

Water-based Engineering & Fabrication: Large-Scale Additive Manufacturing of Biomaterials

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ABSTRACT

In nature, water assembles basic molecules into complex multi-functional structures with nano-to-macro property variation. Such processes generally consume low amounts of energy, produce little to no waste, and take advantage of ambient conditions. In contrast digital manufacturing platforms are generally characterized as uni-functional, wasteful, fuel-based and often toxic. In this paper we explore the role of water in biological construction and propose an enabling technology modeled after these findings. We present a water-based fabrication platform tailored for 3-D printing of water-based composites and regenerated biomaterials such as chitosan, cellulose or sodium alginate for the construction of highly sustainable products and building components. We demonstrate that water-based fabrication of biological materials can be used to tune mechanical, chemical and optical properties of aqueous material composites. The platform consists of a multi-nozzle extrusion system attached to a multi-axis robotic arm designed to additively fabricate extrusion-compatible gels with graded properties. Applications of the composites include small and medium-scale recyclable objects, as well as temporary large-scale architectural structures.

INTRODUCTION

While contemporary digital fabrication tools are able to produce geometrically sophisticated objects and structures, such constructs are typically not sustainable insofar as material and energy use are considered [20]. In contrast, water-based assembly observed in nature employs mild chemicals, produces little to no waste, and uses small amounts of energy to produce multifunctional and adaptable systems [6].

Water exists throughout nature and in all biological materials [1]. It provides for an invisible scaffold designed to assemble basic molecules into structures with complex functions and property gradients. Examples include the giant squid beak where water content contributes to a significant stiffness gradient [5, 6, 8]. The squid's beak is one of the hardest and stiffest wholly organic materials known. Water-storing proteins, and polymers are carefully combined to generate its internal structure contributing to exceptionally graded material properties. When hydrated the beak exhibits an extreme functional gradient across its structure: it is sharp and firm at the tip with a tensile strength of 35MPa, and 10 times more compliant at the rim with a tensile strength of 3.5MPa [8]. Another example of water-mediated structural performance is the chitin-made insect cuticles and crustacean shells. These structures accomplish dual functionality enabled by variable hydration. Chitin can be found, at once, in hard composites that shield insects, and in the flexible tissue found in their joints. Despite chitin's extraordinary properties,

and in spite of its abundance, it is mostly used in pharmaceutical and dietary products [2, 5, 6, 9, 11], and has not yet been deployed in large scale manufacturing of consumer goods [12, 18].

Man-made plastics are challenging to reuse or degrade [4]. Only about 9% of plastic waste generated in the US is recyclable, while 27% of glass, 34% of metal, and 65% of cardboard are routinely recycled [4]. In the construction industry, synthetic plastics derived from petrochemicals are vastly used and make up most of pollutant non-recyclable waste [4]. While it could provide an alternative to fuel-based plastic materials, the use of regenerated biomaterials for product, architectural, and engineering applications is still not widespread [12]. This low use rate exists in spite of the fact that natural materials display exceptional mechanical properties [12, 13, 3]. Cellulose provides structure for plants, and chitin supports the exoskeleton of insects and crustaceans [5,6]. The elastic moduli and tensile strength of structural polysaccharides such as chitin and cellulose are similar to those of engineering ceramics and metal alloys [3]. Natural polymers and polysaccharides provide for a vast renewable resource produced at much higher rates than man-made synthetic polymers. Consequently, polysaccharide derivatives could replace existing synthetic fuel-based polymers, provide new property combinations for relevant applications, and play a key role in future manufacturing implementations [5, 3].

Indeed, water is known to initiate or activate chemical reactions in biological materials and, in the engineering disciplines, it is especially relevant in the context of programmable materials [21, 22, 23]. Within traditional building construction, water can be found in common construction materials such as clay, concrete or plaster, where it also acts as an initiator/activator. Metals and glass too, involve water as a lubricator and cooler for efficient manufacturing. More recently, water-as-activator has been used in programmable composites where hydrophilic polymers, which expand 150 percent when exposed to water, are used at the joints of segmented strands for underwater 2D or 3D shaping processes [23]. Additionally, recent research demonstrates a new way to utilize wood as a responsive building envelope. Wood is a hygroscopic material that can absorb water molecules causing it to shrink and swell in the tangential direction of the fibers [21]. As a result, thin wooden sheets can be induced to find their shape in response to humidity changes when tuning the fiber direction in the exposed components [21, 22]. Common to all of these examples is the use of water as an agent for material processing and object shape change. This is contrary to its use in the biological world as a building block for internal organization, environmental tunability and biodegradability.

In this paper we demonstrate the use of water as the *fundamental* building block in additive fabrication. Specifically, we use water as; (1) an initiation agent, to chemically formulate the composite solution; (2) an activation agent, achieving optimal viscosity and fabricability properties; (3) a shape formation agent; (4) a recycling agent for the reuse of the deposited materials; and (5) a life sustaining agent, enabling the containment of living micro-organisms for biological augmentation. Our research lies at the intersection of biomaterials, digital design and additive manufacturing. We present a *Water-based Engineering & Fabrication* platform and its associated methods for the design and production of small to large-scale multifunctional constructs that have the capacity to interact with their environment, and that are fully recyclable upon contact with water.

EXPERIMENTAL DETAILS

Chitosan at 85% of de-acetylation, acetic acid, and microcrystalline cellulose powder were purchased from Alfa-Aesar; sodium alginate was purchased from Melecule-R; chitin powder was purchased from NutriCargo LLC. The solutions were prepared with a 0.1 mg resolution analytical balance, model Mettler Toledo ML54 with 0.1 mg resolution and 0.2 mg linearity, are composed of chitosan 3%, 6% and 10% w/v in 1% acetic acid aqueous solution, sodium alginate 4% w/v in water, cellulose 5% in 10% chitosan solution, and 16% chitin powder [19].

The viscosity of 85% de-acetylated chitosan is 20–300cP, 1 wt. % in 1% acetic acid (25°C, Brookfield)(lit.). In order to determine composite properties, oscillatory shear measurements were carried out at shear rates of 1–100 Pa over 10 min with a minimum normal force limit of 0.10 N and a maximum of 50.00 N, to the polysaccharide matrixes in an AR-G2 viscometer (TA Instruments) employing a cone aluminum. All measurements were performed at a constant temperature of 25°C (**Figure 1c**). The ultimate tensile strength tests were performed under an Instron mechanical tester with a 9071.85 kg (20.000lb) reversible load cell, with a rated load/speed capability of 20.000lb (10.000 kg, 100 kN) at speeds of up to 50 mm/min (2.0 in./min) and speed accuracy of $\pm 0.1\%$ of set speed at all loads and speeds, using a routine setup at a rate of 200 mm/min, sampling 120 times per minute and a load threshold of 500 N. Manufactured results were measured with a digital caliper with an accuracy of 0.0254 mm (0.001 in.) [19] (**Figure 1d**).

A computer-controlled pneumatic extrusion system was attached to an existing motion platform's end-effector. The platform is a Kuka KR AGILUS robotic arm; model KR 10 R1100 SIXX WP. It weighs 54kg with a 10kg payload and a maximum reach of 1101mm. It has 6 axes, a ± 0.03 mm repeatability and it employs the KR C4 compact control system. At the pneumatic extrusion end-effector, different materials were contained in six 300cc clear plastic dispensing syringe barrels with hard rubber plungers, and extruded through 0.7 to 9mm plastic nozzles. Flow valves, gauges and tubing were dimensioned to 4mm 10PSI to 120PSI pneumatic circuitry [16] (**Figure 1a**).

DISCUSSION

We have successfully designed, developed and provisionally patented (US PPA Num. 17388T, 2014) an enabling additive manufacturing technology for water-based design and manufacturing of large scale structures [16, 18, 19]. It is composed of a computer-actuated pneumatic tool-head that can extrude paste and gel-like materials, and is tightly synchronized with a robotic arm (**Figure 1a**). The technology enables the use of raw natural polysaccharides - such as chitosan, cellulose, or sodium alginate - combined with fillers and diluted with low impact chemicals and water. The objects presented in this section, are fabricated and cured at room temperature, dramatically reducing the need for external energy sources other than air-actuated extrusion and displacement of the nozzle head [16, 18, 19]. Initial results of deposited and dried chitosan bio-plastic films show an ultimate tensile strength (UTS) of 40mPa comparable to nylon or wood in the direction of the fiber (**Figure 1d**). Natural thickeners such as sodium alginate powder can be incorporated into chitosan gels to generate shear thinning effects in the material barrel, allowing for the materials to extrude easily under shear forces, and to

become more viscous once extruded effectively defining the extruded geometry (**Figure 1c**). Various other fillers such as sand, soil, hemp fiber, seeds, calcium carbonate, sodium bicarbonate or polyacrylamide storing crystals, have been combined with chitosan and sodium alginate hydrogels (**Figure 1b**). Such structures display integrity after drying due to the binding capabilities of polysaccharide gels. Hemp long fibers, sodium bicarbonate, and polyacrylamide chitosan-based composites display irregularities, material heterogeneity, and pose extrusion issues due to the difficult control of chemical reactions or filler distribution at the nozzle. Sand, soil, and calcium carbonate chitosan-based composites display sub-millimeter surface resolution when dried due to the dense packing of their grains. These initial results encourage further research into natural volumetric fillers for 3D printing of fully recyclable and naturally biodegradable objects such as compost containers or vegetation planters harvesting chitosan's fertilizer and plant growth promoting properties. Moreover, the antimicrobial effects of chitosan gels, combined with fibrous or granular fillers, could be applied to food packaging, exo-prosthetic devices, toys, or single-use consumer products such as cups or tableware.

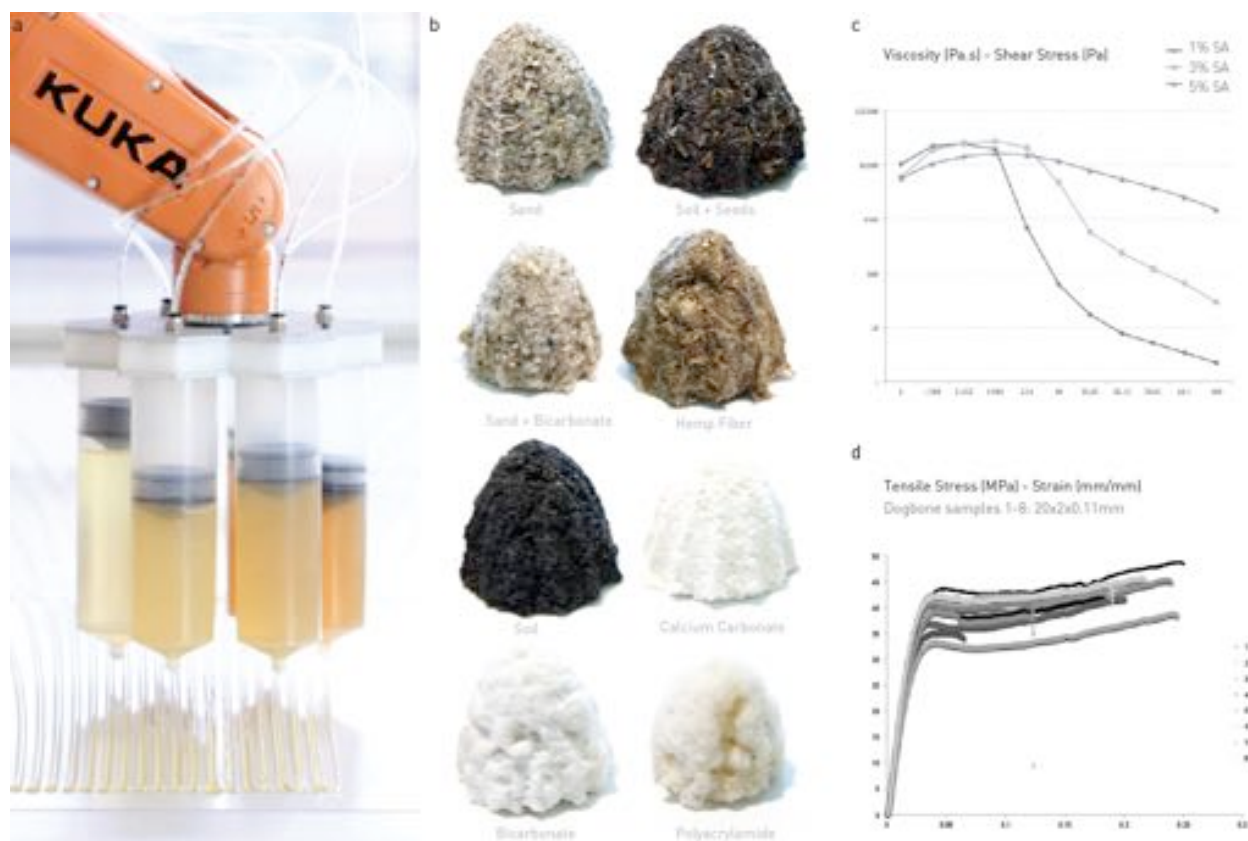


Figure 1: (a) A customized pneumatic multi nozzle natural composites extruder mounted on a positioning robotic arm system. (b) Granular and fibrous fillers combined with polysaccharide hydrogels can enable 3D printing of fully biodegradable and recyclable objects. (c) Shear thinning effects of sodium alginate powder in chitosan gels reduce axial forces needed to extrude colloids out of the barrel. (d) Chitosan bio-plastic films show an ultimate tensile strength (UTS) of 40mPa comparable to nylon or wood in the direction of the fiber.

In order to test and evaluate some of the materials designed, constructs were digitally fabricated layer by layer with composite materials containing; chitosan (CHI) in diverse

concentrations (3%, 6% and 10% w/v) in acetic acid aqueous solution (1% w/v); cellulose microfibers (CEL) in CHI solution (100% w/v in 3% CHI solution); and sodium alginate powder (SA) in CHI solution (4% w/v). The multi-material 3D printing system is equipped with 6 material containers that can be connected to nozzles of varying sizes (from 0.7 to 9mm inner diam.) in order to achieve different resolutions along the printed objects. Importantly, due to the chemical makeup of the composites used, the platform can harness shrinking forces for naturally induced shape formation. The wet depositions are layered flat and constructs find dry 3D shape by responding to internal directional evaporation stresses. Those stresses can be defined by geometrically designed heterogeneous patterns and computer-controlled material distribution along the extrusion process. Further detail about the novel computational control behind this deposition system can be found in [16, 18, 19].

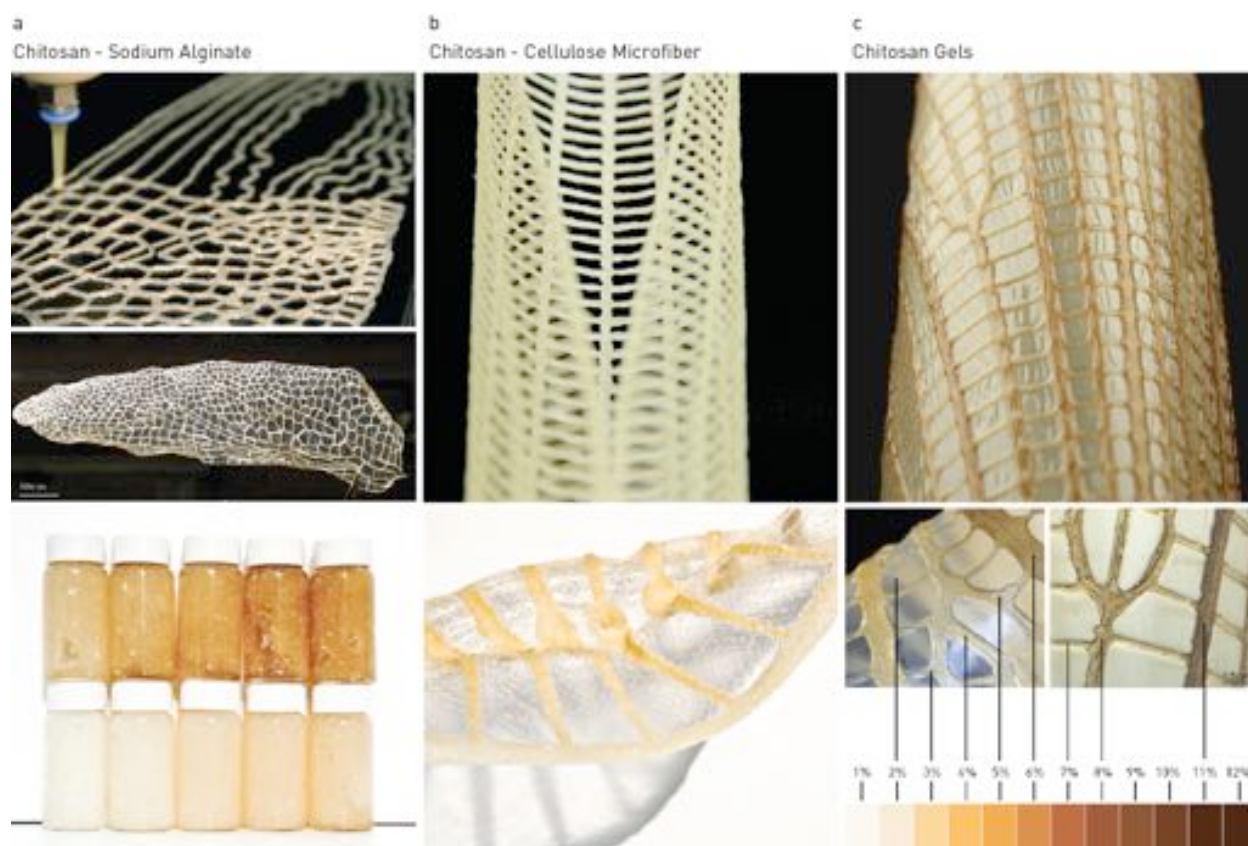


Figure 2: (a) CHI-SA composite defining a 50cm long construct inspired in dragonfly wing architecture. (b) CHI-CEL composites defining helical and cylindrical 50cm and 1m long grids and surface structures. (c) CHI multi-concentration composite describing a 3m long leaf venation pattern.

The resulting deposited objects display variable mechanical, optical, and biodegradability properties. For instance, in a 50cm long design inspired by the dragonfly wing, CHI and SA composites can be printed as structural bending-resistant venations, and clear CHI 3% solutions can be deposited and bonded to such venations to create a tension-resistant membrane in the construct [18] (**Figure 2a top**). The concentration of SA in CHI solution can be graded to provide for optical density variation from: 1% CHI and 10% SA, to 10% CHI and 1% SA (**Figure 2a bottom**). In another example, cellulose microfiber (CEL) in 100% w/v in 3% CHI

solution is deposited in a 5x15mm grid and left to dry obtaining a fine 50cm length cylindrical structure (**Figure 2b top**). CEL extrusions can also be combined with 3% CHI depositions as in the membrane of a strong 1m long object with CEL spine-like venations (**Figure 2b bottom**). The combination of strong CEL members and tensile 3% CHI membrane results in a higher degree of structural performance of the final dried object. Finally, CHI-only depositions can be mechanically and optically graded by using different concentration CHI gels in 1% w/v acetic acid aqueous solution (from 1% to 12% w/v) (**Figure 2c bottom**). Mechanical functional gradients can be accentuated by designing variable thickness extrusion path arrangements, or by using different nozzle sizes (0.7 to 9mm) for each extrusion path. **Figure 3c** shows part of a 3m tall construct inspired by leaf venations. The structure combines CHI with varying concentrations organized as structural members and tensile membrane areas. Both areas are bonded by the self-repairing characteristics of the materials used [16]. These material systems and their properties can be deployed into temporary architectural panels, lightweight biodegradable car parts, wearable devices, or even bacterial scaffolds for biofuel production.

Finally, we evaluated that a 15g dry conical chitosan composite sample of 30mm base and height, will dissolve in 200ml of water at room temperature after 20min [18, 19]. Objects can have longer stability to moisture by being submerged in 4% NaOH w/v aqueous solution, or coated with natural waxes once dried. Nevertheless, natural water-based composites will biodegrade over time once exposed to water [18]. This feature supports the design of temporary and highly sustainable architectural-scale parts that can interact with the environment; for instance, by contributing to soil nutrient levels or nourishing marine life. Grass growth from embedded seeds on a composite disc of chitosan and soil was observed over a week with no integrity loss [18].

CONCLUSIONS

The role of water in the biological world far exceeds its role in current digital manufacturing methods. *Water-based Engineering & Fabrication* proposes the use of water as key ingredient in all phases of the design and production process: initiation, activation, shape formation and biodegradation. The platform and its associated methods serve to advance digital manufacturing platforms and propel them towards biologically inspired, informed and engineered manufacturing. Initial outcomes demonstrate the design and production of sustainable and self-supporting structural components. Combining the use of natural regenerated abundant materials with a computer-controlled additive technology, we can design and manufacture structural and material hierarchies achieving sustainable products and building components characterized by high spatial resolution in manufacturing that are multifunctional and can biodegrade upon contact with water. The design of the platform dramatically reduces the need for external energy sources for fabrication other than air-actuated extrusion and displacement of the nozzle head, pointing towards new possibilities for sustainable additive manufacturing.

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REFERENCES

1. Wiggins P.M. Role of water in some biological processes. *Microbiology and Molecular Biology Reviews* 1990; 54:(4)432-449.
2. Lieleg O., Ribbeck K. Biological hydrogels as selective diffusion barriers. *Trends in Cell Biology*, 2011; 21:9: 543-551 10.1016/j.tcb.2011.06.002.
3. Ashby M. F., Gibson L. J., Wegst, U., et al. *The Mechanical Properties of Natural Materials: Material Property Charts. Proceedings: Mathematical and Physical Sciences. The Royal Society.* 1995;450;1938;123-140.
4. US Environmental Protection Agency, *Municipal Solid Waste (MSW) in the United States: Facts and Figures. MSW Characterization Reports 2012* (online resource: <http://epa.gov>.)
5. Dumitriu S. *Polysaccharides: Structural Diversity and Functional Versatility.* Marcel Dekker, New York, NY, 2005.
6. Vincent, J.F.V. *Structural biomaterials.* Macmillan, London, 2012.
7. Raven, P.H., Evert R.F., and Eichhorn S.E. *Biology of Plants.* W. H. Freeman and Company, New York, 1999.
8. Miserez A. et al. The Transition from Stiff to Compliant Materials in Squid Beaks. *Science* 2008; 10.1126/science.1154117.
9. Rinaudo M. Chitin and chitosan: Properties and applications. *Progress in Polymer Science* 2006; 10.1016/j.progpolymsci.2006.06.001.
10. Kieback B., Neubrand A., Riedel H. Processing techniques for functionally graded materials. *Materials Science and Engineering* 2003; 10.1016/S0921-5093(03)00578-1.
11. Gutowska, A., Jeong, B. and Jasionowski, M. Injectable gels for tissue engineering. *The Anatomical Record* 2001; 10.1002/ar.1115.
12. Fernandez J. G. and Ingber D. E. Manufacturing of Large-Scale Functional Objects Using Biodegradable Chitosan Bioplastic. *Macromolecular Materials and Engineering* 2014; 10.1002/mame.201300426.
13. Fernandez J. G. and Ingber D. E. Bioinspired Chitinous Material Solutions for Environmental Sustainability and Medicine. *Advanced Functional Materials* 2013; 10.1002/adfm.201300053.
14. Fernandez J. G. and Ingber D. E. Unexpected Strength and Toughness in Chitosan-Fibroin Laminates Inspired by Insect Cuticle. *Advanced Materials* 2012; 10.1002/adma.201104051.
15. Omenetto, F. G. and Kaplan, D. L. New opportunities for an ancient material. *Science* 2010; 10.1126/science.1188936.
16. Duro Royo J., Mogas Soldevila L. and Oxman N. Flow-based Robotic Fabrication: Model for Design and Fabrication of Functionally Graded Structures, *Computer-Aided Design*,

Elsevier (in review).

17. Hiller, J., Lipson, H. Design and analysis of digital materials for physical 3D voxel printing. *Rapid Prototyping Journal* 2009; 10.1.1.375.6436.

18. Mogas-Soldevila L., Duro-Royo J., Oxman N. Water-based Robotic Fabrication: Large-Scale Additive Manufacturing of Functionally-Graded Hydrogel Composites via Multi-Chamber Extrusion. *3D Printing and Additive Manufacturing* 2014; 1:1- 11.

19. Duro Royo J., Mogas Soldevila L. and Oxman N. Methods and Apparatus for Integrated Large Scale Robotic Fabrication of Functionally Graded Materials and Structures. US PPA Num. 17388T, 2014.

20. Oxman N. Variable property rapid prototyping. *Virtual and Physical Prototyping* 2011; 10.1080/17452759.2011.558588.

21. Krieg, O., Christian, Z., Correa, D., Menges, A., Reichert, S. et al. HygroSkin: Meteorosensitive Pavilion, in Gramazio, F., Kohler, M., Langenberg, S. (eds.). *Fabricate: Negotiating Design and Making*, Zurich 2013; 272-279 (ISBN 978-3-85676-331-2).

22. Reichert, S., Menges, A., Correa, D. Meteorosensitive Architecture: Biomimetic Building Skins Based on Materially Embedded and Hygroscopically Enabled Responsiveness. *CAD Journal*, Elsevier 2014; 10.1016/j.cad.2014.02.010

23. Tibbits S. 4D Printing: Multi-Material Shape Change. *AD* 2014; 84.1:116-121.