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1. REPORT DATE (DD-MM-YYYY) 03-01-2017	2. REPORT TYPE Final Report	3. DATES COVERED (From - To) 1-Jun-2015 - 29-Feb-2016
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4. TITLE AND SUBTITLE Final Report: STIR: Novel magnetically responsive and self-repairing particle-lipid-water gels: Exploring nanocapillarity as a tool for making materials with extraordinary properties	5a. CONTRACT NUMBER W911NF-15-1-0115
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER 611102

6. AUTHORS Orlin D Velev	5d. PROJECT NUMBER
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAMES AND ADDRESSES North Carolina State University 2701 Sullivan Drive Admin Srvcs III, Box 7514 Raleigh, NC 27695 -7514	8. PERFORMING ORGANIZATION REPORT NUMBER
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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS (ES) U.S. Army Research Office P.O. Box 12211 Research Triangle Park, NC 27709-2211	10. SPONSOR/MONITOR'S ACRONYM(S) ARO
	11. SPONSOR/MONITOR'S REPORT NUMBER(S) 67015-CH-II.3

12. DISTRIBUTION AVAILABILITY STATEMENT Approved for Public Release; Distribution Unlimited
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13. SUPPLEMENTARY NOTES The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT This exploratory project resulted in the discovery and testing of two responsive materials with extraordinary properties and wide areas of potential technological applications. The first one is a new smart gel system containing ultraflexible chains of magnetically responsive nanoparticles formed in multiphase water-oil systems. Liquid lipid shells condensed on the nanoparticles lead to directed assembly of microfilaments and networks via nanocapillary bridges. These liquid bridges allow for particle rolling and sliding, and the resulting chain flexibility was measured to be orders of magnitude higher than any other linear structures reported to date. The nanoparticles' binding

15. SUBJECT TERMS Responsive materials, magnetic materials, soft matter, smart gels, 3D printing, PDMS, magnetic nanoparticles

16. SECURITY CLASSIFICATION OF:	17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON Orlin Velev
a. REPORT UU	b. ABSTRACT UU	c. THIS PAGE UU	19b. TELEPHONE NUMBER 919-513-4318

Report Title

Final Report: STIR: Novel magnetically responsive and self-repairing particle-lipid-water gels: Exploring nanocapillarity as a tool for making materials with extraordinary properties

ABSTRACT

This exploratory project resulted in the discovery and testing of two responsive materials with extraordinary properties and wide areas of potential technological applications. The first one is a new smart gel system containing ultraflexible chains of magnetically responsive nanoparticles formed in multiphase water-oil systems. Liquid lipid shells condensed on the nanoparticles lead to directed assembly of microfilaments and networks via nanocapillary bridges. These liquid bridges allow for particle rolling and sliding, and the resulting chain flexibility was measured to be orders of magnitude higher than any other linear structures reported to date. The nanoparticles' binding through soft, "snappable" capillary forces provides facile means of creating self-repairing gels and new types of responsive multiphase composites. On the basis of the characterization of these capillary interactions, Velev et al. then introduced a new method for 3D printing with polydimethylsiloxane (PDMS). In their new method PDMS microbeads are bound through formation of capillary bridges to form an ink for three-dimensional printing. The 3D-printed PDMS structures exhibit high elasticities after crosslinking. These self-standing and highly flexible 3D printed PDMS structures can find applications in biomedical scaffolds and devices, novel electronics and soft robotics.

Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
08/27/2016	1 Bhuvnesh Bharti, Anne-Laure Fameau, Michael Rubinstein, Orlin D. Velev. Nanocapillarity-mediated magnetic assembly of nanoparticles into ultraflexible filaments and reconfigurable networks, Nature Materials, (): 1104. doi:
08/27/2016	2 Anne-Laure Fameau, Stephanie Lam, Audrey Arnould, Cédric Gaillard, Orlin D. Velev, Arnaud Saint-Jalmes. Smart Nonaqueous Foams from Lipid-Based Oleogel, Langmuir, (): 13501. doi:
TOTAL:	2

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

<u>Received</u>	<u>Paper</u>
TOTAL:	

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Orlin D. Velev, 90th ACS Colloid & Surface Science Symposium. Cambridge, MA, June 2016. Keynote talk: Dynamically reconfigurable and self-propelling assemblies from engineered microparticles: Principles and emerging applications).

Orlin D. Velev, 251st ACS National Meeting, San Diego, CA, March 2016. Invited talk: Design of new classes of responsive soft matter by embedding nanoparticle structures in Pickering foams and multiphasic gels.

O. D. Velev, B. Bharti and M. Rubinstein, PACIFICHEM 2015, December 2015. Nanocapillary bridging as a new tool for binding of ultraflexible reconfigurable nanoparticle filaments and gel networks).

Orlin D. Velev, MRS National Fall Meeting, Boston, November 2015. Invited talk: Nanocapillary Liquid Bridging: A New Tool for Making Ultraflexible Filaments and Reconfigurable Gel Networks from Nanoparticles.

Orlin D. Velev, Magnetically Stimulated Soft Matter Conference, Athens, GA, May 2015 Invited talk: Magnetic Assembly and Dynamics of Metallo-Dielectric Janus Spheres, Cubes and Nanoparticles: From Colloidal Origami to Motile Microbots.

Orlin D. Velev, Faraday Discussion on Nanoparticle Synthesis and Assembly, Argonne, IL, April, 2015. Magnetophoretic assembly of flexible nanoparticles/lipid microfilaments.

Number of Presentations: 5.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

<u>Received</u>	<u>Paper</u>
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TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

“3D printing with silicone elastomer via capillary bridging of PDMS microbeads into thixotropic gel,” filed July 13, 2016,
~~U.S. Patent Application No. 62/361,729.~~

Patents Awarded

Awards

Orlin D. Velev, Chancellors' Innovation Fund Award, NC State University 2016.

Graduate Students

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Sangchul Roh	1.00	
FTE Equivalent:	1.00	
Total Number:	1	

Names of Post Doctorates

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
FTE Equivalent:	
Total Number:	

Names of Faculty Supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	National Academy Member
Orlin D Velez	0.00	
FTE Equivalent:	0.00	
Total Number:	1	

Names of Under Graduate students supported

<u>NAME</u>	<u>PERCENT SUPPORTED</u>	Discipline
Christopher Guardiola	0.00	Chemical Engineering
FTE Equivalent:	0.00	
Total Number:	1	

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:..... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):..... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:..... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:..... 0.00

Names of Personnel receiving masters degrees

<u>NAME</u>
Total Number:

Names of personnel receiving PHDs

<u>NAME</u>

Total Number:

Names of other research staff

<u>NAME</u>	<u>PERCENT SUPPORTED</u>
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Bhuvnesh Bharti	0.00
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FTE Equivalent:	0.00
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Total Number:	1
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Sub Contractors (DD882)

Inventions (DD882)

5 3D PRINTING WITH SILICONE ELASTOMER VIA CAPILLARY BRIDGING OF PDMS MICROBEADS INTO THIN

Patent Filed in US? (5d-1) Y

Patent Filed in Foreign Countries? (5d-2) N

Was the assignment forwarded to the contracting officer? (5e) N

Foreign Countries of application (5g-2):

5a: ROH, SANGCHUL

5f-1a: North Carolina State University

5f-c: EB1

Raleigh

NC 27695

5a: VELEV, ORLIN D.

5f-1a: North Carolina State University

5f-c: EB1

Raleigh

NC 27695

Scientific Progress

This exploratory project resulted in the discovery and testing of two responsive materials with extraordinary properties and wide areas of potential technological applications.

(1) A new smart gel system containing ultraflexible chains of magnetically responsive nanoparticles formed in multiphase water-oil systems. Liquid lipid shells condensed on the nanoparticles lead to directed assembly of microfilaments and networks via nanocapillary bridges. These liquid bridges allow for particle rolling and sliding, and the resulting chain flexibility was measured to be orders of magnitude higher than any other linear structures reported to date. The nanoparticles' binding through soft, "snappable" capillary forces provides facile means of creating self-repairing gels and new types of responsive multiphase composites. These new developments are reported in the paper in the prestigious journal Nature Nanotechnology, as well as the paper in Langmuir, which are already uploaded as a part of this report.

(2) New compositions for 3D printing with the highly desirable elastomer polydimethylsiloxane (PDMS). On the basis of the characterization of these capillary interactions, our team introduced a new method for 3D printing with PDMS. In this new method PDMS microbeads are bound through formation of capillary bridges to form an ink for three-dimensional printing. The 3D-printed PDMS structures exhibit high elasticities after crosslinking. These self-standing and highly flexible 3D printed PDMS structures can find applications in biomedical scaffolds and devices, novel electronics and soft robotics. We attach as a file in the next section of this report the draft of a manuscript describing these results and achievements, which will be submitted to a high impact peer-reviewed journal.

Technology Transfer

We are presently seeking, together with the NC State University office of Technology Transfer, industrial and government collaborators, users and licensees, who can use the new 3D printing technology for which we filed a provisional patent.

STIR: Novel magnetically responsive and self-repairing particle-lipid-water gels: Exploring nanocapillarity as a tool for making materials with extraordinary properties

Pi: Orlin D. Velev, North Carolina State University

Abstract

This exploratory project resulted in the discovery and testing of two responsive materials with extraordinary properties and wide areas of potential technological applications. The first one is a new smart gel system containing ultraflexible chains of magnetically responsive nanoparticles formed in multiphase water-oil systems. Liquid lipid shells condensed on the nanoparticles lead to directed assembly of microfilaments and networks via nanocapillary bridges. These liquid bridges allow for particle rolling and sliding, and the resulting chain flexibility was measured to be orders of magnitude higher than any other linear structures reported to date. The nanoparticles' binding through soft, "snappable" capillary forces provides facile means of creating self-repairing gels and new types of responsive multiphase composites. On the basis of the characterization of these capillary interactions and the thixotropic gels, Velev et al. then introduced a new method for 3D printing with polydimethylsiloxane (PDMS). Their new method uses 3D printable, capillary suspension inks, based on aqueous suspension of pre-cured PDMS microspheres, which are held together by liquid PDMS capillary bridge, to form a gel-like ink for three-dimensional printing. The 3D-printed PDMS structures exhibit high elasticities after crosslinking. These self-standing and highly flexible 3D printed PDMS structures can find applications in biomedical scaffolds and devices, novel electronics and soft robotics.

Results and discussion

Our preliminary data demonstrate that attractive capillary bridging forces in conjunction with external magnetic field provide a facile tool for assembling flexible filaments, responsive gels and self-repairing networks. The first part of the research on this project led to the development and testing of novel gels that are magnetically responsive and demonstrate basic self-repairing capabilities. During the development of these gels we found that they can also serve as excellent novel materials for 3D printing with a thixotropic paste. These two groups of results are described in the following two sections of the Report.

1. Development of novel “smart” magnetically responsive and self-repairing thixotropic gels based on nanocapillary binding

The first result of this STIR project was a class of new smart gel systems containing ultraflexible chains of magnetically responsive iron oxide nanoparticles formed in multiphase water-oil systems. Liquid lipid shells condensed on the nanoparticles lead to directed assembly of microfilaments and networks via nanocapillary bridges (Figure 1). These liquid bridges allow for particle rolling and sliding, and the resulting chain flexibility allowed making highly reconfigurable structures and materials. The nanoparticles’ binding through soft, “snappable” capillary forces also provides facile means of creating novel networks with unusual magnetic and rheological responses. These nanocapillary-bridged magnetically responsive structures served as new types of matrices of self-repairing gels and responsive multiphase composites.

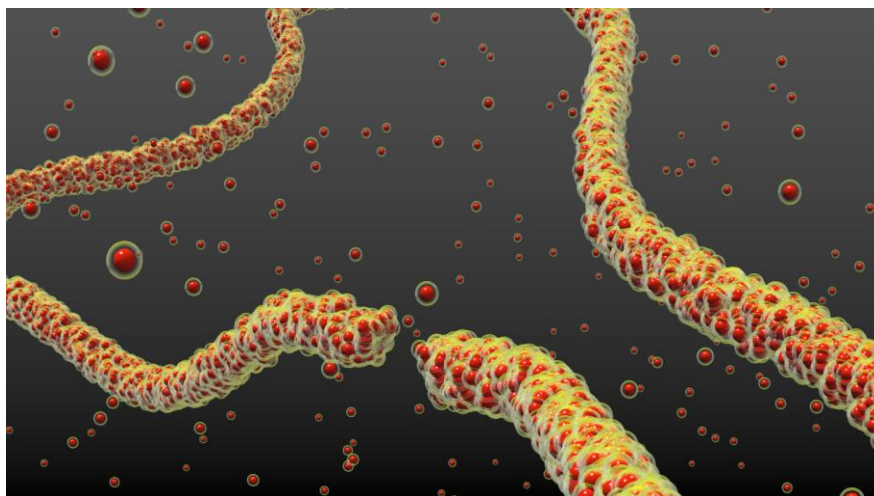


Figure 1. Schematic rendering of the new lipid-bridged magnetic Fe_2O_3 nanoparticles filaments that form the basic system of this project.

The first part of the investigation made possible to harvest the unusual properties of the nanocapillary interactions within new magnetically responsive and self-repairing bulk gels. One of the first goals of this project was to identify a basic 3D gel system that can be used as a test-bed for the role of the capillary forces and the unique features that they can deliver to new responsive soft materials. We showed that the nanocapillary forces can be used to make interconnected and reconfigurable structures upon application of magnetic fields (Figure 2). The nanocapillary bridges can be broken at a well-defined “snap-off” force that depends on the type of the lipid phase used for binding the particles and its interfacial tension with water. However, these links are reversible and can be re-formed when the particles are brought back together by the magnetic field and the

liquid shells merge again (Figure 2). The lipid shells enable the formation of new liquid bridges between the nanoparticles in near contact. These insights were reported in the paper in the prestigious journal *Nature Nanotechnology*,¹ as well as the one in *Langmuir*,² which are uploaded as a separate part of this report.

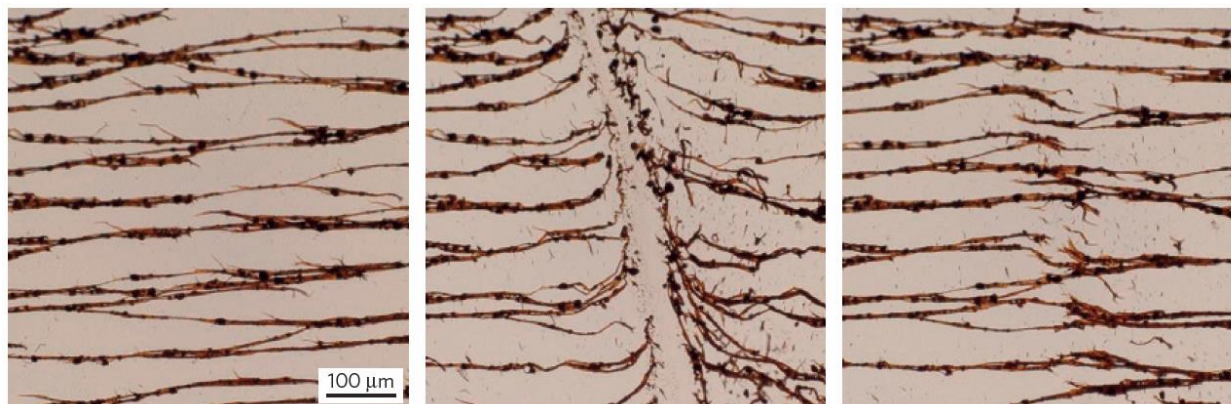


Figure 2. Example of a 2D system of nanocapillary-bound filaments that can form a self-repairing percolated network thanks to their responsiveness to magnetic field: **(left)** Magneto-responsive 2D gel-like percolated network formed by the sticky filaments following an initial burst of magnetic field. **(center)** Mechanically fractured network cut with a sharp stylus. **(right)** After applying a magnetic field of intensity $1,200 \text{ A m}^{-1}$, the filaments are reconnected again owing to their “stickiness”, highlighting the self-repairing properties of this network.

At the next stages of the research we sought to replace the relatively expensive, small volume, and research-oriented, nanoparticles with a simple basic polymeric particulate that could serve as a basis for larger volume gels and soft materials. In order to achieve this, we synthesized hydrophobic microparticles from the most common and widely used elastomer polydimethylsiloxane (PDMS) and formed gel-like materials by binding these particles with small amount of liquids. The procedure for fabrication of PDMS microparticles is described in Figure 3. By embedding the magnetic nanoparticles in PDMS matrix, the magnetic nanoparticle can be fixed in position. More specifically, 0.5 g of Fe_2O_3 (Sigma-Aldrich, USA) nanoparticles were dispersed in 9.5 g of tetrahydrofuran (THF) using a sonicator for 1 hr. While the Fe_2O_3 /THF mixture was sonicated, 9.5 g of PDMS liquid precursor was added in the mixture. The sonicated Fe_2O_3 /THF/PDMS mixture was immediately dried with a rotary evaporator. After removing THF, the mixture was cooled at room temperature. At the next step, 10 g of the mixture was further mixed with 1g of PDMS crosslinker. The mixture was then emulsified with 0.01 M of myristic acid and 0.01 M of ethanolamine aqueous solution using a homogenizer. The emulsified solution was then cured while stirring at 85°C .

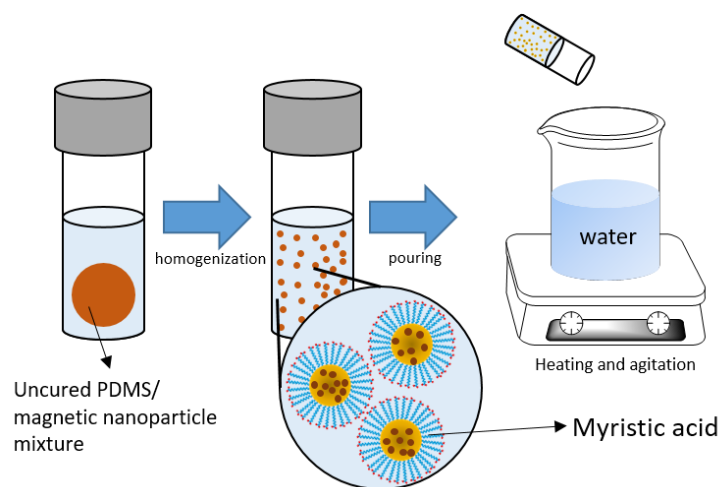


Figure 3. Schematics of the procedure for fabrication of PDMS microparticles that are made to be field-responsive by having embedded magnetic nanoparticles.

The fabricated PDMS microparticles with embedded magnetic nanoparticles are shown in Figure 4. The optical microscope image provides a confirmation that each PDMS microspheres contains brown colored magnetic nanoparticles. When external magnetic field was applied, these particles responded to the field by forming chains along the magnetic field gradient. Moreover, when we brought a magnet near to the vial which contained the particle suspension, the PDMS spheres were dragged and collected close to the magnet forming chains along the magnetic field gradient. The ensemble of collected PDMS microparticles then behaved like a gel in water with a well-defined yield stress. In spite of the high volume fraction, these gels demonstrated remarkable fluidity. By virtue of having only 5% of magnetic nanoparticles into the PDMS microparticle cores, these gel-like materials could be easily manipulated with a magnet, where they rearrange in response to the magnetophoretic force extending in the direction of the field gradient (Figure 4).

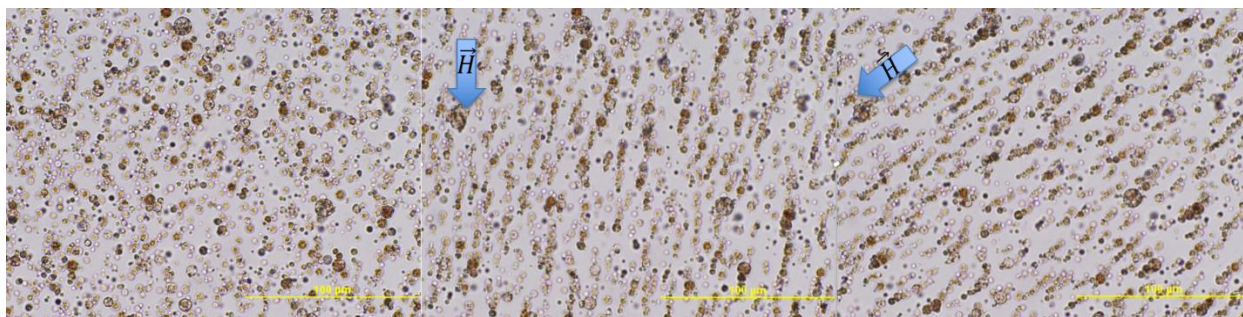


Figure 4. Optical microscopic images of PDMS microspheres containing in their elastomer bulk 5 wt.% of magnetic nanoparticles. When magnetic field is applied, the PDMS microparticles respond to the external magnetic field by forming chains as shown in the middle and right frames.

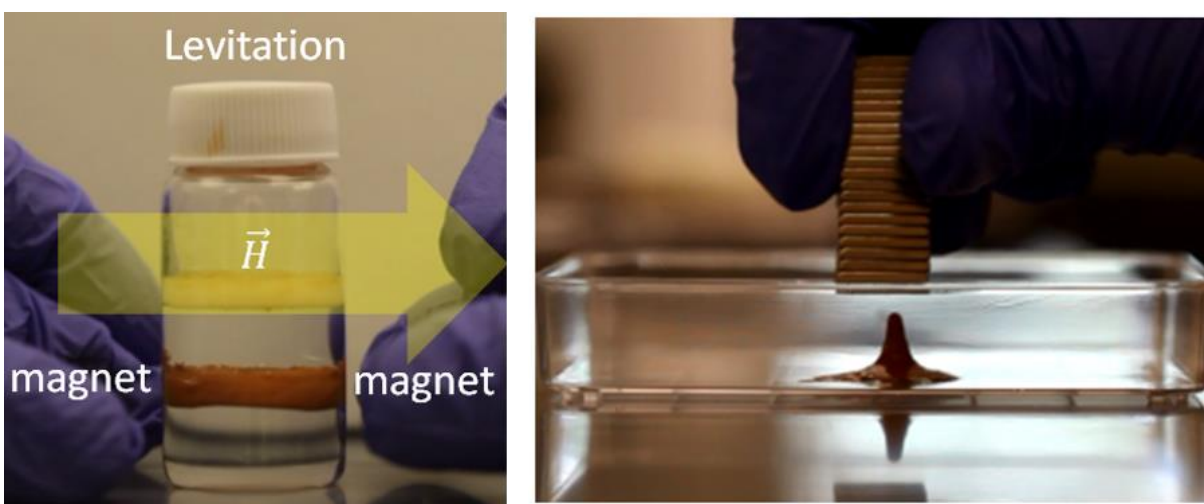


Figure 5. Magnetic responsive capability of PDMS beads bound into nanocapillary gels. The gel exhibit levitation with parallel magnetic field (left) and can be stretched with external magnetic field (right).

The most unusual and potentially useful feature of these gels is their magnetic responsiveness. Figure 5 illustrates the magnetic reconfiguration and pliability of these gels under water and as a separate phase. The gel can be easily shaped along the bulk of the vessel with parallel magnetic field. The soft material could also be taken out from the water and placed on a Petri dish. As a magnet approaches from above, the gel deformed its shape by stretching toward magnet. In other words, these gels had such a low yield stress that they could be deformed with moderately strong external magnetic field. The fluidity of the gel enables not only their re-shaping, but also self-repairing properties.

We proved the ability of these gels to re-form and reconstitute their continuous matrix under the action of a magnetic field. This is illustrated in the experiment shown in Figure 6. The gel in the left-hand image has been originally assembled by magnetic field on the bottom of the sample vial. We then break it by intense stirring and shaking into millimeter-size pieces freely floating around the excess amount of water in the vial. However, when the dispersed

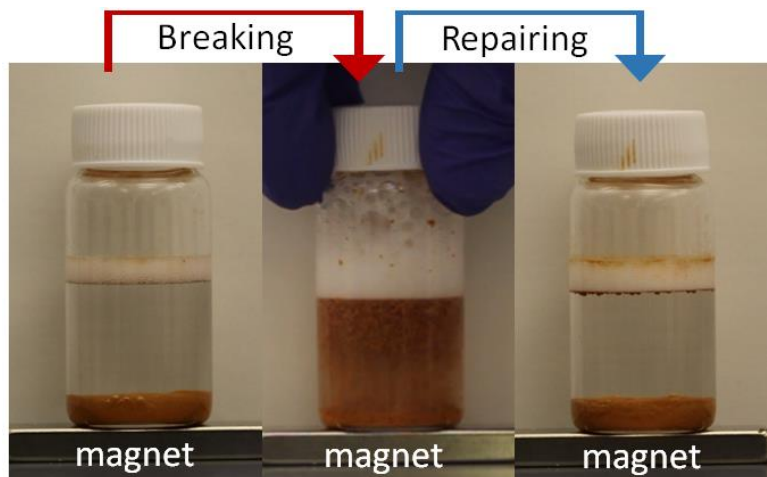


Figure 6. Example of magnetically responsive particle-lipid-water gel. The gel-like phase responds to magnetic field even though it has a very high volume fraction of PDMS particles. The dispersed gel re-forms when a magnet is re-introduced from the bottom of the vessel.

pieces of gel are brought back together by a combination of gravity sedimentation and magnetic gradient towards the vessel bottom, we obtain a re-formed single gel phase with a characteristic cohesiveness and yield stress. The process can be repeated multiple times and demonstrates features that are not common with the present molecularly assembled lipid and biomolecular gels.

These newly developed gel compositions could also be very suitable for 3D printing as PDMS is a highly desirable common elastomer. In the new 3D printing method that we report in the next section, our PDMS microbeads are bound through formation of capillary bridges to form a thixotropic gel-like ink for three-dimensional printing. By harvesting of the unusual capabilities of the capillary interactions, our group introduced a new powerful method for 3D printing with PDMS.

2. Three-dimensional printing via capillary bridging of PDMS microbeads into thixotropic gel

Introduction

Three-dimensional (3D) printing is a revolutionary technique for rapid prototyping and engineering of complex architectures at micro and macroscale. It can be used to create very complex 3D structures at micro and macroscale with desirable local topographical features.²⁻⁹ Depending on the application, various “inks” have been used, based on ceramics, plastics and even

metals. In the case of polymer inks the choice is often limited to thermoplastics as the “polymer” should solidify fast after the extrusion so that the printing process can proceed, which is not the case with the conventional curable polymer melts, which require much longer curing times. One such “conventional” material is Polydimethylsiloxane (PDMS), which is widely used in manufacturing of electronics and biomedical devices, but unless special curing agents are used, it is a challenge to 3D print with it. We have overcome this limitation by developing novel 3D printable, capillary suspension inks, based on aqueous suspension of pre-cured PDMS microspheres, which are held together by liquid PDMS capillary bridges, thus turning the suspension into 3D printable, shape retaining paste, that can be further strengthened by post curing at an elevated temperature, after the printing process is complete, thus creating self-standing, stretchable 3D meta structures.

The present-day 3D printing inks are mostly limited to thermoplastics, which allow hot melt nozzle extrusion, followed by rapid cooling and solidification at desired, pre-determined shape, which in turn allows fast 3D printing. Elastomeric polymers are normally liquid at ambient conditions and can be solidified upon curing or heating. This makes them more difficult to use in 3D printing. PDMS is one of the most widely used elastomeric polymers, with wide range of applications in the area of advanced materials for biomedical and soft robotics applications¹⁰⁻¹⁴, but is challenging to 3D print with unless special or fast curing agents are used, which respond to other stimulus than temperature^{6,15,16}. These however can be quite expensive, often not available commercially and might not be compatible with all of the applications. Finding a way to circumvent this limitation by using conventional PDMS, could significantly expand its 3D printing applications. Indeed, direct 3D printing of nonflowable PDMS precursor was used to fabricate synthetic spider web and microfluidic channels.^{12,14} In another study, wax microparticles were incorporated to impart PDMS precursors with gel-like property to have stable structures after extrusion.¹⁷ More recently, PDMS liquid precursors were injected into hydrophilic thixotropic gel, “Carbopol gel,” via 3D printing.¹⁸

Our capillary method of binding particles has materials analogies in sandcastles formed by mixing sand with right amount of water. The structural stability of sandcastles is attributed to the formation of capillary bridges upon direct surface contact of the wetted sand particles.¹⁹⁻²⁶ Similar capillary bridges are found in concentrated multiphase suspensions, containing small amount of immiscible liquid with $< 90^\circ$ contact angle on solid particles.²⁷⁻²⁹ The interparticle capillary bridge forces, confine the adjacent particles movements, thus leading to formation of 3D particle networks, with paste like consistency, that have significant elasticity and static yield stress.^{28,29} At low stresses, such pastes behave as elastic, shape retaining solid and as visco-elastic flowable liquids at high stresses, which makes them suitable candidates for 3D printing inks. Indeed, recently,

Chopin et al. showed several 3D structures such as sphere and filament by ejecting glass microparticles in water suspensions.³⁰ In their report, the deposited glass bead suspensions retained stable 3D structure by means of capillary bridges between the glass beads. The capillary bridges were formed after extruded through a nozzle by absorbing water instantaneously through a super-absorbing surface. An obvious disadvantage is that such 3D printed structures are soft and fragile, unless they are post cured or sintered, which will make them more rigid and brittle. Also, multiple materials must be used as solid suspension phase and wetting and continuous fluids, which complicates the process as for some applications they might need to be removed. This begs the question if we can create capillary suspension inks, that use elastomeric material as suspension phase and curing precursor as wetting fluid phase and water as continuous phase, which could be cured by temperature, thus allowing solidification and water removal in one step?

We developed a new class of PDMS based inks, containing pre-cured PDMS microparticle suspension in water, linked together by capillary bridges from liquid PDMS precursor. The capillary structure, turns the ink into flowable paste, with strong shape retention properties (due to the large yield stress of the material), thus allowing them to be extruded through nozzle and thus 3D printed as soft, self-standing and shape retaining 3D structures, with controllable micro porosity. The mechanical properties of the final 3D structures are set by final curing of the liquid capillary bridges and removing continuous water phase, thus allowing us to separate the printing and curing steps in time. To best of our knowledge no such capillary interaction based printable inks with cross-linkable binder have been reported.

Methods

Synthesis of PDMS microbeads: The synthesis of PDMS microbeads is based on two steps: 1) emulsification of PDMS precursors (Sylgard 184, Dow Corning) and 2) crosslinking of the polymer in the droplets. 10:1 mixtures of PDMS precursors and curing agents were mixed and degassed in a desiccator under vacuum. The PDMS precursors were pre-emulsified in a 50 ml centrifuge tube containing 30 ml of 14 wt.% polyvinyl alcohol aqueous solution using a vortex. The pre-emulsified PDMS emulsions were then emulsified finely with a mechanical mixer whose rotation rate is controllable digitally from 150 rpm to 6,000 rpm for 30 mins. After emulsification, the PDMS emulsions were poured and stirred in DI water at 85 °C for 2 hrs. The crosslinked PDMS microbeads were then rinsed 10 times with 50 ml of Tween 20 (0.1 wt.%) aqueous solution.

Preparation of PDMS microbeads suspension/precursor mixtures: Desired amount of 10:1 mixture of PDMS precursors and curing agents were then added into PDMS suspension and mixed using Vortex and the mechanical mixer. PDMS suspensions were blended with desired amount of

PDMS precursor. The mixtures were then loaded in syringes (50 ml) and they were extruded through a nozzle. Extruded PDMS mixtures were cured at an oven at 85 °C.

Characterization of PDMS suspensions: For the rheological analysis of PDMS suspensions, a 25 mm plate-plate geometry was used for both dynamic shear measurements with 1.0 mm gap size (AR 2000, TA instrument). Every measurement was performed after oscillatory pre-shearing at 1 rad/s for 10 mins with a strain of 0.5 and equilibrium for 10 mins and 1.0 Hz for reproducible data. The tensile testing of the cured (at 85°C for 2hrs) PDMS suspensions were conducted after molding the suspensions into dog bone shape (ASTM D412). The crosshead speed of the testing was 5.0 mm/min (5943 Instron). Fluorescent microscopy and Field Emission Scanning Electron Microscopy (Verios 460L FE-SEM, FEI) were used to visualize and analyze the morphology of the deposited PDMS structures. Here the PDMS particles were tagged in red color with Nile red dye, and the capillary bridges were colored in yellow by addition of Coumarin 6 dye (Scale bar = 20 µm). After each color component was mapped by Fluorescence microscope, two color channels were merged through ImageJ.

Results

The conceptual schematic for overall procedure for fabricating PDMS inks is described in Fig. 7. First, PDMS microbeads (hereinafter MBs) suspension is prepared by emulsification and thermal curing. We used polysorbate 20 for dispersion stabilizer. The suspension is then mixed with the PDMS liquid precursor (hereinafter LP) via a mechanical mixer allowing the surface wetting of MBs with uncured LP. A direct surface contact between the wetted MBs leads to the formation of LP capillary bridges between cured PDMS MBs (Figure 7). The formation of capillary bridges results into the transformation of the free-flowing PDMS suspension into viscoelastic paste. The paste is extrudable through an orifice and printed into a desired 3D structures. The printed structure was further heat-cured at 85°C to selectively crosslink PDMS capillary bridges between the PDMS MBs and removing of the continuous water phase, resulting into semi-flexible reconfigurable 3D architectures.

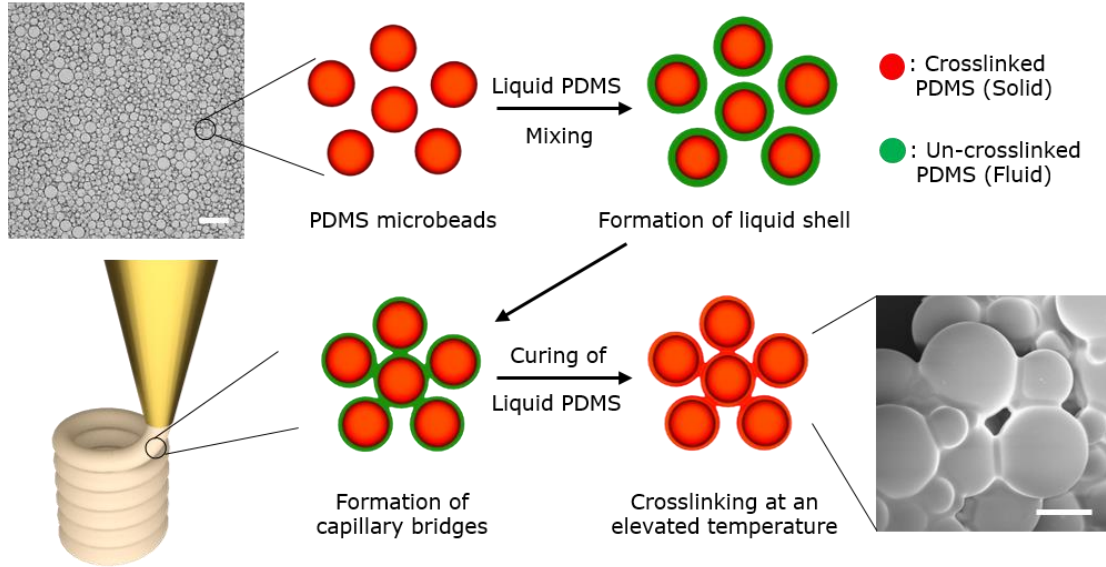


Figure 7. Schematic of 3D printing process of PDMS particle suspensions with capillary bridges. PDMS microbeads suspension in water are mixed with liquid-PDMS precursor. The suspensions turned into gel as liquid-PDMS precursor formed capillary bridges among adjacent PDMS microbeads. The gel-like PDMS suspension is extruded into 3D shape via a nozzle. The 3D printed PDMS structure is heat-cured at 85°C to solidify capillary bridges to enhance shape stability of the structure. The scale bars are top: 100 μm and bottom: 20 μm , respectively.

The mechanical stability of the printed structure is strongly correlated with the viscoelastic property of the uncured PDMS ink. We evaluated the viscoelastic properties of the inks using dynamic oscillatory measurements.³¹ Addition of a small amount of LP into prepared PDMS MB suspensions resulted large change in the rheological characteristics of the suspension. The dynamic elastic modulus (G') versus frequency (ω) of PDMS microbead suspensions (50% v/v) with and without 2 vol.% of LP are shown in Fig. 8a. Both suspensions, with and without the addition of LP exhibited frequency independent elastic modulus. The suspension with 2 vol.% of LP had three order of magnitude higher storage modulus and forms the stronger visco-elastic paste (Fig. 8b), in line with previously established in the literature^{29,32}. Therefore, the increase in the G' upon the addition of LP to PDMS microbead suspension can be attributed to the formation of capillary bridges,^{27,29} which has been confirmed by using fluorescence microscopy (Fig. 8c), where the PDMS microbeads are tagged with Nile red, and the capillary bridges contain Coumarin 6 (yellow dye).

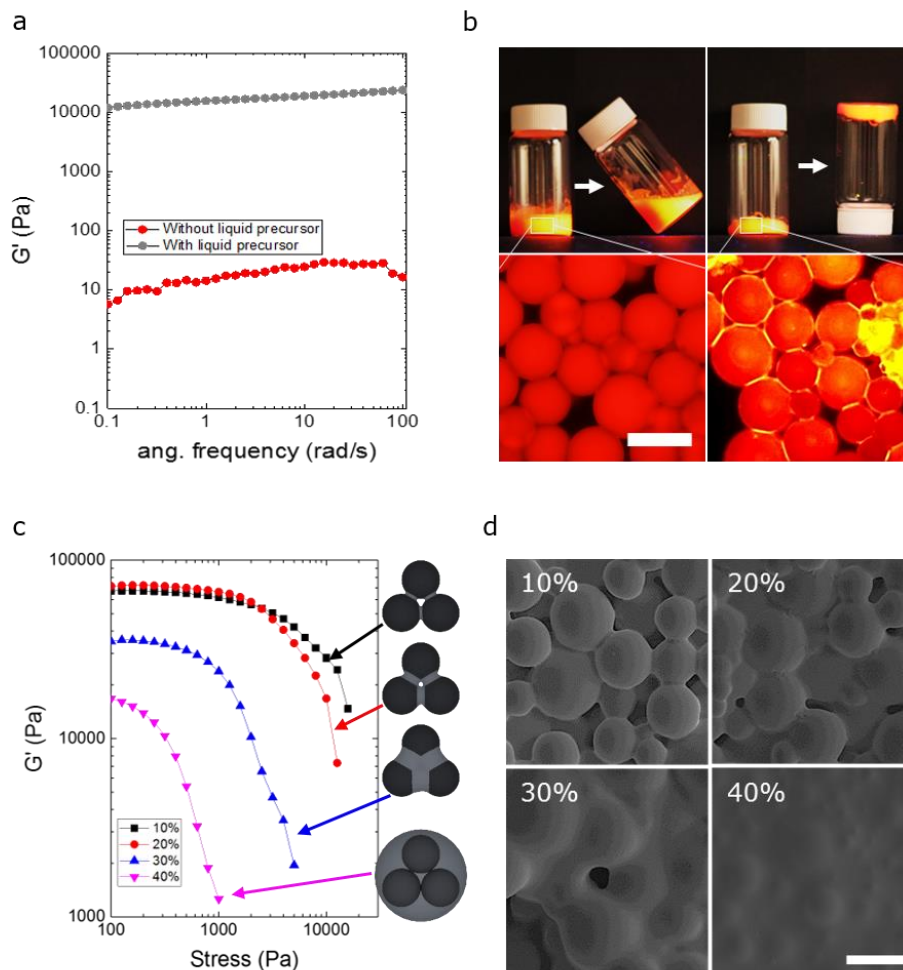


Figure 8. Characterization of capillary bridged PDMS microbead suspension. **a**, Change in the storage modulus with the frequency of PDMS MB in water suspensions (50% v/v) with/without 2 vol.% of additional liquid PDMS precursor. **b**, Photographs of PDMS suspension without (left) and with (right) 2 vol.% of PDMS precursor. The suspension with 2 vol.% of PDMS liquid precursor does not flow when it is tilted or flipped showing a gel-like behavior. Fluorescence micrograph showing the structure of PDMS microbeads without (left) and with (right) additional PDMS precursor. The PDMS precursor (yellow) forms capillary bridges between the particles (red). **c**, The elastic modulus of PDMS suspension mixed with various amount of PDMS LPs plotted against the oscillation stress. From the plot, the yield strength of the mixture can be estimated by reading the point where the elastic modulus decrease abruptly. At 10-20 vol.% of PDMS liquid precursor, both storage modulus and yield stress remained similar. Above 20 vol. %, the storage modulus and yield stress decreases as the amount of PDMS liquid precursor increases. **d**, Scanning electron micrograph of the suspensions with increasing amount of PDMS liquid precursor. As the amount of surface wetting PDMS precursor increases (> 20 vol.%), the capillary bridges vanish, and the microparticles are engulfed in the matrix of liquid PDMS.

The rheological characteristics of PDMS suspension pastes was further measured with incremental addition of PDMS LP (0-40 vol.% with respect to the vol. of PDMS microbeads). The G' versus the oscillatory shear stress of the suspensions were measured as is depicted in Fig. 8c.

All compositions of MB suspensions showed gel-like behavior at low shear stress and yielding at high shear stresses. The MB suspensions containing up to 20% of PDMS LP showed both high yield stress and storage modulus (G'). However, yield stresses and storage moduli decrease as the amount of PDMS LP increased > 20 vol.% resulting weaker gels. This can be attributed to the morphological change of the PDMS suspension.^{33–35} Up to 20 vol.% of PDMS LP, capillary bridges of PDMS liquid were clearly observed in the electron micrographs (Fig. 8d). Meanwhile, as the concentration of PDMS LP increases, almost all pores between particles were filled and capillary bridges were diminished as shown in Fig. 8d. Nevertheless, 30 vol.% of PDMS LP in PDMS suspension still has high yield stress behaving like a gel. This could be attributed to the curvatures of the LP between the MBs on the surface of ink which is able to induce negative capillary pressure.^{36,37} When the added PDMS LP exceeded 40%, the suspension behaved like a weak gel with a low yield stress and low elastic modulus. In summary, capillary pressures are likely to operate in our PDMS suspension gel system at 2–30 vol.% resulting in mechanically stable gels that are suitable for 3D printing inks.

The PDMS suspension pastes with 10 – 30% PDMS additional LP were utilized as 3D “inks”. For example, when they were ejected through the nozzle (Inner diameter $\approx 410 \mu\text{m}$, Fig. 9), the extruded microwires were stable and composed of very small number of PDMS microbeads along the radial direction, indicating the presence of strong capillary attraction between the individual particles.³⁸

Afterwards, the PDMS suspension pastes (in form of microwires) were thermally cured and became elastic rubbery materials. The LP PDMS capillary bridges were crosslinking by curing the microwires at 85°C for 2 hrs. The chemical crosslinking of PDMS bridges resulting into permanent binding of PDMS microbeads and immobilization of the extruded structure. This thermal curing reduced the thixotropic response of the suspension but newly induce more obvious elasticity like rubbery polymers. The tensile testing was performed with cured PDMS suspensions after molding them into dog-bone shapes. Fig. 9c illustrates the tensile stress versus strain curves of the specimen. Notably, the PDMS specimens mixed with less than 10% of PDMS LP were fragile. Meanwhile, the PDMS specimen with more than 10% of PDMS binders had elasticities even with a strain above 50%. As higher amounts of PDMS LPs were added, the tensile modulus and maximum elongation at break also increased. Increase in the tensile modulus of cured PDMS suspension with the increasing amount of PDMS binder can be correlated with the rheological properties of uncured PDMS suspensions (Fig. 9c). While mechanical strength of the ‘uncured’ PDMS suspension increased with the capillary bridging forces, it also makes more porous morphology, which is detrimental for the tensile modulus of a materials.³⁹

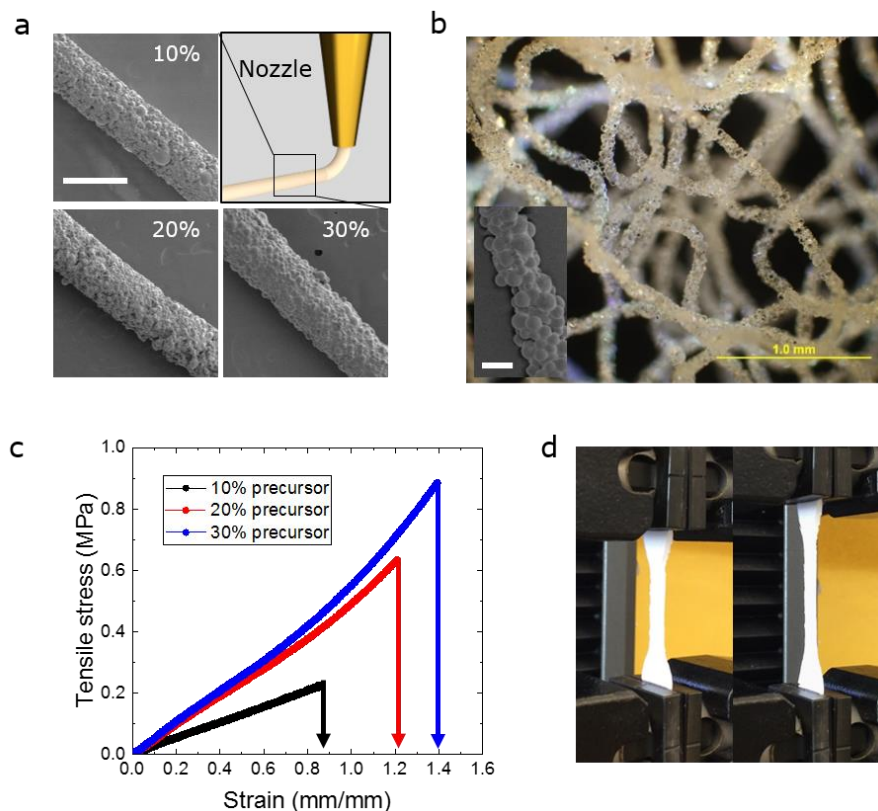


Figure 9. Mechanical properties of cured PDMS capillary gel. **a**, SEM of ejected PDMS suspensions with the various LP amounts. **b**, Optical and scanning electron microscope images of freely ejected PDMS ink. The wires preserve their shape even after ejection and crosslinking at 85 °C, **b**, The extensional tensile stress vs. strain at increasing amount of PDMS LP precursor. As the amount of the additional precursor decreases, the slope (Young’s modulus) and maximum strain at break decreases. **c**, A photograph of extension of dog bone shaped PDMS with 10% of liquid precursor.

To illustrate the applicability of these novel, capillary suspension based PDMS inks, we deposited them using controlled air pressure pump on a computer-controlled translational X-Y-Z stage (retrofitted from a CNC machine), which resulted in various three dimensional structures via a process known as direct-writing which is a syringe/needle-based microdeposition 3D printing method used quite commonly in fields of bio-printing that use similar viscoelastic inks. In our setup we printed a multi-layered spiral structure consisting of PDMS inks with 25% of PDMS LP (Fig. 10a). This structure retained its as-printed shape. As another illustration of the 3D stability, a tetrahedral PDMS composed of six vertices with a nozzle with diameter of 500 μm could be printed on a substrate (Fig. 10b). The maximum height (h_{crit}) of stable self-standing structures is linearly correlated with elastic modulus of structure.²¹ Thanks to high elastic modulus and static yield stress of capillary ink, those printed structures show significant shape retention property, which in turn facilitates fast 3D printing of consecutive layers.

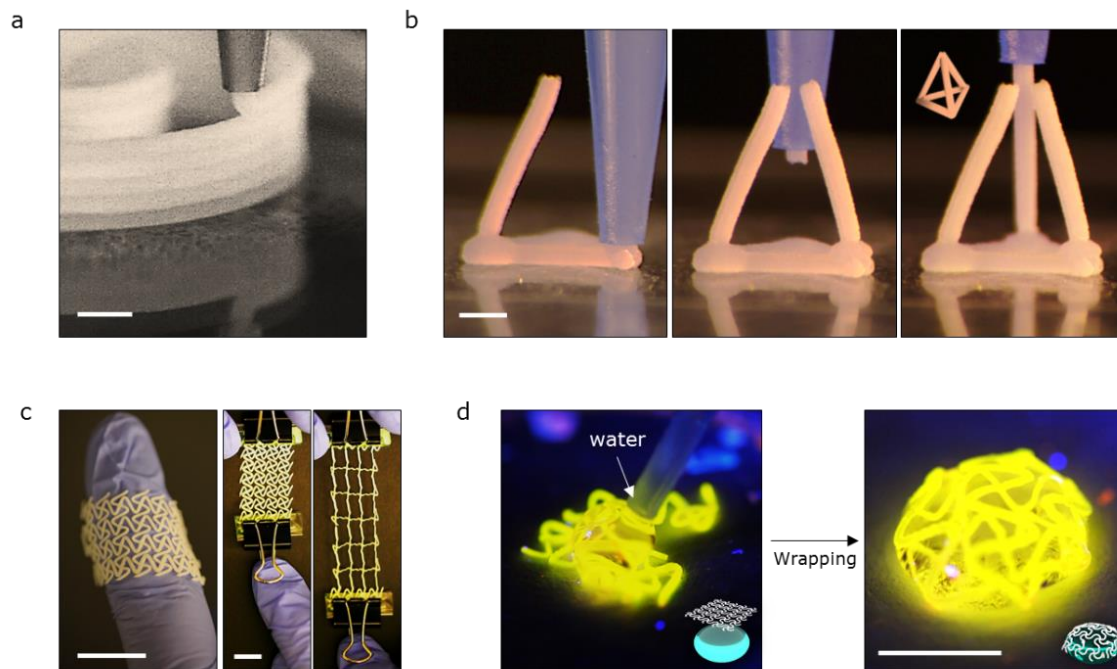


Figure 10. Examples of 3D printed PDMS structures using capillary-bridged particle suspensions. a, Printing of multi-layered spiral structure (scale bar, 1.0mm). **b,** A photograph of printing of tetrahedral structure of PDMS (scale bar, 1.0mm). The ejected structure shows self-standing property. **c,** Printed ‘elastin-like structure’ (scale bar, 5.0mm). The structure has high elasticity. **d,** Water encapsulation of PDMS elastin structure (scale bar, 5.0mm). Dominated by the surface force between PDMS and water, the elastin-like structure is deformed wrapping up the droplet on superhydrophobic surface.

As father example that illustrates the unique property of our novel 3D printed PDMS structures, we have created designed 3D printed metamaterial structure,^{16,40} where demonstrate that we can modify macroscopic material elasticity using structure design. Fig. 10c shows an example of a macroscopic elastin-like structure printed and cured with the PDMS inks. The PDMS elastin-like structure exhibits being adopted to various types of surfaces by changing its shape due to its ultra-flexibility at various length scales. Depending on the applied macroscopic stress, different topological features expand defiantly thus allowing creation of novel metamaterials with pre-programmed, non-linear response and shape memory properties (refs). Furthermore, when the these 3D printed PDMS elastin-like meta-structure are exposed to water droplet, they can wrap around surface of the droplet by changing their structure into something what people use to call ‘Capillary origami’^{41,43} as shown in Fig. 10d. This is an example of electrocapillarity interplay, occurring when the surface capillary forces are comparable to the bulk elasticity of the 3D printed structures. Given the fact that the later can be pre-programmed by the hemistichal 3D printed topological

structure as well by the property of the “ink” (i.e. elastomer concentration and property, capillary suspension volume fraction, particle size, etc.), this offers an unprecedented capability of designing new metamaterials.

Conclusions

We have introduced a new type of 3D printable ink purely consisting of PDMS granules and uncrosslinked PDMS as a secondary fluid for gelation. Triggered by capillarity among PDMS microbeads, the suspension behaved like a paste showing Bingham plastic property with a certain range of the amount of PDMS liquid precursor with high storage moduli and yield stresses. The PDMS suspension paste was directly extruded with air pressure and shaped with 3D printer. The extruded PDMS inks have porosities between their microbeads. Due to its mechanical stability, a multi-layered spiral and free-standing filament structures could be printed. The liquid PDMS bridges were further crosslinked after printing. The crosslinked PDMS exhibited elasticity without brittleness. This process can find applications in extrusion-type 3D printing, as well as other additive manufacturing processes for biological, medical, and consumer products. These self-standing and highly flexible 3D printed PDMS structures can find applications in biomedical scaffolds and devices, novel electronics and soft robotics. The results described in this report will form the basis of a manuscript, which will be submitted to a high impact peer-reviewed journal.

References cited

1. B. Bharti, A.-L. Fameau, M. Rubinstein and O. D. Velev. Nanocapillarity-mediated magnetic assembly of nanoparticles into ultraflexible filaments and reconfigurable networks. *Nature Mater.*, **14**, 1104–1109 (2015).
2. A.-L. Fameau, S. Lam, A. Arnould, C. Gaillard, O. D. Velev and A. Saint-Jalmes. Smart Nonaqueous Foams from Lipid-Based Oleogel. *Langmuir* **31**, 13501–13510 (2015).
3. Ladd, C., So, J.-H., Muth, J. & Dickey, M. D. 3D printing of free standing liquid metal microstructures. *Adv. Mater.* **25**, 5081–5 (2013).
4. Lewis, J. A. & Gratson, G. M. Direct writing in three dimensions. *Mater. Today* **7**, 32–39 (2004).
5. Lewis, J. A. Direct ink writing of 3D functional materials. *Adv. Funct. Mater.* **16**, 2193–2204 (2006).
6. Tumbleston, J. R. *et al.* Continuous liquid interface production of 3D objects. *Science*. **347**, 1349–1352 (2015).
7. Hong, S. *et al.* 3D Printing of Highly Stretchable and Tough Hydrogels into Complex, Cellularized Structures. *Adv. Mater.* **27**, 4035–4040 (2015).
8. Highley, C. B., Rodell, C. B. & Burdick, J. A. Direct 3D Printing of Shear-Thinning Hydrogels into Self-Healing Hydrogels. *Adv. Mater.* **27**, 5075–5079 (2015).
9. Parekh, D. P. *et al.* 3D printing of liquid metals as fugitive inks for fabrication of 3D microfluidic channels. *Lab Chip* **16**, 1812–1820 (2016).
10. Kokkinis, D., Schaffner, M. & Studart, A. R. Multimaterial magnetically assisted 3D printing of composite materials. *Nat. Commun.* **6**, 8643 (2015).
11. Wehner, M. *et al.* Entirely Soft, Autonomous Robots. *Nature* **536**, 451–455 (2016).
12. Qin, Z., Compton, B. G., Lewis, J. A. & Buehler, M. J. Structural optimization of 3D-printed synthetic spider webs for high strength. *Nat. Commun.* **6**, 8038 (2015).
13. Shan, S. *et al.* Multistable Architected Materials for Trapping Elastic Strain Energy. *Adv. Mater.* **27**, 4296–4301 (2015).
14. Kolesky, D. B. *et al.* 3D bioprinting of vascularized, heterogeneous cell-laden tissue constructs. *Adv. Mater.* **26**, 3124–3130 (2014).
15. Gratson, G. M., Xu, M. & Lewis, J. A. Direct writing of three-dimensional webs. *Nature* **428**, 386 (2004).
16. Clausen, A., Wang, F., Jensen, J. S., Sigmund, O. & Lewis, J. A. Topology Optimized Architectures with Programmable Poisson’s Ratio over Large Deformations. *Adv. Mater.* **27**, 5523–5527 (2015).
17. Lipton, J. I., Angle, S. & Lipson, H. 3D Printable Wax-Silicone Actuators. *2014 Annu. Int. Solid Free. Fabr. Symp. Austin, TX* 848–856 (2014).
18. Hinton, T. J., Hudson, A., Pusch, K., Lee, A. & Feinberg, A. W. 3D Printing PDMS Elastomer in a Hydrophilic Support Bath via Freeform Reversible Embedding. *ACS Biomater. Sci. Eng.* **2**, 1781–1786 (2016).
19. Scheel, M. *et al.* Morphological clues to wet granular pile stability. *Nat. Mater.* **7**, 189–193 (2008).
20. Kudrolli, A. Granular matter: sticky sand. *Nat. Mater.* **7**, 174–175 (2008).

21. Pakpour, M., Habibi, M., Møller, P. & Bonn, D. How to construct the perfect sandcastle. *Sci. Rep.* **2**, 2–4 (2012).
22. B. Bharti, D. Rutkowski, K. Han, A. Kumar, C. H. Hall and O. D. Velev. Capillary Bridging as a Tool for Assembling Discrete Clusters of Patchy Particles. *J. Am. Chem. Soc.*, **138**, 14948–14953 (2016).
23. Kralchevsky, P. A. & Nagayama, K. Capillary interactions between particles bound to interfaces, liquid films and biomembranes. *Adv. Colloid Interface Sci.* **85**, 145–192 (2000).
24. Bharti, B., Fameau, A.-L. & Velev, O. D. Magnetophoretic assembly of flexible nanoparticles/lipid microfilaments. *Faraday Discuss.* **181**, 437–448 (2015).
25. Bharti, B. *et al.* Capillary Bridging as a Tool for Assembling Discrete Clusters of Patchy Particles. *J. Am. Chem. Soc.* jacs.6b08017 (2016).
26. Velev, O. D., Denkov, N. D., Paunov, V. N., Kralchevsky, P. a & Nagayama, K. Direct Measurement of Lateral Capillary Forces. *Langmuir* **9**, 3702–3709 (1993).
27. Van Kao, S., Nielsen, L. E. & Hill, C. T. Rheology of concentrated suspensions. II. Suspensions agglomerated by an immiscible second liquid. *J. Colloid Interface Sci.* **53**, 367–373 (1975).
28. Butt, H.-J. Controlling the flow of of Suspensions. *Science.* 868–869 (2011).
29. Koos, E. & Willenbacher, N. Capillary forces in suspension rheology. *Science* **331**, 897–900 (2011).
30. Chopin, J. & Kudrolli, A. Pearling and arching instabilities of a granular suspension on a super-absorbing surface. *Soft Matter* **11**, 659–64 (2015).
31. Li, Q. & Lewis, J. A. Nanoparticle Inks for Directed Assembly of Three-Dimensional Periodic Structures. *Adv. Mater.* **15**, 1639–1643 (2003).
32. Israelachvili, J. N. *Intermolecular and surface forces.* (Elsevier Inc., 2011).
33. Iveson, S. M., Litster, J. D., Hapgood, K. & Ennis, B. J. Nucleation, growth and breakage phenomena in agitated wet granulation processes: A review. *Powder Technol.* **117**, 3–39 (2001).
34. Iveson, S. M. & Litster, J. D. Fundamental studies of granule consolidation. Part 2: Quantifying the effects of particle and binder properties. *Powder Technol.* **99**, 243–250 (1998).
35. Iveson, S. M. & Litster, J. D. Liquid-bound granule impact deformation and coefficient of restitution. *Powder Technol.* **99**, 234–242 (1998).
36. Newitt, D. M. & Conway-Jones, J. M. A contribution to the theory and practice of granulation. *Trans. Inst. Chem. Eng.* **36**, 422–441 (1958).
37. Mitarai, N. & Nori, F. Wet granular materials. *Adv. Phys.* **55**, 1–45 (2006).
38. Conrad, J. C. *et al.* Designing colloidal suspensions for directed materials assembly. *Curr. Opin. Colloid Interface Sci.* **16**, 71–79 (2011).
39. Wang, J. Young’s modulus of porous materials. *J. Mater. Sci.* **19**, 801–808 (1984).
40. Jang, K.-I. *et al.* Soft network composite materials with deterministic and bio-inspired designs. *Nat. Commun.* **6**, 6566 (2015).
41. Py, C. *et al.* Capillary origami: Spontaneous wrapping of a droplet with an elastic sheet. *Phys. Rev. Lett.* **98**, 2–5 (2007).
42. Paulsen, J. D. *et al.* Optimal wrapping of liquid droplets with ultrathin sheets. *Nat. Mater.* **14**, 1206–1210 (2015).