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Abstract

Either processed or in their native form, sugars are ubiquitous in food, and are among the main sources of energy for almost all forms of life. Sugars and their derivatives can also form structural building blocks such as cellulose in plants or chitin in crustacean shells. Because of their inherent degradability, resorbability and biocompatibility characteristics, sugars are compelling constituent materials in transient devices and robotics. Here, we introduce an additive manufacturing approach for the 3D production of magnetic sugar-based composites. First, we show that sugar-based 3D architectures can be 3D printed by selective laser sintering (SLS). Importantly, we show that this approach enables one to adjust not only their caramelization chemistry but also the mechanical properties of the sugar 3D architectures as a function of the energy input of the laser. Capitalizing on these results, we demonstrate that power mixtures of sugars and magnetic particles can also be processed as 3D composites. As a proof of concept, we fabricate a sugar-based helical millimeter-scale swimmer, which is able

to perform corkscrew locomotion in a solution with a viscosity comparable to those of biological fluids. The millirobot is able to quickly dissolve in water while being manipulated trough external magnetic fields. We believe that the present fabrication method could pave the way to a new generation of transient small-scale robots based on sugars that would allow new approaches in minimally invasive procedures. Due to their rapid dissolution, sugars could be used as an intermediate step for transporting swarms of particles to specific target locations.

Wireless small-scale robots hold great promise for diagnosis and treatment of certain diseases and/or pathologies in a minimally invasive way.[1] These mobile systems are engineered to improve the efficacy of therapeutic payloads and to reduce their systemic toxicity by delivering them at affected sites of the human body. While these devices have demonstrated many potentially biomedical *in vitro* and *in vivo* applications, current designs exhibit limited features that impede their translation to actual clinical scenarios. For example, most of reported small-scale robots have been manufactured with materials that are difficult to degrade, resulting in their undesired accumulation in tissues.[2–8] Accordingly, there is a current upsurge of interest in addressing aspects such as biodegradability and bioresorbability of small-scale robots.[9–11] Recently, Wang and co-workers presented transient self-destroyed catalytic magnesium- and zinc-based Janus micromotors for applications in the gastrointestinal track.[12] After accomplishing their tasks, these machines were degraded into nontoxic products in relevant biological media. Wilson and coworkers demonstrated that catalytic block-copolymer stomatocyte nanomotors could be engineered to degrade after cellular internalization by glutathione.[13]

Soluble saccharides or sugars are biomolecules that have been used in drug delivery applications due to their specific interactions with proteins.[14] They have been combined with polymers to enhance the biocompatibility of drug carriers and biodegradation. In the area of fabrication, sugars have also been tested as water-soluble sacrificial building blocks in surface micromachining.[15] Interestingly, sugar structures have also been shaped using 3D printing technologies, mostly for customized food fabrication. For example, Chen, Bathia and coworkers have shown the printing of 3D filament networks of carbohydrate glass consisting of a mixture of glucose, fructose and dextran. The networks acted as sacrificial templates for perfusable 3D tissues capable of tolerating high- pressure pulsatile flows of blood.[16] Because

of their inherent biocompatibility and biodegradability characteristics and low cytotoxic effects, sugars are potential candidate materials for designing transient devices.

Here, we describe for the first time the fabrication of free-form designed (3D printed) saccharide-based magnetic composite structures via selective laser sintering (SLS). We chose sugars as the main component of the magnetically active small-scale robots, because they are inherently biocompatible and biodegradable.[1] In a typical fabrication process, sugar crystal powders (specifically glucose or sucrose) and barium ferrite ($BaFe_{12}O_{19}$) or carbonyl iron microparticles, both commercially available, were used. We chose $BaFe_{12}O_{19}$ and carbonyl iron as both are prototypical hard- and soft-magnetic materials.

Figure 1a shows the fabrication of saccharide-based structures by SLS. The printing machine comprises a reservoir unit (RU) containing the powder (i.e. sucrose crystal powder or sucrose crystal powder with magnetic microparticles), which is transferred to the building unit (BU) by a roller or a scraper. Both units use a stationary laser with mobile platforms. An additional aluminum plate is located on the bottom platform of the BU to enable the reflection of the infrared (IR) laser beam. The aluminum plate minimizes the energy dispersion and was roughened using sandpaper to enhance the adhesion of the first sintered layer to the surface. To form the structures, cross-sections generated from a 3D model are scanned by the laser, which melts and fuses the powder into solid pieces (Figure 1b). After printing each cross-section, the platforms of both RU and BU move vertically by one layer thickness (RU moves up and BU moves down). Additionally, the roller conveys a new layer of powder from the RU to the BU. This process is sequentially repeated for each layer until the structure is completed. Figure 1c–e show examples of saccharide-based 3D printed structures produced with our method. Particularly, Figure 1c and 1d shows glucose-based 3D printed logo characters and a helical structure. Figure 1e exhibits sucrose-based 3D printed gear structures. We observed that sucrose provided a smoother and better homogenous finishing of the 3D printed structures. Additionally, and in sharp contrast to glucose, sucrose allowed for the fabrication of 3D printed objects at

least two times smaller than those printed with glucose. We conjecture that the larger crystal size of glucose powder is responsible for the rougher finishing of the printed structures in comparison with those printed from sucrose powders. Note that the crystal sizes of the sugar powders are 40 μm and 400 μm for sucrose and glucose, respectively. Accordingly, we focused our work on the fabrication of sucrose-based small-scale structures.

To design the pattern required for the production of 3D printed sugar structures, we used a set of software consisting of CAD program to design the 3D structure (**Figure 2**a), a slicer to decompose the 3D model in 2D layers and vector graphics software to combine the 2D layers in a single master image (Figure 2b), which was finally transferred to the laser control software. The specific software procedure can be found in the experimental section.

To successfully achieve sucrose-based 3D printed structures, we first assessed how sintering parameters such as the power of the laser beam, the scan speed, and the scan pitch affect both their mechanical properties and the finishing characteristics (**Figure 3** and Figure S1, respectively). Accordingly, 3×10 mm rectangular slabs of sintered sucrose were fabricated for these studies. A cantilever beam test was used to examine the effect of the aforementioned parameters on the strength and robustness of the sucrose sintered slabs (Figure 3a). Note that the slabs are not perfectly rectangular due to the balling effect (vide infra) and the limitations derived from the laser spot size. We observed that our 3D printed sugar structures had a deviation in dimensions in this order of magnitude (-/+ 400 μm in the XY plane). Figure 3b and Figure 3c show the Young's modulus and ultimate strength (σ) of the sugar sintered slabs, respectively, as a function of the printed parameters, which are represented by the linear energy density (Δ), which is the ratio of the laser power percentage (P) to the scan speed (v):

$$\Delta = \frac{P}{v} \quad (1)$$

The Young's modulus (*E*) values are approximately in the range of 1 to 2.5 GPa, which roughly correspond to those obtained from compression tests on sugar pellets.[17] Intuitively, it is expected that structures printed at higher laser powers would exhibit a higher stiffness as a more complete melting of the powder is expected. However, the results obtained contradict this hypothesis. This is clear when plotting σ as a function of Δ. Figure 3c shows that the samples obtained from the lowest Δ display the highest ultimate strength values. Interestingly, when increasing Δ, printed structures evolved from a whitish or pale-yellow dull appearance to an opaque brownish color characteristic of caramelized sugar. It appears that caramelization, which implies amorphization of sugar crystals, impairs the mechanical strength measured in the corresponding printed sucrose structures. Additionally, the cantilever beam test also indicated that the scan path pattern (i.e.: separation between printed lines) used during the fabrication process impacted significantly the mechanical properties of the slabs produced. For example, the structures ruptured upon detachment from the printing bed and also displayed balling effect (see Figure S2), as encountered in direct metal laser sintering.[18] Interestingly, the best and most reproducible results were obtained by printing the structures using a zigzag path pattern and continuously printing the entire cross-section of the sucrose sintered slabs. We found that low powers (< 5 W) and high scan speeds (> 2.5 cm s^{-1}) resulted in a non-uniform welding between subsequent printed cross-sections, and hence, resulted into an unsatisfactory finishing of the printed structures. High powers (> 25 W) and low scan speeds (< 0.4 cm s^{-1}) also led to unsatisfactory finishing; in this case, the printed layers were damaged with the laser, leading to deterioration of the printed structure.

In order to identify the reasons for the counter-intuitive changes in the mechanical properties observed, we further investigated the crystallinity and chemical composition of sucrose-based 3D printed structures. **Figure 4**a shows characteristic sucrose-based 3D printed slabs sintered at 6.75 J cm^{-1}, 9 J $cm^{-1,}$ 10 J cm^{-1} and 11.5 J cm^{-1}. In Figure 4b, the X-ray

diffraction pattern of the sucrose precursor used in our experiments is presented, which corresponds well to the standard reference pattern (JCPDS: 24-1977). The peaks of the sucrose powder were also observed in the printed structures, indicating that the printing process did not transform the monoclinic crystalline phase of sucrose to other polymorphs. Additionally, no significant peaks from other crystalline chemical species were induced during the fabrication process, which means that the main crystalline chemical component in the printed structures is still sucrose. One obvious change observed in the XRD patterns is the rise of a broad band around 20° by increasing laser density, indicating that the sintered samples have a lower degree of crystallinity. Note that some amorphous derivatives of sugars, such as caramel, also exhibit a wide band at around 20°.[19] Besides, the full width at half maximum (FWHM) of the peaks of the sucrose-based 3D printed structures were slighter larger than those of the pristine samples, which also indicates the amorphization of the printed specimens. For example, the strongest peak at 24.77°, which corresponds to the reflection of (211) crystalline plane, has a FWHM of 0.12° for the precursor (i.e. pristine sucrose), and of 0.14° for structures prepared with a linear energy density of 6.75 J cm^{-1} or 9 J cm^{-1}, and of 0.15° for structures sintered at 11.5 J cm^{-1} (see SI Table S1 for additional details). Additionally, we also conducted differential scanning calorimetry (DSC) measurements to assess the crystalline nature of the printed structures as a function of the laser density used during their fabrication. As shown in Figure 4d, we observed that the 3D printed structures exhibited lower melting temperatures and melting enthalpies than those of pristine sucrose crystals. This result indicates that the printed structures exhibit a certain degree of defects and a lower crystallinity compared to the pure crystalline sucrose.

To shed light into the chemical composition of the 3D printed structures, we performed infrared (IR) spectroscopy measurements. Figure 4c shows the IR spectra of the pristine sucrose crystals used in the fabrication process as well as the IR spectra of the samples printed with different linear energy densities. In all samples, the positions of the absorption bands are almost equal. However, the intensity of some bands is slightly decreased in the IR spectra when the

linear energy density used during the fabrication process is increased. For example, the bands at 3560 cm^{-1}, 3384 cm^{-1} and 3327 cm^{-1}, which represent the OH stretching modes are less obvious in the printed samples than in the pristine sucrose crystals. A similar trend is also observed for the bands representing scissoring modes of CH_2 (1477 cm^{-1} and 1460 cm^{-1}), twisting mode of CH_2 (908 cm^{-1}), CO stretching modes (1129 cm^{-1}, 1116 cm^{-1}), and C-C stretching modes (1171 cm^{-1}, 1066 cm^{-1}, 943 cm^{-1}).[20] It has been reported that the intensity of the IR absorption bands for sucrose are reduced when its crystallinity decreases.[21,22] Additionally, note that there is an absorption band at 833 cm^{-1} in the sucrose-based 3D printed structures, which cannot be observed in sucrose. This absorption band might be assigned to glucose that can form due to the thermal decomposition of sucrose.[23] Therefore, these results suggest that, while the laser mainly melts the sucrose crystals, the heat generated by the laser could trigger other chemical reactions via a thermal decomposition, resulting, for example, in the formation of glucose. Clearly, we demonstrated that when the temperature decreases, the melted powder sintered, leading to objects with an amorphous crystalline nature. This result is not surprising, as it has been reported that when sugars are melted and subsequently cooled, they can become amorphous instead of crystalline.[24] All these data are in accordance with the observed melting enthalpies in our samples, which are lower at higher laser energy densities because a larger amount of sucrose was melted and sintered into an amorphous phase. Besides, during the melting process, there is also a concomitant decomposition and caramelization reaction.[24,25] Note that melting of sucrose takes place at 160 °C, while its caramelization occurs at a temperature range between 180 °C and 190 °C.[26] Importantly, when sucrose is heated, enolization and dimerization reactions can occur, and volatile molecules (such as furans, maltol, diacetyl, ethyl acetate) as well as nonvolatile compounds (e.g. D-fructose dianhydride) can form.[27] Therefore, upon heating, polymerization reactions can lead to the formation of oligomers such as caramelan (hexose tetramers), caramelen (glucose hexamers), and caramelin. These compound families form dark orange and brown particulate aggregates of around 0.46,

0.95 and 4.33 μm for caramelan, caramelen and caramelin, respectively.[26] Interestingly, we observed this brown color on the structures printed with a linear energy density higher than 30 J cm^{-1} (Figure S3). In fact, caramelin is the darkest compound among them and it can exist in three forms: soluble in cold water, soluble in hot water or insoluble in water and other conventional solvents[26]. It is therefore reasonable to expect that the dissolution of our sucrose-based 3D printed structures may be compromised, to some extent, due to the formation of insoluble species. Accordingly, the linear energy density will not only influence the mechanical properties and finishing of the sucrose-based 3D printed structures but also their chemistry, and, eventually their solubilization behavior and disintegration. This hypothesis was investigated looking at the dissolution rate of sintered sucrose-based 3D printed structures as a function of the linear energy density used during their fabrication. In this study, four different squared-shape sucrose-based 3D printed structures fabricated at different Δ of 6.75 J cm^{-1}, 9 J cm^{-1}, 10 J cm^{-1} and 11.5 J cm^{-1} were considered. The study was conducted at room temperature by placing each specimen in a well containing 5 ml of water (Figure 4e and Video S1). Three replicates for each condition were evaluated. The dissolution was monitored in time and recorded (Table S2). Interestingly, we observed that all the structures produced were dissolved roughly at around 11 min (see supporting information for details). Therefore, these results indicate that no insoluble species were formed using these printing conditions, thus ensuring the entire dissolution of the 3D printed structures in aqueous media.

To successfully accomplish the generation of sucrose-based 3D printed structures that can actively respond to external magnetic fields, we combined sucrose crystal powder with commercial hard-magnetic polyhedral $BaFe_{12}O_{19}$ microparticles with an average size of 5 μm (see SI for data regarding the morphology, crystalline structure and magnetic properties of the particulates). The printing procedure for the magnetic composite followed the same procedure as indicated in Figure 1. Due to the presence of $BaFe_{12}O_{19}$ microparticles, an increase in Δ was required compared to that employed for printing of pure sucrose structures. Note that the

presence of $BaFe_{12}O_{19}$ microparticles enhanced the scattering and reflection of the laser beam thus reducing the total energy transferred. Compared to pure sucrose, an increase in Δ (18 J cm^{-1}) was required to successfully produce sintered magnetically active sucrose-based 3D printed structures. Additionally, we observed that a mixture containing 50 wt% of $BaFe_{12}O_{19}$ microparticles resulted in very brittle 3D printed structures. In this case, we presume that the amount of sugar is not sufficient to lead to the fabrication of stable composite architectures. In contrast, structures made with a mixture containing 10 wt% of $BaFe_{12}O_{19}$ microparticles could be successfully fabricated. However, the amount of $BaFe_{12}O_{19}$ microparticles was not enough to perform magnetic manipulation. While different weight percentages were tested, a 1 to 3 weight ratio (25 wt% of $BaFe_{12}O_{19}$ microparticles) resulted in the best tradeoff between magnetic properties and structural integrity of the printed structure. Next, we analyzed if the printing process affected the $BaFe_{12}O_{19}$ microparticles. We confirmed by SEM, XRD and EDX that both the particles morphology and composition were not altered during the printing process (see Figures S4, S5 and S6 in SI). Additionally, vibrating sample magnetometry (VSM) revealed that the saturation magnetization of the composite corresponded to 42% of the saturation magnetization of pure $BaFe_{12}O_{19}$, which is only a 17% higher than expected considering the physical mixture of magnetic particulates and sugar (Figure S7).

As a magnetically active sucrose-based 3D printed small-scale robot, we chose a helical structure for the magnetic manipulation (**Figure 5**a). This type of design, also known as artificial bacterial flagella (ABF), shows favorable swimming characteristics at low Reynolds number and requires low rotating magnetic fields for their actuation. Once the magnetically active sucrose-based composites are printed, a homogenous 22000 Gauss DC magnetic field was used to magnetize the printed magnetic sucrose composite. This magnetization is possible due to the hard-magnetic nature of $BaFe_{12}O_{19}$ microparticles, which can retain a significant remnant magnetization ($M_r \sim 15$ emu g^{-1}, Figure S7a) after being subject to a premagnetizing magnetic field. A transversal magnetization was chosen to program the preferential

magnetization direction perpendicular to the screw axis of the printed helical structure. In this way, when applying a rotating magnetic, the magnetically active sucrose-based ABF can rotate around the screw axis (Figure 5b). In order to conduct magnetic manipulation with the sucrose-based ABF, a custom made electromagnetic navigation system (eMNs) called Octomag was used.[2] In order to generate relevant magnetic forces for magnetic manipulation, it is necessary to generate strong magnetic field gradients. In contrast, magnetic torque is directly proportional to the generated magnetic field, which allows for generating reasonable torques on a magnetic structure with relatively low magnetic field magnitudes. Note that, in addition to the aforementioned dependencies, both force and magnetic torque are also directly proportional to the volume of the structure and the total magnetization.

$$F_m = V(\vec{M} \cdot \nabla)\vec{B} \quad (2)$$

$$T_m = V \cdot \vec{M} \times \vec{B} \quad (3)$$

The combination of transversal magnetization and geometric shape allows the sucrose-based ABF structures to exploit the external magnetic torque as main mean of locomotion. By applying a rotating magnetic field parallel to the screw axis of the sucrose-based ABF, it is possible, given a large enough field, to induce a rotating motion along on the sucrose-based ABF. If the sucrose-based ABF is immersed in a liquid that is viscous enough, this rotating motion transforms itself in a corkscrew motion that results in a net displacement of the sucrose-based ABF structure. When a rotating magnetic field of 30 mT at a frequency of 5 Hz was applied from the eMNS, the magnetically active sucrose-based helix starts to move along the same screw axis while rotating around it, displaying a corkscrew like motion. By changing the direction of the field is then possible to consequently change the direction of the swimming ABF structure. This type of response allows for the precise guidance of the miliswimmer through the fluid. In order to prevent the ABF structure from contacting the bottom of the

container, an out of plane gradient of 100 mT m^{-1} was also applied. This gradient provides a small but supportive vertical force that improves the overall achievable motion. While the force generated by the gradient is not sufficient to lift off the structure from the container bottom surface, the combination of rotating field and gradient allows the ABF structure to move freely in the water/glycol (W/G) pool (Figure 5c and Video S2).

During the experiment, the ABF structure was manually guided using the eMNS along a 2D square path inside the W/G container. As expected, once the ABF structure begins to move, the sugar matrix starts to slowly dissolve in the DI water, and it is possible to observe the ABF structure thinning out. After several minutes (20 min), the sugar matrix of the ABF structure dissolves resulting in the fragmentation of the swimmer in a multitude of fragments, which causes the fragmented magnetic ensemble to lose its ability to corkscrew (Figure S8). As soon as the external field is removed the remaining magnetic particles disperse in the W/G container. The relatively fast dissolution of the proposed sugar-based swimmers could be exploited in treatments where the delivery of therapies or small-scale implanted assemblies of particulates should occur very quickly, such as in thrombosis or aneurysms.

We also fabricated carbonyl iron-based helical devices containing a 25 wt% of particles (Figure S9). Interestingly, the carbonyl iron particles were not damaged or corroded during the printing process. See the SEM, XRD and EDX results comparing both pure carbonyl iron and sugar-based composites in SI (see Figures S5, S6 and S10). VSM results show that the saturation magnetization of the composite corresponds to a 25 wt% of the saturation magnetization of pure carbonyl iron, which matches the composition of the printing powder (Fig. S7b). Regarding their manipulation, the carbonyl iron composites were not ideal as it is challenging to achieve a corkscrew motion with a soft-magnetic helix. Nevertheless, the proposed process could be used to print transient iron-based soft-magnetic parts without issues such as corrosion or deterioration.

Here, we have demonstrated that complex structures of biomolecules such as sucrose can be successfully shaped and combined with other materials such as magnetic particles to from printed composites. This approach will not only open new avenues in the use of sucrose-based biodegradable smalls-scale robots, but will also enable the realization of other transient devices for a wealth of biomedical applications. Importantly, by tailoring the caramelization degree of the sugar structures, it is possible to adjust their mechanical and chemical characteristics. Additionally, the transient properties of the printed robot can be further tailored by playing with the caramelization conditions and/or exploiting the rich chemistry of sugars to add polymeric coatings. We envision that the combination of sugar printed structures with other therapeutic particles will strongly impact the field of biodegradable and bioresorbable smart drug delivery systems and small-scale swimmers, and will also contribute to other fields such ingestible devices in which transient sugar components could be integrated. Sucrose-based composites could be an attractive approach to carry swarms of particles and distribute them upon reaching specific target positions such as small capillaries and vasculature bifurcations.

Experimental Section

Software used to design the 3D helical structures

For the printing process, the following software were used: (i) Siemens UGS NX10; (ii) 123D Make; (iii) Coreldraw X6; and (iv) Trotec Job Control. The first step consists of designing the 3D model for the structure. For a helix, a cylinder was swept long a helical guideline, created with the "*helix command*", using the "*sweep along line"* feature in Siemens UGS NX10. The resulting 3D model is then exported using the embedded STL exporter. The exported 3D stl model is then imported in 123D Make, which is used to slice the 3D model in multiple superimposed 2D slices. By choosing appropriate manufacturing settings and selecting the fabrication method "*stacked layers"* is possible to subdivide the helix 3D model in a specified number of 2D slices. The number of slices is given by the total model height divided by the

single layer height, which is set in the manufacturing option for the substrate. The resulting 2D slices are then arranged on multiple sheets that are subsequently exported in PDF format. The exported PDF is imported in Coreldraw X6 using the pdf importer. Due to the 2D limitation of the Trotec Job Control software in reading input model, Coreldraw X6 is used to compose a 2D image, which is made by manually assembling stacks of multiple 2D layers generated in a single 2D master image in X6. Color coding is used to distinguish between the different helix layers (Figure 2b), where for example red is the first layer to be lasered and blue corresponds to the third one (Figure 2a). By using this strategy is possible to use the Trotec Job Control software to produce 3D structures from plain 2D images stacked on top of each other. The full 2D helix master image is composed by 16 different stacked layers, each one with its own unique RGB color (Fig 2b). The 2D master image is then sent from CorelDraw X6 to the Trotec Job Control via the printing function. Once in the Trotec Job Control the master image appears as a set of superimposed paths distinguished by their RGB color. To enable the Trotec Job Control to laser all the 16 layers, a new custom material is prepared. The custom material is prepared using Trotec material wizard. Each RGB color is assigned a cut operation with the corresponding linear energy density. The created custom material has different cut operations (maximum is 32), one per RGB color. For the particular case of the printed helices, 16 layers were used. Using this custom color approach is possible to send the control input from the Trotec Job Control directly to the laser unit electronics, and therefore start to laser the 3D structure.

Fabrication of the 3D printed structures

The sucrose fine powder used in the experiment was acquired from COOP (confectionary sugar). The sucrose powder contains 98% sucrose and 2% corn starch. The corn starch is added from the sugar manufacturer to reduce caking. The magnetic $BaFe_{12}O_{19}$ and the carbonyl iron powder were purchased from Hoosier magnetic and Alfa Aesar, respectively. The $BaFe_{12}O_{19}$ hard-magnetic particles exhibit a polyhedral morphology, an average size of 2 μm in diameter,

a coercitivity of ca 3000 Oe and a saturation magnetization of 70 emu/g, The soft-magnetic iron carbonyl particles present a spherical shape, an average size of 1–3 μm in diameter, a coercivity of 2.5 Oe and a saturation magnetization of 200 emu/g. The powders where weighted using a precision lab scale (VWR Lag 164i) and mixed in a beaker by agitation in a custom made vibrating table for 15 minutes. Before the mixing occurs, the sugar powder is passed through a sieve and dried in an oven (Binder APT BD) at 50 degrees for two hours. The drying procedure helps reducing the balling effect encountered during the laser melting procedure. For the fabrication procedure, a custom container system is inserted on the cutting plane of a Trotec 75W laser cutter. The Trotec laser cutter has a CO_2 laser (λ = 10.6 μm) with tunable power. The laser is equipped with a 1.5-inch collimating lens that results, at focus plane, in a 150-μm beam width (spot size 300 μm). The mixed powder is filled in the reservoir tank in the SLA system. Next, the powder is slightly compressed by using a squared plate Plexiglas plate. After compressing the powder, the roller is used to homogenize the surface of the powder reservoir. While the powder container is lowered to accommodate the filled in powered, the printing container is raised up to the starting printing height. After the containers are in the correct starting position, the powder container is raised by one layer, the roller moves than from the powder container to printing container transferring exact quantity of powder necessary for one layer. The data are passed to the laser control software in the form of color coded lines on an image (Figure 2a). The laser cutter is then able to discern between the different trajectories based solely on the color of these. The printing procedure starts by lasering the first trajectory contained in the image. The first layer uses unique laser parameters that are otherwise not used for the remaining layers. For the first layer the speed is reduced by 30% and the power is increase by 20%. This initial step ensures that the molten sucrose adheres sufficiently well to the roughed aluminum plate. This is necessary to avoid any movement of the structure when the subsequent powder layers are dispensed over it. Once the first lasering is completed, the powder container is lifted up, and the printing container is lowered by an equal amount. The

roller moves again from the powder container to the printing container and transfers the powder necessary for the next layer. Subsequently, the next layer is lasered, and the melted sucrose adheres on the previous layer. The entire process is repeated until all layers on the image have been lasered in the sucrose bed. Once the fully laser procedure is completed, the aluminum plate of the printing container can be removed. The bulk of the non-melted sucrose can be recycled back in the powder container. To fully remove the non-melted sucrose from the laser structures a compressed air gun was used. A metal spatula is then used to gently pry the lasered structures away from the aluminum plate. The aluminum plate is then rinsed with water and placed back in the printing container.

Characterization of sucrose-based 3D printed structures

The XRD patterns were acquired on a Bruker D8 Advance X-ray diffractometer equipped a Cu target with the wavelength of 1.542 Å. The DCS was obtained using a Q1000 from TA Instruments, on a sample weight of 2 mg. The samples were heated from 25 to 300 C° at a rate of 10 C°/min. The infrared spectrums where obtained using a Tensor 27 (Bruker) performing a attenuated total reflection Fourier transform infrared spectroscopy (ATR-FT-IR) using a platinum single reflection diamond ATR accessory (Bruker). The recorder scans have a 4 cm^{-1} resolution with a spectral range ranging from 4000 to 400 cm^{-1} for each sample. For the determination of the young modulus a custom setup equipped with a Femto Tool FT-S10000 sensor was used to press on the sucrose structures. The sensor is capable of determining force and displacement, from which the Young modulus is then calculated. The SEM images of the particles were obtained using a Zeiss ULTRA 55. Previously, the samples were dispersed in EtOH, casted on a silicon substrate and coated with 4nm of gold. The EDX spectra were acquired using Ultim Max Silicon Drift Detector (Oxford Instruments).

Magnetic manipulation of the magnetic sucrose-based composite small-scale robots

The eMNS used for the magnetic navigation, is a custom development eMNS composed by eight electromagnets. The electro magnets are separated in two groups of four, arranged in a semispherical pattern. This type of arrangement allows 5 degrees of freedom. The system is capable of generating, at the work space center, field in the excess of 40 mT with frequencies up to 20 Hz. Gradients up to 500 mT/m are also possible at the center of the system. A Plexiglas holder is available at the center of the system workspace to place the container with the structures. The ABF structure was immersed in an aqueous solution containing 30 wt% of glycerol. Glycerol simulates the characteristic fluid viscosity of blood[2]. The glycerol was acquired from Sigma Aldrich. To prepare the mix glycerol was added to room temperature DI water and vigorously stirred using a rotating magnetic bar for 15 minutes. After 15 minutes of mixing the solution is fully homogenous and it is ready for the magnetic manipulations. In a first step a single structure was immersed in the glycerol solution by means of tweezers on the bottom of the W/G container. Subsequently, the rotating field is started and the ABF structures starts to rotate along its screw axis. Additionally, an out of plane gradient is applied. As the gradient is applied, the structure starts to move in a corkscrew motion along his screw axis. The ABF sucrose structure is manually swam in a square pattern along the container, the guidance is accomplished by rotating the field rotation axis of the rotating field in different directions. The position of the structure is returned using via camera feedback. The camera is combined with a microscope objective and it is placed directly above the center of the system workspace.

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Figure Captions

Figure 1. a) Schematic drawing of the SLS device used in our work. The illustration shows the fabrication of sucrose-based structures. The container on the left is the reservoir unit (RU). The left container is the building unit (BU) were the structures are manufactured by laser melting. Both containers can be raised and lowered to transfer the correct amount of powder into every layer. The roller is used to move the powder from the RU to the BU. b) Schematic illustrations showing a sequence of steps followed during the printing of a sugar-based helical structure with the SLS technique. The illustration includes a micrograph of a 3D printed sucrose-based helical structure. From c) to g), micrographs of saccharide-based 3D printed structures obtained with different laser powers (P) and different scan speeds (v): c) a glucose-based logo (P = 22.5 W; v = 1.4 cm s^{-1}), the scale bar is 20 mm; d) a glucose-based helix (P = 22.5 W; v = 1.4 cm s^{-1}), the scale bar is 10 mm; e) sucrose-based gears (P = 22.5 W; v = 1.4 cm s^{-1}), the scale bar is 10 mm; f) a sucrose-based set of caramelized helices (P = 14 W; v = 1 cm s^{-1}), the scale bar is 10 mm; and g) sucrose/ $BaFe_{12}O_{19}$ composite-based helices (P = 21 W; v = 1 cm s^{-1}), the scale bar is 10 mm.

Figure 2. a) Schematic illustration of the 2D layer stacking process required to generate the 3D helix model compatible with the laser control software. This illustration provides an insight on how the 2D input image correlates with the actual 3D printed object. In the dashed square inserts, the laser path for each structure layer is represented by a different color. One single color path is executed by the laser for each layer. By stacking up the needed numbers of layers, a 3D structure can be printed. b) A 3D model is sliced horizontally in order to generate the required 2D color-coded layers. Example of the final 3D helix model composed of 16 2D stacked layers used to produce the sugar helical structures. Each colored line represents the path followed by the laser beam to print one of the stacked 2D layers.

Figure 3. a) Schematic representation of the cantilever beam test setup. The sucrose slabs are fixed on a plexiglas support, the FemtoTool sensor tip comes vertically down and presses on each slab. b) Young's modulus (E) of the sucrose slabs as a function of Δ. The scale bar is 10 mm. c) Ultimate strength (σ) of the sucrose-based slabs as function of Δ.

Figure 4. a) Sucrose-based slabs printed at 6.75 J cm^{-1}, 9 J cm^{-1}, 10 J cm^{-1} and 11.5 J cm^{-1} (from left to right). The scale bar is 10 mm. In b), c), and d), XRD patterns, DSC and infrared (IR) spectra, respectively, of the precursor and of the 3D printed samples. e) Dissolution of a sucrose-based slab printed at 6.75 J cm^{-1}, scale bar 10 mm.

Figure 5. a) Batch of printed sucrose-based $BaFe_{12}O_{19}$ composite ABFs on the aluminum printing bed used in the printing container. The scale bar is 10 mm. The inset shows a magnified image of the surface. b) Schematic representation of the movement of the sucrose-based magnetic helix under a rotating magnetic field of 30 mT at a frequency of 5 Hz. c) The manipulation procedure seen from the top during the experiments. The scale bar is 10 mm.