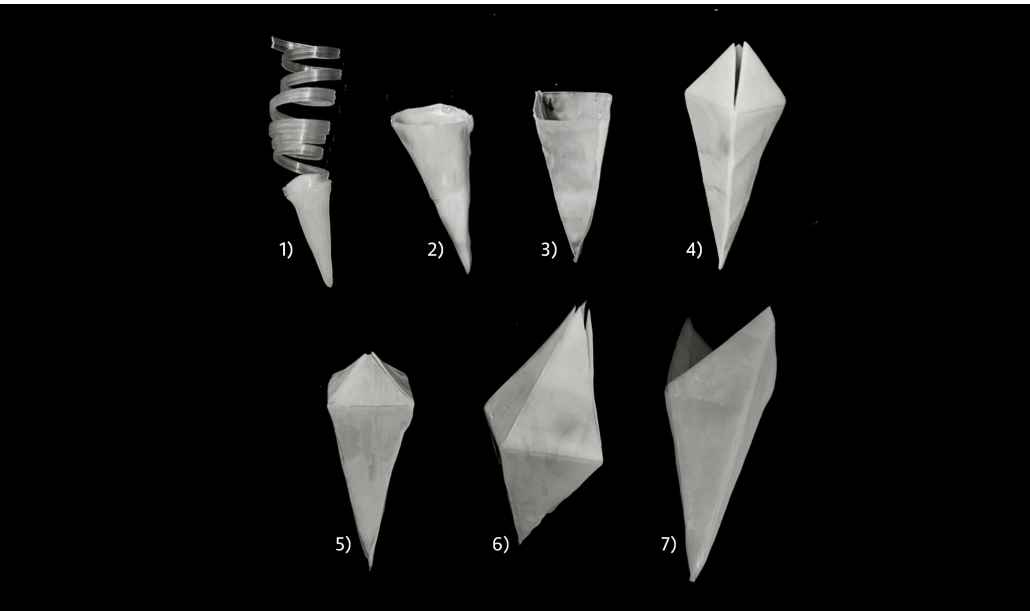


Figure 14. First drop test capsules

Capsule shape	1	2	3	4	5	6	7
Success rate (%)	0%	10%	0%	15%	15%	10%	45%

Table 1. Soil penetration success rates of drop test 1

Soil Penetration

Two drop tests were conducted to determine the soil penetration success rate of the PCL containers. All the capsules perceived to have potential (Figure 14, 15) were dropped a total amount of ten times. The drop height was 50cm for drop test 1 (Table 1), and 100cm for drop test two (Table 2). The results can be found in the tables below.

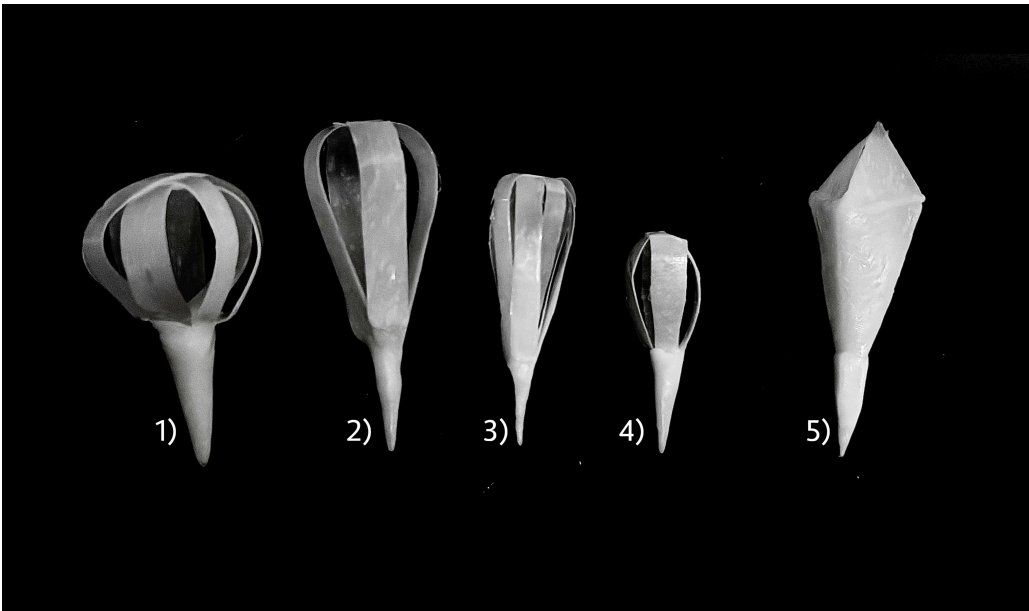


Figure 15. Second drop test capsules

Capsule shape	1	2	3	4	5
Success rate (%)	37.5%	52.5%	60%	27.5%	35%

Table 2. Soil penetration success rates of drop test 2

Seed Growth Evaluation

Four different experiments were conducted to evaluate the seed growth and germination when they are placed in different PCL capsules: seeds melted into PCL, capsule with an open top, capsule with an open bottom, and a capsule with both an open top and bottom (Figure 16). Radish seeds were used for their rapid growth; a total of approximately 20 radish seeds were used, 5 seeds per experiment. The results can be seen in Figure 17 and Table 3.



Figure 16a. Radish seeds in various PCL capsules



Figure 16b. Radish seeds in various PCL capsules in soil



Figure 17. Radish seeds in various PCL capsules after one week. 1) Seeds melted into PCL. 2) Seeds in capsule with open top. 3) Seeds in capsule with open bottom. 4) Seeds in capsule with open top and bottom

	Seeds melted into PCL	Seeds in capsule with open top	Seeds in capsule with open bottom	Seeds in capsule with open top and bottom
Did all the seeds grow?	No	Yes	Yes	Yes
How big was the plant after 1 week? (cm)	8.3 cm	3.2 cm	2 cm	8.5 cm

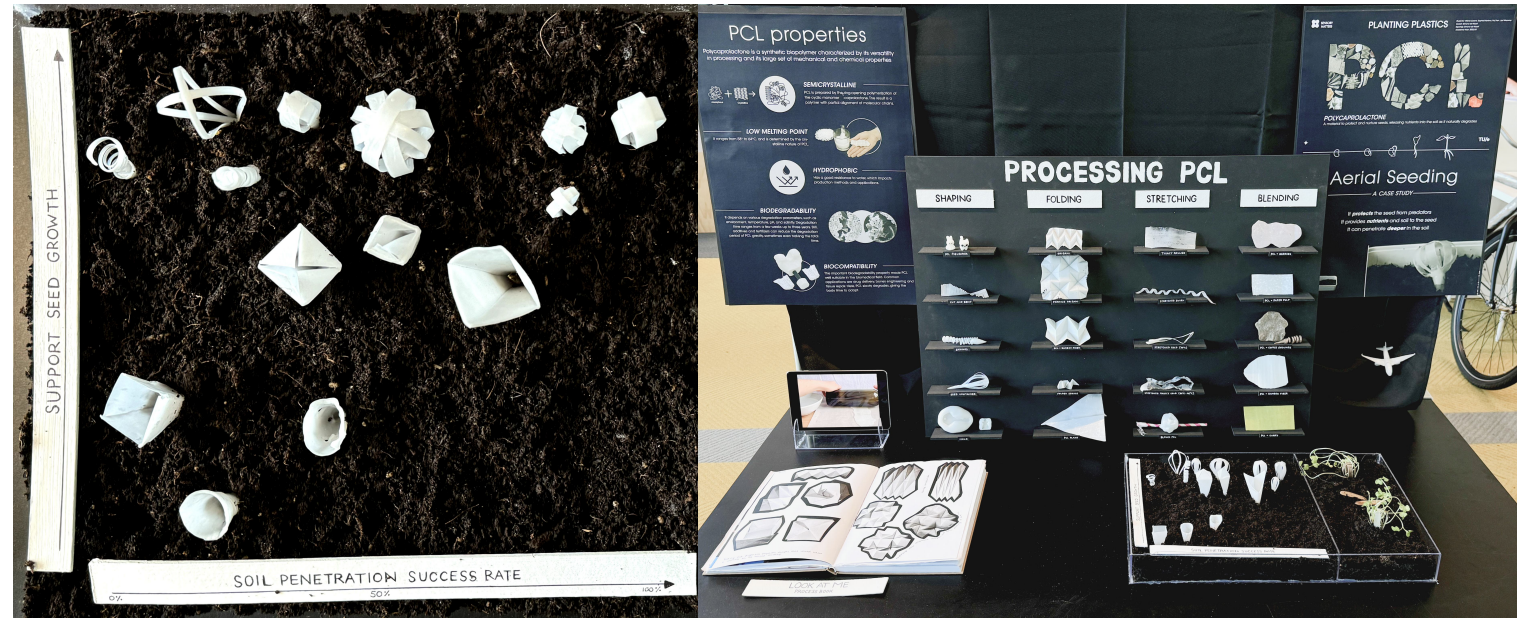
Table 3. Seed growth evaluation

Overview

An overview of all the results can be seen in the physical graph we created in Figure 18, showcasing all the capsules on a x-axis of 'soil penetration success rate' and y-axis of 'support seed growth'.

Figure 18. Physical graph tank

Figure 19. Demo Day set-up



Biodegradability

To assess the biodegradability of PCL, we created thin sheets and placed them in natural soil to monitor their degradation (Figure 21). Two samples were tested: a pure PCL sample, and a 30% coffee ground and 70% PCL composite (Figure 20).

However, due to the slow degradation rate of PCL and the limited timeframe of our study, we were unable to obtain conclusive results, since the samples showed no signs of degradation yet.

Figure 20. Coffee ground capsules

Figure 21. PCL sheet into soil for degradation test

DISCUSSION

PCL can provide various benefits as a material for design. Its ease of use and malleability make the material accessible and convenient, qualities that are important in rapidly iterating design processes. The ability to easily create material composites widens the range of applications as the material can be given a natural texture, color, or shape while remaining reusable and malleable. As shown in the case study, where the PCL-Coffee grounds composite was applied as a controlled-release fertilizer [3, 23], the advantages of PCL composites extend further than just sensorial improvements. Another benefit is found in how well the material folds while retaining its strength, which is due to its high flexibility, bendability, and plasticity [3]. This proves also useful for both aesthetic and practical use cases, as folded or origami structures are recurring themes in both design and engineering. Naturally, PCL being both biodegradable and biocompatible significantly increases its number of possible use cases as the material can be used in nature as well as within the human body. Finally, the ability of the material to stretch both while molten and solid as well as its ability to act like a spring in shapes where that was not necessarily to be expected, may serve additional benefits, as these qualities have not been thoroughly investigated in this study.

A limitation of the material can be found in applications that require very short-term biodegradation, as the material can remain intact for several months before showing significant signs of degradation. Another limitation is the synthetic sourcing of PCL, which reduces the future potential of the material [11, 17]. Another property that should be considered is PCL being hydrophobic, which is an advantage in many cases but can make the material unsuitable for (design) applications that require a more permeable or porous structure. Finally, based on the findings in this study it cannot be concluded that localized heating of PCL



will be advantageous for design.

Placing the findings within the context of existing research, this study both highlights additional applications and presents successful processing methods for PCL. Currently, PCL is mainly used in biomedical applications, but it seems this could be extended to other fields as well as PCL lends itself as a suitable biodegradable (although not renewable) material for agriculture, nature, and prototyping applications. In these contexts, PCL can form a suitable biodegradable alternative in cases where no long-term wear should be resisted (as PCL will degrade).

A number of different suggestions for further research have been identified. Firstly, the case study could be continued by further exploration of shapes, particularly shapes that make use of the flexibility and compressibility of folded PCL sheets, as well as shapes that utilize the spring capabilities

of the material. In addition, there could be a possibility to use biodegradation to achieve shape change after seed deployment, such as shapes that have outer walls with varying thicknesses to achieve quicker degradation in certain locations for improved root growth. A second suggestion for further research is the actual testing of design proposals in an aerial seeding context to learn more about PCL as a material and its behavior in nature. Finally, we advise further exploration of two material qualities: the blending of PCL with natural materials is bound to be supportive in other applications similar to blends and copolymers presented in *Degradation mechanisms of polycaprolactone in the context of chemistry, geometry and environment* [2], and the ease of folding of such a strong but biodegradable material, as well as its applications, suggest additional opportunities within the design field.

Focusing on this study, different limitations can be

identified. Firstly, the study was conducted part-time over the duration of less than 6 months. If the time spent on material tinkering, benchmarking, and the case study could be extended, the study would benefit from more in-depth as well as broader material understanding. In addition, because of a lack of scientific equipment and budget, it was not possible to accurately test material properties (for example of different material blends), to test different shapes highlighted in the case study in real-life settings, or to experiment with toxic chemicals, such as solvents for PCL [18].

Taking all the things mentioned into consideration, we are able to highlight a few design implications for which PCL suits itself well. Firstly, as shown in the case study, PCL can be a strong and resistant material for short-term applications in nature or agricultural settings. Secondly, the material's strength and flexibility while being thin make it a suitable material for biodegradable origami or other folding applications for example in the packaging industry. In addition, the accessibility and malleability of the material make it suitable for prototyping plastic objects with more organic results compared to 3D-printed plastics, which is partly due to how well PCL blends with other materials [2]. Finally, as has been previously known, PCL is able to be placed safely inside or on living organisms, which may, in addition to the current biomedical applications, be useful for design projects focused on wearables or health.





CONCLUSION

This study explored the properties and potential applications that polycaprolactone brings to design. The primary findings indicate that PCL exhibits high blend compatibility, which serves aesthetical and sensorial qualities that are useful in product design and may provide additional practical benefits such as controlling fertilizer release; high malleability, which can also be utilized for both aesthetic and practical applications, as folded or origami structures are recurring themes in both design and engineering; as well as biodegradability and biocompatibility, making PCL a suitable material to be used in, on, and around nature, agriculture, and living organisms.

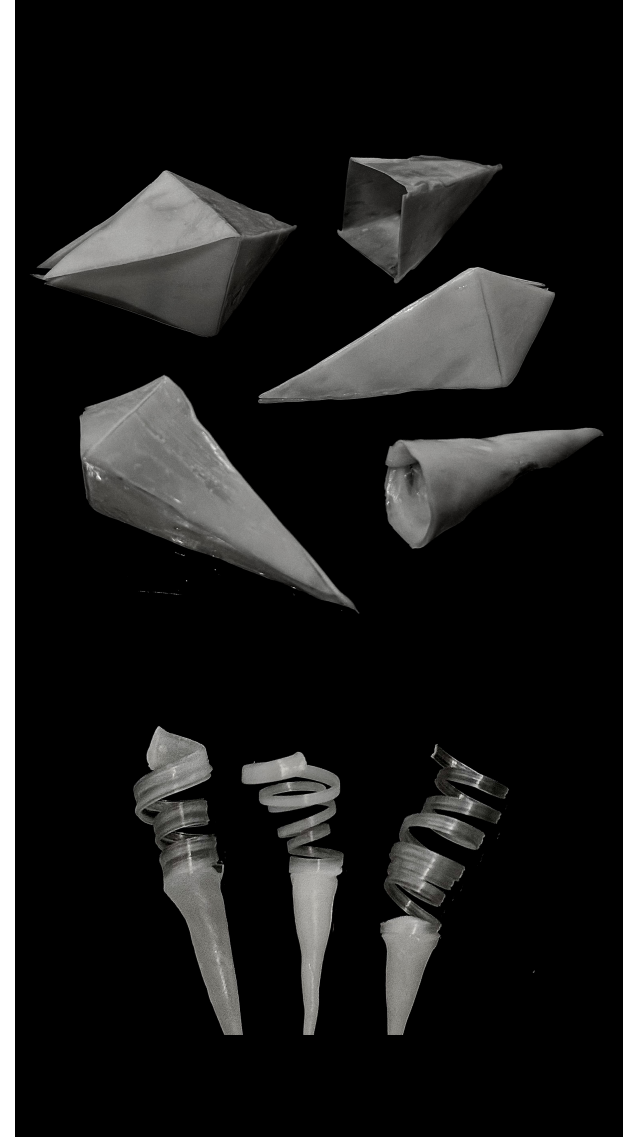
Additional research could further explore the material's flexibility and spring behavior, or could build upon the presented case study by exploring how degradation can be utilized to further support plant growth, and both measuring and testing suggested container shapes to learn more about the behavior of the material. Additionally, deepened investigation of natural material blends and the folding of PCL as a biodegradable material may forward impactful results.

Finally, reflecting on this study's goal, it can be concluded that the intentions of exploring PCL as a design material and providing different design implications for further use and investigation have been fulfilled.

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APPENDIX 1: PROCESS BOOK

GELATINE

animal based bioplastic



60ml water
12g gelatine

60ml water
12g gelatine
7.2g glycerine

FINDINGS

gelatine	glycerine	curry
<ul style="list-style-type: none">• stretchy• flexible• breaks easily	<ul style="list-style-type: none">• stretchier• sturdier	<ul style="list-style-type: none">• brittle• less stretchy

23-2-2020M

ADDING CURRY


WATER + GELATINE


WATER + GELATINE
+ GELATINE

ADDING RADISH


WATER + GELATINE


WATER + GELATINE
+ GELATINE

ADDING ONION


without
glycerine


half a cup
glycerine


one cup of
glycerine


two cups of
glycerine

PCL

PCL POLYCAPROLACTONE

PCL HOLD OF WATER + FLOUR

Research Possibilities PCL

Created 22/02/2024 10:24 by Jort Wiersma
Notabene logging

PCL and PLA

- (1) PCL-gelatin nanofibres crosslinked with genipin can modulate proliferation and differentiation of Myoblasts, potentially preventing applications in muscle tissue engineering
 - Genipin (chemical compound) is a natural cross linking agent, extracted from gardenia fruit myoblast is a progenitor cell that when it stops dividing enters myogenesis to develop into a muscle fiber of the skeletal muscles
 - So PCL can be used as Muscle engineering
- (2) PCL can be Electrospun to create PCL Fiber meshes that show a fast degradation rate in vitro, making them suitable for wound dressing and tissue regeneration applications.
 - Electrospinning involves an electrospraydynamic process, during which a liquid droplet is electrified to generate a jet, followed by stretching and elongation to generate fibers(s)

(LLM Source) How can material qualities be altered

- adding fillers like nanoparticles or reinforcements such as glass fibers can increase strength, stiffness and toughness
- adding plasticizers can increase flexibility and reduce brittleness (crates, glycerine)
- blending PCL with other polymers or additives can improve compatibility with other components, so adhesion and dispersion
- crosslinking can increase thermal stability and chemical resistance
- chain extenders
- surface modifications can change wettability, adhesion, biocompatibility
- polymer blending
- nucleating agents
- functional additives (UV stabilizers, antioxidants)
- processing conditions

(LLM Source) Naturally occurring plasticizers and materials affecting strength and toughness

Natural plasticizers:

- plant oils
 - <https://www.sciencedirect.com/science/article/pii/S095861732030077>
 - <https://doi.org/10.1016/j.mbs.2020.100548>
 - <https://pubs.rsc.org/en/content/articlehtml/d3bm00001a>, successfully used for antibacterial coatings.
- <https://www.mdpi.com/2073-4360/7/102/165> shape memory polymeric material created by combining PCL as Epoxidized soybean oil - resulting materials are expected to contribute to the development of biodegradable intelligent materials
- <https://www.tandfonline.com/doi/full/10.1080/14613551.2016.1151514> coffee, cocoa, and cinnamon extracts tested to alter the Tg of the PCL. Its use improved the melt flow rate, tensile strength, and hardness

7-3-2024

SHAPING PCL

The thinner, the easier to fold

Springlike

FOLDING PCL

PCL holds its shape (add marks are visible)

it pops (not like paper)

BRAIDING PCL

STRETCHING PCL

PCL can get very thin

Arches/bubbles triggered in the PCL indicate the direction it will move

when it is thin - it is HIS RESILIENCE

STRETCHING PCL

When stretched a lot, it gets transparent like-line properties

WOVEN PCL

Strips are strings like threads, the more transparent

ROLLING PCL

Strings are strings like threads, the more transparent

STRINGS OF PCL

Shows like properties

PCL beads not shape

8-3-2024

light green
↑
faded

ANNOTATIONS

① after 6 days, color faded
smell faded
where we fold it, it looks like it's breaking (under the surface)
to me it brought me where it was
was disintegrated

② very strong smell
when looking, it looks a white, bold mark
brown orange color

③ smell almost
completely faded
no disintegrated with
light brown color

④ after 6 days, the smell was still strong
orange color
color is now more disintegrated

⑤ slightly more gray

⑦ looks as shape when looking
bringing color was less apparent

① PCL + GREEN LEMON TEA SPICES

② PCL + CINNAMON SPICES

③ PCL + BERRY EXTRACT

④ PCL + PEANUT-BUTTER

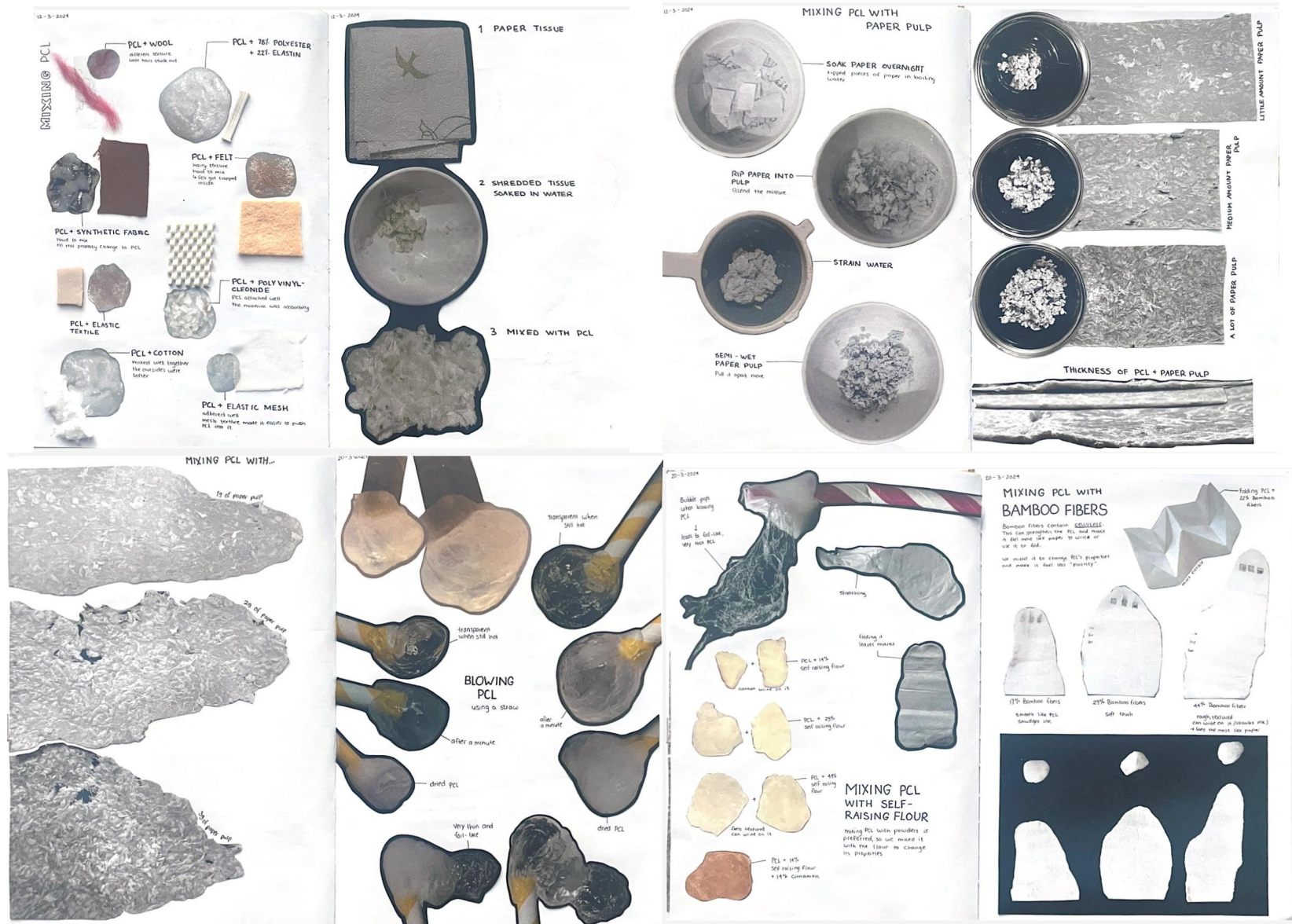
⑤ PCL + CHOCOLATE

⑥ PCL + SOAP

⑦ PCL + SALT

COLORING
PCL

APPENDIX 1: PROCESS BOOK



APPENDIX 1: PROCESS BOOK

Blowing

Casting

FEEDBACK

- THE PCL + CELLULOSE SAMPLE FEEL MORE NATURAL BIODEGRADABLE WHEN COMPARED TO 100% PCL
- MAKE A BENCHMARK TO SEE WHICH QUALITIES PCL HAS AND HOW WE COULD IMPROVE THESE
- PLACE THE MATERIAL IN A CONTEXT
- MAPPING
- HOW IS PCL MADE
- DO MORE LITERATURE RESEARCH
- LOOK INTO THE BIODEGRADABILITY OF PCL
- LOOK INTO THE PROCESSING TECHNIQUES

New Team Structure

Meetings are prepared

Fixed Notetaker

Chair

Better Preparation

Who	Does?	Details
Jort	X	12:00
Sophia	X	12:00
My	X	12:00
Vittoria	X	12:00
Chair	X	12:00
Notetaker	X	12:00

Now What?

NEW EXPERIMENT

PCL WITH A BLACK STRIPE. THE IDEA WAS THAT WHEN YOU HEAT IT WITH A HEATLAMP, THE BLACK WOULD ABSORB MORE HEAT AND BECOME FLEXIBLE FASTER THAN THE WHITE, MAKING THE PCL DEFORM/BEND.

UNFORTUNATELY, THIS DID NOT WORK IN PRACTICE DUE TO THE BLACK STRIPE THAT WAS NOT FULLY BLACK & THE HEATLAMP THAT DID NOT WORK OPTIMAL.

WE ALSO TRIED TO IRON THE PCL, TO SEE IF WE COULD GET THINNER SHEETS

THIS WORKED REALLY WELL & IT MADE THE SHEETS MORE CONSISTENTLY FLAT

BENCH-MARKING OF PCL

THIS DOCUMENT IS A WORK IN PROGRESS, IT IS CONSTANTLY BEING UPDATED

PCL, The material

HOW IS PCL MADE

Properties

Strengths

Weaknesses

Biodegradability

PCL in the medical field

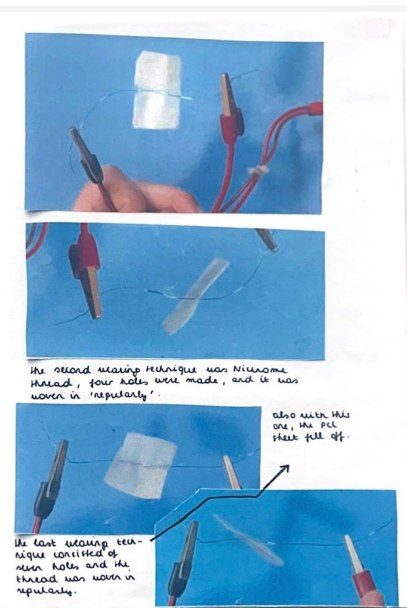
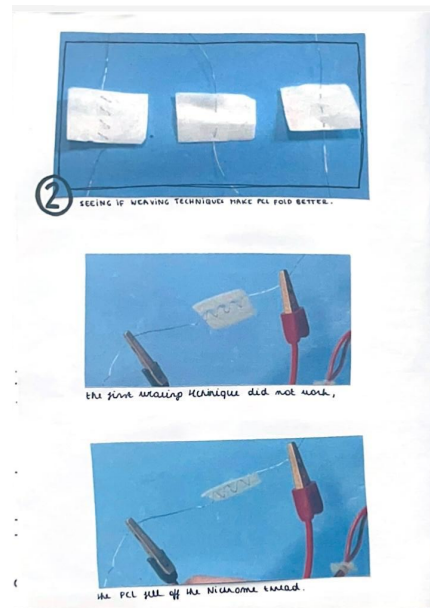
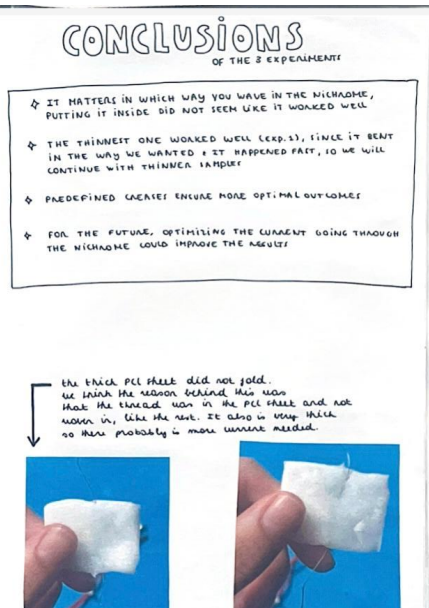
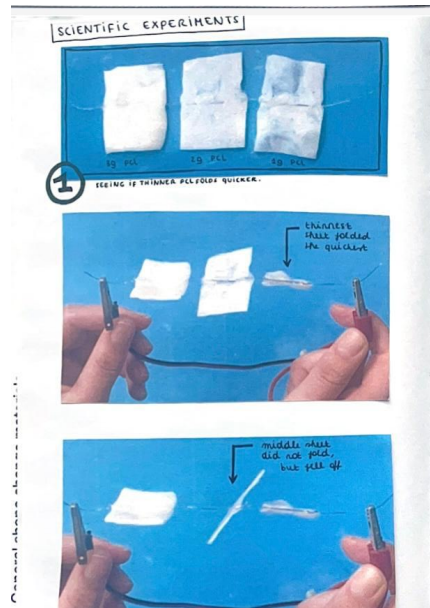
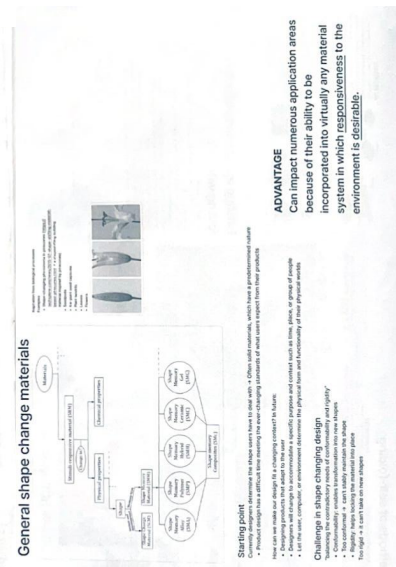
3D printing

Blow molding

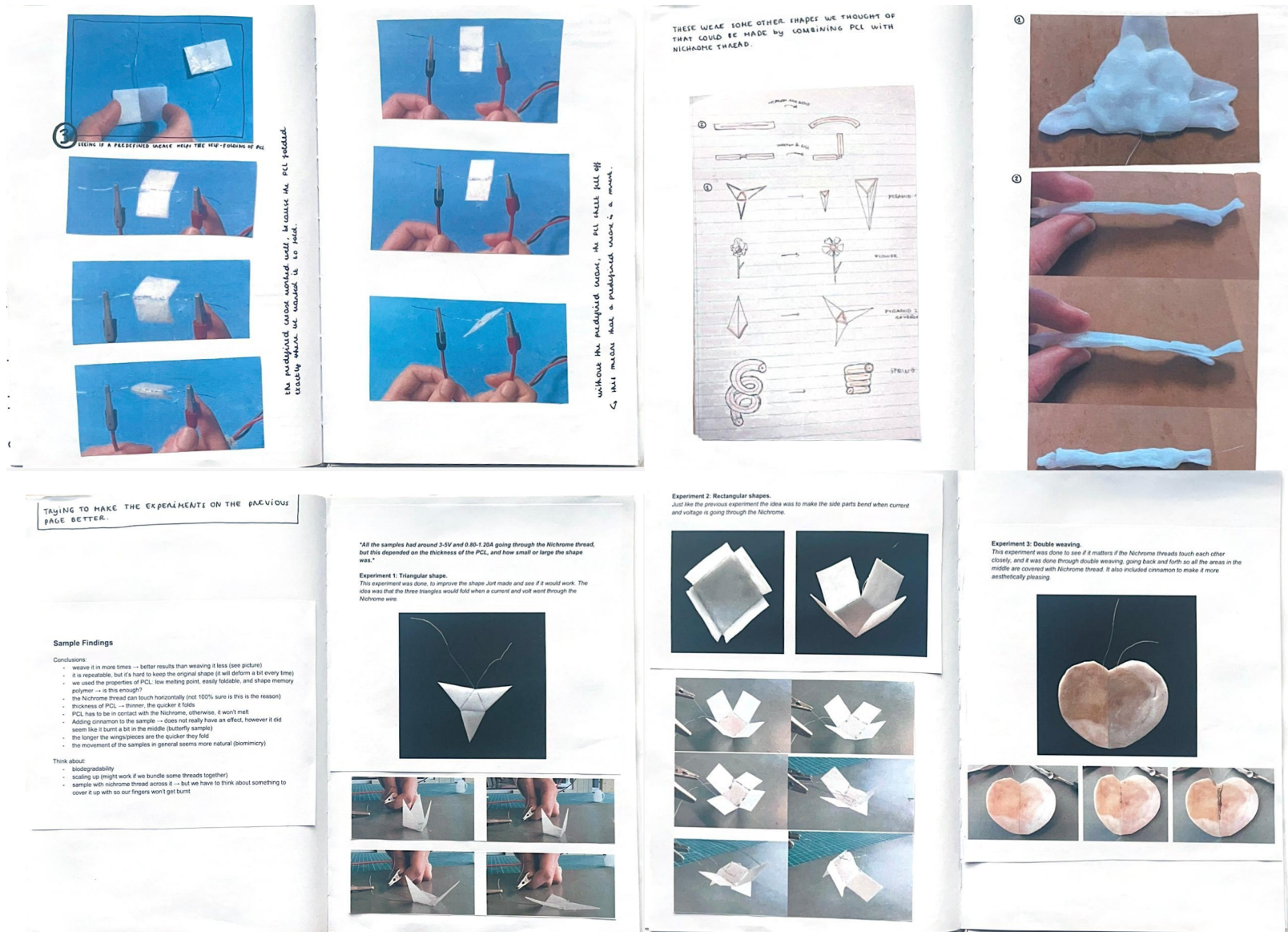
Electrospinning

Mixing with additives

APPENDIX 1: PROCESS BOOK



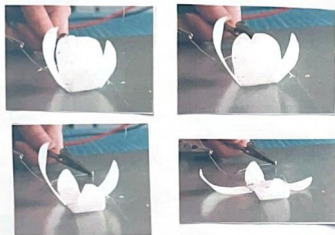
APPENDIX 1: PROCESS BOOK



APPENDIX 1: PROCESS BOOK

Experiment 4: Floral shaped PCL

This shape was made to mimic the natural shape of a flower. The idea also with this one was that the side pieces would go down once the Nichrome thread was heated.



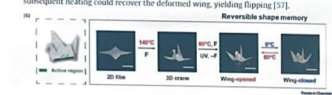
DOING HOME RESEARCH

Organi-PCL Research

<https://www.sciencedirect.com/science/article/pii/S2669597419302564>
PCL is a shape-memory polymer (SMP) by itself, and can be combined with other materials to become a two-way or triple state shape memory polymer.

- One-way shape memory: a material that exhibits shape memory only upon heating (Polysyan)
- Two-way shape memory: a material that exhibits shape memory at heating as well as cooling (Polysyan)
- Triple-shape-memory polymers will switch from one temporary shape to another at the first transition temperature, and then back to the permanent shape at another, higher activation temperature (Wikipedia, etc).

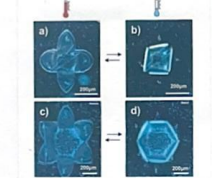
into a new set of temporary shapes [45,55,55,58]. As shown in Figure 46, a flat sheet made from PCL/PJ based two-way SMP can undergo bond exchange and be folded into a 3D crane. When the active region of the wing underwent photo-induced dimerizations, subsequent heating could recover the deformed wing, yielding flipping [57].



SMPs	Material	Shape Memory	Thermal	Medical devices, consumer products, drug delivery, smart packaging
PCL/PJ based SMPs	PCL, PCL/PJ, PCL/PJ/PJ	One-way shape memory	Thermal	Medical devices, consumer products, drug delivery, smart packaging
PCL/PJ based SMPs	PCL, PCL/PJ, PCL/PJ/PJ	Two-way shape memory	Thermal	Medical devices, consumer products, drug delivery, smart packaging
PCL/PJ based SMPs	PCL, PCL/PJ, PCL/PJ/PJ	Three-way shape memory	Thermal	Medical devices, consumer products, drug delivery, smart packaging



<https://www.ncbi.nlm.nih.gov/pmc/articles/PMC7807481/>



Could PCL be of use in reforestation? The ability of PCL to fold flat, it being biodegradable and non-toxic (important when reforesting lands affected by wildfires) can perhaps create a foldable container for aerial seeding of tree saplings for reforestation of wildfire-affected lands. Through organ techniques, we could create a self-burying seed carrier that can also hold soil-improving and plant-supporting resources, that is ultra-small and perhaps foldable, cheaply made and hopefully effective.

Aerial seeding is a technique that throws seeds out of airplanes or drones to reforest or seed difficult-to-reach grounds. It is less effective than drilled seeding and thus only useful for these areas. <https://www.youtube.com/watch?v=3AaKvnm5d0> is an example of a self-burying seed carrier. It is made of wood and molded into the shape of Erodium seeds.

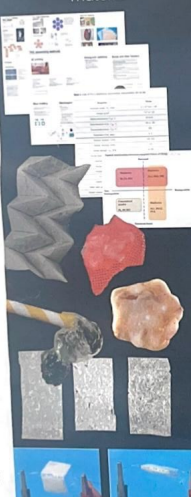


Erodium cicutarium seeds

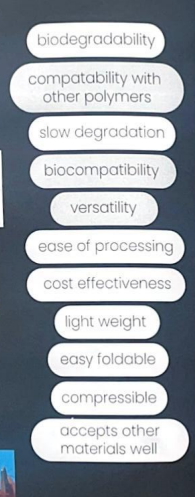


Material Driven Design Process

1 understanding the material



2 creating materials experience vision



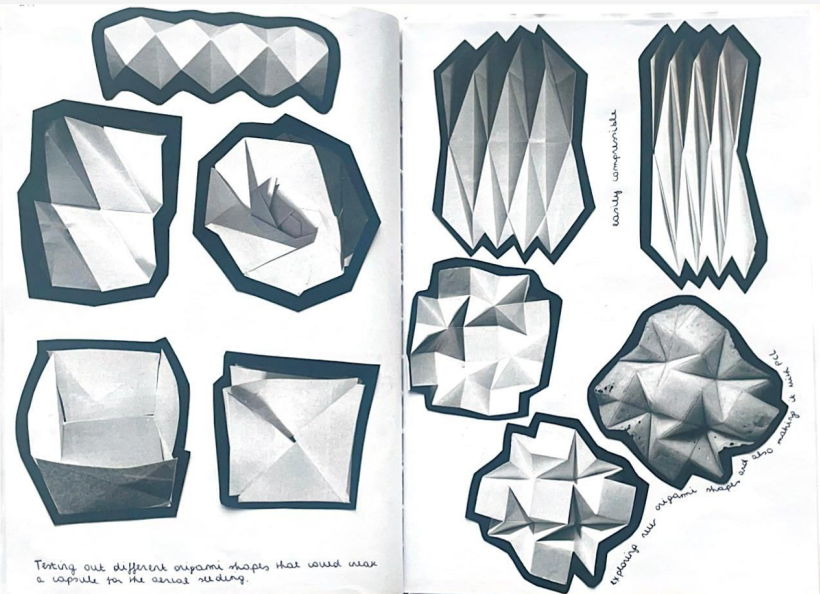
3 manifesting materials experience patterns



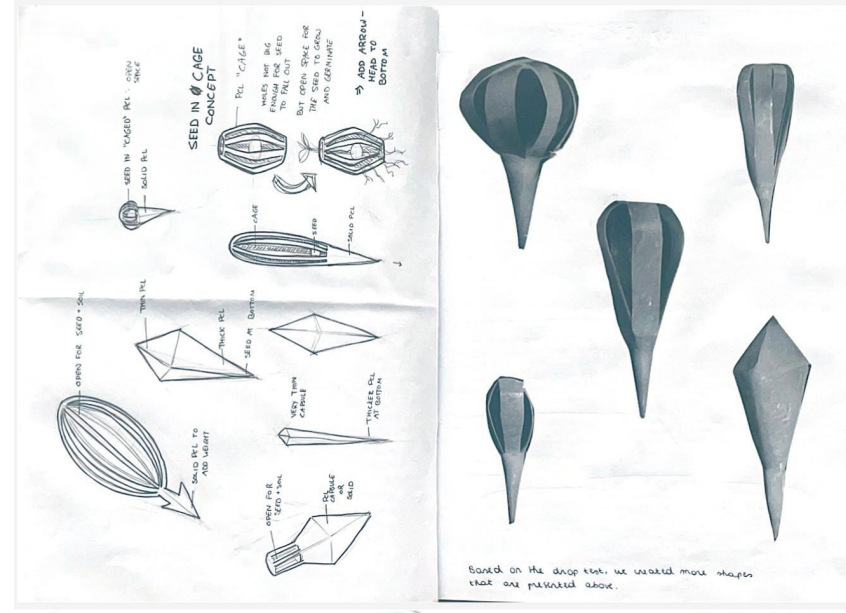
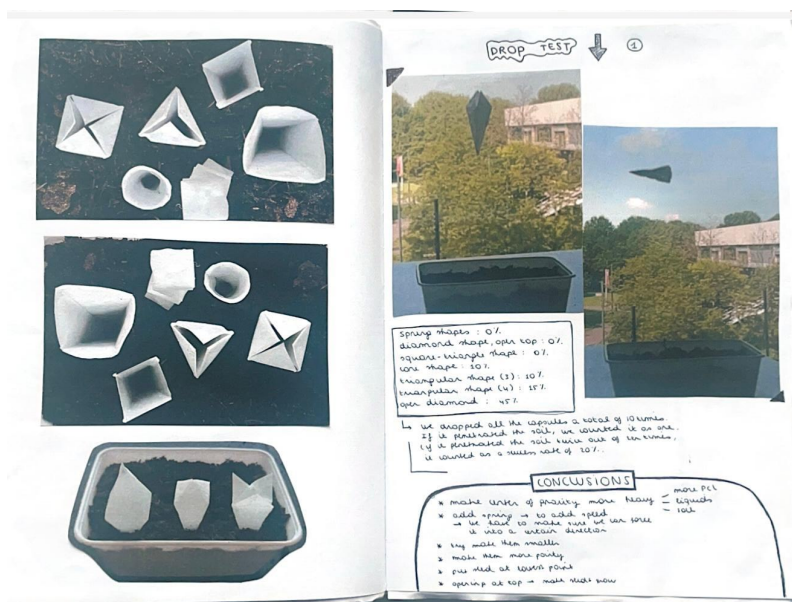
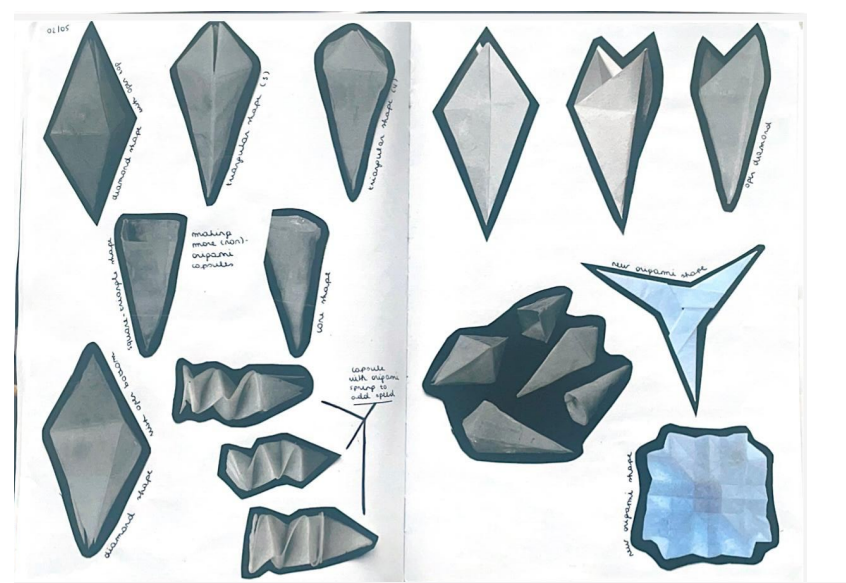
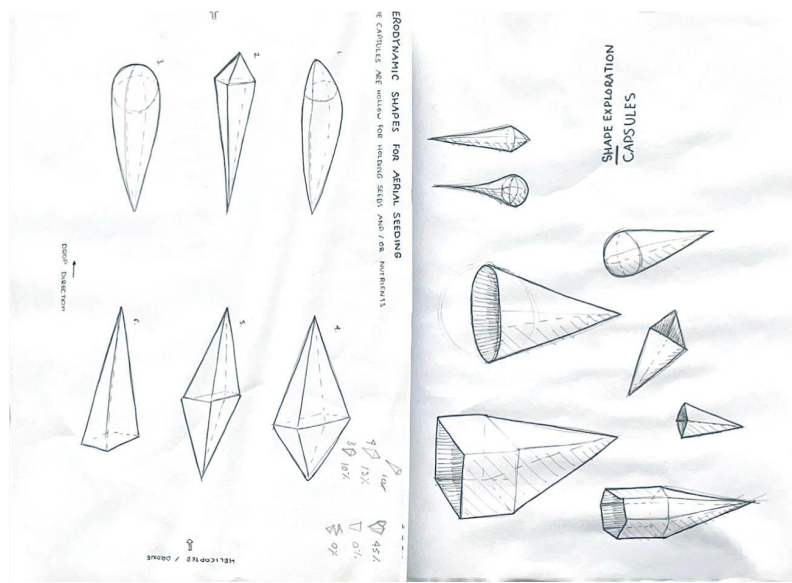
4 designing material/product concepts



How can the folding properties of PCL be used in the novel delivery of drugs, nutrients or seeds?



APPENDIX 1: PROCESS BOOK



APPENDIX 1: PROCESS BOOK



APPENDIX 2: SAMPLE CIRCLES



APPENDIX 2: SAMPLE CIRCLES



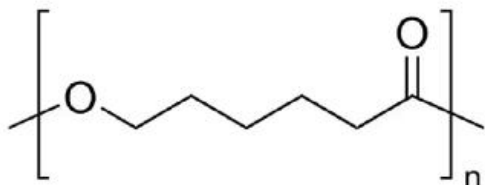
APPENDIX 2: SAMPLE CIRCLES



APPENDIX 3: VISUAL BENCHMARK

PCL, The material

- Biodegradable, petroleum-based
- Semicrystalline → highly ordered molecular structures with sharp melt points
- Hydrophobic
- Low transition temperature (around 60 degrees)
- Chemical structure of PCL:
- Biocompatible

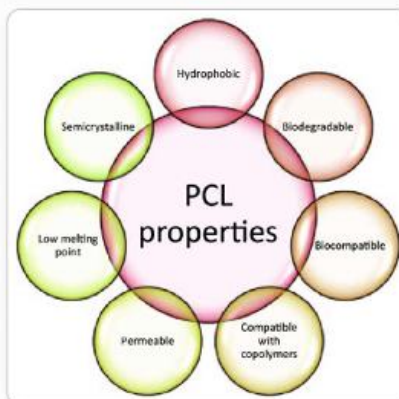


HOW IS PCL MADE

PCL is formed through a process called ring-opening polymerization

Process:

1. An initiator [tin(II) 2-ethylhexanoate and stannous octoate] starts the reaction by reacting with the cyclic monomer
2. Once the initiator has reacted with the cyclic monomer, it forms an active species that reacts with additional monomer molecules. This reaction continues, with each monomer adding to the growing polymer chain
3. Eventually the reaction stops, either when all the monomer has been consumed, or when a terminating agent is introduced. In the case of PCL, the terminating agent could be a chemical that reacts with the active species, halting further polymerization
4. The end result of this process is a long chain polymer made up of repeating units of ϵ -caprolactone, forming PCL



Biodegradability

"The capacity for biological degradation of organic materials by living organisms down to the base substances, such as water, carbon dioxide, methane, basic elements and biomass."

- PCL degrades more slowly in soil
- The degradation time of PCL varies based on factors such as molecular weight, environmental conditions, and the presence of enzymes or microorganisms
- In natural environments: PCL can take several years to biodegrade completely
- In controlled environments, like composting facilities, where the temperature, humidity, microbial activity are optimized: PCL can degrade more rapidly: within a few months to a year
- Compared to some other biodegradable polymers like polylactic acid (PLA) or polyhydroxyalkanoates (PHA) → PCL generally degrades more slowly
- Proper disposal methods should be considered for PCL products to minimize environmental impact and ensure effective biodegradation

[https://www.nature.com/articles/s41428-020-00396-5.pdf?](https://www.nature.com/articles/s41428-020-00396-5.pdf?error=cookies_not_supported&code=fbbc7442-caa1-427b-9e2b-0c85fda1f3d8)

<https://www.sciencedirect.com/topics/chemistry/biodegradability#:~:text=Biodegradability%20is%20the%20capacity%20for,methane%2C%20basic%20elements%20and%20biomass.>

<https://www.sciencedirect.com/topics/chemistry/biodegradability#:~:text=Biodegradability%20is%20the%20capacity%20for,methane%2C%20basic%20elements%20and%20biomass.>

Strengths

- High strength
- High biocompatibility
- Good electrospinning properties
- Synthetic material: ability to achieve high material purity
- High drug permeability
- Undergoes microbial and enzymatic degradation under external conditions
- Degraded very slowly in vitro in the absence of enzymes and in vivo as well
- Can easily blend with other polymers
- Soluble in a wide variety of chlorinated/fluorinated organic solvents, as well as partially soluble in acetone and dimethylformamide
- Low degradability in aqueous environments
- Degrade over a period of 2-4 years depending on its molecular weight and degree of crystallinity

Weaknesses

- Less versatility due to a lack of chirality in the PCL chain
 - Non-functionalized polymer, except at the chain ends
 - Toxic solvents
 - Poor adhesion to cells due to hydrophobic surface
- <https://www.ncbi.nlm.nih.gov/pmc/articles/PMC9653691/>
https://www.researchgate.net/figure/Key-advantages-and-disadvantages-of-the-selected-polymer-materials.tsl3_288671121

APPENDIX 3: VISUAL BENCHMARK

PCL in the medical field

PCL braces



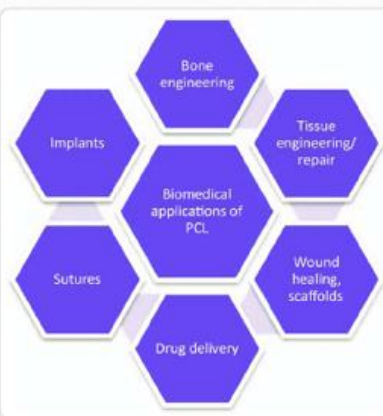
3D-Printed Polycaprolactone Mechanical Characterization and Suitability Assessment for Producing Wrist-Hand Orthoses. <https://doi.org/10.3390/polym15030576>



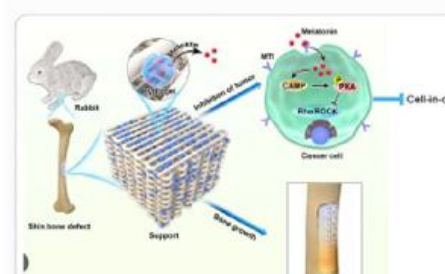
PCL can be used as a carrier for in-eye drug delivery
<https://www.sciencedirect.com/science/article/pii/S0168365919305632>



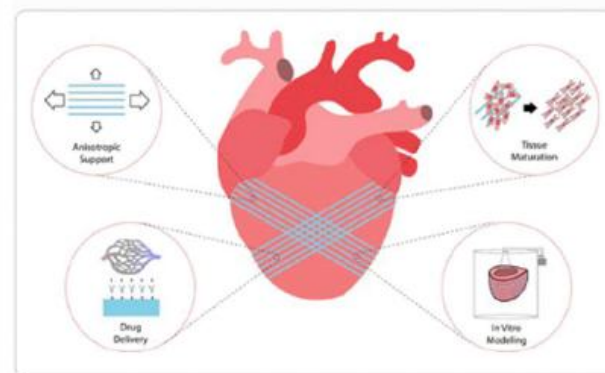
Absorbable surgical sutures (stiches)
<https://www.huidainstrument.com/surgical-sutures-needles/polycaprolactone-surgical-sutures-absorbable.html>



PCL is a widely recognized biodegradable and biocompatible petroleum-based polymer with numerous applications in packaging, scaffolds, prosthetics, sutures, drug delivery, films, carry bags, pouches, trays, reusable dishes, membranes, and other fields. It can be degraded without polluting the environment by hydrolysis of ester bonds or by microorganisms [6]. It is also easily blended with other polymers and is soluble not in water but in a number of different organic solvents [7].
https://www.researchgate.net/figure/Biomedical-applications-of-polycaprolactone_fig4_348902304



3D-printed magnesium-PCL stops bone cancer
<https://nanobiotechnology.biomedcentral.com/articles/10.1186/s12951-021-01012-1>
(osteosarcoma is the most common type of cancer that starts in bones)



<https://pubs.acs.org/doi/10.1021/acsabm.2c00174>

APPENDIX 3: VISUAL BENCHMARK

Other PCL Products



PCL model making <https://www.youtube.com/watch?app=desktop&v=shq8vXk7U6I>



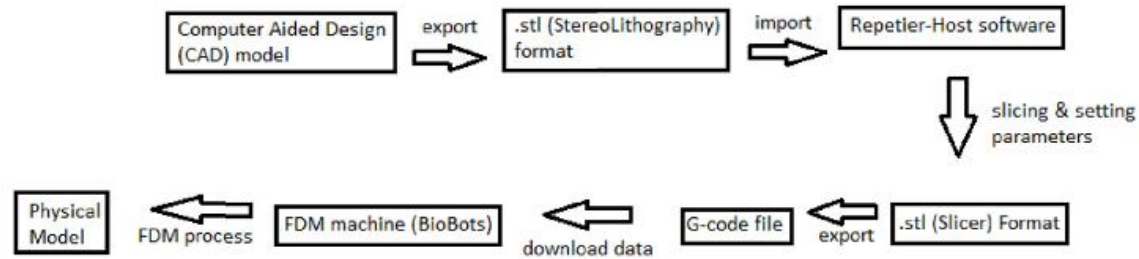
Waste bags
<https://www.brighton.net/en/product/item-142.htm>



3D Printing https://www.researchgate.net/figure/3D-printed-complex-anatomical-structures-based-on-polycaprolactone-PCL-with-polyvinyl_fig2_244481636

APPENDIX 3: VISUAL BENCHMARK

3D printing



FDM: Fused Deposition Modeling

- Most common method for 3D printing
- PCL as filament material
- Heated Nozzle
- Layer-by-layer deposition
- Support structures if needed
- Post processing (example: removal of supports structures)

https://www.researchgate.net/figure/Basic-steps-of-the-FDM-process-for-producing-3D-printed-PCL-scaffolds_fig5_316860984

SLS: Selective Laser Sintering

- PCL as a powdered material
- Layer-by-layer sintering
- Building up layers
- Cooling and solidification
- Supports structures if needed

https://www.researchgate.net/figure/SLS-processed-PCL-test-part-fabricated-at-optimally-determined-process-parameters-a_fig2_245368580

SLA: Stereolithography

- PCL as resin material
- Layer-by-layer photopolymerization
- Building up layers
- Supports structures if needed
- Post curing

https://www.researchgate.net/figure/Photograph-of-a-PCL-based-scaffold-prepared-by-SLA-63_fig12_226142574

Mixing with additives

Some additives for mixing it with PCL and why:

- Polylactic acid (PLA) is more rigid: increases stiffness of PCL (<https://www.frontiersin.org/articles/10.3389/fmats.2019.00206/full>)
- Polyethylene glycol (PEG) is hydrophilic: enhances water absorption and biocompatibility of PCL
- Glycerol, glycerin: improve flexibility of PCL
- (Bamboo) fibers: adds considerable toughness, flexibility, easy processing, recyclability and eco-friendliness. Longer fibers mean more tensile strength and durability

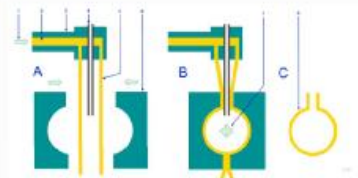
Blow molding

Blow molding is a process for forming hollow plastic parts.

There are three types of blow molding: extrusion blow molding, injection blow molding and injection stretch molding.

Process:

1. Softening plastic by heating a preform or parison
 - a. parison = tube-like piece of plastic with a hole in one end through which compressed air can enter
2. Plastic workpiece is clamped into a mold and air is blown into it, the air pressure inflates the plastic which conforms to the mold
3. Once cooled and hardened the mold opens and the part is ejected



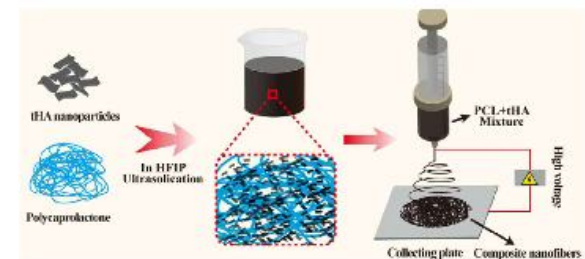
Electrospinning

Process:

1. Preparation of PCL solution
 - a. Dissolve PCL polymer in suitable solvent to form a viscous solution
2. Setup of electrospinning apparatus
 - a. Mount a syringe containing PCL solution onto a syringe pump (pump controls the flow rate of the solution)
 - b. Connect high-voltage power supply to the syringe needle → creates an electric field between the needle and a grounded collector
 - c. Position the collector a suitable distance away from the syringe needle
3. Electrospinning process
 - a. Turn on the syringe pump to start the flow of the polymer solution
 - b. Apply a high voltage between the syringe needle and the collector
 - c. As the solution is pumped through the needle, the electrostatic repulsion overcomes the surface tension, forming a charged jet of polymer solution
 - d. The charged jet stretches and elongates as it travels towards the grounded collector due to the electric field, forming ultrafine fibers
 - e. The solvent evaporates during the flight, leaving behind solid PCL fibers on the collector
4. Collection of electrospun fibers
 - a. Fibers are collected on the grounded collector in the desired arrangement (random, aligned, patterned)
 - b. Once the desired thickness or amount of fibers is obtained, the electrospinning process is stopped

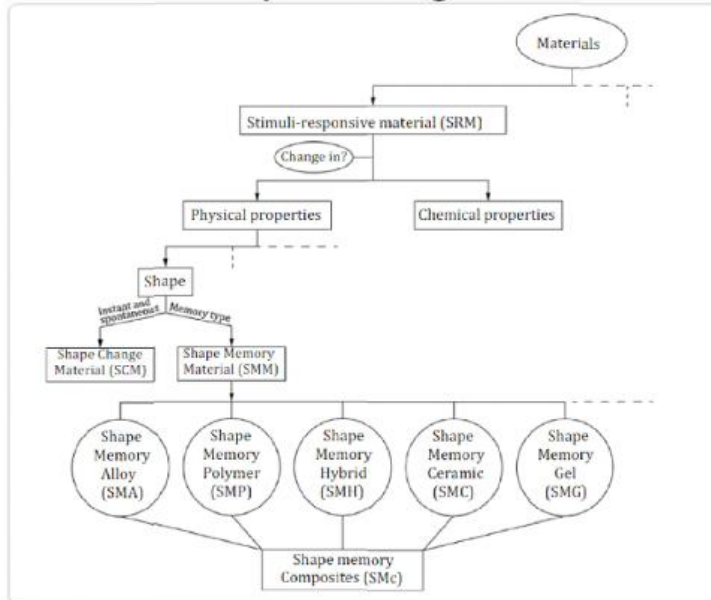
https://www.wikilectures.eu/w/Tissue_engineering

<https://www.semanticscholar.org/paper/Polydopamine-Templated-Hydroxyapatite-Reinforced-Gso-Song/99102cc27855621074c4684528ae3a29be63af56/figure/2>



APPENDIX 3: VISUAL BENCHMARK

General shape change materials

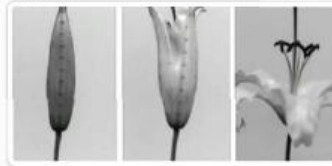


Inspiration from biological processes

Examples:

- Shape-changing phenomena in pinecones (<https://techxplore.com/news/2015-07-shape-shifting-material-based-pinecones.html> → a shapeshifting building material inspired by pinecones)

- Seedpods
- Ice-plant seed capsules
- Plant tendrils
- Leaves
- Flowers



Starting point

Currently designers determine the shape users have to deal with → Often solid materials, which have a predetermined nature

- Product design has a difficult time meeting the ever-changing standards of what users expect from their products

How can we make our design fit a changing context? In future:

- Designing products that adapt to the user
- Designers will change to accommodate a specific purpose and context such as time, place, or group of people
- Let the user, computer, or environment determine the physical form and functionality of their physical worlds

Challenge in shape changing design

"balancing the contradictory needs of conformability and rigidity"

- Conformability: enables transformation into new shapes
- Too conformal → can't stably maintain the shape
- Rigidity: helps locking the material into place

Too rigid → it can't take on new shapes

ADVANTAGE

Can impact numerous application areas because of their ability to be incorporated into virtually any material system in which responsiveness to the environment is desirable.

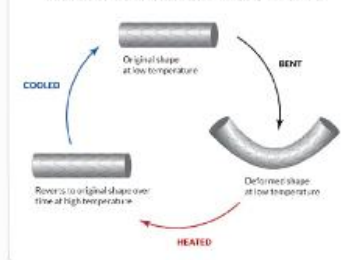
APPENDIX 3: VISUAL BENCHMARK

Methods of self-folding

Shape Memory Polymers (SMP):

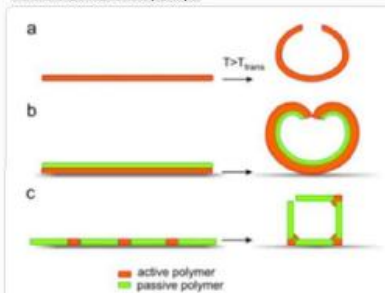
- Original shape → shape change → stimuli → return to original shape

The Phase Transformation Process for SMAs

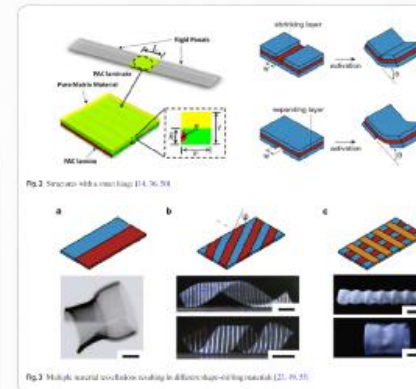
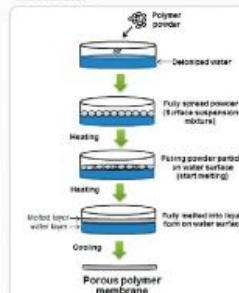


Polymer bilayer

- Active and passive polymer
- Active polymer → stimuli → active polymer changes shape/volume while passive polymer stays the same → bilayer shape change
- https://www.tfd.de/fileadmin/user_upload/nm/stamny/Praktikum/2_Jenox_manuscript_rev.pdf



Creating porous PCL membrane for bilayer
<https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6273409/>



4D PRINTING

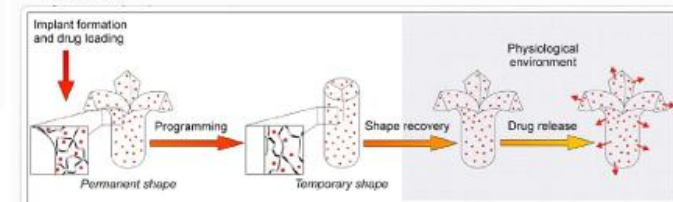
4D printing involves creating objects using smart materials that can change shape or properties over time in response to external stimuli like heat or light. The main advantage is size reduction, since objects can be "folded" or "compressed" during printing to fit within machine constraints. Also, 4D printing enables precise designs and control over material distribution.

https://www.researchgate.net/publication/332059109_A_taxonomy_of_shape-changing_behavior_for_4D_printed_parts_using_shape-memory_polymers

Existing applications of self-folding with PCL

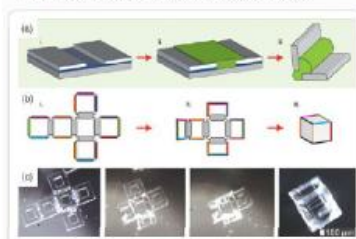
Some examples of applications:

- Drug delivery systems: controlled encapsulation and release of drugs, particles and cells
- Smart plasters: for medical applications, improve drug transport
- Tissue engineering scaffolds
- Micro- and nano-actuators for applications in robotics or microsurgery. actuators can respond to external stimuli such as temperature, pH, or light to perform specific movements or tasks
- Soft robotics: create robots with adaptive, shape-changing capabilities
- Responsive textiles: Self-folding polymers can be incorporated into textiles to create fabrics that respond dynamically to changes in environmental conditions



Thermo-responsive polymers:

- Original shape → temperature change → shape change



pH-responsive polymers

- Original shape → change in pH → shape change

Solvent-responsive polymers

- Original shape → solvent mixture → shape change

STIMULI

- Temperature
- Water (hydrophilic vs hydrophobic)
- pH
- Solvents
- Forces

