

PARAMETRIC CHEMISTRY

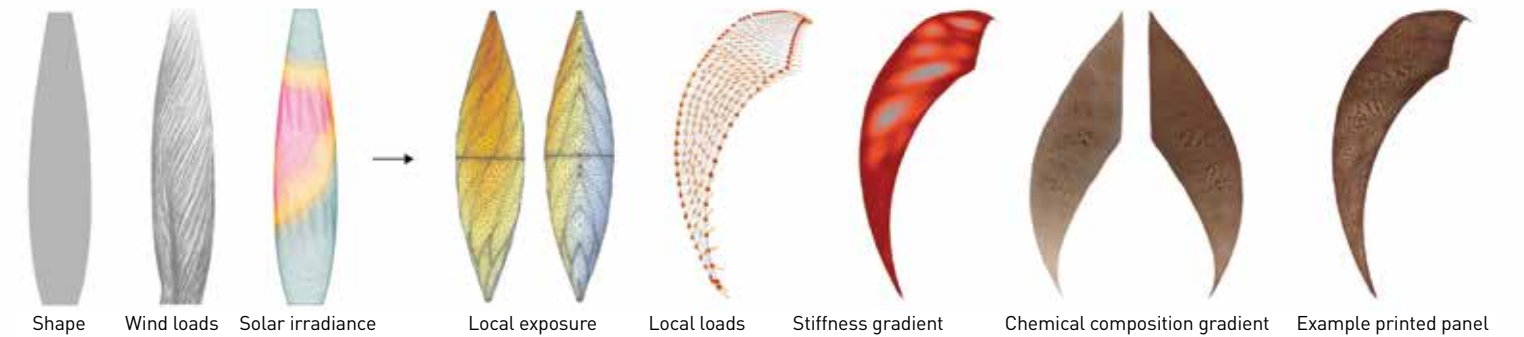
Reverse engineering biomaterial composites for robotic manufacturing of bio-cement structures across scales

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At the close of the Digital Age, the fields of digital design and fabrication remain constrained by the canons of manufacturing and mass production. Products, structures and architectural constructions are still designed in terms of discrete elements with distinct functions and homogeneous properties (Oxman, 2016). By contrast, living structures grow from cells programmed to tune their own physical and chemical properties, as well as those of the materials they synthesize—through growth and remodeling—as a function of genetic, intracellular and environmental constraints and across spatial and temporal scales (Oxman, 2015). In this paper, we propose a novel design approach and technology enabling integration between geometrical complexity, material behavior and robotic fabrication at scales that approach—and often match—those of Nature.



a) ENVIRONMENTAL MAPPINGS & HIERARCHICAL PROPERTY DESIGN for prototypical panel shapes and material distributions



b) INITIAL SHAPE, PANEL ASSEMBLY & PATTERN EXPLORATION:

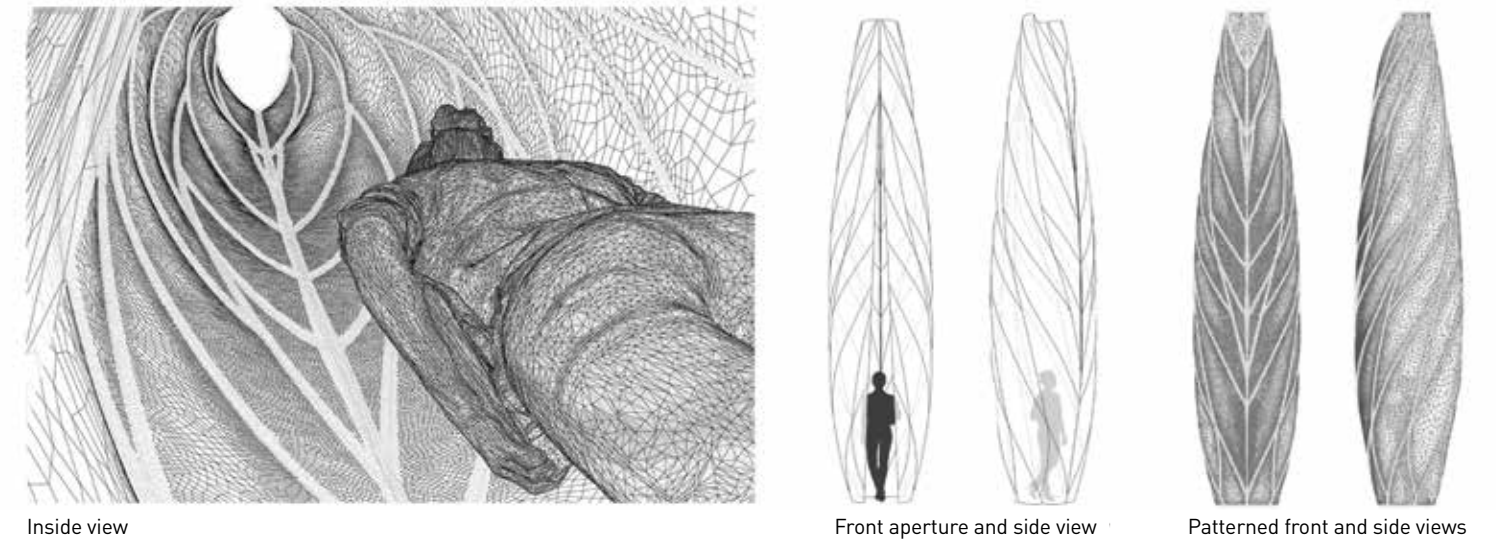


Fig.1 (opposing page). Detail of material differentiation via deposition parameters and curing time; Fig. 2 (above). a) Global shape and textures were generated from environmental mappings for the City of Cambridge, MA (April 2017). In response, hierarchical material distributions, patterns, layering strategies and other design decisions were deployed to optimize local, regional and global responses to changing environmental conditions. b) Initial drawings of experiential qualities both within and outside of the biomaterial pavilion prototype.

We coin the term “parametric chemistry” to denote, describe and demonstrate the ability to control the composition, structure and properties of physical matter across multiple-length scales, using a customized multi-material, robotically actuated additive manufacturing platform and its associated parametric environments. As a proof-of-concept, a tunable bio-cement composite has been engineered via parametrically controlled deposition of organic and inorganic elements including—but not limited to—chitosan, calcium carbonate, pectin, cornstarch and cellulose. The chemical, mechanical and optical properties of prototypical bio-composites were evaluated and implemented as inputs for computational design and digital fabrication, thereby facilitating nearly full integration between robotic fabrication platforms, material modeling and form generation. Toward this end, we have demonstrated a set of parametrically tuned and chemically altered surface-based structures embodying hierarchical behavior informed by geometry and material composition.

Specifically, in order to utilize strategies that enable parametric tunability for digital fabrication, we have developed a novel bio-composite that can be digitally tuned and fabricated using the previously developed water-based digital fabrication platform (Duro-Royo et al., 2015; Duro-Royo et al., 2014), which has been configured to facilitate the digital design and fabrication of large-scale bio-composite architectures using multiple materials with varying properties (Appendix A).

In this study, we focus on two natural biopolymers—chitosan and cellulose—which are widely abundant in nature and exhibit extraordinary mechanical properties, especially when combined with organic and inorganic substances (Fernandez & Ingber, 2013; Mogas-Soldevila et al., 2014; Vincent, 2012). However, architects and engineers have yet to establish the methods by which to reconfigure biopolymers into useful composites across functional length-scales that match—and even transcend—the properties and functionality of traditional building materials (Fernandez & Ingber, 2012).

2. DESIGN & TECHNICAL APPROACH

The water-based digital fabrication platform was developed by The Mediated Matter Group at the MIT Media Lab to enable multilateral additive manufacturing of hierarchical biomaterial structures across scales using a robotic platform (Duro-Royo et al. 2015; Duro-Royo et al., 2014). The development of this technology has furthered our research approach—Material Ecology, and one of its key enablers—Fabrication Information Modeling (Duro-Royo & Oxman, 2015; Oxman, 2013).

2.1 MATERIAL ECOLOGY

Conventional product- and architectural-design prioritize a ‘shape first’ approach, assigning materials to shape in a retroactive manner. Moreover, established design practices do not typically enable design generation and digital fabrication of functionally graded materials across scales (Oxman, 2010; Oxman, 2011). As a result, structural components are generally fabricated from, and manufactured as, single materials with homogeneous properties subse-

quently formed into predefined shapes, performing predetermined, specific functions (Oxman, 2010).

Inspired by the natural world, we believe that multivalent wholes designed to match nature’s nuances will in the future far surpass the performance of antiquated assemblies of mono-material parts. We explore this design approach by combining environmentally informed numerical simulation, data-driven material modeling and multi-material robotic manufacturing of biomaterial composites.

We define material ecology as the interrelationship between human-made (or designed) structures—fabricated with property gradients at the resolution of nature, enabling multi-functionality that matches nature and their environs (White House, 2014). This design approach promotes the conceptualization of holistic products, characterized by property gradients and multi-functionality (Oxman et al., 2015).

In attempting to recreate processes and properties found in nature that support spatial and temporal tunability, the material ecology approach builds on the underlying logic of biological fabrication to conserve energy and materials by parametrically varying ratios of universal ingredients thereby designing their shape through physical behavior. The goal is to enable different

elements of a material to adapt to various specific environmental conditions, ultimately feeding energy and nutrients back into the planet, through dissociation and bio-degradation.

As such, the range of properties given by a material—including its biodegradation—must be utilized to express and respond to specific environmental conditions. Further, distributed fabrication ‘agents’—such as cells, minerals and organic compounds—are often integrated into the materials they synthesize to allow for dynamic feedback and remodeling using various types of environmental data, which can be used to locally modulate the material over time. For instance, after osteoclasts digest old bone, mononuclear cells migrate to the surface, at which point osteoblasts deposit new bone until the old bone is completely replaced (Hadjidakis, 2006). Such bone remodeling enables cell networks to tune a bone’s architecture to varying mechanical needs, while repairing damage within the bone matrix.

In a similar way, stem cells in the plant kingdom repair and remodel plant tissue in response to changing seasons and environmental stresses. The sequoia sempervirens, the tallest tree in the world, holds stem cell reservoirs that can function for more than 2,000 years within one tree. In fact, all plants carry small stem cell reservoirs at the growing ends of shoots and roots that can be deployed when repair or regrowth is needed (Mayer, 1998). This intimate relationship between design and biology, digital fabrication and natural growth or adaptation, points toward a shift from consuming nature as a geological resource to editing it as a biological one (Oxman, 2015).

Designers and architects are empowered as a result to “program” material behavior, directly informed by digital fabrication parameters. As a conceptual methodology that calls for parametric-based communication between form generation, manufacturing, the environment and the material itself, material ecology promotes the design of fabrication platforms designed to inform both the shape and the properties of the final construct.

2.2 FABRICATION INFORMATION MODELING

Fabrication information modeling is a design approach and a technical framework that facilitates the design and robotic fabrication of geometrically complex and materially heterogeneous structures with tunable mechanical, optical and chemical properties across scales. The water-based digital fabrication platform embodies the principles of the fabrication information modeling framework by enabling real-time feedback across physical and digital platforms including computational form finding, material modeling and robotic fabrication. This feedback can be triggered in response to interactions between the molecular structure of the substrate material—such as molecular density and organization—and the surrounding environment, resulting in structures that inform and/or are informed by the extra-structural matrix. For instance, a thermal camera has been used to evaluate regional heat distributions in order to modulate the temperature gradient of printed material as it dries at room temperature. Doing so can both mitigate warping due to uneven evaporation and solidification, as well as communicate to robot operators when to deposit the next layer.

Design iterations based on real-time feedback of this nature may involve, by example, variation in nozzle pressure as a function of an anticipated load profile. Variability in nozzle pressure would, in turn, result in structural member thickness variation representing and corresponding with the load profile. Here, the encoded chemical information within a designed material dynamically communicates with—and is inseparable from—its fabrication processes and expressions. Consequently, shape and material composition can be directly informed by physical properties (e.g., stiffness and opacity), environmental conditions (e.g., load, temperature and relative humidity), and fabrication constraints (e.g., degrees of freedom, arm speed and nozzle pressure). Through this process, designers are able to maximize mechanical, optical and environmental material performance such as strength, thereby accounting for contractile forces due to drying, among other environmental fluctuations. As such, the platform and its related software environment are designed to bridge the gap between virtual design and digital fabrication (Duro-Royo et al., 2015; U.S. Patent Application 16/20160075089—2015).

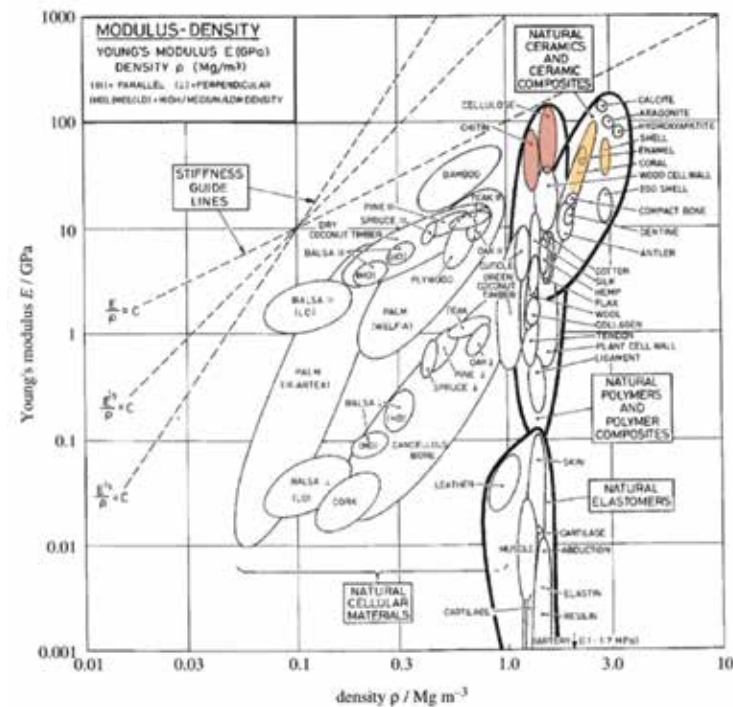
2.3 WATER-BASED DIGITAL FABRICATION

The water-based digital fabrication platform consists of a custom extrusion system attached to an existing robotic arm, for which we have programmed and integrated real-time instruction feed and feedback capabilities (Duro-Royo et al., 2015). Designs are generated computationally to tailor speed and motion paths, nozzle sizes, air pressure, material selection and distance from the substrate. Modulating such parameters enables us to tune the weight and height of extruded material down to sub-millimeter tolerances (Duro-Royo et al., 2015). Specifically, the platform is configured to deposit water-based materials such as polysaccharide blends, clays and cements, as well as various colloids, in 2.5- and 3-dimensions. Using molds with extreme curvature and irregular geometry, we have been able to engender purposeful three-dimensionality within large, panelized components (Fig. 6b). Furthermore, taking advantage of multiple robots simultaneously extruding material has facilitated quick and expansive experimentation and fabrication (Fig. 5b).

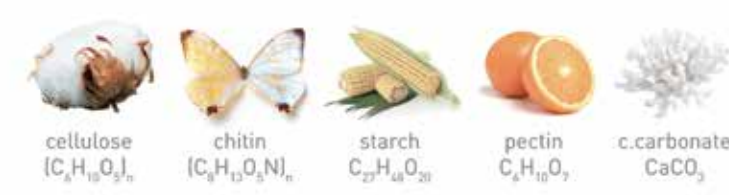
Recently, we have achieved intermediate goals in large-scale manufacturing of fully biodegradable, lightweight, and self-supporting structures based on chitosan-cellulose blends (Mogas-Soldevila et al., 2015). (Fig. 6, 7) These robotically fabricated bio-composite structures have been inspired by natural shell structures in their integration of organic and inorganic materials derived from our previous work in composite-based hierarchical constructs (Mogas-Soldevila, Duro-Royo, et al., 2015). The resulting properties of these designed materials will drive immediate improvements in the water-based digital fabrication platform, which will allow for extended extrusion capabilities as well as novel biological functionality within the fabrication platform.

Fig. 3. a) An Ashby chart depicting material properties of the composite building blocks comparing their density and Young’s modulus with those of other architectural materials. b) Natural origin of materials of interest: cellulose pulp from trees, chitosan from chitin in insect wings, starch from corn and calcium carbonate from mining or quarrying c) Requirements for function and ‘fabricability’ to enable an integrated design for large-scale biomaterial structures.

a) Material properties chart [M.F. Ashby, L.J. Gibson et al. 1995]



b) Natural origin of our materials of interest:



c) LARGE-SCALE STRUCTURES design requirements

Design parameters:

- fully-tuned optical and mechanical behavior
- future support of biological augmentation
- overall lightweight
- full biodegradability

Digital fabrication constraints:

- constant physical-to-virtual feedback
- nano-to-macro material behavior control
- integration of trans-disciplinary data sets

2.4. BIOMATERIALS PAVILION

We are currently at work on the design and digital fabrication of a full-scale pavilion made entirely of biomaterials utilizing dynamic, data-driven communication between the computational design environment and the robotic platform (Fig. 4). This project demonstrates the flow of data throughout the entire lifespan of biological materials from synthesis to degradation. Furthermore, material-based data relayed to the robotic platform is utilized to drive design strategies and fabrication parameters at various length scales, from sub-millimeter resolution for patterning to the overall shape and its spatio-structural and environmental performance. Below we present initial experiments and research related to the process of robotically fabricating large-scale biomaterial structures. This initial design for a first-of-its-kind biomaterial pavilion elucidates economical and energy-based budgets relating to embodied energy within functional building blocks to encode for varied functional properties (Fig. 2).

2.4.1 BIOMATERIALS BACKGROUND

Natural biopolymers are abundant, biocompatible, biodegradable and nontoxic, making them appealing as stock materials for use in additive manufacturing of sustainable products (Tran et al., 2013). The bio-cement composites discussed in this paper utilize a chitosan-cellulose backbone, with organic and inorganic additives. The synthesis of these structural biomaterials is a promising step toward large-scale digital manufacturing of economically viable, non-toxic, biocompatible and biodegradable products and structures.

Specifically, we have digitally designed and synthesized various blends of cellulose, chitosan, cornstarch, pectin and calcium carbonate to elicit specific mechanical and optical properties by varying the proportional chemistry through novel fabrication strategies, as prescribed below. In doing so, we have endowed a novel bio-cement with precise and tunable material properties that perform differently at multiple scales, with locally tailored characteristics for desired performance-based outcomes across length scales.

2.4.2 NOVEL BIO-CEMENT

Chitosan is a natural biopolymer found in the shells of crustaceans such as shrimp and lobster. It is the second most abundant natural polysaccharide on the planet, after cellulose (Dawsey, 1994). Cellulose is a natural biopolymer found predominantly in the plant kingdom and is structured as a long chain of linked sugar molecules, which give wood its stiffness. It is also the main structural component of plant cell walls and a building block for textiles (Augustine, 1990). (Fig. 3)

Calcium carbonate is widely used in the pharmaceutical, agricultural, construction and paper industries. It comes mainly from powdered marble and limestone but can also be found in mollusk shells and stony corals (Cho et al., 2016). Importantly, calcium carbonate can endow a strong material with a high stiffness-to-weight ratio (Ofem, Umar, & Muhammed, 2015), which—in nature—

allows for the formation of lightweight, easy to carry shells. Applied on a larger scale, calcium carbonate can enable reductions in the mass of structures, which can allow for smaller and lighter supports, formal freedom, precise and purposeful geometric patterning and low embodied energy (Mo et al., 2016).

Pectin is a carbohydrate in the skin and core of fruit that acts as structural ‘glue’ holding cell walls together. In a solution, pectin can form a fibrous network that traps liquid and sets upon cooling. Combined with acid and sugar, pectin can form a hydrogel (Lopez-Sanchez et al., 2016). In layering bio-cement on top of pectin films—utilizing the water-based digital fabrication platform—a mechanical bond counteracts the bio-cement’s propensity for contraction and curling. In a favorable proportion, its elasticity dominates the bio-cement’s rigidity and strength, thereby allowing for additional control, as well as relatively high levels of spatial tenability, over both the local and global shape of large bio-cement pieces. Furthermore, pectin’s natural translucency allows it to act as skin in patches.

Cornstarch is a powder made by pulverizing corn grains after soaking and removing the embryo and outer covering (Crawford et al., 2013). Cornstarch is used here as a shear-thickening liquid which gives the bio-cement added rigidity and cohesion.

3. MATERIALS AND METHODS

3.1 BIO-CEMENT PREPARATION

A solution of 4-10% cornstarch (w/v) (VWR, Radnor, PA) is heated to 95°C for 20 minutes while stirring vigorously. The temperature is then lowered to 78°C, at which point 8-18% chitosan (w/v) (85% de-acetylated VWR, Radnor, PA) is added to the mixture. The temperature of the solution is then lowered to 37°C, and acetic acid is added in a ratio of 2 parts chitosan to 1-part acetic acid (v/v). At this point, 1-8% calcium carbonate (w/v) is stirred in while folding vigorously to avoid rapid expansion. Finally, 40-70% cellulose (v/v) is added in small amounts to acquire an extremely viscous hydrogel, which is then homogenized with a drill mixer.

3.2 COMPUTATIONAL DESIGN

Line patterns are elaborated in 2.5 dimensions within a putative computer-aided design environment (Rhinoceros3D®) and its parametric modeling tool (Grasshopper®). Here, toolpath instructions are seamlessly sent to the fabrication agent—a robotic additive manufacturing platform—by embedding geometries with abundant meta-data corresponding to nozzle size, direction and height, as well as mechanical pressure and positioning speed. Further detail can be found in (Duro-Royo et al., 2015).

In turn, a material ecology emerges from the flow of data between two convergent scales of design considerations: molecular and environmental. As in growing organisms, molecular dynamics within materials inform the param-

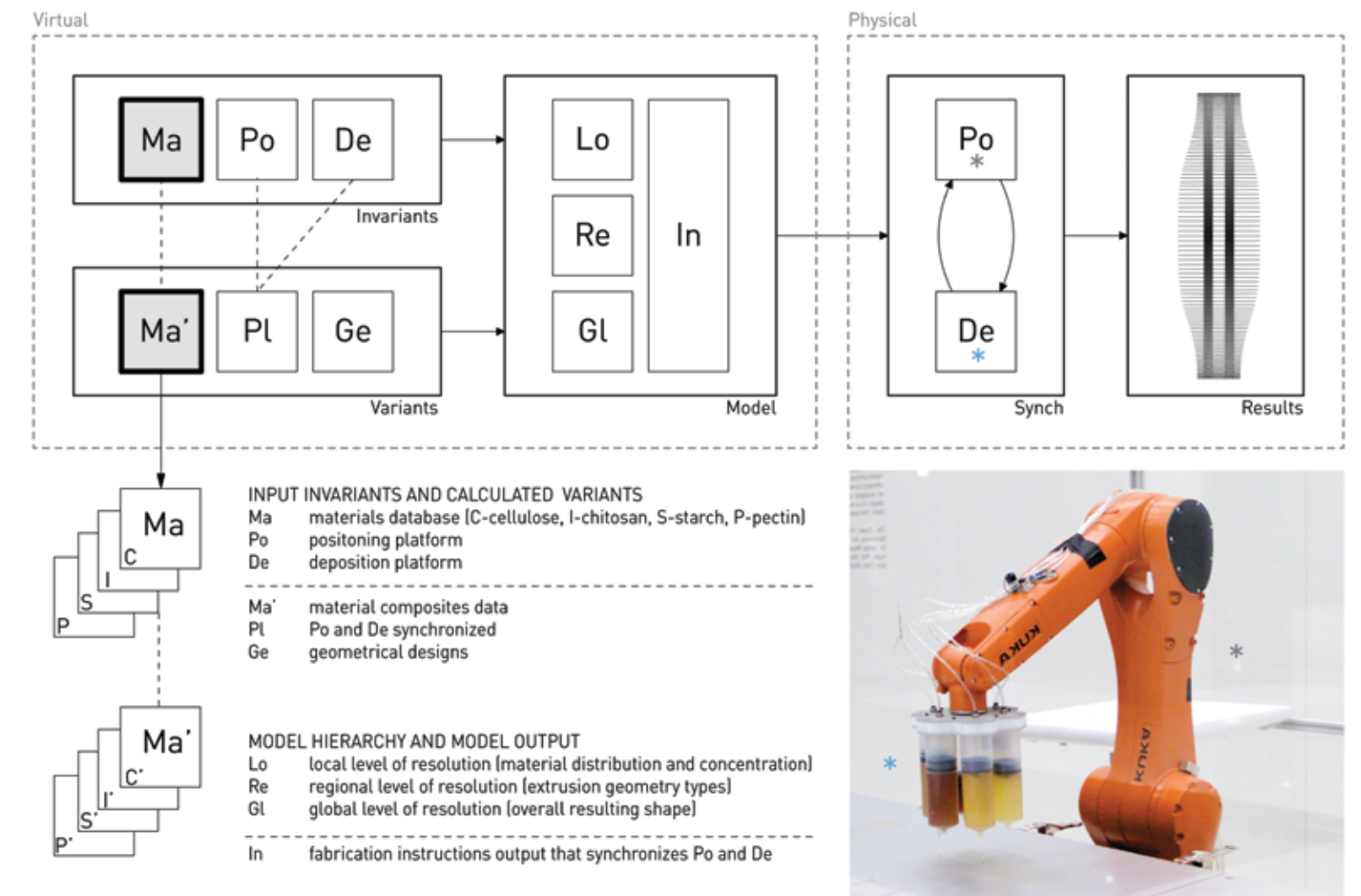


Fig. 4. The workflow diagram of the water-based digital fabrication platform contains parameters associated with the robotic fabrication process, including nozzle positioning, robotic (arm) speed, air pressure and time delays. These parameters are integrated and processed in real time to construct databases that communicate instructions to hardware components, thereby enabling feedback between software and hardware (graphics extended and adapted from Duro-Royo et al., 2015).

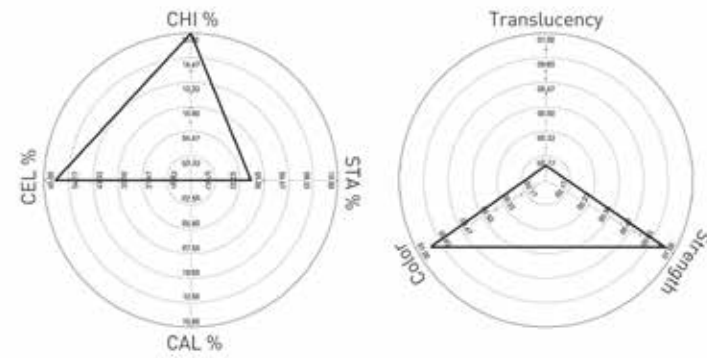
eters of their fabrication using logic similar to DNA, while environmental mappings—such as temperature and rain (Fig. 2a)—dictate the micro-, meso- and macro-scale patterns and shapes in which materials are distributed and layered, just as growing cells form larger constructs in response to local extracellular cues. Combined, this gradient of scalar considerations drives distributions of optical and mechanical properties, producing adaptive, rather than homogenized, form and behavior.

3.3 ROBOTIC FABRICATION PARAMETERS

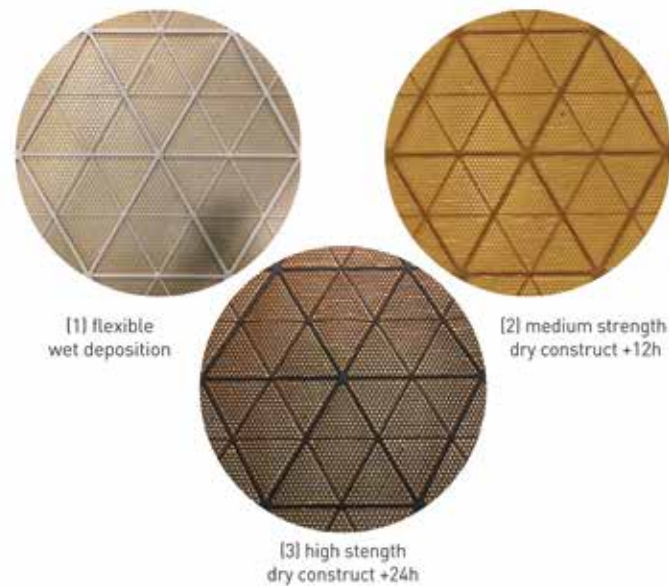
The water-based digital fabrication platform can integrate both the pneumatic extrusion of materials and the precise positioning of a nozzle in space via a custom virtual interface (Duro-Royo et al., 2015). To smoothly deposit material structures, robotic interface distributes serial-based signals and valve response delays to inform the custom extrusion system. Simultaneously, an Ethernet-enabled data stream locates feedback for the existing robotic arm system (Duro-Royo et al., 2015).

Integrating both CAD and CAM files is typically achieved by exporting a design file as a G-Code, e.g. a machine file format for numerically controlled digital fabrication (Chang, 2004; Sass & Oxman, 2006; Sheil, 2013). Subse-

a) MATERIAL-PROPERTY relationships in Parametric Chemistry:



c) STRENGTH, TRANSLUCENCY, & COLOR VARIATION over time:



b) TIME-DEPENDENT MATERIAL TEMPLATING deposition process and setup:

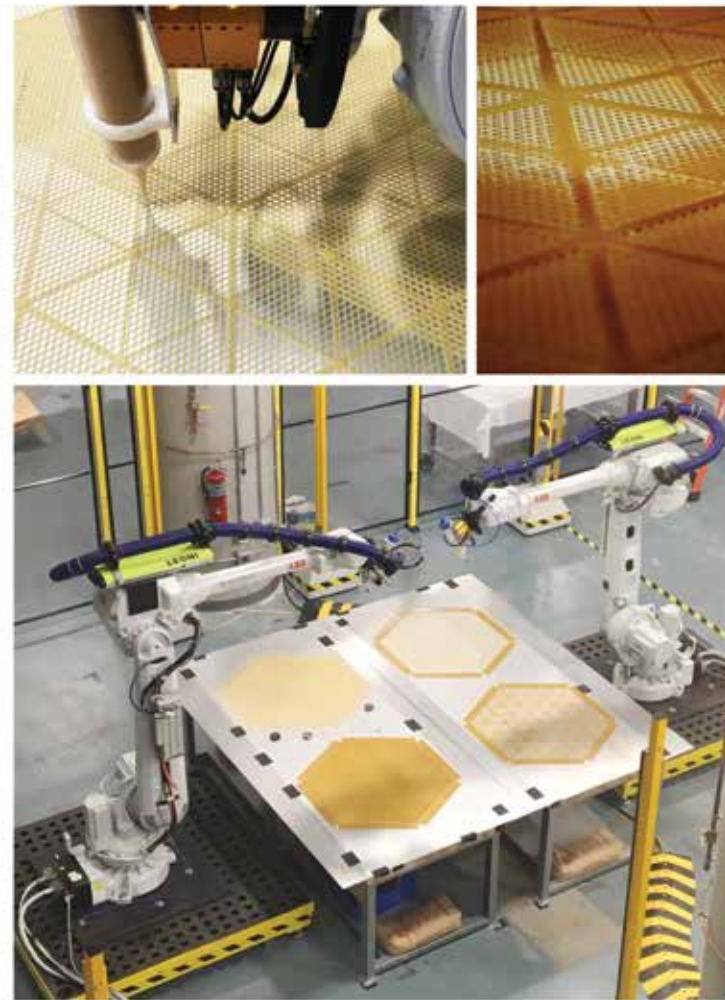


Fig. 5. a) Utilization of parametric chemistry to endow a panel with specific thermal, mechanical and optical properties (CEL: cellulose 60%, STA: starch 4%, CHI: chitosan 20%). Further detail is provided in Appendix A. b) Top – Details of tuning material deposition and curing time to yield hierarchical materiomic differentiation. Bottom - Fabrication process depicting different stages of component construction. c) Medium-scale structural panels composed of chitosan-cellulose blends, which have been hierarchically distributed and differentially tuned to optimize material properties such as strength, elasticity, thermal equilibrium and dissociation. Time-dependent optical properties emerge due to the diffusion of water between dry and wet layers, as well as surface-air interactions while curing.

quently, materials and tool paths are set within the machine's software, but with limited-to-no options for editing. Consequently, this often results in miscommunications between the original CAD environment and the machine logic assigned to execute the design. Such discrete processes end up constraining the design workflow, especially in the context of designs with complex shapes and, heterogeneous material compositions (Oxman, 2011).

In the current client-based communication interface associating design computation based operations with robotics, we implement the geometric kernel library for Grasshopper to write custom C# code that transmits XML instructions controlling fabrication parameters to a central interface. The communication applet is written in C++ using the Qt open-source platform (2014,

Qt project, Norway). Its function is to process input and output data generated from the design platform to and from mechanical parts. An Ethernet UDP socket enables transmission parametric information to the motion and extrusion systems via a serial USB signal. The pneumatic tool firmware is developed in C code using the Eclipse IDE environment (2014, The Eclipse Foundation, Canada) and the cross-platform open-source Arduino library (2014, Arduino Software, Italy).

Specifically, the flow of data is initiated through a combination of variant design parameters as well as invariant system constraints defined by the system's building blocks (Fig. 4). These include the materials to be extruded (Ma, Ma'), the positioning platform (Po), the deposition platform (De), and the geometric designs (Ge). Here, basic rules can include envelope size, global cur-

vature, intersections of members, etc., each of which can be reached by varying local properties and fabrication strategies, resulting in graded micro details that optimize materials for local environmental conditions and functions. In addition, the printing substrate can be manipulated in terms of temperature, morphology, electrical current and magnetism for various fabrication typologies and material compositions.

Beginning as a wet, off-white, clay-like mass, our current biomaterials are packed into cartridges that are loaded into a holster within a rotating, multi-material end-effector. A nozzle diameter is then chosen in relation to the viscosity and cohesive forces within the material. Subsequently, air pressure, the distance of the nozzle from the substrate and the speed of the robotic arm are set in the design code's variants. Each of these parameters is also informed by the resolution and turning radii of the tool path geometry. Following extrusion, the material is left to dry at room temperature.

Thus, the system is defined as generally as possible according to variant and invariant constraints that are extrinsic to the hardware system in use with the goal of enabling it to be implemented using various DDM platforms. In our current testing system, a 6-axis robotic arm is used as a positioning platform (Po), and a multi-barrel pneumatic extruder is used as a deposition platform (De) (Duro-Royo et al., 2015). In our current work, diverse large-scale curved molds can be placed in the print bed to deposit materials in 3D for enhanced shape-based structural inertia. The robotic arm can easily cover curved areas with specific wrist motions while conserving orthogonal positioning to the substrate.

4. RESULTS AND DISCUSSION

This research integrates multiple disciplines to realize large-scale design and digital fabrication with biomaterials. We have coined "parametric chemistry" the method by which aspects of materials science, engineering, architecture, physics, biology, mathematical modeling and chemistry are utilized to parametrically tune the chemical components and fabrication methods to design and digitally produce a wide range of bio-composites.

We have digitally fabricated material blends at various scales using the WDF platform, which enables 2.5- and 3-dimension flat and molded deposition of water-based materials forming hierarchical structures. In this case, we have layered multiple materials—oriented in a semi-parallel or semi-perpendicular configuration—to control local-to-global mechanical properties (Appendix A). Such geometric patterning has been configured to either enhance or compensate for the mechanical and optical properties of the bio-cement material blends described below.

This research has informed our strategy for fabricating a biomaterial pavilion, which will highlight how a scalar gradient of data—from molecular to environmental—can drive design decisions, fabrication parameters, functional properties, and, finally, degradation. Upon completion, this pavilion will demonstrate the value and efficacy of biological materials and fabrication logic – enabled by robotic agents.

4.1 MATERIAL CHARACTERIZATION

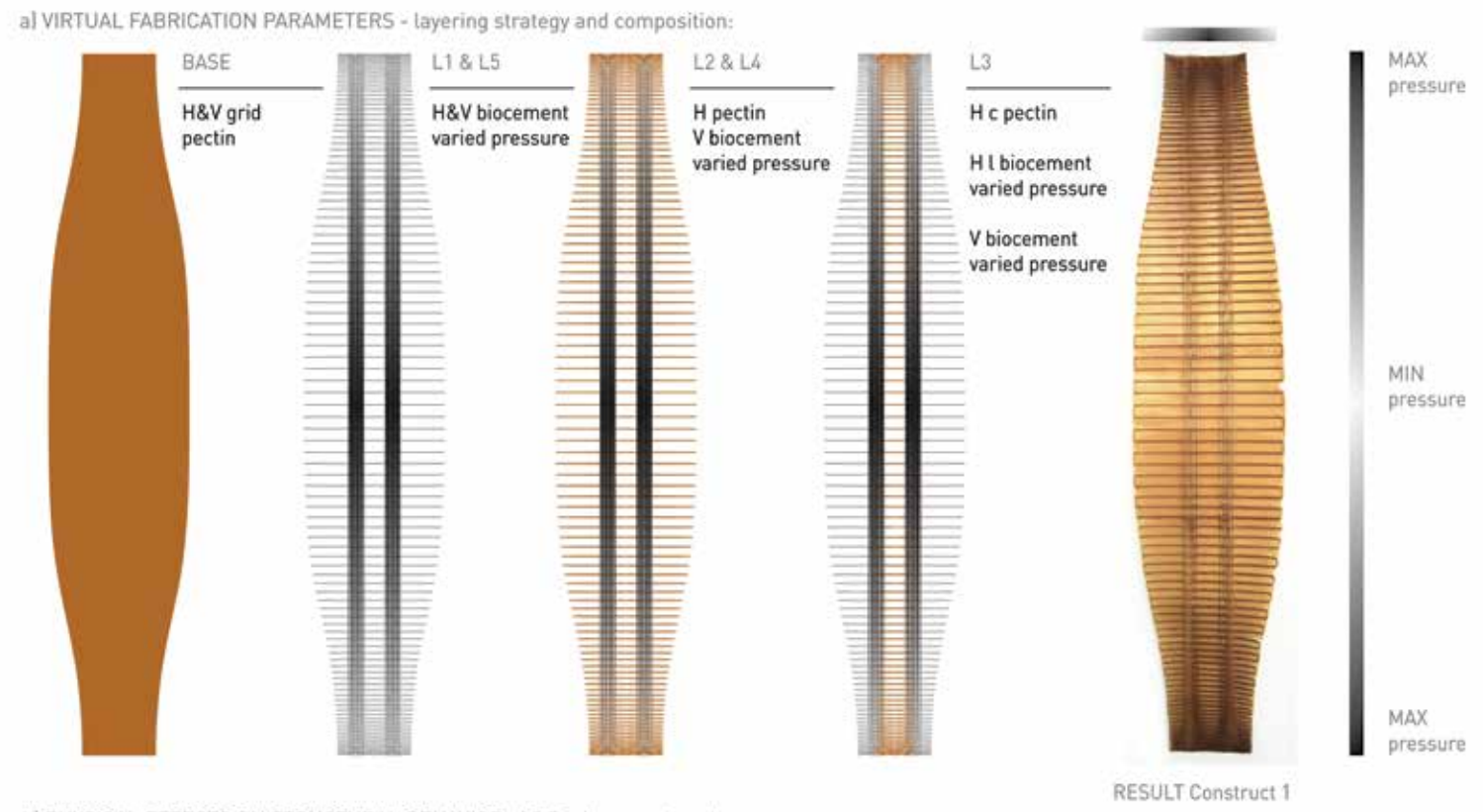
We have identified and demonstrated a direct relationship between the mechanical properties of our prototypical bio-cement structures and the relative proportions of cellulose, chitosan, calcium carbonate, and starch (Fig. 5, Appendix A). By observing the controlled layering of organic and inorganic materials found in natural shells, we have been able to tailor material properties as well as drying durations of constructs to local and global prerequisites through chemical interactions.

A high proportion of cellulose (40-70% v/v) provides the material with additional mechanical strength; likely due to the distributing of cellulose fibers contributing to an increase in anisotropy. Adding cellulose to the solution turns it into a more viscous, quick-drying hydrogel. Material tests of intricate geometry printed using this material show little-to-no spreading on the substrate. The hydrogel is squeezed through a ~1.0mm nozzle with 40-90 psi of air pressure, resulting in an ability to print at a higher resolution. Increasing the amount of cellulose relative to the amount of chitosan results in a whiter, slightly translucent material. Conversely, the speed at which the robotic arm is programmed to move decreases with increasing amounts of cellulose because the printed geometries stick together so well that turning corners and making curves drag the material out of place.

A greater proportion of chitosan (8-22.5% w/v) results in a global increase in both strength and elasticity. A high ratio of chitosan relative to cellulose and starch makes the material more golden brown in color and opaque. However, this ratio also results in a more viscous hydrogel that does not keep its shape well when printed, thereby reducing our ability to print at high resolutions. Conversely, the robotic arm could move at a higher speed because the hydrogel does not stick together as well, nor does it dry as quickly.

Increasing the amount of calcium carbonate (1-10% w/v) yields a lighter weight material with the same, or an even better, mechanical strength; a whiter, more translucent color; faster drying time; and added stiffness. The hydrogel also becomes much lighter—likely due to chemical reactions with the acetic acid—and holds its shape very well. This allows for a high printing resolution (~1.0mm) but again necessitates a slower printing speed and more air pressure (40-90psi). Adding calcium carbonate also results in a higher pH (4-7.3) which may create a more hospitable environment for bacteria and other organisms.

Finally, increasing the amount of cornstarch (4-10% w/v) results in added stiffness as well as a whiter color and slightly more translucency. We have also empirically determined that the use of pectin can dominate chitosan's mechanical properties and endow the material with more flexibility and translucency.



b) PHYSICAL EFFECTS ON STRUCTURAL BEHAVIOR of 2.5m long constructs:

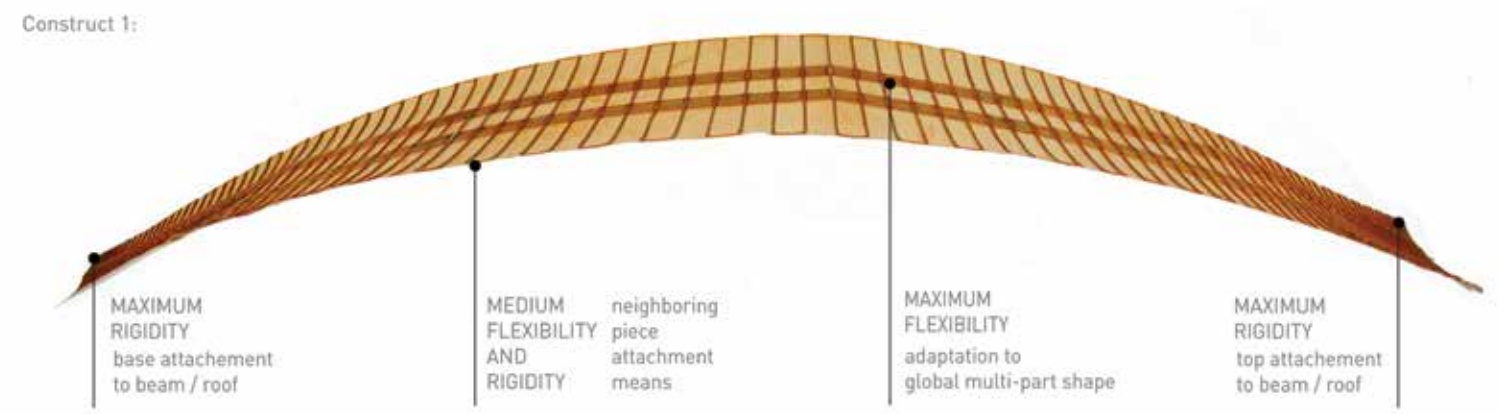
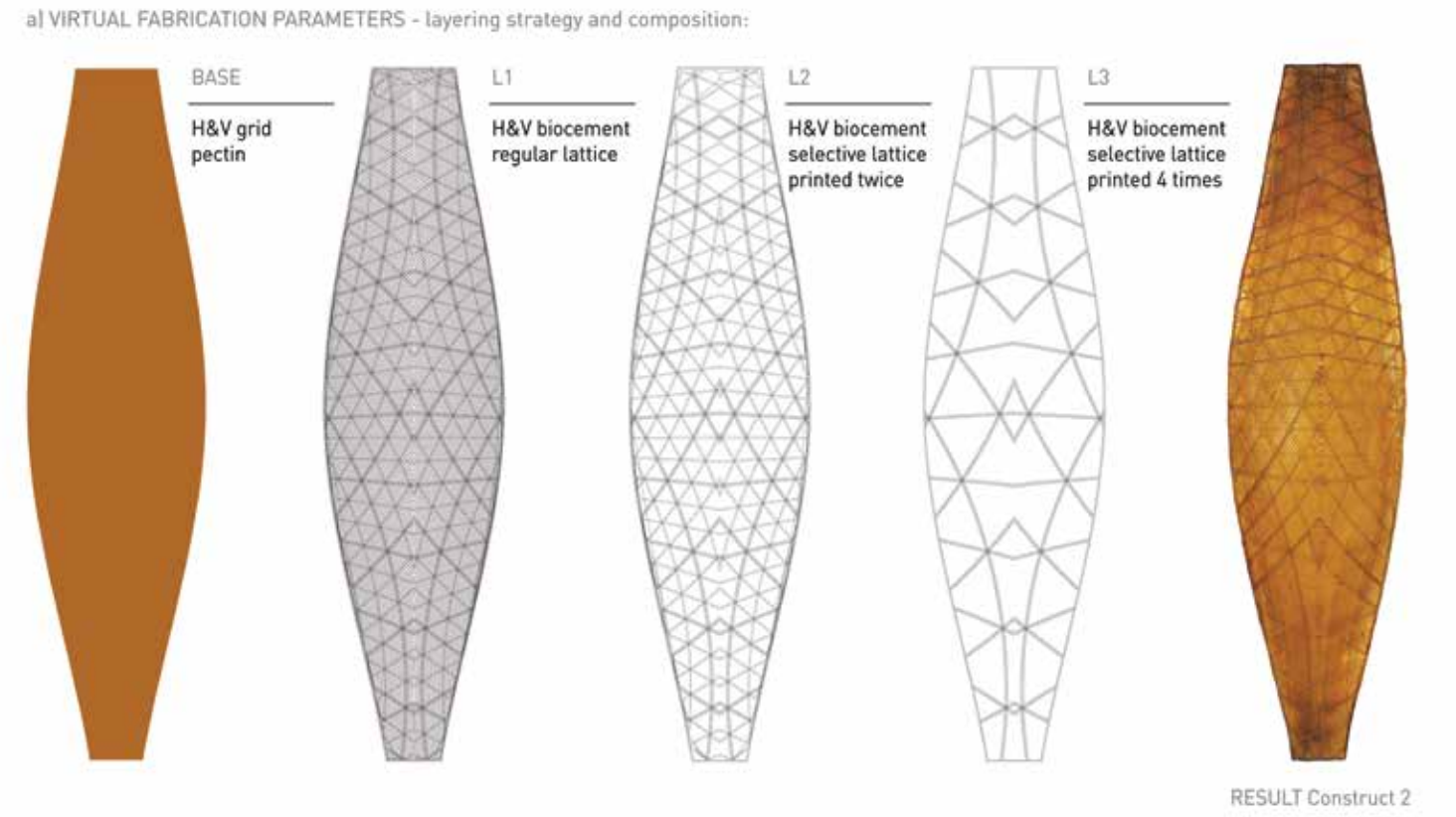


Fig. 6. a) Digital fabrication parameters and material composition data within a large-scale panel. b) Experimental large-scale results of a 2.5m-long prototypical panel exhibiting differential flexibility and strength within one material system. Local and global behavior is designed and expressed within a single physical construct.



b) PHYSICAL EFFECTS ON STRUCTURAL BEHAVIOR of 2.5m long constructs:

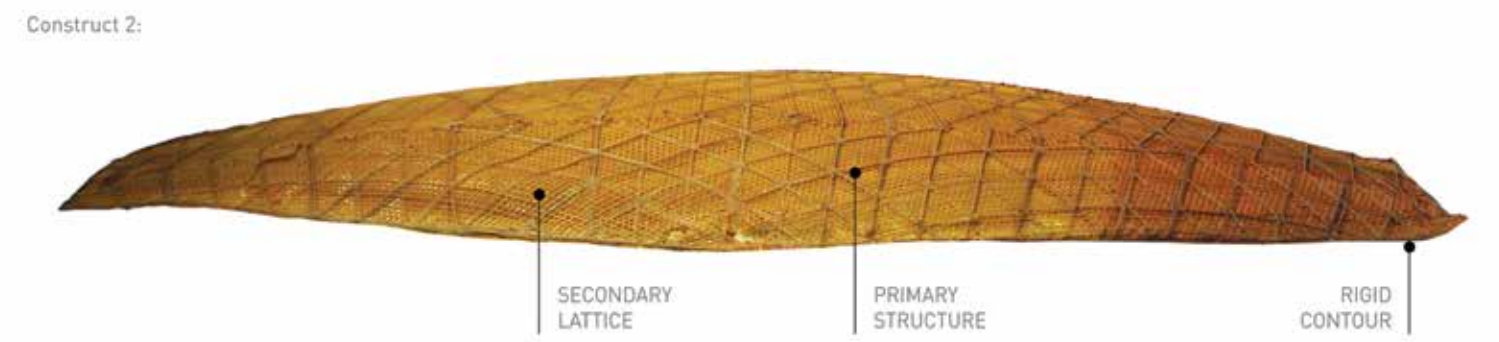


Fig. 7. a) Digital fabrication parameters and geometric hierarchy strategy within a single large-scale prototype. b) Experimental large-scale results shown for a 2.5m-long prototype deposited on top of a 3D mold and designed for structural bracing to preserve the molded shape.

4.2 MATERIAL BEHAVIOR TESTING

We have analyzed the material behavior of eight geometric lattices with varying chemical proportions (Appendix A). Geometric design, number of layers, and printing nozzle diameter are kept constant for every lattice, while pressure and speed are varied depending on the material's shear stress and flow. Appendix A illustrates material composition of each lattice, including its performance-based attributes in terms of color, translucency, and strength.

We have found the concentration of calcium carbonate is a determining factor for both the strength and stiffness of the material (Fig. 6, 7). We observed a higher ultimate tensile strength in materials with greater concentrations of chitosan; whereas, increased stiffness can be largely attributed to higher concentrations of starch. Alternatively, higher concentrations of cellulose added both strength and a higher elastic modulus to the composite; most likely due to its fibrous structure (Appendix A, Fig. 6-7). It is important to note that—within the scope of this paper—potential interactions between materials were not further analyzed.

It should also be noted that the bio-cement was cross-linked with acetic acid to form a hydrogel, which was left to dry at room temperature after being deposited in 2.5- and 3-dimensions via the water-based digital fabrication platform. Both heat and humidity led to embrittlement and large contractile deformations in the material, respectively. Further curing, crosslinking, and deprotonating experiments will be conducted. Regardless of material composition, a thicker line weight and an increase in layer count typically result in increased mechanical strength and rigidity. Similarly, more complex geometrical features could be used to compensate for the contractions of the material as it dries, as well as a strengthening agent. Printing successive layers in opposite orientations could endow the material with additional resistance to lateral forces. We have experimented with some of these strategies in a large constructs described in Figure 6 and Figure 7.

Mechanical data—including data relating to properties such as strength, rigidity, and viscosity—has informed deposition parameters such as speed, air pressure, nozzle diameter and height relative to the substrate. Moving forward, we plan to further functionalize multi-scale material properties using data-driven material mixing and deposition within a rotating extruder with coaxial mixing and extruding capabilities, using real-time intrinsic and extrinsic sensing of molecular and environmental dynamics, respectively. Such dynamic material transformations within a single tool-path can engender truly reactive—rather than prescribed—properties of materials and the structures they form.

4.3 LARGE-SCALE RESULTS

We have designed and manufactured two large proof-of-concept constructs with differentiated geometric and material distribution to respond to varied structural behavior along its construction. One construct was printed in 2.5D and 3D shape was found via local strengthening and shrinking forces due to differential material distribution. Another construct was directly printed in a

3D mold to ensure controlled shape. This can further drive structural inertia and enhance strengthening strategies tested in the first construct. In both cases, material deposition was achieved utilizing the water-based digital fabrication platform in subsequent layers of cured multi-material colloids. Specifically, a base layer combining pectin (35% w/v) (BASE), acetic acid (15% v/v), and glycerin (2% v/v) was coarsely deposited and left to dry to accommodate subsequent hierarchical extrusions. A 1mm nozzle is used for all depositions. Differential extrusion thickness is achieved by incrementally varying air pressure from 40 to 80 PSI (Fig. 6, 7).

PHYSICAL CONSTRUCT 1:

The first lattice-like layer (L1) is composed of vertical and horizontal bio-cement extrusions. Vertical extrusions are printed with differential pressure to ensure a rigidity gradient with maximal material content toward the top and bottom of the construct. Doing so will—in the future—allow us to design and construct connections to ground as well as the top of an architectural pavilion's crowning. At the structure's center, additional flexibility was achieved by layering less material amounts and higher polymer concentrations allowing the piece to behave in an arch-like configuration (Fig. 6b). The horizontal bio-cement extrusions in the first layer (L1) also follow a pressure gradient, with a maximum at the edges. The same strategy was applied in the final and external layer—layer five (L5)—to accommodate for deformation in the center of the construct (Fig. 6a).

In between layers one (L1) and five (L5), layers two (L2) and four (L4) carry vertical bio-cement depositions with varied pressure as in L1. They also contain added horizontal extrusions of pectin to ensure flexibility of cross ribs and provide longitudinal, arch-like behavior, as displayed in Figure 6b. Layer three (L3) contains a combination of pectin and bio-cement in its horizontal lines. Pectin is placed at the center ribs and bio-cement at the lateral ribs. The center of the construct is expected to achieve maximal folding in longitudinal and transverse directions, so its material composition is kept as flexible as possible. L3 also contains vertical bio-cement extrusions with pressure gradients for differential rigidity from the extremes towards the center (Fig. 6a).

PHYSICAL CONSTRUCT 2:

The second structure is designed with an overall shape and size similar to the first but is directly printed in a 3D single-curved mold. The layering strategy for the structure is based on the geometrical hierarchy shown in Figure 7a. We begin by depositing a lattice substrate (L1) on top of a pectin base. It is selectively densified in subsequent layers L2 and L3. Depositions are achieved on top of a 3D mold by calculating angular robotic wrist motions to ensure orthogonal deposition to the substrate. Toolpath patterns are designed in a structural bracing manner to preserve the desired molded shape after curing and removal from substrate (Fig. 7a). The resulting hierarchical dried structure appears to have conserved its shape after printing and performs as a structural shell (Fig. 7b).

Qualitative observations regarding the physical behavior of the fully cured, large-scale 3D prototypes displayed in Figure 6b and Figure 7b confirm

the capacity for the tunability of flexibility/rigidity enabled by the multi-material water-based digital fabrication system. The results shown here will inform future designs of multi-functional structures for a full-scale biomaterial pavilion.

5. CONCLUSIONS & FUTURE WORK

Robotically fabricated parametric reconfiguring of chemical properties has been shown to inform mechanical and optical hierarchies of a given material system. Such chemically induced design is typical of shell and other natural structure formations. We demonstrate the ability to tune and optimize the properties and behavior of novel bio-cements using a customized additive manufacturing platform. In doing so, we demonstrate the capacity to obtain geometrically complex constructs with tunable structural and environmental properties.

We have coined the term parametric chemistry, to describe the nano-to-macro control of bio-material blends integrated with on-the-fly mechanical performance evaluations executed within a single fabrication environment. By differentially configuring nozzle pressure and speed, thereby tuning geometrical organization during fabrication, we compensate for structural weaknesses identified in various bio-cements, enhancing desired properties—such as strength or flexibility—by design. We have demonstrated our techniques in the design and robotic fabrication of medium-to-large scale lattices exhibiting high strength to weight ratios. Moreover, we have shown control of shape formation vis-a-vis 3-dimensional folding of large-scale structures by implementing robotically informed 2.5- and 3-dimensional deposition informing stiffness distribution while curing.

This research has enabled the design and digital fabrication of large-scale architectural structures that demonstrate:

1. Differentiated mechanical and optical qualities within a single material system;
2. High weight to surface area ratios;
3. Complete biocompatibility and biodegradability.

As demonstrated through mechanical tests, by utilizing a wide array of tunable bio-composites, we have demonstrated the ability to precisely control the shape and properties of 3D printed constructs. Using this approach, we can leverage user-defined, small-scale and chemistry-based control of structure-function relationships on architectural scale.

Additional progress achieved in the context of ongoing research will inform our next steps toward designing and digitally fabricating biomaterial structures in architectural scales. Doing so will help guide the next iteration of the water-based digital fabrication platform with improved extrusion capabilities and real-time material property feedback. Moreover, natural bio-cements developed as part of this research have been configured to support living organisms as a way of enabling geometrical and structural temporal tunability via bio-augmentation of large-scale biomaterial structures. Toward this end, we aim to embed microorganisms that can perform functions such as bio-mineralization, microbial digestion, tissue formation and ambient sensing (Bader et al., 2016).

6. ACKNOWLEDGMENTS

This research was primarily sponsored by The Mediated Matter Group at the MIT Media Lab. Ideas, methods, products and techniques included herein were developed to support an ongoing project and research platform focusing on large-scale biodegradable additive manufacturing, originally commissioned by the TBA-21 Academy (Thyssen-Bornemisza Art Contemporary). Research and scientific exploration related to this project was partly sponsored by GettyLab. The authors would like to thank Prof. Tim Lu and the Lu Lab based at the Research Laboratory of Electronics at MIT for a fruitful collaboration. The authors also wish to thank undergraduate researchers Matthew Bradford, Loewen Cavill, and Emily Ryeom as well as Shaymus Hudson in the Materials Science and Engineering Department at MIT for his help with tensile testing. Finally, we thank the Autodesk Build team at the Boston Design Center for facilitating this project and providing workspace.

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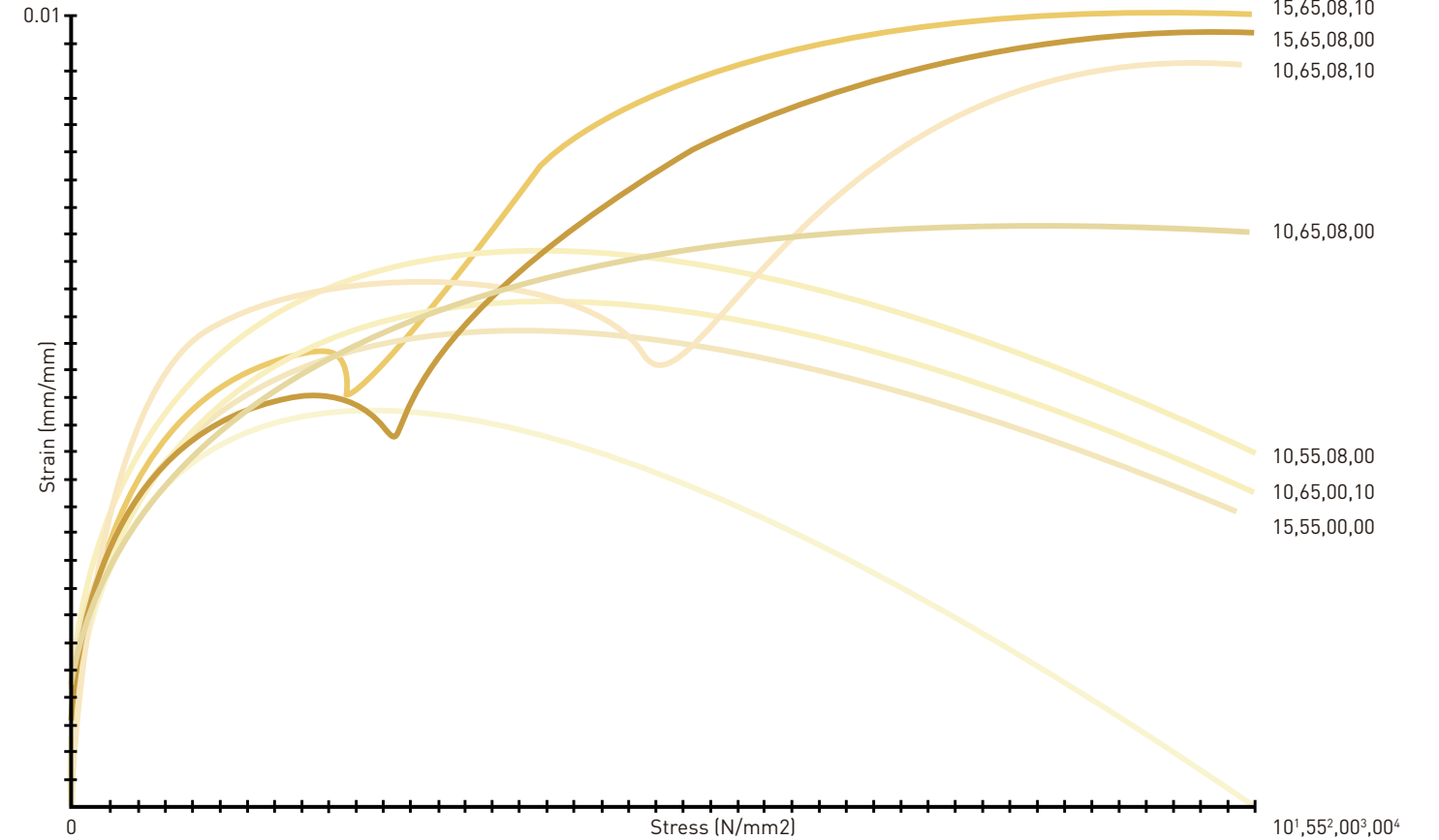
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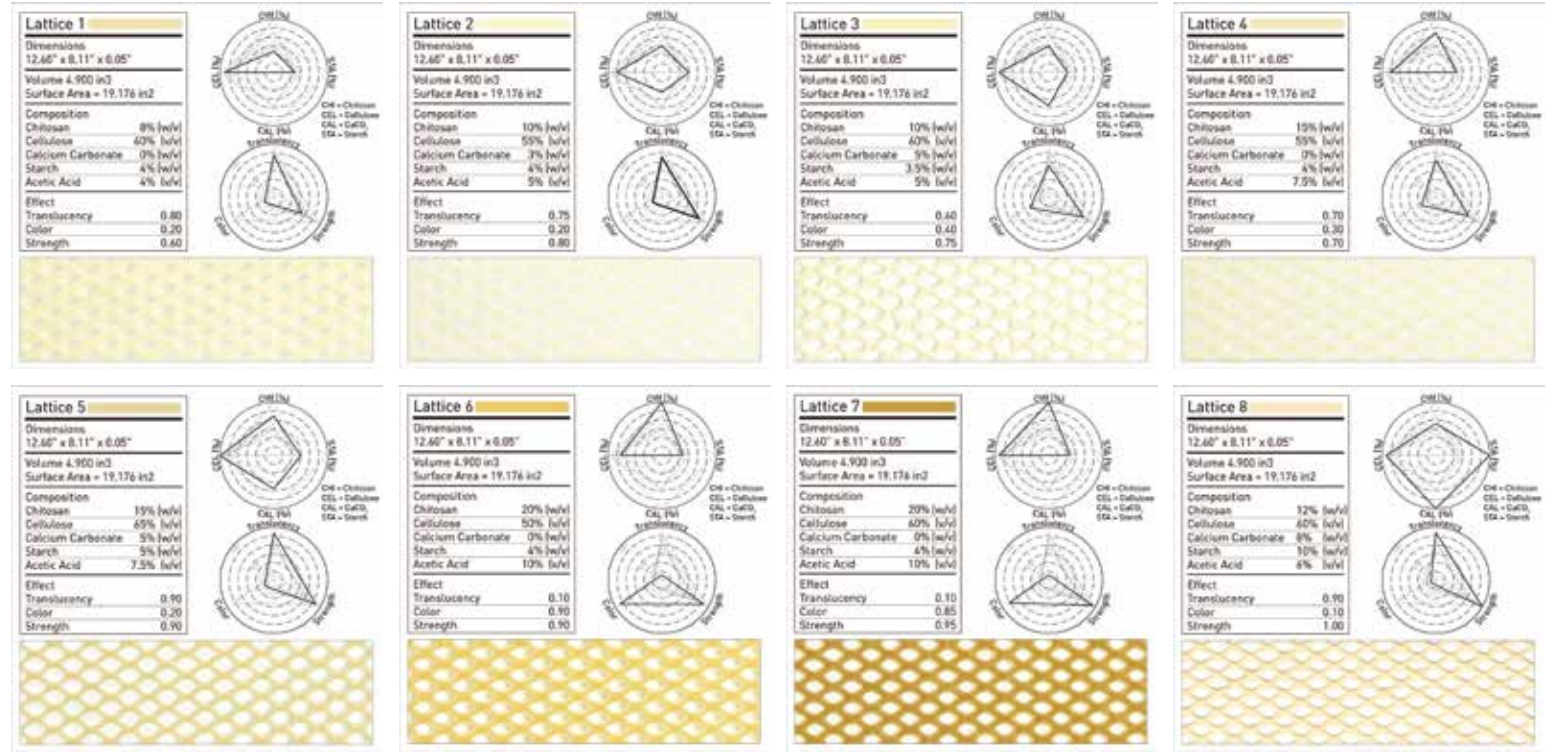
Tensile Testing of Various Biocement Compositions



Material composite mixes:
 1 % Chitosan (w/v)
 2 % Cellulose (v/v)
 3 % Calcium Carbonate (w/v)
 4 % Cornstarch (w/v)

Appendix A. Continued

a)Qualitative effects of material composition on printed lattices:



Appendix A.