

# Biocompatible, 3D Printable Magnetic Soft Actuators – Ink Formulation, Rheological Characterization and Hydrogel Actuator Prototypes

Fatih Puza, Lukas Barth, Marc-Christopher Thiel, Ralf Seemann, and Karen Lienkamp\*

3D printable inks for the preparation of magnetic hydrogel actuators are difficult to formulate because magnetic nanoparticles tend to aggregate without stabilization through other ink components. At the same time, such inks need to be shear-thinning and recover their high viscosity state sufficiently fast to be suitable for the printing process. Here, the use of chitosan as dispersing agent for Fe<sub>2</sub>O<sub>3</sub> nanoparticles is reported. Combined with Pluronic F127 as a rheology modifier and acrylamide as the base monomer, thermo-responsive and shear-thinning magnetic inks containing well-dispersed particles are obtained. The ink viscosity is tuned over two orders of magnitude by varying the chitosan and Pluronic F127 content. 3D-printed shapes with good shape fidelity are obtained at a print bed temperature of 50 °C, where aggregation of the Pluronic F127 micelles occurs. This leads to a fast recovery of the high viscosity state of the material, so that the printed shape can then be locked in by UV cross-linking. This treatment yielded magneto-responsive prototypes which are promising for soft robotics applications. Thanks to the simplicity of the ink formulation, it is easily transferable also to nonspecialist laboratories, and the concept is potentially applicable also to other types of nanoparticles.

different external stimuli, and as such are promising for soft robotics applications.<sup>[1]</sup> They can be actuated by external stimuli that affect the state of hydration of their crosslinked polymer constituents (e.g., temperature or pH changes),<sup>[2,3]</sup> or by addressing built-in stimulus-responsive components (e.g., magnetic nanoparticles, by using external magnetic fields).<sup>[4,5]</sup> Hydrogels which show predetermined, complex motion in response to changes in their environmental conditions are referred to as programmed or programmable hydrogel actuators. Programmed actuation, such as the rolling or folding of structured hydrogel sheet into cubes, twisted ribbons, or tubes requires structural anisotropy of the actuator material. This is achieved either by local modulation of the polymer network structure of the material (e.g., by local variation of the cross-linking density), or by introducing a pattern into the material during fabrication (e.g., material grids with different grid shapes, spacings and/or angles). In this manner, locally different mechanical properties and hence actuation responses are generated.<sup>[6–8]</sup>

## 1. Introduction

Hydrogels are hydrophilic, often biocompatible polymer materials that can be designed to respond to a number of

It is not straightforward to introduce localized anisotropies into materials with conventional polymer processing techniques such as molding or casting. They can be realized with photolithographic processes, yet this technique requires stepwise fabrication and alignment, which is slow and expensive. 3D printing, on the other hand, provides access to soft actuators with anisotropic materials composition and/or patterning and a complex structural design, all in a highly automated process.<sup>[9,10]</sup> As a processing technique, 3D printing of polymer materials has reached disproportionate levels of maturity: While 3D printing of thermoplastic materials has become a main-stream technique, 3D printed hydrogels are much less common. They are mainly found in the biomedical field, where “bioprinters” are used to manufacture biopolymer-based scaffolds, e.g. for tissue engineering or drug delivery. 3D printing of programmable hydrogel actuators is a newly emerging field, as reviewed recently.<sup>[6]</sup> For successful 3D printing, the printed material must have a low viscosity during the printing process, and a high viscosity directly afterwards, so that shape distortions due to flow are avoided. When printing thermoplasts, this is straightforwardly

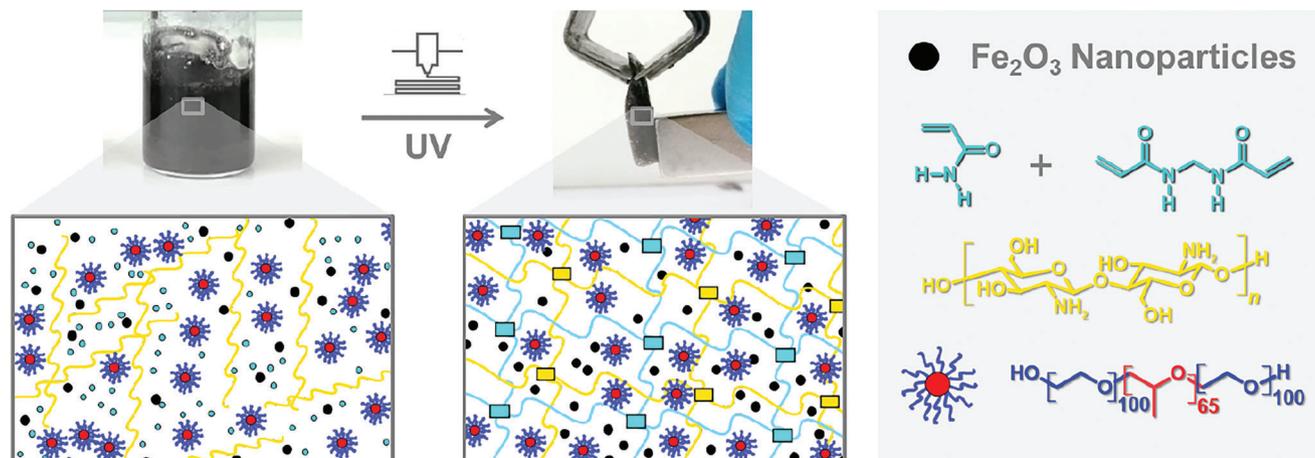
F. Puza, L. Barth, M.-C. Thiel, K. Lienkamp  
Chair of Polymer Materials  
Department of Materials Science and Engineering  
Saarland University  
66123 Saarbrücken, Germany  
E-mail: karen.lienkamp@uni-saarland.de

R. Seemann  
Chair of Geometry of Fluid Interfaces  
Department of Physics  
Saarland University  
66123 Saarbrücken, Germany

 The ORCID identification number(s) for the author(s) of this article can be found under <https://doi.org/10.1002/mame.202300322>

© 2023 The Authors. Macromolecular Materials and Engineering published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

DOI: 10.1002/mame.202300322



**Figure 1.** Study design: a 3D printable hydrogel ink consisting of acrylamide and N,N-methylene(bisacrylamide) crosslinker (both cyan), iron oxide nanoparticles (black) dispersed in chitosan (yellow), and the rheology modifier Pluronic 127 (blue-red) was formulated. After 3D printing and UV cross-linking, a double hydrophilic network of physically cross-linked chitosan and covalently cross-linked polyacrylamide was obtained, in which the nanoparticles and the rheology modifier micelles are dispersed. This hydrogel can be actuated by a permanent magnet.

achieved by heating the thermoplastic filament or granulate to obtain a viscoelastic polymer melt, which rapidly solidifies when deposited onto a cool print bed. The formulation of suitable polymer inks for hydrogel printing is more complicated, especially if stimulus-responsiveness is required in addition to printability. The base formulation for printing hydrogels is a viscoelastic, gel-like ink consisting of at least one hydrophilic polymer and a suitable solvent. The ink must be sufficiently shear-thinning (i.e., decreasing in viscosity with increasing shear rate) to be printable, and thixotropic (i.e., decreasing in viscosity under constant shear, with a fast recovery of the high viscosity state when the shear stress is removed) to avoid flow after printing.<sup>[6,11]</sup> Often a post-printing step (e.g., UV cross-linking) is required to enhance the mechanical stability of the printed hydrogel objects, therefore suitable functional groups for supramolecular structure formation or polymerization must be present in the ink. For actuation, either the polymer itself or an additional component must be stimulus-responsive. Thus, the formulation of polymer inks for 3D printing requires much fine-tuning of the composition to meet the requirements of the printing process and to obtain the desired mechanical properties and stimulus-responsiveness of the target hydrogels.

Shear-thinning of polymer solutions is observed if the polymer chains undergo supramolecular interactions that are broken at high shear rates. If the polymer used in the ink is not shear-thinning itself, rheology modifiers can be added. Examples are specific block copolymers or nanoclays.<sup>[12,13]</sup> Such additives have multivalent supramolecular interactions with themselves or the polymer component. These are reversibly broken at the high shear rates of the printing process but are recovered when at rest on the print bed. Thus, flow is avoided, and the geometry of the printed object is stabilized for the post-printing treatment. For example, the amphiphilic triblock copolymer poly(ethylene oxide-block-propylene oxide-block-ethylene oxide) (Pluronic F127) undergoes micellization in aqueous environments, which leads to an increased ink viscosity due to hydrogen bonding between

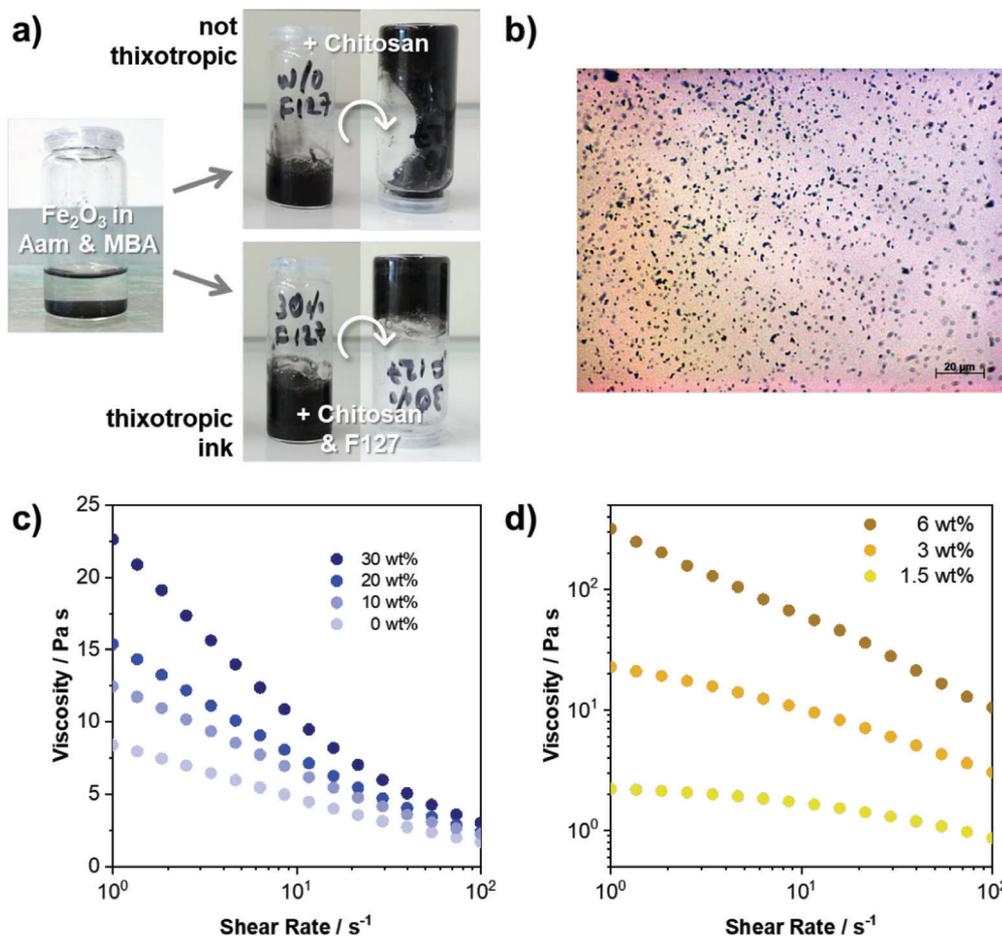
the micelles.<sup>[14]</sup> Pluronic F127 is widely used in hydrogel systems due to its biocompatibility and temperature-induced sol-gel transition.<sup>[15]</sup> It can even be used as a sacrificial rheology modifier to 3D print low-viscosity solutions, where it is removed afterward by a suitable solvent. For example, thermoresponsive PNIPAm inks with low viscosity were 3D printed with the help of Pluronic F127, which was afterward extracted.<sup>[16]</sup>

We here report the formulation of a polymer ink for 3D printable magnetic soft actuators consisting of acrylamide, N,N-methylenebis(acrylamide), an UV initiator to trigger free radical polymerization, the dispersing agent chitosan, magnetic iron oxide nanoparticles, and Pluronic F127 as a rheology modifier (**Figure 1**). Thus, the resulting hydrogel actuator contains only poly(acrylamide), chitosan, iron oxide, and Pluronic F127, all of which are deemed to be biocompatible. In the ink formulation, Pluronic F127 was used as a structural component and therefore not extracted after printing. The hydrogel ink obtained was shear-thinning and had a temperature-dependent viscoelasticity. By adjusting the 3D printing parameters, 3D printed objects with a resolution of  $\leq 1$  mm in  $x$ - $y$ -direction were obtained. UV polymerization and cross-linking of the acrylamide led to stable 3D-printed objects that could be actuated by magnetic fields.

## 2. Results and Discussion

### 2.1. Study Design

The aim of this work was to formulate an ink for 3D printing of magnetic hydrogels which could be actuated by an external magnetic field and consists only of biocompatible components (Figure 1). Iron oxide nanoparticles were used as magnetoactive components. Poly(acrylamide) (PAAm) was chosen as hydrogel matrix. Two main requirements had to be met: a good dispersion of the nanoparticles in the ink to get a homogeneous material, and a suitable shear-thinning behavior during the printing process. As the nanoparticles did not disperse in an aqueous solution of the PAAm precursors (acrylamide monomer, AAm, and the

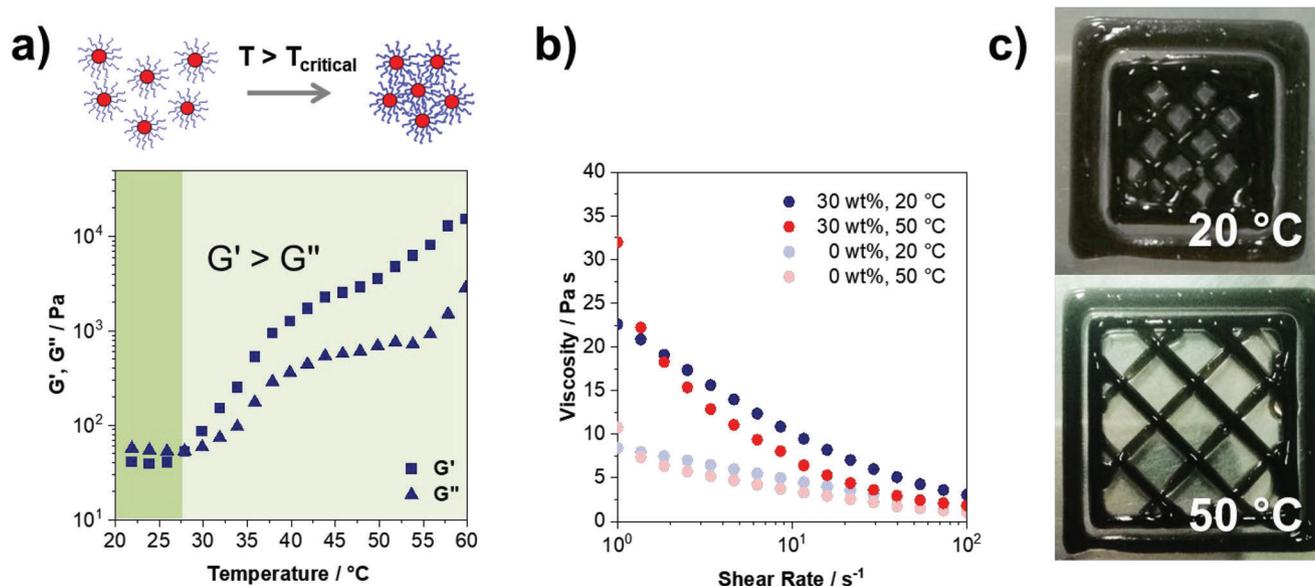


**Figure 2.** a) Formulation of inks for 3D printing of magneto-responsive hydrogel actuators. Neither AAm/MBA nor a combination of AAm/MBA/F127 (not shown) can stabilize iron oxide nanoparticles in an aqueous solution. Addition of chitosan helps disperse the particles but does not yield sufficient thixotropy. The formulation AAm/MBA/CH/F127/Fe<sub>2</sub>O<sub>3</sub> contained well-dispersed particles and had a resistance to flow, as desired for 3D printing applications. b) Light microscopy image of the ink formulation AAm/MBA/3% CH/30% F127/Fe<sub>2</sub>O<sub>3</sub>, scale bar = 20 μm. c) and d) Shear rate tests (viscosity versus shear rate) of different ink formulations. c) Variation of the F127 concentration of AAm/MBA/F127/Fe<sub>2</sub>O<sub>3</sub> (no CH), and d) variation of the CH concentration in AAm/MBA/F127/Fe<sub>2</sub>O<sub>3</sub>/CH.

cross-linker N,N-methylene(bis-crylamide), MBA), the biopolymer chitosan was added as a dispersing agent. As this composition did not yield a sufficiently shear-thinning ink, Pluronic F127 was chosen as a rheology modifier. Thus, the ink formulation consisted of AAm, MBA, the UV initiator 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone, iron oxide nanoparticles dispersed in chitosan, and Pluronic F127 (Figure 1). First, the influence of the ink composition on its rheological properties was studied by varying the concentration of Pluronic 127 and chitosan. Next, the printing temperature was optimized to minimize the ink flow on the build plate/print bed. Printing each layer consisted of two steps: deposition and UV irradiation. The UV irradiation initiated the free radical polymerization of AAm and MBA to PAAm. Thus, a double hydrophilic network of physically cross-linked chitosan within a covalently cross-linked PAAm matrix was obtained, in which iron nanoparticles and Pluronic 127 micelles were dispersed (Figure 1). As demonstrators, hydrogel grids were fabricated, and a hydrogel sheet was printed as a prototype for a hydrogel actuator.

## 2.2. Ink Formulation Experiments

As shown in Figure 2a, iron oxide nanoparticles did not disperse well in an aqueous solution of AAm and MBA. Furthermore, it has been reported that the viscosity of such small molecule solutions is too low for 3D printing.<sup>[16]</sup> Pluronic 127 (called F127 in the following) was added as a rheology modifier, as it had been previously shown to make low viscosity solutions printable.<sup>[17]</sup> While F127 was successfully used in the context of other actuator system due to its thermoresponsiveness, it has not yet been used in the context of magnetic actuators. As we found here, iron oxide particles do not disperse well in F127. Therefore, to stabilize and disperse the iron oxide nanoparticles in the aqueous AAm/MBA/F127 solution, the carbohydrate polymer chitosan (CH) was added to the ink. CH carries multiple hydroxyl groups, and with these ligates the polar, high surface-energy nanoparticles. With this ligand, an optically homogeneous dispersion of the particles was obtained (Figure 2b). An ink containing CH but no F127 was not sufficiently thixotropic for printing, but the



**Figure 3.** a) Temperature-dependent aggregation of the F127 micelles and its effect on the viscoelastic properties of the ink formulation with 30 wt.% F127. At an oscillation frequency of 1 Hz, a temperature sweep test between 20 and 60 °C indicated a transition from  $G' < G''$  to  $G' > G''$  at 28 °C. b) Shear rate test performed at 20 °C (blue symbols) and 50 °C (red symbols) using ink formulations with 0 and 30 wt.% F127, respectively. c) Optical micrographs of 3D printed hydrogel meshes using the ink formulation with 30 wt.% F127 and 3 wt.% CH onto a print bed kept at 20 °C ( $< T_{critical}$ ) and when heated to 50 °C ( $> T_{critical}$ ). Heating the print bed drastically increased the resolution of the printed object. The overall dimensions of the 3D-printed meshes were 30 mm x 30 mm.

combination of CH and F127 united the desired shear-thinning and thixotropic properties, as indicated by finding that a vial containing that formulation could be turned upside down without flow (Figure 2a).

### 2.3. Rheological Properties

To quantify the above-described visual observations, different rheological measurements were performed. First, the viscosity and shear-thinning behavior of different ink formulations were evaluated by shear rate tests (i.e., measurements of viscosity as a function of shear rate). For these tests, inks with the formulation AAm/MBA/F127/Fe<sub>2</sub>O<sub>3</sub> were investigated (Figure 2c). As expected, the sample without F127 (0 wt.%) had a low viscosity (8 Pa·s at a shear rate of 1 s<sup>-1</sup>, which decreased to 2 Pa·s at 100 s<sup>-1</sup>) and was not particularly shear-thinning. Increasing the F127 concentration to 10, 20, and 30 wt.%, respectively, increased the viscosity successively, with 23 Pa·s at a shear rate of 1 s<sup>-1</sup> for the 30 wt.% formulation. This sample was also sufficiently shear-thinning, with a viscosity reduction to 3 Pa·s at 100 s<sup>-1</sup>. Thus, both the viscosity and the extent of shear-thinning depended on the F127 concentration. Viscosity and shear-thinning further depend on the CH concentration, as shown for inks with the formulation AAm/MBA/30 wt.% F127/Fe<sub>2</sub>O<sub>3</sub>/CH (Figure 2d). At a CH concentration of 6 wt.%, the viscosity at 1 s<sup>-1</sup> was as high as  $3.2 \cdot 10^{[2]}$  Pa·s. To avoid potential clogging problems during printing, the ink formulation with a concentration of only 3 wt.% CH was chosen for further use. This ink had a viscosity of 23 Pa·s at 1 s<sup>-1</sup>, which decreased to 3.0 Pa·s at 100 s<sup>-1</sup> due to shear-thinning (Figure 2d). The developed ink formulation was thus promising for the targeted printing process. Further measurements showed

that the viscosity did not significantly depend on the nanoparticle concentration (Figure S1, Supporting Information).

### 2.4. Influence of Temperature on the Rheological Properties and 3D Printing Results

It is well-known that F127 is thermoresponsive. While the F127 micelles are dispersed in aqueous media below a certain critical temperature ( $T_{critical}$ ), they aggregate to larger supramolecular structures above that temperature (Figure 3a). As this would also affect the viscosity of the ink formulation, the temperatures used during the printing process (both within the print head and on the print bed) relative to  $T_{critical}$  are crucial parameters. To determine  $T_{critical}$  of the ink formulation with 30 wt.% F127, its complex shear modulus  $G^*$  (reported as storage and loss moduli  $G'$  and  $G''$ , respectively) as a function of temperature was determined in a dynamic temperature sweep test at a constant oscillation rate of 1 Hz. As shown in Figure 3a, at a critical temperature of 28 °C, there was a transition from  $G' < G''$  to  $G' > G''$ . Thus, below 28 °C, the ink behaves as a liquid, while  $G'$  becomes dominant at higher temperatures, and the ink becomes more like a viscoelastic solid.

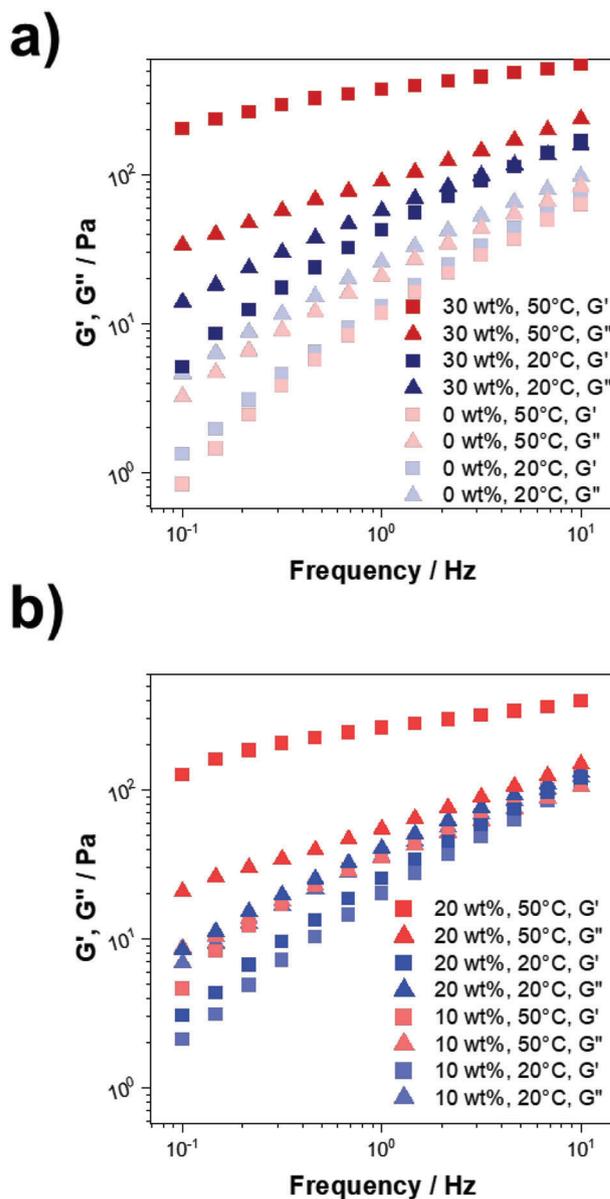
To further understand how this transition affects the ink viscosity during printing, measurements of viscosity versus shear rate at 50 °C were performed for ink formulations with 0 and 30 wt.% F127, respectively, and compared to the measurements obtained at 20 °C (Figure 3b). It was observed that an ink without F127 had a similar viscosity versus shear rate profile for both temperatures. On the other hand, the ink with 30 wt.% F127 had a notably higher viscosity at 1 Hz at 50 °C compared to 20 °C, and was overall more strongly shear-thinning at the higher

temperature than at 20 °C. This indicates that aggregated F127 micelles were present at 50 °C at low shear rate, but that these aggregates were broken as the shear rate increased. This type of measurement can be considered as a simulation of the ink viscosity inside the print head at different printing speeds. To make sure that the ink viscosity was near-independent of the printing speed, it was decided to maintain the print head at 20 °C. As the data indicated that the ink viscosity increased at low shear rates at the higher temperature, the temperature of the print bed was set to 50 °C to reduce the flow of a just printed object. As shown in Figure 3c, this greatly improved the shape fidelity and resolution of the printed object.

To further evaluate this aspect, dynamic frequency sweep tests were conducted for ink formulations with 0, 10, 20, and 30 wt.% F127 at 20 °C and 50 °C, respectively (Figure 4). In these measurements, the samples were exposed only to low shear forces. Thus, they model the situation of the inks after deposition on the print bed. For the ink with 0 wt % F127, the loss modulus  $G''$  was larger than the storage modulus  $G'$  at all frequencies for both temperatures (Figure 4a), indicating that this ink behaves as a liquid throughout and is thus unsuitable for printing. The ink with 10, 20, and 30 wt.% F127 also had  $G' < G''$  at 20 °C. For the 10 wt.% sample, the values of both moduli were similar at 50 °C, indicating a more viscoelastic solid-like behavior at the higher temperature (Figure 4b). For both the inks with 20 and 30 wt.% F127 at 50 °C,  $G'$  was substantially larger than  $G''$  for the entire frequency range (Figures 4a,b), indicating sufficient viscoelastic solid-like behavior at that temperature. Thus, 20 wt.% F127 was found to be the minimum concentration of the rheology modifier to have a sufficient resistance to flow on the heated print bed. The data also explains the flow observed for the 30 wt.% ink when the print bed was kept at 20 °C (Figure 3c).

## 2.5. Prototype Printing

Following the rheological characterization, different prototypes were printed using the ink formulation with 30 wt.% F127 (Figure 5). In-situ UV treatment was performed directly after printing to cross-link the acrylamide monomer. While the printing process was successful at the chosen printing conditions, the printed, cross-linked structures strongly adhered to the glass print bed and could not be removed without damage. For this reason, different methods to remove the prototypes were evaluated. Immersion of the entire print bed in ultrapure  $H_2O$  led to partial dissolution of the chitosan moieties of the hydrogel (Figure 5a). When placed into 1 M  $Na_2SO_4$  solution, the chitosan chains were physically cross-linked by the negatively charged ions sulfate ions (in addition to the chemical cross-linking), so that the hydrogel shape was stabilized (Figure 5b) and could be removed by another bath in pure water. Besides the prototype with the mesh structure shown in Figure 5b, a rectangular hydrogel was fabricated and detached from the print bed by this method (Figure 5c). When the rectangular hydrogel was held near a permanent magnet, it oriented in the magnetic field by bending (Figure 5d, and Video S1 in the supporting information). This demonstrated that the printed hydrogel prototypes could indeed be actuated by this external stimulus.

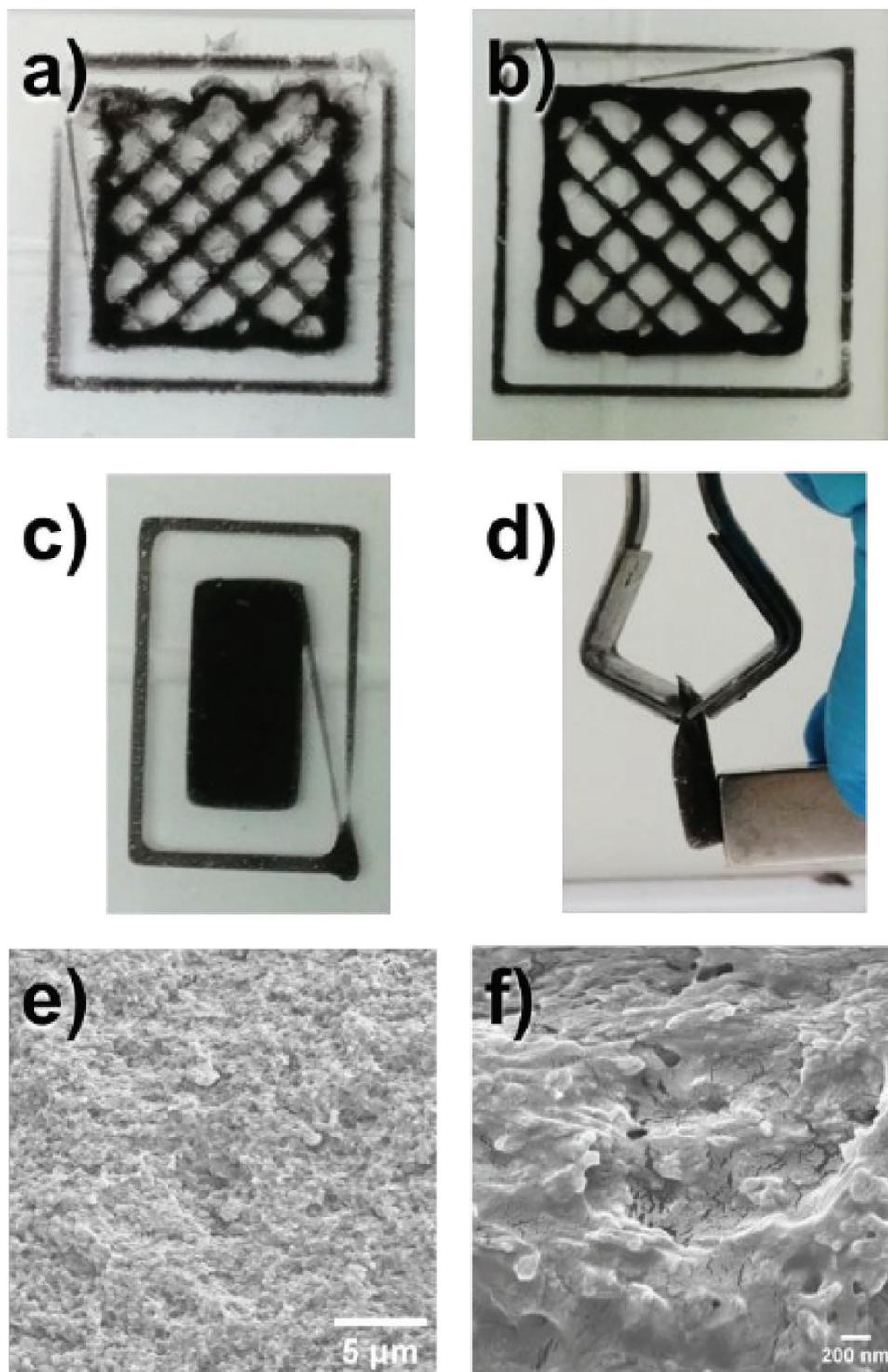


**Figure 4.** Dynamic frequency sweep tests for ink formulations with 0, 10, 20, and 30 wt.% F127. Storage moduli  $G'$  (squares) and loss moduli  $G''$  (triangles) in a range from  $10^{-1}$  to  $10^{[1]}$  Hz at 20 °C (blue symbols) and 50 °C (red symbols) are shown. a) Inks with 0 and 30 wt.% F127; b) inks with 10 and 20 wt.% F127.

To investigate the microstructure of the material, a rectangular hydrogel sheet was investigated by scanning electron microscopy (Figure 5,f). The images of the freeze-fractured cross-section of the material indicated a dense, but still porous structure. The rugged edges are attributed to the nanoparticles which are embedded and distributed evenly in the hydrogel matrix.

## 3. Conclusion

The above-presented study offers a simple procedure to formulate inks for 3D printing of magneto-responsive soft actuators.



**Figure 5.** Different 3D printed shapes, their actuation and microstructure. a) When immersed into pure water, the 3D-printed mesh disintegrated within minutes. b) Treatment with 1 M  $\text{Na}_2\text{SO}_4$  stabilized the printed mesh structure. The dimensions of both meshes were 30 mm  $\times$  30 mm, with a 5 mm grid sizes. c) A rectangular shape was 3D printed and immersed into 1 M  $\text{Na}_2\text{SO}_4$ , then detached using a spatula for an actuation test. d) The rectangular hydrogel bent in the static magnetic field of a permanent magnet. e) and f) Scanning electron microscope images of the freeze-dried hydrogel material. The material has a porous structure. The embedded nanoparticles are evenly distributed.

Importantly, the carbohydrate polymer chitosan was used as a dispersing agent to evenly disperse the magneto-responsive iron oxide nanoparticles, which is a prerequisite for successful 3D printing. By adding the rheology modifier Pluronic F127 to the aqueous suspension of acrylamide monomer, *N,N*-methylenebis(acrylamide), a UV initiator, chitosan and the iron oxide nanoparticles, inks with a suitable viscosity range were obtained. We demonstrated that both the rheology modifier F127 and the stabilizer chitosan were needed to obtain such a combination of properties. Both the ink viscosity and the shear-thinning behavior could be adjusted by changing the chitosan and the Pluronic F127 concentration. Importantly, this ink formulation did not require chemical modification of the nanoparticles themselves and is thus easily transferable also to laboratories that are not specialized in modification of particle surface properties.

Besides being shear-thinning, ink formulations with at least 20 wt.% Pluronic F127 had also the properties of a viscoelastic solid at elevated temperatures due to the thermo-responsiveness of the rheology modifier. The inks showed too much fluidity when used at room temperature. When the print bed was heated to 50 °C, the viscoelastic properties of the ink became dominant and prevented flow, so that prototype structures with high shape fidelity could be obtained. Further rheological characterization showed that inks with only 10 wt.% F127 were mainly viscous at 20 °C and 50 °C and thus unsuitable for 3D printing.

After UV treatment (to polymerize the acrylamide monomer) and swelling in sodium sulfate solution (to cross-link the chitosan), a free-standing rectangular 3D printed prototype was obtained, which bent in the magnetic field of a permanent magnet. Thus, the here presented ink formulations are promising materials for the fabrication of magneto-responsive hydrogel actuators by 3D printing. Further studies are needed to quantify the magnitude of the actuation response, and to assess the magnetic field strengths needed for actuation. Actuators with structural anisotropy should be accessible by printing anisotropic structures, or by using a combination of inks with different amounts of nanoparticles. The concept of using chitosan as a dispersing agent in combination with Pluronic F127 as a rheology modifier should be transferable also to other high-surface energy (nano)particles, and as such can probably be generalized for the formulation of a whole family of 3D printable polymer inks containing stimulus-responsive particles.

## 4. Experimental Section

**Materials:** Acrylamide ( $\geq 99\%$ ) (AAm), *N,N*-methylenebis(acrylamide) (99%, MBA), 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone (98%), chitosan (medium molecular weight, 75%–85% deacetylated), iron(II,III) oxide nanopowder (particle size: 50 to 100 nm), Pluronic F127 (bioreagent grade) and acetic acid ( $\geq 99\%$ ) were purchased from Sigma-Aldrich/Merck, Taufkirchen, Germany. All chemicals were used as received. Ultrapure H<sub>2</sub>O was obtained from TKA MicroPure water purification system (JWT GmbH, Jena, Germany) and had a resistivity of 18.2 M $\Omega$  cm.

**Ink Preparation:** Hydrogel inks were prepared by dissolving all components in ultrapure H<sub>2</sub>O. As the chitosan used was not soluble in H<sub>2</sub>O, a small amount of acetic acid was added to solubilize it. In a typical preparation, 0.1 ml (2.5 v/v %) acetic acid was added to the 4 mL ultrapure H<sub>2</sub>O and stirred. 1.20 g AAm (30 wt.% of H<sub>2</sub>O), 25 mg of MBA crosslinker (2 wt.% of AAm), and 120 mg (3 wt.% of H<sub>2</sub>O) chitosan polymer were added sequentially. After each addition, the solution was

stirred until the added component had completely dissolved. Next, the rheology modifier Pluronic F127 (30 wt.% of H<sub>2</sub>O) was slowly added into the solution under continuous stirring. After obtaining a homogeneous solution, 40 mg iron(II,III) oxide nanopowder (1 wt.% H<sub>2</sub>O) of was added into the solution. The mixture was ultrasonified for 10 min to eliminate visible nanoparticle aggregates and was then stirred. Just before starting the printing process, 15 mg of the UV initiator 2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone was added into solution, which was stirred for another 10 min. Details of the compositions of all ink formulations can be found in Table S1 in the Supporting Information.

**Rheological Characterization:** All rheological measurements were performed using a Haake Mars 40 Rheometer (Thermo Fisher Scientific, Karlsruhe, Germany) with a parallel plate setup and a Peltier temperature control system. The radii of both the upper plate and lower plate were 25 mm. The gap between the plates was set to 1 mm before the experiments. Unless otherwise stated, the temperature was 20 °C. To determine the shear-thinning profile of the inks, shear rate sweep tests were performed. The viscosity was recorded at different shear rates from 1 to 100 s<sup>-1</sup> at 1 Hz. For the shear modulus versus temperature measurements (temperature sweep test), the oscillation frequency was set to 1 Hz. A frequency sweep test was used to evaluate the viscoelastic behavior of the magnetic inks, i.e., to obtain a curve of shear modulus versus oscillation frequency. The storage modulus  $G'$  and the loss modulus  $G''$  were determined within a frequency range of 0.01 to 10 Hz at 0.1% strain.

**4.0.0.1. Printing:** 3D Printing was performed using a Reg4Life 3D printer (Regemat, Granada, Spain) using a print head with a bioink extrusion syringe. Before starting to print, the print bed/build plate temperature was set to 50 °C. The print bed was coated with a solution of 15 wt.% of poly(vinyl alcohol) (PVA) in water as a soluble sacrificial layer. The overall dimensions of the printed mesh structure (Figure 3c) were set to 30 mm x 30 mm. The infill pattern was a diagonal grid with a tilt angle of 45 °. The grid size was 5 mm. The layer height was 0.25 mm; the flow speed was 2 mm s<sup>-1</sup>. UV light with a wavelength of 365 nm was used for cross-linking. The curing speed was 1 mm s<sup>-1</sup>. After printing, the obtained hydrogel and glass print bed were immersed into 1 M Na<sub>2</sub>SO<sub>4</sub> for 1 hour to induce physical crosslinking of chitosan polymer. They were then immersed into H<sub>2</sub>O to remove the sacrificial PVA layer. After 10 min, the printed hydrogels were gently detached from the glass print bed.

**Optical Microscopy and Scanning Electron Microscopy:** The dispersion of the nanoparticles in the ink was imaged using a Zeiss Axio Observer equipped with a CCD camera (Zeiss, Oberkochen, Germany). The hydrogel microstructure was studied using a Zeiss Sigma 300 VP scanning electron microscope (Zeiss, Oberkochen, Germany). A 3D-printed and UV-irradiated rectangular hydrogel was swollen in 1 M Na<sub>2</sub>SO<sub>4</sub> for 1 h to induce physical crosslinking of the chitosan polymer. It was then washed with water and dried. The dried material was mounted onto a sample holder with conductive carbon adhesive tape and then sputtered with gold using a Cressington Sputter Coater 108 Auto (Tescan GmbH, Dortmund, Germany; process parameters: 20 mA, 0.1 mbar, 30 s). Images were taken at 3 kV.

## Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

## Acknowledgements

This work was supported by funding from Saarland University, by the Heisenberg Program of the German Research Foundations (DFG, Grant ID LI 1714/9-1), and by the IPROM research cluster (Zeiss-Foundation).

Open access funding enabled and organized by Projekt DEAL.

## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

## Keywords

actuators, hydrogels, magnetic actuators, polymers, soft robotics

Received: September 7, 2023  
Published online: September 29, 2023

- 
- [1] Y. Lee, W. J. Song, J.-Y. Sun, *Mater. Today Phys.* **2020**, *15*, 100258.  
[2] W. J. Zheng, N. An, J. H. Yang, J. Zhou, Y. M. Chen, *ACS Appl. Mater. Interfaces* **2015**, *7*, 1758.  
[3] P. Techawanitchai, M. Ebara, N. Idota, T.-A. Asoh, A. Kikuchi, T. Aoyagi, *Soft Matter* **2012**, *8*, 2844.  
[4] C. Gong, Y. Zhai, J. Zhou, Y. Wang, C. Chang, *J. Mater. Chem. C* **2022**, *10*, 549.  
[5] Y. He, J. Tang, Y. Hu, S. Yang, F. Xu, M. Zrinyi, Y. Mei Chen, *Chem. Eng. J.* **2023**, 142193.  
[6] F. Puza, K. Lienkamp, *Adv. Funct. Mater.* **2022**, *32*, 2205345.  
[7] W. Sun, S. Schaffer, K. Dai, L. Yao, A. Feinberg, V. Webster-Wood, *Front Robot AI* **2021**, *8*, 673533.  
[8] A. Zhang, F. Wang, L. Chen, X. Wei, M. Xue, F. Yang, S. Jiang, *Chin. Chem. Lett.* **2021**, *32*, 2923.  
[9] M. Champeau, D. A. Heinze, T. N. Viana, E. R. De Souza, A. C. Chinellato, S. Titotto, *Adv. Funct. Mater.* **2020**, *30*, 1910606.  
[10] J. Siminska-Stanny, M. Niziol, P. Szymczyk-Ziółkowska, M. Brozyna, A. Junka, A. Shavandi, D. Podstawczyk, *Addit. Manuf.* **2022**, *49*, 102506.  
[11] X. Wan, L. Luo, Y. Liu, J. Leng, *Adv. Sci.* **2020**, *7*, 2001000.  
[12] J. Li, C. Wu, P. K. Chu, M. Gelinsky, *Mater. Sci. Eng.: R: Rep.* **2020**, *140*, 100543.  
[13] Y. Jin, Y. Shen, J. Yin, J. Qian, Y. Huang, *ACS Appl. Mater. Interfaces* **2018**, *10*, 10461.  
[14] *Tissue Eng., Part B* **2022**, *28*, 451.  
[15] S. Dutta, D. Cohn, *J. Mater. Chem. B* **2017**, *5*, 9514.  
[16] H. Arslan, A. Nojoomi, J. Jeon, K. Yum, *Adv. Sci.* **2019**, *6*, 1800703.  
[17] M. Müller, J. Becher, M. Schnabelrauch, M. Zenobi-Wong, *Biofabrication* **2015**, *7*, 035006.