

Material Assembly from Collective Action of Shape-Changing Polymers

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Abstract

Some animals form transient, responsive, and solid-like ensembles through dynamic structural interactions. These ensembles demonstrate emergent responses such as spontaneous self-assembly, which are difficult to achieve in synthetic soft matter. Here we use shape morphing units comprised of responsive polymers to create solids that self-assemble, modulate volume, and disassemble on demand. The ensemble is composed of responsive hydrogel, liquid crystal elastomer (LCE), or semicrystalline polymer ribbons that reversibly bend or twist. Dispersions of these ribbons mechanically interlock inducing reversible aggregation. Aggregated LCE ribbons have a 12-fold increase in yield stress as compared to the cooled dispersion and contract by 34% on heating. Ribbon type, concentration, and shape dictate aggregation and govern the global mechanical properties of the solid that forms. Coating LCE ribbons with liquid metal begets photo-responsive and electrically conductive aggregates, while seeding cells on hydrogel ribbons enables self-assembling 3D scaffolds, providing a versatile platform for design of dynamic materials.

Main Text

Materials capable of autonomous assembly, reconfiguration, and disassembly in response to changes in environmental conditions may enable new functionality in robotics^{1,2}, medicine³, and other engineering disciplines⁴⁻⁷. Inspiration for these materials can be found in animals that form transient structures through collective action to perform tasks not achievable by individual agents. Fire ants (*Solenopsis Invicta*)⁸, honeybees (*Apis Mellifera*)⁹, and California blackworms (*Lumbriculus Variegatus*)¹⁰ all mechanically interlock into entangled swarms to accomplish various collective functions such as raft formation¹¹, colony unification¹², and thermal regulation¹³. In doing so, these animals form porous structures with viscoelastic mechanical properties¹⁴ that exhibit adaptive self-assembly and reorganization due to each member's ability to physically attach and detach to its neighbors^{12,15-17}.

The key characteristics of these living aggregates, such as autonomous aggregation, solid-like viscoelasticity, internal motion, adaptability, and reversible disassembly, are highly sought after in engineering materials⁵. Like their biological counterparts, synthetic aggregates can form free-standing structures with tunable mechanical properties^{18–21}. For example, injectable hydrogel microspheres^{22,23} that crosslink after injection form porous macroscopic solids; however, chemical crosslinking between units restricts disassembly. Colloidal systems, such as Janus particles²⁴ and microbubbles²⁵, demonstrate reversible transitions from dispersed to clustered states under the influence of various stimuli^{26–28}. These colloids generally exhibit negligible cohesive strength. Improved cohesion is, however, achievable via mechanical entanglement. Entangled hydrogel microstrands²⁹ can form structures with sufficient cohesion to remain solid-like after molding or 3D printing. However, these aggregates are inactive and thus incapable of autonomous assembly, internal reconfiguration, adaptive response, and disassembly.

We describe a general approach to creating transient, responsive solids by exploiting the shape change of stimuli-responsive polymers^{30–32}. Specifically, we employ hydrogel, elastomer, and semicrystalline ribbons that undergo reversible, thermo-responsive transitions from straight to bent and/or twisted configurations upon a change in environmental conditions^{33–36}. This local transformation causes neighboring ribbons to mechanically interlock and form solid-like ensembles with viscoelastic properties. Removing the stimulus causes the ribbons to straighten such that the aggregates redisperse into a disentangled suspension with negligible elasticity. We modulate ribbon material type, shape, and concentration to control the formation, mechanical properties, and reversibility of aggregates. Ultimately, we demonstrate a largely material agnostic strategy to assemble materials using shape-changing elements.

Actuating ribbons form programmable, entangled aggregates

Liquid crystal elastomer (LCE) ribbons undergo a broad nematic-paranematic phase transition upon heating, causing local contraction along the director³⁷ (Fig. 1a). We synthesize ribbons with controlled bending and twisting on heating due to a 90° rotation of the nematic director through the ribbon's thickness (Supplementary Fig. 1). By varying the relative angle, θ , of the ribbon's long axis to the orientation of the nematic director of the top surface, the relative degree of bending and twist upon actuation may be tuned, where $\theta = 0^\circ$ induces pure bending while $\theta = 45^\circ$ induces pure twisting (Supplementary Fig. 2). When these ribbons are suspended in a fluid at sufficiently high concentrations and heated, ribbons mechanically interlock and contract to form solid-like ensembles, paralleling the activity-driven contraction of fire ant rafts (Fig. 1b)^{8,14,38} or the O₂ concentration-modulated aggregation of California blackworms¹³. At high temperatures (150 °C) the aggregates have a greater storage than loss modulus up to shear strains of $4.1 \pm 0.43\%$, constituting solid-like behavior (Fig. 1c,d). Upon cooling, the LCE ribbons return to the nematic state, driving the ribbons towards their straight configurations, enabling redispersion into the liquid-like state. Specifically, when cooled to 50 °C, the system exhibits a greater loss than storage modulus from low strain amplitudes ($> 0.19 \pm 0.04\%$) (Fig. 1d).

Thermoresponsive hydrogel and semicrystalline LCE ribbons can also be programmed to reversibly transition from a straight to bent configuration and therefore form transient aggregates in response to temperature (Supplementary Fig. 3). These responses occur over different temperature ranges enabling aggregate formation at 25 °C (for semicrystalline LCEs), 37 °C (for hydrogels), and 175 °C (for LCEs). Furthermore, the elastic modulus of the constituents contributes to the mechanical properties of the aggregate. As the elastic modulus of the shape-changing material increases from 0.045 ± 0.002 MPa (hydrogels) to 22.16 ± 3.74 MPa (LCEs) to 382.17 ± 78.28 MPa (semicrystalline LCEs)³⁹, the yield stress of the aggregate increases from 2.35 ± 0.96 Pa (hydrogels) to 9.13 ± 4.90 Pa (LCEs) to 390.71 ± 78.24 Pa (semicrystalline LCEs) (Fig. 1e, Supplementary Fig. 4,5). After dispersion, the yield stress reduces to 0.32 ± 0.28 Pa for hydrogels, to 0.16 ± 0.04 Pa for elastomers, to 1.60 ± 0.19 Pa for semicrystalline LCEs (Fig. 1e).

Aggregates formed from the entanglement of ribbons exhibit unusual thermomechanical responses. Entanglement-induced solidification occurs upon heating, analogous to the heat-induced solidification

observed in some polymer solutions with a lower critical solution temperature (LCST)⁴⁰. These aggregates also exhibit large decreases in volume upon heating (Supplementary Movie 1). By contrast bulk LCEs undergo nearly isochoric deformation by contracting along the nematic director and expanding perpendicularly. This volumetric contraction is driven by the underlying ribbons' decrease in end-to-end distance as they physically entangle and continue to twist during heating. Cooling allows the actuated ribbons to extend, lengthening the distance between physical entanglements and causing volumetric expansion. Materials that demonstrate volume contraction on heating are useful for applications where managing thermal stresses is required. However, fabrication of such materials can be difficult as thermal expansion coefficients must be patterned within a single structure⁴¹. Here, we achieve emergent volume contraction on heating within a self-assembled structure composed of a single material. The combination of a controlled phase transition and volumetric contraction enables LCE aggregates to reform structurally after damaged without external manipulation (Supplementary Fig. 6). Furthermore, this combination enables LCE aggregates to form in confined environments such as fluidic channels (see Supplementary Information Note 1, Supplementary Fig. 7-9).

Aggregate formation is not ubiquitous amongst all ribbon suspensions. Rather, it depends on factors such as ribbon length and concentration. Short ribbons and suspensions with low ribbon concentration fail to aggregate. Utilizing both experimentation and Monte Carlo simulations, we find that the initial suspensions of ribbons must exhibit percolated geometric overlap before actuation to form cohesive solids after heating (see Supplementary Information Note 2, Extended Data Fig. 1). However, once cohesive solids are formed, aggregates resist dilution, compression, shear, and tension. Qualitative tensile (Supplementary Movie 2) and dilution tests were conducted to explore the difference between the formed aggregates and solely jammed granular matter, which can be stiff in compression⁴² yet cannot withstand tension or dilution⁴³. To illustrate that these aggregates' structural stability goes beyond jamming, samples were transferred to a large, heated silicone oil bath with a rotating spin vane. Aggregates remain intact, indicating strong cohesion (Supplementary Movie 3). In contrast, aggregates in cold, agitated silicone oil disperse.

Aggregate properties are tunable through ribbon design

The aggregates' mechanical properties are highly influenced by the aspect ratios of the underlying ribbons. To map this dependence, we first conducted mechanical testing on aggregates formed from ribbons with conserved offset angles, cross-sectional areas, and packing densities, while sweeping their lengths over 3-mm, 6-mm, and 12-mm (Fig. 2a). We find that increasing the ribbon length increases the number of turns within each ribbon in the heated state (Supplementary Fig. 10). Longer ribbons form aggregates with higher yield strains, yield stresses, and penetration forces (Fig. 2b-d, Supplementary Fig. 11, 12). As the ribbon length is increased from 3-mm to 6-mm to 12-mm, the yield stress of the heated aggregate increases from 221 ± 61 Pa (at 2.1 ± 0.59 % strain) to 300 ± 50 Pa (at 4.15 ± 0.43 % strain) to 701 ± 114 Pa (at 6.98 ± 1.35 % strain), respectively (Fig. 2b,c). After cooling without any other intervention, the yield stress decreases to 21 ± 17 Pa (at 0.06 ± 0.05 % strain) for 3-mm ribbons, 25 ± 5 Pa (at 0.19 ± 0.04 % strain) for 6-mm ribbons, and 92 ± 28 Pa (at 0.27 ± 0.05 % strain) for 12-mm ribbons (Fig. 2c, Supplementary Fig. 11). Furthermore, formed aggregates resist probe penetration, having a normal force of 3.5 ± 1 N for 3-mm ribbons, 11 ± 1 N for 6-mm ribbons, and 17 ± 2 N for 12-mm ribbons (Fig. 2d, Supplementary Fig. 12). Once cooled, the penetration force decreased to 0.03 ± 0.02 N for aggregates constructed from both 3-mm and 6-mm ribbons. However, the penetration force only decreased to 4.94 ± 0.9 N for samples constructed from 12-mm ribbons. This indicates that there is a limit to dissociation of the aggregates as will be discussed further. Since increasing a ribbon's length increases the number of twists it achieves upon unfettered actuation, we hypothesize that aggregates comprised of longer ribbons achieve more entanglements per ribbon, thus increasing their penetration resistance and yield stresses.

In addition to ribbon length, ribbon offset angle also influences aggregate mechanics (See Supplementary Information Note 3). An offset angle of 0° induces pure bending, and an offset angle of 45° leads to pure twisting. Offset angles between 0° and 45° lead to some combinations of bending and twisting (Fig. 2e, Supplementary Fig. 2). While aggregation occurs for ribbons with offset angles of 0° or 10° , ribbons with

45° offset do not cohere and exhibit negligible change in mechanical properties with temperature (Fig 2fh, Supplementary Fig. 11, 12). As the offset angle is increased from 0° to 10°, the yield stress of the aggregates decreases from 516 ± 162 Pa (at $5.36 \pm 1.25\%$ strain) to 300 ± 50 Pa (at $4.15 \pm 0.04\%$ strain) (Fig. 2f, g). After cooling, yield stress decreases to 36 ± 4 Pa (at $0.3 \pm 0.03\%$ strain) and 25 ± 5 Pa (at $0.19 \pm 0.04\%$ strain) for 0° and 10° ribbons, respectively (Fig. 2g, Supplementary Fig. 12). The decrease in yield stress with respect to increasing offset angle suggests that bending, and not twist, is the requisite geometric trait required to induce entanglement in these aggregates. We note the values in yield stress between the heated and cooled dispersions of both the 0° ($p = 0.01$, $n = 3$, paired t-test) and 10° ($p = 0.04$, $n = 3$, paired t-test) ribbons are significantly different; however, no significant difference in yield stress is observed for the 45° ($p = 0.2$, $n = 3$, paired t-test) ribbons (Supplementary Fig. 13).

Aggregation reversibility is governed by ribbon actuation

Ribbon length and offset angle impact the degree of volumetric contraction and reversibility of the aggregate. Ribbons of varying lengths and 10° offset angle were placed into a well with a packing density of 0.075 mg/mm^3 and subjected to 2 heating and cooling cycles. Volume enveloped by the aggregates was measured with respect to temperature. Initially at room temperature, dispersed ribbons occupied the entire volume of the well. However, after heating, the aggregates comprised of 3, 6, and 12 mm-long ribbons contracted to $70.41 \pm 0.49\%$, $66.21 \pm 1.65\%$, and $56.50 \pm 1.82\%$ of their original volume, respectively (Fig. 3a). While aggregates comprised of 3-mm and 6-mm ribbons fully redisperse after cooling, the 12-mm ribbon only returned to $76.56 \pm 3.23\%$ of their original volume when cooled. While the greater degree of volumetric contraction for the 12-mm ribbons is perhaps indicative of higher entanglement density, the inability to disperse upon cooling is indicative of entanglement irreversibility. Ribbons of varying offset angles and 6-mm length were also placed in wells at the same packing density and subjected to the same thermal cycling (Fig. 3b). While ribbons with 45° offset exhibited negligible thermal contraction, ribbons with 10° offset exhibited fully reversible contraction and expansion. However, ribbons with 0° offset (i.e., no twist), only occupy $73 \pm 6.7\%$ of the initial volume after their first heating and cooling cycle again suggesting entanglement irreversibility. Importantly, irreversibility is not observed in individual ribbons undergoing the same thermal loading (Supplementary Fig. 14), affirming topological changes as the source of aggregate irreversibility.

To quantify the degree of reversibility as well as its temperature dependence, we employ a simple empirical model and find that normalized volume evolves with temperature following a modified logistic function (see Supplementary Information Note 4, Supplementary Fig. 15-18). We deduce the approximate threshold for reversibility by cyclically heating a dispersion of 12-mm ribbons between 50 °C and 150 °C (Fig. 3c). As these thermal conditions yielded nearly fully reversible aggregates, we deduced that the reversibility threshold is on the order of 0.67 ± 0.02 . We leverage this approximate threshold and use it as a fitting parameter for each cycle of the system heated to 175 °C. Fitting the equation with the data for 12mm ribbons from Fig. 3a, we empirically model the cyclic behavior of 12-mm ribbons heated between 50 °C to 175 °C (Fig. 3d). Therefore, aggregation reversibility is programmable through features such as ribbon length, ribbon offset angle, and temperature.

Light-responsive & conductive aggregates

Coupling LCE ribbons with functional coatings enables multi-stimuli response and conductive aggregates (Fig. 4a)^{44,45}. In the presence of NIR light, ribbons coated with a strain-tolerant metal coating⁴⁶ (Supplementary Fig. 19) demonstrate photothermally induced shape change⁴⁴ and aggregate (Fig. 4b). The volume occupied by the ribbons decreases to $49 \pm 3\%$ of its original value when exposed to NIR light and returns to $86 \pm 8\%$ original volume when the NIR light is switched off (Fig. 4c, Supplementary Movie 4). Temporal control of volume change is used for collective grasping (Fig. 4d). When the light is off, a screw can be independently removed from a dispersion of coated LCE ribbons. However, when the light is on, the ribbons entangle, forming an aggregate around the screw; therefore, removal of the screw leads to removal of the aggregate. These aggregates are also capable of healing damage (Supplementary Fig. 20). Upon

NIR light exposure, dispersed ribbons form an aggregate that is then severed. By toggling off the NIR light, stirring, and then reintroducing NIR light, the ribbons redisperse and then reaggregate.

Mechanical entanglement of conductive ribbons leads to a reversible transition from electrically insulating to conducting (Fig. 4a,f). Conductance increases from 0 ± 0 S to 0.85 ± 0.14 S as temperature is increased from 50°C to 175°C (Supplementary Fig. 21) and then decreases back to 0 ± 0 S after cooling (Supplementary Movie 5). Ribbon packing density plays an important role in forming conductive pathways, as aggregates must be capable of attaching to both leads while maintaining structural integrity (Fig. 4g). At a low packing density of 0.02 mg/mm^3 , ribbons are incapable of achieving electrical continuity between the two fixed leads in response to photo-thermal heating. However, at a packing density of 0.06 mg/mm^3 , aggregates form a continuous network between leads giving rise to a switchable soft conductor. Upon cyclic NIR illumination, conductance initially increases from 0 ± 0 S to 0.45 ± 0.12 S in the presence of light, with an increase from 0 ± 0 S to 0.27 ± 0.16 S by the third cycle. At the highest packing density of 0.11 mg/mm^3 , conductance increases from 0 ± 0 S to 0.66 ± 0.16 S upon irradiation; however, residual conductance of 0.04 ± 0.08 S then occurs in the dark due to residual contacts between ribbons. By exploiting these aggregates' re-processability and conductance, healable, photo-responsive electronic circuits are realized (Fig. 4h, Supplementary Fig. 22, Supplementary Movie 6).

Aggregation near room temperature

The shape of liquid crystal polymer networks depends not only on temperature, but also on the presence of solvent. Liquid crystalline gels (LCGs) were synthesized to create aggregates stable at room temperature. The swelling or deswelling of LCG films enables isothermal, programmed shape change used to irreversibly form aggregates stable at room temperature (see Supplementary Information Note 5, Supplementary Figs. 23-27)^{47,48}. Reversible aggregates stable at room temperature are formed using semicrystalline liquid crystal polymer ribbons that are bent and twisted at room temperature and flat at elevated temperatures³⁹ (see Supplementary Information Note 5, Supplementary Figs. 28,29). While semicrystalline LCEs enable reversible aggregates stable at room temperature, high temperatures are needed to redisperse the ribbons which hinders the use of this mechanism for sensitive environments, such as biomedical applications.

Hydrogel bilayer ribbons enable the formation and dispersion of aggregates at lower temperatures and in water, thereby making them potentially well-suited for biomedical applications. Individual ribbons are bilayers of a thermoresponsive hydrogel layer with a passive polymeric layer^{49,50} (Fig. 5a, Supplementary Fig. 3). When a dispersion of these ribbons is suspended in water and heated, ribbons mechanically interlock and contract (Fig. 5b). At the higher temperature of 37°C , a ribbon dispersion loaded at an initial packing density of 0.06 mg/mm^3 aggregates exhibiting a yield stress of 4.03 ± 2.05 Pa at a yield strain of $16.44 \pm 11.64\%$. After cooling, the ribbons redisperse and exhibit a yield stress of 0.48 ± 0.17 Pa at a yield strain of $1.38 \pm 0.39\%$ (Fig. 5c, Supplementary Fig. 30, 31). Furthermore, the initial packing density and length of ribbons determine aggregate formation and mechanical properties (Fig. 5d, Extended Data Fig. 1, Supplementary Fig. 30-33). As the initial packing density of the dispersion increases from 0.03 to 0.06 to 0.12 mg/mm^3 , the yield stress of the aggregate increases from 2.35 ± 0.96 Pa (at a strain of $12.37 \pm 3.61\%$) to 4.03 ± 2.05 Pa (at a strain of $16.44 \pm 11.64\%$) to 39.43 ± 4.82 Pa (at a strain of $48.97 \pm 22.39\%$) (Fig. 5d, Supplementary Fig. 30). Along with aggregation induced increases in yield stress and yield strain, ribbon dispersions also demonstrate a decrease in volume upon heating (Fig. 5e, Supplementary Fig. 17, 18, 34). The volume occupied by the aggregates decreases to $59.03 \pm 3.96\%$ at a loading density of 0.12 mg/mm^3 , to $32.59 \pm 4.69\%$ at a loading density of 0.06 mg/mm^3 , and to $22.57 \pm 4.47\%$ at a loading density of 0.03 mg/mm^3 (Fig. 5e).

Self-assembling scaffolds are made by seeding mouse 3T3 fibroblasts on planar hydrogel ribbons. Fibroblasts are seeded onto the ribbons by incorporating RGD within the hydrogel layer (Figure 5f)⁵¹. After cell culturing, fibroblasts can be found mainly along the ribbon edges, and individual ribbons transition from a straight to a bent configuration upon heating to 37°C (Fig. 5g). Dispersions of cellcoated ribbons, with

high cell viability, transition into an aggregate in response to heating to 37 °C (Fig. 5h, Supplementary Fig. 35, 36). Metabolic activity of the fibroblasts was maintained for at least 10 days (Supplementary Fig. 37). Furthermore, responsive hydrogel ribbons may also be used as injectable blood clotting agents due to their ability to self-assemble into porous structures with high surface areas⁵². Responsive hydrogel ribbons can induce a blood clot with no significant difference in time when compared to the kaolin positive control (Supplementary Fig. 38). The clotting time of blood exposed to the bulk hydrogel is significantly longer than the blood exposed hydrogel aggregate ($p = 0.0006$). The effect of surface area of a synthetic material on blood clotting is known⁵³. However, the combination of injectability and self-assembled macroporosity that is enabled by entanglement is unique amongst previously described materials. This combination of properties, allows the hydrogel ribbons to be injected, fill a model aneurysm, and induce a blood clot (Supplementary Fig. 38, 39).

Summary & Conclusions

We report a simple yet powerful method to create macroscopic aggregates capable of autonomous assembly and disassembly. Hydrogels, elastomers, and semicrystalline ribbons are programmed to reversibly transition from straight to bent and twisted configurations in response to heating, NIR irradiation, or presence of a solvent. By allowing multiple ribbons to actuate in proximity, the ribbons entangle and produce transient, viscoelastic solids. The initial packing density, shape, and mechanical properties of the individual ribbons dictate both the ability to form aggregates and the aggregate's mechanical properties. We introduce the parameters available for ribbon design and – through a combination of experimentation and stochastic simulations – predict and explain the onset of aggregation as a function of ribbon length, offset angle, loading temperature, and packing density. Additionally, we examine the reversibility of aggregation and utilize an empirical model to explore observed plasticity in a subset of these systems. Furthermore, coating ribbons with liquid metal produces units that aggregate in response to NIR light and exhibit electrical conductance. Aggregation is a common trait in dispersions of stimuli-responsive ribbons. This may enable a wide range of materials to be assembled on demand enabling a range of potential applications from stimuli-responsive circuits to injectable biomaterials.

Acknowledgments

This material is based upon the work supported by the Army Research Office under grant no. W911NF1810150, National Science Foundation under Grant nos. 2041671, 2147830, 2023179 and the Dr. Dionel E. Avilés '53 and Dr. James E. Johnson '67 Graduate Fellowship. A.K.G. acknowledges financial support from the National Institute of Biomedical Imaging and Bioengineering (NIBIB) of NIH, the Director's New Innovator award (DP2 EB026265), Peer Reviewed Medical Research Program (PRMRP) of Department of Defense (DOD) (W81XWH2210932), President's Excellence Fund (X-Grants) from Texas A&M University. We would like to also acknowledge the Cardiovascular Pathology Laboratory at Texas A&M University (CVP-TAMU) for Micro-CT imaging and analysis. We acknowledge the use of the Materials Characterization Facility at Carnegie Mellon University supported by Grant MCF-677785. We would also like to thank Professor Sarah Bergbreiter for the use of her lab's Phenom SEM. We would also like to acknowledge Kyle J. Weishaar for intellectual discussions. Information release number LLNLJRN-843254.

Author Contributions:

M.K.A. and T.H.W. designed the research. M.K.A. conducted most of the experiments. R.J.W. and F.J.V. performed simulations. M.S.K., M.Z., and C.M. performed and/or designed experiments involving conductive ribbons. L.K.J. performed experiments involving Micro CT imaging. M.S.K., S.W., M.J., and A.D. assisted with experiments involving mechanical testing. A.K.G., M.H.K., and K.A.S. performed and/or designed experiments involving cell seeding. A.K.G. and S.E.H. performed and/or designed experiments involving blood clotting. The article was written through the contributions of all authors. All authors have given approval to the final version of the article.

Competing Interest Statement: The authors declare no competing financial interest.

Figure Legends:

Fig. 1 | Inspiration and construction of synthetic aggregates. **a**, Schematic illustrating mechanism driving shape change in liquid crystal elastomers. An initially straight ribbon having a 90° transition in the orientation of the nematic director from the bottom surface to the top surface of the ribbon and an angle of θ between the ribbons longitudinal axis and the orientation of the nematic director on the top surface **b**, Top view of a biological system consisting of fire ants (*S. invicta*) undergoing global volumetric contraction (scale bar = 20 mm) and **c**, top view of a synthetic system consisting of LCE ribbons, with a length of 6 mm and an offset angle of 10° , submerged in silicone oil at a ribbon packing density of 0.075 mg/mm^3 transitioning from dispersed to aggregated after being heated from 25°C to 175°C (scale bar = 5 mm). **d**, Representative graph of oscillatory rheology strain sweeps plotting storage modulus and loss modulus as a function of shear strain of ribbons with a length of 6 mm and on offset angle of $\theta = 10^\circ$ at an initial density of 0.075 mg/mm^3 . **e**, Yield stress plotted as a function of ribbon type at the aggregated state (red) and at the dispersed state (blue). Data are presented as individual data points and mean values $\pm$ SD. Hollow circles represent individual data points, solid circles represent the mean, and error bars represent the standard deviation. $N = 3$. All ribbons were loaded at an initial packing density of 0.03 mg/mm^3 . Hydrogel ribbons were dispersed in water, while elastomers and semicrystalline ribbons were dispersed in silicone oil.

Fig. 2 | Individual ribbon parameters affect global mechanical properties. **a**, Schematic of individual ribbons with varying lengths in their heated, actuated state. Offset angle for ribbons is 10° . **b**, Representative graph of oscillatory rheology strain sweeps ($\omega = 10 \text{ rad/s}$) plotting storage modulus and loss modulus as a function of shear strain in the heated, aggregated state of ribbons with varying lengths having an offset angle of 10° . **c**, Yield stress plotted as a function of ribbon length at 150°C (orange) and after cooling to 50°C (purple). Hollow circles represent individual data points, solid circles represent the mean, and error bars represent the standard deviation. $N = 3$. Offset angle of ribbons is 10° . **d**, Representative graph plotting normal force as a function of gap for penetration tests of aggregates formed of ribbons with different lengths and an offset angle of 10° . **e**, Schematic of individual ribbons with varying offset angles in their heated, actuated state. The length of the ribbons is 6 mm. **f**, Representative graph of oscillatory rheology strain sweeps ($\omega = 10 \text{ rad/s}$) plotting storage modulus and loss modulus as a function of shear strain in the heated state of ribbons with varying offset angles and a length of 6 mm. **g**, Yield stress plotted as a function of offset angle at 150°C (orange) and after cooling to 50°C (purple). Hollow circles represent individual data points, solid circles represent the mean, and error bars represent the standard deviation. $N = 3$. Length of ribbons is 6 mm. **h**, Representative graph plotting normal force as a function of gap for penetration tests in the heated state of a dispersion of ribbons with varied offset angles and a length of 6 mm. All experiments were conducted at a ribbon packing density of 0.075 mg/mm^3 . Error bars represent the standard deviation. $N = 3$.

Fig. 3 | Contractile reversibility. **a**, Normalized volume plotted as a function of temperature cycling from 25°C to 175°C of 3 mm ribbons (red), 6 mm ribbons (green), and 12 mm ribbons (blue). Offset angle of ribbons is 10° . Hollow circles represent individual data points, solid circles represent the mean, and error bars represent the standard deviation. $N = 3$. **b**, Normalized volume plotted as a function of temperature cycling from 25°C to 175°C of ribbons with varied offset angles. Length of ribbons is 6 mm. Hollow circles represent individual data points, solid circles represent the mean, and error bars represent the standard deviation. $N = 3$. **c**, Normalized volume plotted as a function of temperature for a dispersion of 12 mm ribbons, having an offset angle of 10° , cyclically heated and cooled from 50°C to 150°C . Circles indicate experimental data. Blue circles indicate the first cycle, green circles indicate the second cycle, and red circles indicate the third cycle. **d**, Normalized volume plotted as a function of temperature for a dispersion of 12 mm ribbons, having an offset angle of 10° , cyclically heated and cooled from 50°C to 175°C . Solid line indicates the empirical model and circles indicate experimental data. Blue curves indicate the first cycle, green curves indicate the second cycle, and red curves indicate the third cycle. All experiments were conducted at a ribbon packing density of 0.075 mg/mm^3 .

Fig. 4 | Metal coating enables emergent functionalities. **a**, Schematic illustrating the process of coating ribbons with liquid metal, enabling NIR responsive aggregates and conductive aggregates. **b**, Dispersion of coated ribbons with an offset angle of 10° and a length of 6 mm at a ribbon packing density of 0.075 mg/mm^3 aggregating in the presence of NIR light (scale bar = 3 mm). **c**, Normalized volume plotted as a function of NIR light state of coated ribbons with an offset angle of 10° and a length of 6 mm at a packing density of 0.075 mg/mm^3 for 3 cycles. Data are presented as individual data points and mean values $\pm$ SD. Hollow, black circles represent individual data points, solid, grey circles represent the mean, and error bars represent the standard deviation. $N = 3$. **d**, Aggregation can be used to form a solid-like aggregate around a foreign object and latch on (scale bar = 5 mm). **e**, Percent of ribbons attached to the foreign object plotted as a function of the NIR light state. Data are presented as individual data points and mean values $\pm$ SD. Hollow, black circles represent individual data points, solid, grey circles represent the mean, and error bars represent the standard deviation. $N = 3$. **f**, Schematic illustrating that ribbons can transition from an insulating state to a conductive state depending on the state of the NIR light. **g**, Conductance measured as a function of time for 3 cycles of turning the NIR light from off to on for 3 different packing densities (scale bar = 8 mm). Data are presented as individual data points and mean values $\pm$ SD. Hollow, black circles represent individual data points, solid, grey circles represent the mean,

and error bars represent the standard deviation. N = 3. **h**, Conductive aggregates are capable of healing damage by turning the light off and on. Note that the dispersed ribbons were manually stirred for this experiment only (scale bar = 5 mm). Error bars represent the standard deviation. N = 3.

Fig. 5 | Hydrogel ribbons enable aggregation in physiologically relevant conditions. **a**, Schematic illustrating the mechanism of a single ribbon bending and multiple ribbons aggregating through a hydrogel bilayer system composed of a passive PMMA layer and an active PNIPAm layer in response to heating induced deswelling. **b**, Dispersion of hydrogel ribbons having a length of 10 mm and loaded at a density of 0.06 mg/mm³ aggregating in response to heating from 25 °C to 37 °C (scale bar = 5 mm). **c**, Representative graph of oscillatory rheology strain sweeps plotting storage modulus and loss modulus as a function of shear strain of hydrogel ribbons, having a length of 10 mm at an initial loading density of 0.06 mg/mm³. **d**, Yield stress plotted as a function of ribbon loading density at 37 °C (red) and after cooling to 25 °C (blue). Data are presented as individual data points and mean values +/- SD. Hollow circles represent individual data points, solid circles represent the mean, and error bars represent the standard deviation. N = 3. Length of ribbons is 10 mm. **e**, Normalized volume plotted as a function of temperature cycling from 25 °C to 37 °C of ribbons loaded at an initial density of 0.03 mg/mm³ (red), 0.06 mg/mm³ (green), and 0.12 mg/mm³ (blue). Length of ribbons is 10 mm. Data are presented as individual data points and mean values +/- SD. Hollow circles represent individual data points, solid circles represent the mean, and error bars represent the standard deviation. N = 3. **f**, Schematic illustrating the self assembly of cell seeded scaffolds through the use of bilayer hydrogel ribbon dispersions. **g**, Top and side view of hydrogel ribbon seeded with mouse 3T3 fibroblasts demonstrating transition from a straight to a bent configuration in response to heating from 25 °C to 37 °C (scale bar = 500 µm). Experiment was repeated 3 times yielding similar results. **h**, Fluorescence micrograph of a dispersion of ribbons seeded with mouse 3T3 fibroblasts aggregating in response to increasing temperature from 25 °C to 37 °C demonstrating cell viability within an aggregate (scale bar = 3 mm, inset, 1 mm). 3T3 fibroblasts were seeded on ribbons for 3 days before imaging. Experiment was repeated 3 times yielding similar results.

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Methods

Materials:

The liquid crystal monomers, 1,4-bis-[4-(6-acryloyloxyhexyloxy) benzoyloxy]-2-methylbenzene (RM82) and 1,4-bis-[4-(3-acryloyloxypropyloxy) benzoyloxy]-2-methylbenzene (RM257) were purchased from Wilshire Technologies. The liquid crystal monomer, 1,4-phenylene bis(4-(hex-5-enyloxy)benzoate), was purchased from SYNTHON Chemicals GmbH & Co. KG. The low molecular weight liquid crystal, 4-cyano4'-pentylbiphenyl (5CB), the photoinitiators, Irgacure I-369 and Irgacure I-651, the chain extender, nbutylamine (nBA), the metals, gallium and indium, and polymethyl methacrylate (PMMA) were purchased from Fisher Scientific. Pentaerythritol tetrakis(3-mercaptopropionate) (PETMP), 2,2'-(ethylenedioxy) diethanethiol (EDDT), n-isopropylacrylamide (NIPAM), poly(ethylene glycol) (PEGDA), photoalignable dye, brilliant yellow, kaolin, Irgacure 2959, gelatin (Type A, 300 Bloom), gelatin (Type A, 80-300 Bloom), and methacrylic anhydride were purchased from Sigma Aldrich. Lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LAP) was purchased from TCI America. Methacryloxyethyl thiocarbamoyl rhodamine b was purchased from ALFA Chemistry. Sudan IV powder dye was purchased from Alfa Aesar. Calcium chloride was purchased from Avantor. A two-part polydimethylsiloxane (PDMS) elastomer was purchased from Ellsworth Adhesives.

Silver ink (JS-A102A, Metalon) was purchased from Novacentrix Cell adhesive peptide, Arginylglycylaspartic acid (RGD), was purchased from GenScript (RP20297).

Material Synthesis:

Clean glass slides (VWR) with dimensions 50 mm × 75 mm × 1 mm were subjected to O₂ plasma for 5 min. Subsequently, the slides were spin-coated with a 1 wt.% brilliant yellow in dimethylformamide solution at a spin speed of 3000 RPM for 30 s. Slides were baked for 30 min at 90 °C on a hotplate to ensure evaporation of dimethylformamide. Each coated glass slide was exposed to linearly polarized broadband visible light from a modified projector at an intensity of 10 mW cm² for 3 min to align the brilliant yellow molecules. After alignment, coated glass slides were spin-coated at a speed of 3000 RPM for 30 s with a 9 wt.% RM257 (reactive mesogens) and 1 wt.% I-651 (photoinitiator) toluene solution (10 wt.% solids). The slides were then irradiated with 365 nm UV light at an intensity of 2 mW/cm² for 5 min using a UV oven (UVP Crosslinker CL-3000) for polymerization. Glass cells were prepared by adhering a pair of RM257-coated glass slides together using a 50 µm spacer (USA Sealing) and superglue (498, Loctite). A 1.4:1 molar ratio of RM82 to nBA was heated and mixed with 1.5 wt.% of I-369. The solution was then allowed to partially fill the glass cell through capillary action on a hot plate at 75 °C before placing it in an oven at 75 °C to complete filling and oligomerization. After 15 hrs. of oligomerization, glass cells were allowed to cool to room temperature before exposing the cell to 365 nm ultraviolet light (Lumen Dynamics, OmniCure LX400+) at an intensity of 8 mW cm⁻² for polymerization for 5 min on each side. After polymerization, the top glass slide was released, and the film was cut using a CO₂ laser cutter (Gravograph CO₂ Laser LS100-40W). Additional information on material synthesis can be found in the Supplementary Materials.

Mechanical Characterization:

To measure rheological properties of aggregates or dispersions, previously reported experimental were followed with modification^{14,17}. Briefly, parallel plate rheological scans were conducted utilizing a rheometer (Anton Paar Physica MCR 301). A PDMS well was placed on the base to contain the ribbons and silicone oil in the rheometer (Supplementary Fig. 40). Sandpaper was adhered to both the base of the PDMS well and the top plate (diameter = 8 mm) to minimize slipping. LCE ribbons were placed in silicone oil at a packing density of 0.075 mg/mm³ and heated to 150 °C. Temperature was checked using a thermocouple (Traceable 4015CC). Oscillatory strain sweeps at an angular frequency rate of 10 rad/s with a gap of 3.5 mm were performed measuring storage and loss moduli as a function of shear strain from 0.01% to 100%. The samples were then cooled to 50 °C, and temperature was checked using a thermocouple. The same oscillatory strain sweeps were performed at the lower temperature. No external manipulation of the sample occurred between these tests. Rheological properties of semicrystalline LCE ribbons were conducted in a similar manner to the above. Ribbons were placed in a well with silicone oil heated to 120 °C loaded at an initial packing fraction of 0.03 mg/mm³. After loading, ribbons were cooled to 25 °C to form aggregates. After aggregation, oscillatory strain sweeps at an angular frequency rate of 10 rad/s with a gap of 3.5 mm were performed measuring storage and loss moduli as a function of shear strain from 0.01% to 100%. The samples were then reheated to 120 °C, and temperature was checked using a thermocouple. The same oscillatory strain sweeps were performed at the higher temperature. No external manipulation of the sample occurred between these tests. Rheological properties of hydrogels were performed in a similar manner to LCEs; however, ribbons were dispersed in water heated to 37 °C before conducting oscillatory strain sweeps at an angular frequency rate of 1 rad/s with a gap of 3.5 mm as a function of shear strain from 0.01% to 100%. Yield stress and yield strain values were measured as the shear stress and strain value at the cross over point between the loss modulus and the storage modulus^{54,55}. Three separate batches of ribbons were tested for each condition.

Penetration tests were performed using a rheometer (Anton Paar Physica MCR 301) by replacing the top plate with a cylindrical penetration probe with a diameter of 2.5 mm. A cylindrical PDMS well of dimensions (d = 10 mm, h = 3 mm) was placed on the base to contain the ribbons and silicone oil in the rheometer (Supplementary Fig. 40). Ribbons were dispersed in silicone oil at a packing density of 0.075 mg/mm³. The top of the PDMS well was covered was a glass slide to mold the ribbons into a puck geometry while heating to 150 °C. Temperature was checked using a thermocouple. After reaching 150 °C, the top glass slide was

removed, and the probe penetrated the sample at a rate of 100 $\mu\text{m/s}$. The normal force was measured as a function of the gap. After performing test, the probe was extracted from the sample, and the sample was allowed to cool to 50 $^{\circ}\text{C}$. After cooling, the test was performed under the same conditions. Penetration tests of hydrogels were performed in a similar manner except samples were heated to 37 $^{\circ}\text{C}$ and loaded in water instead of silicone oil. No external manipulation of the sample occurred between these tests. Three separate batches of LCE ribbons were tested for each ribbon shape using the same testing conditions.

Tensile tests of semicrystalline LCE aggregates was performed by molding samples into a rectangular prism. A PDMS well that contained a void with a length of 15 mm, a width of 10 mm, and a depth of 5 mm was fabricated through replica molding of a 3D printed part. Ribbons, having an offset angle of 10 $^{\circ}$ were dispersed into the PDMS well containing silicone oil at an initial loading density of 0.03 mg/mm^3 . The bath was heated to 120 $^{\circ}\text{C}$ and temperature was measured using a thermocouple. After reaching 120 $^{\circ}\text{C}$, ribbons were cooled to 25 $^{\circ}\text{C}$ to develop aggregates. After aggregates were created, silicone oil was removed by submerging aggregates into isopropyl alcohol and rinsing with isopropyl alcohol. After washing, aggregates were dried in an oven set at 37 $^{\circ}\text{C}$ for 4 h. After drying, aggregates were loaded into the DMA. Stress was measured as a function of strain at a strain rate of 0.1 mm/s . Tests were conducted on three separate samples from three separate semicrystalline LCEs.

Volume Change:

Relative volume changes of aggregates composed of LCE ribbons were measured by placing the ribbons in a PDMS well with a diameter of 16 mm and a depth of 5 mm. The ribbons were observed to largely be oriented normal to the thickness of the cylindrical mold. A glass slide was placed on top of the well to encapsulate the ribbons. The ribbons were imaged at the initial temperature of 25 $^{\circ}\text{C}$ and the heated temperature of 175 $^{\circ}\text{C}$. Three thermal cycles were performed. Images were analyzed using ImageJ software. Three separate batches of LCE ribbons were tested for each ribbon shape using the same testing conditions. To measure volume as a function of temperature, experiments were conducted in a similar manner; however, synchronized video recordings were taken of both the temperature readout of the thermocouple and the volume change of the aggregate. Additional information on aggregate volume change can be found in the Supplementary Materials.

Monte Carlo Simulation:

The Monte Carlo simulation was developed in 2D using MATLAB (MathWorks) based on the observation that the ribbons occupy roughly a 2D plane when placed into the cylindrical wells used in experiments, and the assumption that ribbons were approximately evenly spatially distributed. The simulation first defines a discretized grid with prescribed planar concentration, c . It then seeds “ribbons” of length L , so that one ribbon is centered on every grid point. Each ribbon, which is straight to represent the geometry of real ribbons at room temperature, is then prescribed a random angle in the uniform range $[0, \pi)$ rad . The networks are then visually plotted and then image analysis is conducted to determine if the straight ribbons form a fully percolated overlapping 2D network.

Photothermal Response:

Liquid metal coated ribbons demonstrate a photo-thermal response. To analyze NIR light driven aggregation, a circular PDMS well, having a diameter 6 mm and a depth of 5 mm, was placed on top of a NIR light source at distance of 1 mm. Coated ribbons, having a length of 6 mm and an offset angle of 10 $^{\circ}$, were dispersed in silicone oil and placed in the well at a packing density of 0.075 mg/mm^3 . A glass slide was placed on top of the well to encapsulate the ribbons. A 735 nm NIR LED (CBM-120-FR Luminus Devices Inc.) was used to illuminate the sample from the bottom. The IR LED was powered through a laboratory-grade DC power supply with current and voltage adjustment capabilities (Extech). The intensity of the NIR LED was 42 mW/mm^2 at the bottom of the well. A camera was placed on top of the setup to image the volume change. Image was taken before NIR light illumination. NIR light illuminated the sample for 30 s, and the sample was imaged. NIR light was turned off for 90 s, and sample was imaged. This cycle was repeated twice. Images were analyzed using ImageJ software. Three separate batches of coated LCE ribbons were tested.

Conductance:

Measuring conductance of coated ribbons was performed using ambient heating and NIR light exposure. To measure conductance through ambient heating, coated ribbons, having a length of 6 mm and an offset angle of 10°, were dispersed in a circular PDMS well, having a diameter of 16 mm and a depth of 5 mm, at packing density of 0.075 mg/mm³. Within the PDMS well ribbons were dispersed around two copper wire leads spread 5 mm apart that were attached to a multimeter (Fluke 114 Electrical Multimeter). A thermocouple (Traceable 4015CC) was inserted into the well to measure temperature. To measure resistance as a function of temperature, synchronized video recordings were taken of the temperature readout of the thermocouple, the resistance read out of the multimeter, and the ribbon dispersion. Conductance was calculated using this formula:

$$G = \frac{1}{R}$$

To measure conductance of coated ribbons using NIR light, a similar testing procedure was used; however, to ensure flood exposure of the NIR light, the diameter of the circular well was reduced to 10 mm. Additionally, to understand the effect of packing density on conductance, three different ribbon packing densities were used: 0.02 mg/mm³, 0.06 mg/mm³, and 0.11 mg/mm³. Samples were exposed to NIR cyclically at a timeframe of 1 min on, 2 min off. Intensity of NIR light used was 42 mW/mm². Resistance values were collected at the end of each timeframe. Three separate batches of coated LCE ribbons were tested using the same experimental set up for both heat induced conductance and NIR light induced conductance.

Molding:

LCGs were used to mold structures capable of maintaining their shape at room temperature. Briefly, LCG ribbons were placed in a vial containing silicone oil. Ribbons and silicone oil were dropped cast into a PDMS negative mold created by molding from a 3D printed part. Once LCG ribbons filled the mold, the entire structure was heated to 150 °C. As LCG ribbons are heated, 5CB solvent is released from the system causing them to irreversibly deswell and change shape in a way that is similar to heating an LCE ribbon. Once cooled back to room temperature, the molded structure was released. Due to the loss of the solvent, the structure maintains its integrity. After releasing, the structure was submerged in an isopropyl alcohol bath and rinsed with isopropyl alcohol to wash off silicone oil. Structure was then allowed to dry in an oven set at 37 °C for 4 h. before weighing. The density of the molded structure was 0.12 mg/mm³, as calculated by dividing the mass of the molded structure by the internal volume of the mold used. Additional information on aggregate molding can be found in the Supplementary Materials.

Aggregate Reformation After Damage:

Reformation of aggregates after structural damage was performed using both LCE ribbons and metal coated LCE ribbons. Reformation of LCE aggregates was performed by initially dispersing LCE ribbons, that have an offset angle of 10° and a length of 6 mm, into silicone oil bath at an initial packing density of 0.075 mg/mm³. LCE ribbons and silicone oil were contained in a PDMS well that has a diameter of 19 mm and a depth of 3 mm. LCE ribbons, in their dispersed state, were heated from 25 °C to 175 °C to induce aggregation. Once aggregated and at the heated temperature of 175 °C, the aggregate was completely severed by using scissors (Westcott) to cut the aggregate into two separate pieces. After severing the aggregate, the two separate pieces were allowed to disperse independently, without stirring, by cooling the bath to 25 °C. Aggregate reformation was then initiated by heating the bath to 175 °C. Reformed structure was dispersed and reaggregated again to understand the effect aggregation and dispersion cycling has on aggregate reformation after damage. A digital camera was placed above the set-up to record a video. Images represented are snap shots taken from video. Additional information on aggregate reformation can be found in the Supplementary Materials.

Hydrogel Ribbon Injection:

The injectability of hydrogel ribbons was investigated by first heating a bath of 1.5 mL of DI water dyed with blue food coloring in a glass petri dish to 37 °C. The temperature was monitored using a thermocouple (Traceable 4015CC). Once the water reached 37 °C, 40 mg of hydrogel ribbons, previously loaded into a syringe (BD 10 mL syringe) fixed with a 10 G needle tip (Rachel's Closeouts), was injected into the heated bath. A camera was positioned on top and on the side of the petri dish to record hydrogel ribbon aggregation as a function of time.

Cell Culture:

NIH 3T3 Fibroblasts were cultured using HyClone Dulbecco's Modified Eagle Medium (DMEM) with high glucose (Cytiva) supplemented with 10% fetal bovine serum (FBS, Corning), 1% penicillin/streptomycin (P/S, Life Technologies). Bilayer hydrogel samples were prepared using the aforementioned procedure with one difference. After spin coating the PMMA layer, the hydrogel solution was filled into the cell mold and polymerized for 1 min using a UV oven at an intensity of 2 mW/cm². The hydrogel layer of the bilayer sheet was functionalized prior to the cell studies using a secondary modification (2 mM RGD, 20 mg/ml LAP, 9 min UV exposure). After initial polymerization, the glass slide from the hydrogel side of the mold was removed, and a new slide was placed 50 µm above the hydrogel. The integrin binding motifs filled above the hydrogel layer through capillary action and were allowed to swell into the hydrogel at 25 °C for 20 min before further polymerization in a UV oven at an intensity of 2 mW/cm² for 9 min. Bilayer hydrogels were then laser cut and placed under UV light of the biosafety cabinet (Labconco) for 30 min for sterilization. After sterilization, warm cell culture media was pipetted onto hydrogel ribbons, causing the ribbons to release. Ribbons were then transferred from the glass slide to 12 well plates. 3T3 fibroblasts (5 M cells) were then seeded on the flat bilayer hydrogels at 25 °C and set for 30 min. After cell seeding, ribbons were placed in an incubator (37 °C). Media was replaced every other day. After reaching confluence, 3T3 cells that were adhered to the hydrogel ribbons were stained with Celltracker™ Green CMFDA Dye (Thermo Fisher Scientific) using the manufacturer's protocol.

Temperature-responsive ribbons with 3T3 fibroblasts were imaged using Lionheart microscope (BioTek). Dispersion of cell laden ribbons were imaged with temperature control (25 °C/37 °C) to demonstrate self-assembling scaffolds. Cellular viability of the cell-laden ribbons was visualized using a Calcein-AM based Live and dead assay (Invitrogen) at multiple time points (1,3,7 days) after the initial cell seeding, following the manufacturer protocol. Stained cell laden ribbons were imaged using a Zeiss Axiovert A1 fluorescence microscope and Leica SP8 confocal microscope with appropriate filters. The metabolic activity of the cell-laden ribbons was evaluated at multiple time points (1,2,3,5,7, and 10 days) using alamarBlue assay (Thermo Fisher Scientific). For the alamarBlue assay, ribbons were placed in Nunclon™ Sphera™ 96- well plate prior to seeding with 3T3 cells. These well plates prevent cell adhesion to the surface of the well thus allowing for accurate assessment of metabolic activity of cells adhered to the ribbons. Cell laden ribbons were incubated with media containing 10% alamarBlue (v/v) for 2 hrs. Assay media was then collected and fresh media (without alamarBlue) was added back to the cells. Reduction of alamarBlue in the assay media was determined following manufacturers protocols by measuring the absorbance at 570 and 600 nm respectively using a spectrophotometer (BioTek Cytation 5).

Participants and Procedures:

Blood clotting experiments were evaluated using human blood samples from healthy participants in compliance with the protocols that were approved by the institutional review board (IRB2022-0501D) at Texas A&M University. All participants gave informed consent before participation in the study.

Data Analysis:

Statistical analysis for comparison of the yield stress of LCE ribbons with different offset angles was carried out by first testing for normality using the Shapiro-Wilk test using Origin. After normality was confirmed, a paired t-test was performed using Origin 9.9.

Statistical analysis for blood clotting experiments was carried out through an ordinary one-way ANOVA with multiple comparisons using Graphpad Prism 9. Plots were created using IGOR Pro 7, Graphpad Prism 9, and MATLAB 2022a.

Data Availability:

Data supporting the findings of this study are available in the article and its supplementary files. Source data are provided with this manuscript.

Methods Only References

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