Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information:

Mechanochromic Composite Elastomers for Additive Manufacturing and Low Strain Mechanophore Activation

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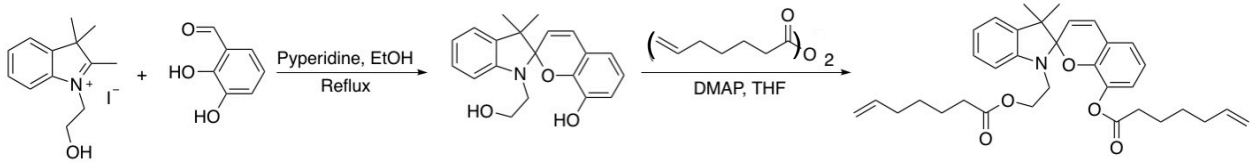
General Procedures:

1. **Synthetic Procedures:** Lab general solvents (dichloromethane, chloroform, hexane, ethyl acetate, acetone, xylene, tetrahydrofuran, ethanol) were purchased from VMR or Sigma Aldrich. Tween 20 and polyvinyl alcohol (Mowiol 18-88) were purchased from Sigma Aldrich. Sylgard®184 was purchased from Ellsworth Adhesives, Germantown, WI. Dragon Skin® 30 was purchased from Smooth-On. Flash chromatography was performed on CombiFlash®200 auto-column system from Teledyne ISCO.

A. Synthesis of Spiropyran

Spiropyran was synthesized according to a previously reported procedure[1].



Scheme S1 - Synthetic scheme of spiropyran-diene.

2. **Molecular Characterizations:** Spiropyran was characterized on ^{1}H NMR spectra were collected on a 400 MHz Varian INOVA spectrometer and ^{13}C NMR spectra were collected on a 500 MHz Varian UNITY spectrometer.

3. **Tensile Testing**: Uniaxial tensile tests were performed on all specimens on a TA Instruments RSA III Dynamic Mechanical Analyzer (Force resolution: 1nm, strain resolution: 1nm) at Duke University's Shared Material Instrument Facility (SMIF). Composite materials were hand extruded. Dragon Skin films were cut to the approximate dimensions of the extruded material. To avoid slipping and to prevent force concentrating at clamp site, two pieces of thin PDMS film were placed between the specimen and clamp on both sides of the specimen.

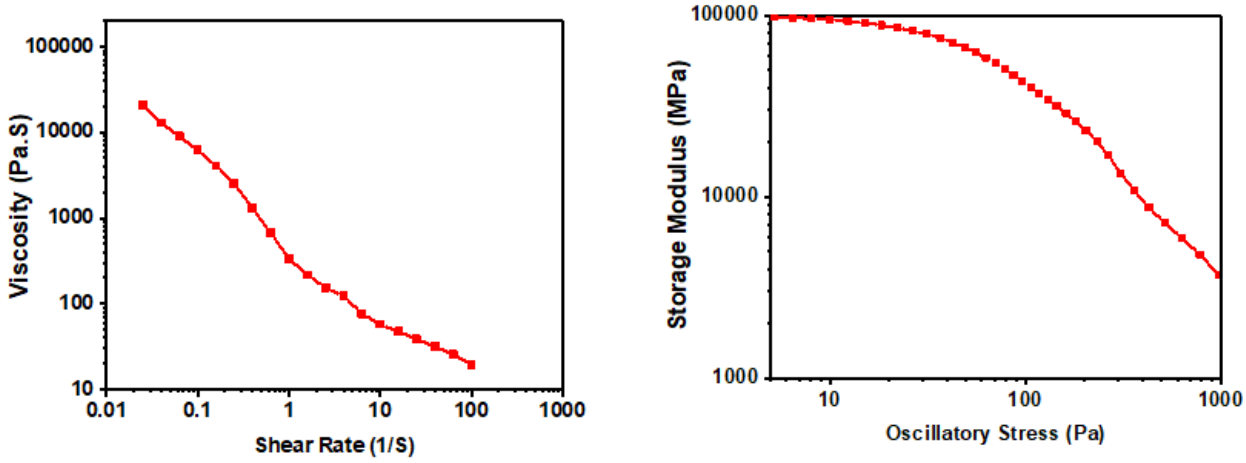


Fig. S1: Rheometrical characterization of mechanochromic ink (a) Viscosity versus shear rate experiment to demonstrate shear thinning nature of the ink. (b) Oscillatory stress ramp experiment demonstrating the yield stress behavior.

Determining Mechanochromic Onset:

We first attempted to determine SP activation by taking images with a Canon EOS Rebel XSi camera at random intervals during a continuous quasi-static uniaxial tensile experiment. The image was white balanced with a color card before being imported in Fiji/ImageJ. A region of interest (ROI) was selected and its approximate position was maintained across all images and color channels. The results from the experiment suggested strain-dependent diffraction (Figure - S1). This was confirmed by repeating the procedure in analyzing color onset in composite materials without SP (Figure – S2).

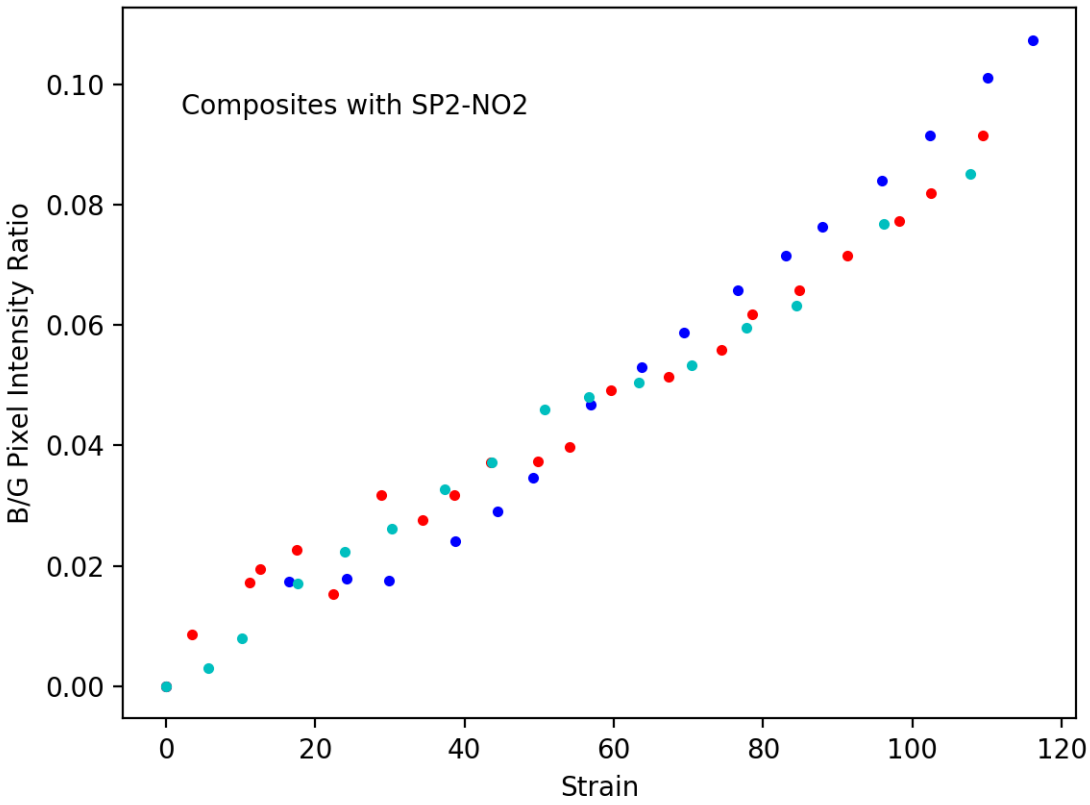


Fig. S2: Results from continuous uniaxial tension tensile experiment of extruded composite materials containing SP. The ratio of the intensities of the blue channel to the green channels are plotted above.

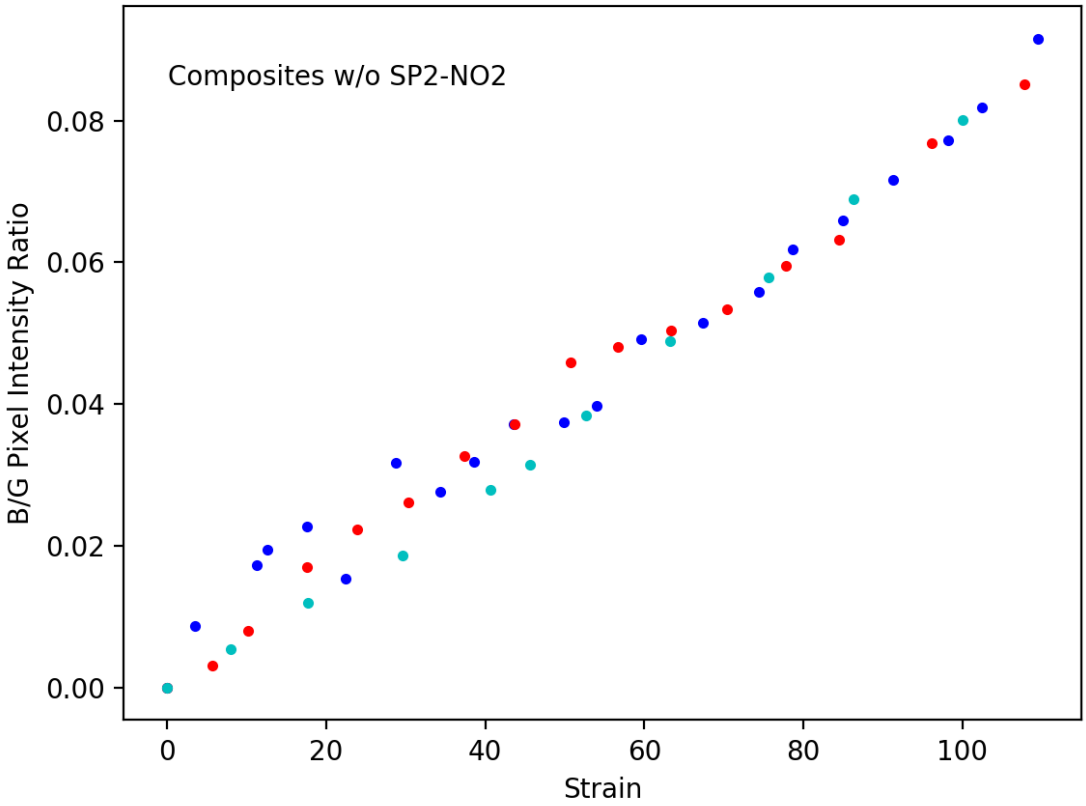


Figure S3: Three extruded composite material without mechanophore. Images were taken at random intervals during continuous quasi-static uniaxial tensile test.

"Zero-Percent" Strain Test:

The previously described experiment was modified to reduce diffraction interference. Instead of continuously straining the specimens until failure, the was stretched to the strain of interest and an image was captured with Canon EOS Rebel XSi. This image was used to confirm strains. The specimen was immediately returned to zero percent strain and another image was taken (Figures S3-S5) . An ROI was selected from the image taken at zero-percent strain and maintained across all color channels and zero strain images. Color ratios were measured from these ROIs with the method described above. The strains measured from the previous image correspond to the B/G measured in zero-strain image that followed (Figure S6). This modified experiment produced data more similar to previously measured mechanochromic onset data from our group[1-3].

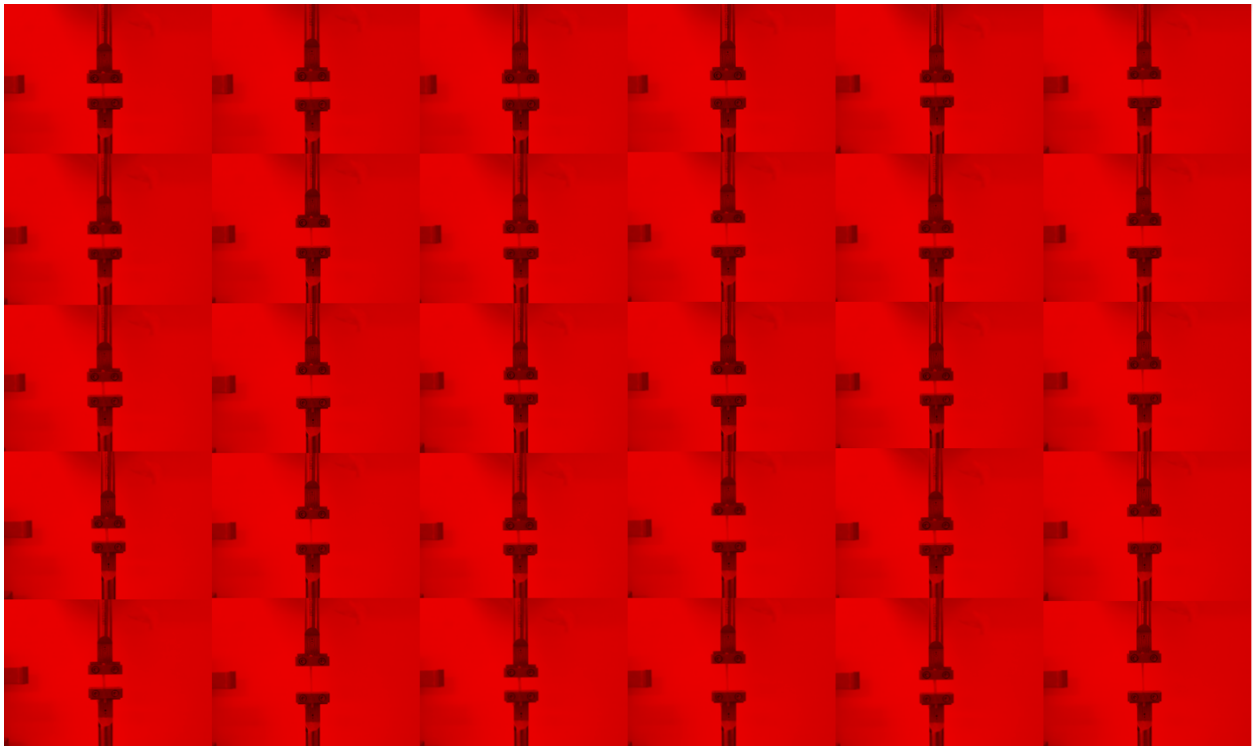


Figure S4: Representative image montage of extruded composite material during the zero-strain experiment in the red channel.

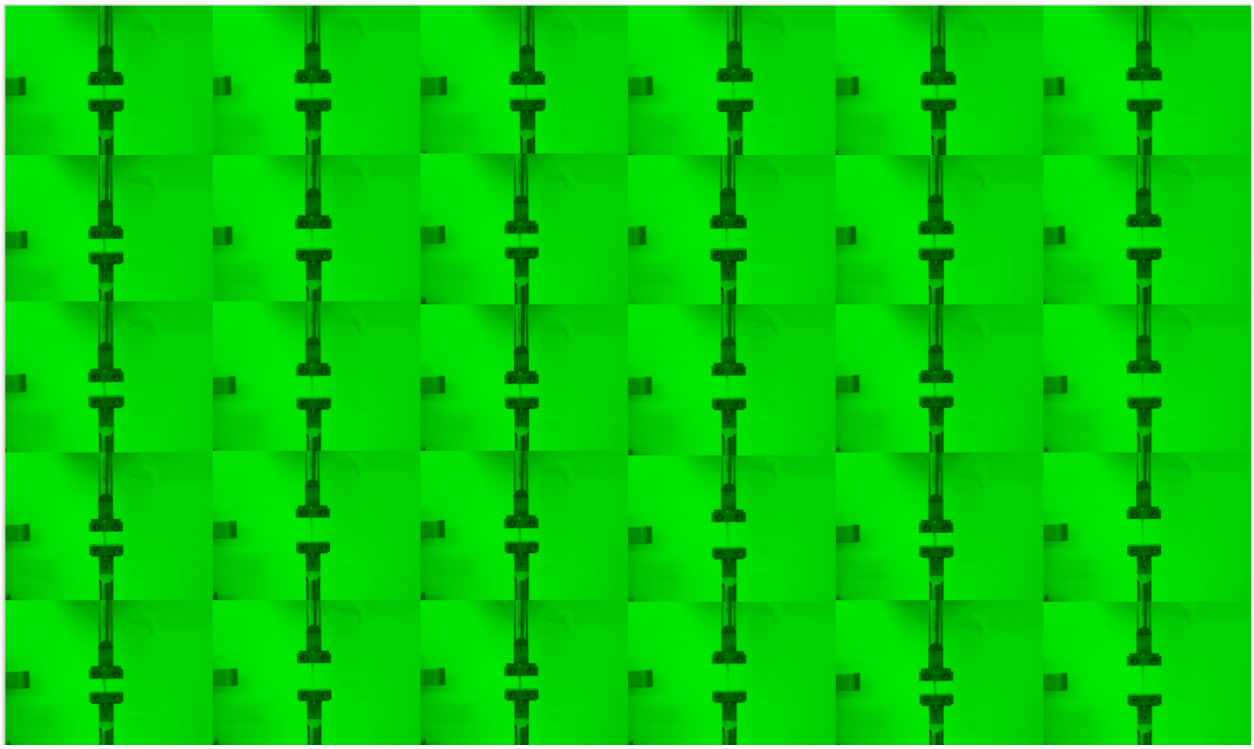


Figure S5: Representative image montage of extruded composite material during the zero-strain experiment in the green channel.

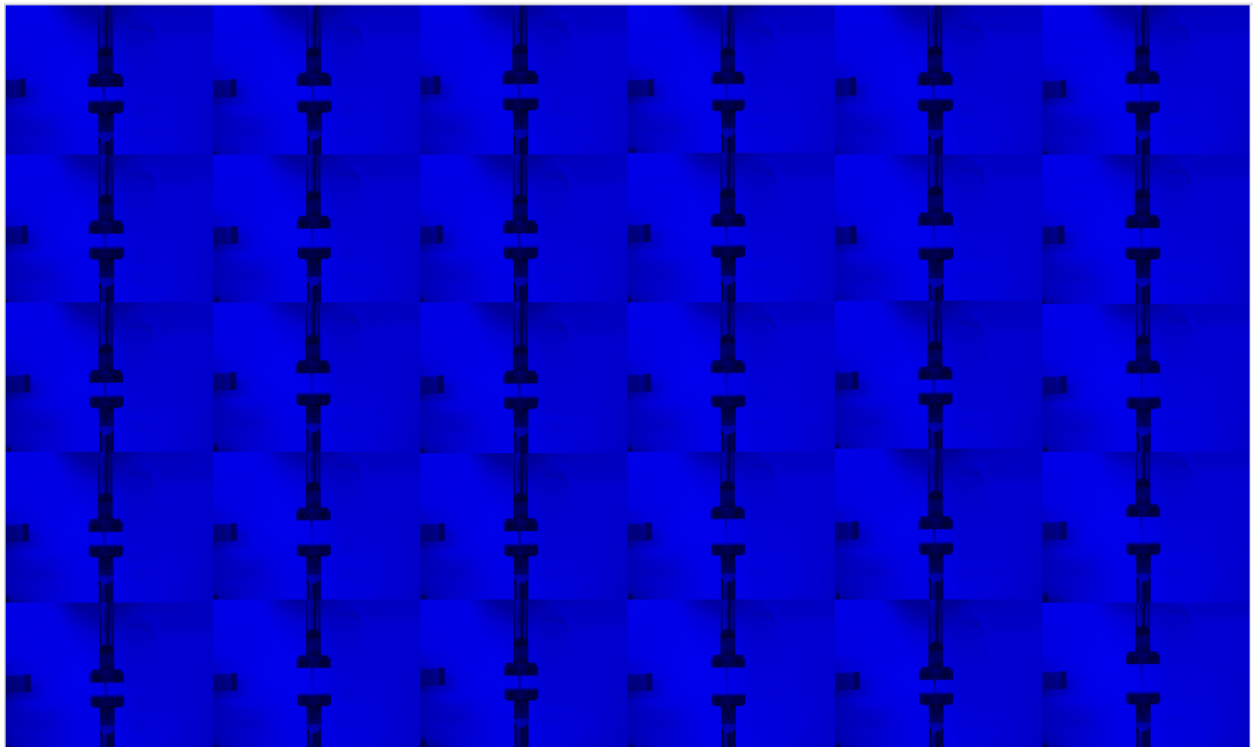


Figure S6: Representative image montage of extruded composite material during the zero-strain experiment in the blue channel.

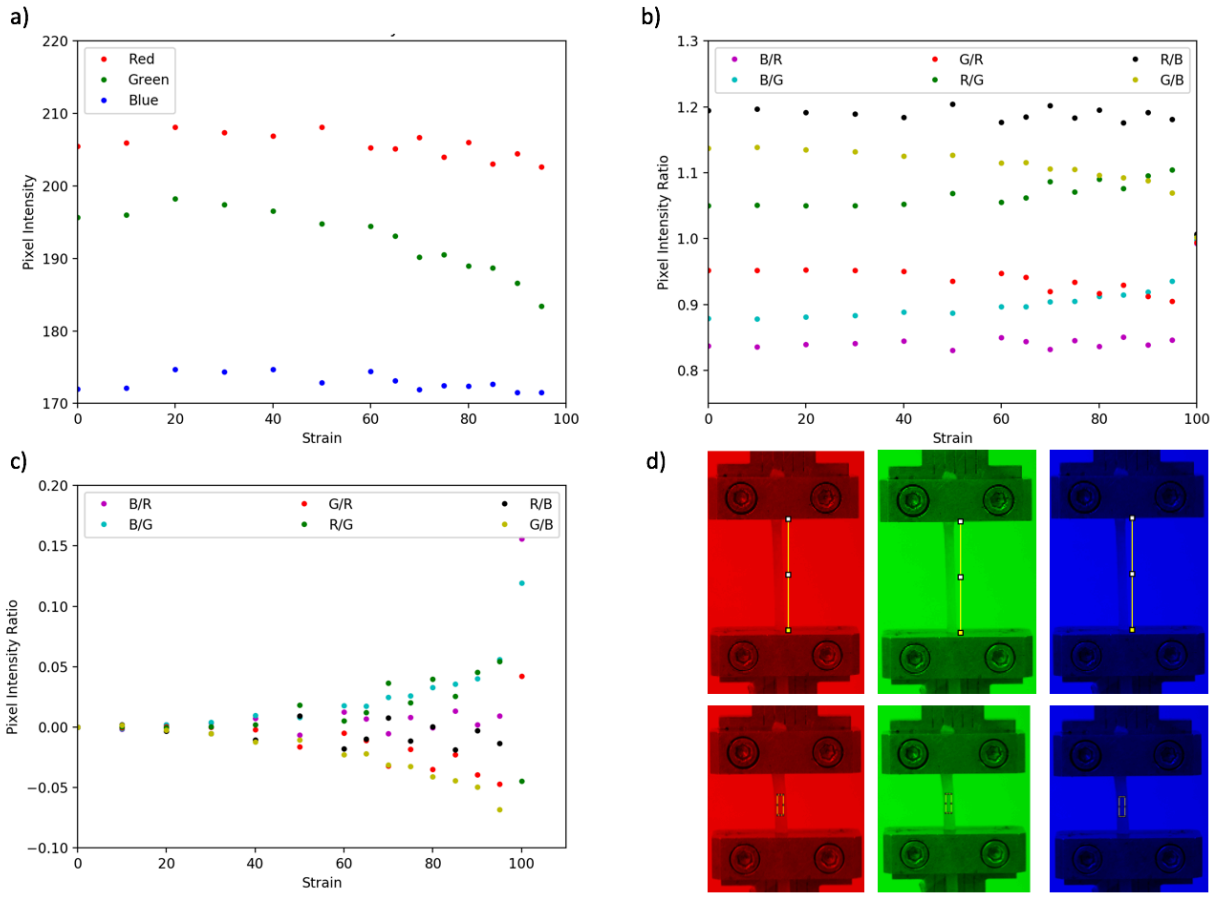


Figure S7: Change in channels as a function of strain. (a) Raw pixel intensities at red, green and blue channels; (b) All possible pixel intensity ratios; (c) All normalized pixel intensity ratios (e.g. $B/G_{ratio} - B/G_{initial}$) (d) Representative image of ImageJ analysis. Strains were determined by the pixel length of strained composite and intensities were taken from rectangular ROI of the corresponding zero-percent strain in red, green and blue channels.

Strain	*R*	*G*	*B*
0	205.486	195.646	172.022
10	205.941	196.006	172.102
20	208.120	198.212	174.683
30	207.357	197.388	174.338
40	206.895	196.572	174.726
50	208.119	194.753	172.857
60	205.262	194.451	174.427
65	205.148	193.104	173.129
70	206.671	190.164	171.927
75	204.000	190.520	172.435
80	206.005	188.973	172.391
85	203.040	188.728	172.685
90	204.423	186.591	171.529
95	202.624	183.400	171.520
100	226.180	224.928	224.562

Table S1: Representative red (R), green (G) and blue (B) pixel intensities at various strains.

Strain	*B/R*	*B/G*	*G/R*	*R/G*	*R/B*	*G/B*
0	0.837147	0.879251	0.952114	1.05029	1.19453	1.13733
10	0.835686	0.878045	0.951758	1.05069	1.19662	1.13889
20	0.839338	0.881294	0.952393	1.04999	1.19142	1.13470
30	0.840763	0.883225	0.951923	1.05050	1.18940	1.13221
40	0.844515	0.888865	0.950105	1.05252	1.18411	1.12503
50	0.830568	0.887570	0.935777	1.06863	1.20400	1.12667
60	0.849777	0.897023	0.947331	1.05560	1.17678	1.11480
65	0.843922	0.896558	0.941291	1.06237	1.18494	1.11538
70	0.831887	0.904099	0.920129	1.08680	1.20209	1.10607
75	0.845270	0.905076	0.933922	1.07075	1.18305	1.10488
80	0.836829	0.912252	0.917322	1.09013	1.19499	1.09619
85	0.850497	0.914994	0.929511	1.07583	1.17578	1.09290
90	0.839089	0.919278	0.912769	1.09557	1.19177	1.08781
95	0.846494	0.935224	0.905125	1.10482	1.18134	1.06926
100	0.992846	0.998373	0.994465	1.00557	1.00721	1.00163

Table S2: All pixel intensity ratios from representative specimen at various strains.

Strain	*D B/R*	*D B/G*	*D G/R*	*D R/G*	*D R/B*	*D G/B*
0	0.000000	0.000000	0.000000	0.00000	0.00000	0.00000
10	-0.001461	-0.001207	-0.000355	0.00039	0.00209	0.00156
20	0.002191	0.002042	0.000279	-0.00031	-0.00312	-0.00264
30	0.003615	0.003974	-0.000190	0.00021	-0.00514	-0.00512
40	0.007368	0.009614	-0.002008	0.00222	-0.01042	-0.01230
50	-0.006579	0.008319	-0.016336	0.01834	0.00946	-0.01066
60	0.012630	0.017772	-0.004783	0.00530	-0.01775	-0.02253
65	0.006775	0.017307	-0.010822	0.01208	-0.00959	-0.02195
70	-0.005260	0.024847	-0.031984	0.03651	0.00755	-0.03126
75	0.008123	0.025824	-0.018192	0.02046	-0.01148	-0.03245
80	-0.000318	0.033001	-0.034791	0.03983	0.00045	-0.04114
85	0.013350	0.035743	-0.022602	0.02554	-0.01875	-0.04443
90	0.001942	0.040027	-0.039344	0.04527	-0.00276	-0.04952
95	0.009347	0.055972	-0.046989	0.05453	-0.01319	-0.06807
100	0.155699	0.119122	0.042351	-0.04473	-0.18733	-0.13570

Table S3: All normalized pixel intensity ratio (e.g. $B/R_{ratio} – B/R_{initial}$) for a representative specimen.

Strain	*Test 1*	*Test 2*	*Test 3*	*Test 4*	*Test 5*	*Average*
0	0.00000	0.00000	0.00000	0.00000	0.00000	0.00000
10	-0.00121	0.00345	-0.00085	-0.00398	0.00057	-0.00040
20	0.00204	0.00228	-0.00222	-0.00010	-0.00200	0.00000
30	0.00397	0.00901	-0.00120	0.00064	-0.00154	0.00218
40	0.00961	0.00886	0.00304	0.00176	0.00008	0.00467
50	0.00832	0.01251	0.00522	0.00141	0.00242	0.00598
60	0.01777	0.01811	0.01452	0.00279	0.00155	0.01095
65	0.01731	0.02204	0.01875	0.01151	0.00597	0.01512
70	0.02485	0.02102	0.02191	0.01452	0.00538	0.01754
75	0.02582	0.03171	0.02664	0.01944	0.02747	0.02622
80	0.03300	0.03320	0.04799	0.02186	0.01465	0.03014
85	0.03574	0.03923	0.05015	0.02361	0.01955	0.03366
90	0.04003	0.04420	0.04697	0.02178	0.01855	0.03431

Table S4: Normalized B/G pixel intensity ratios for all tested specimens.

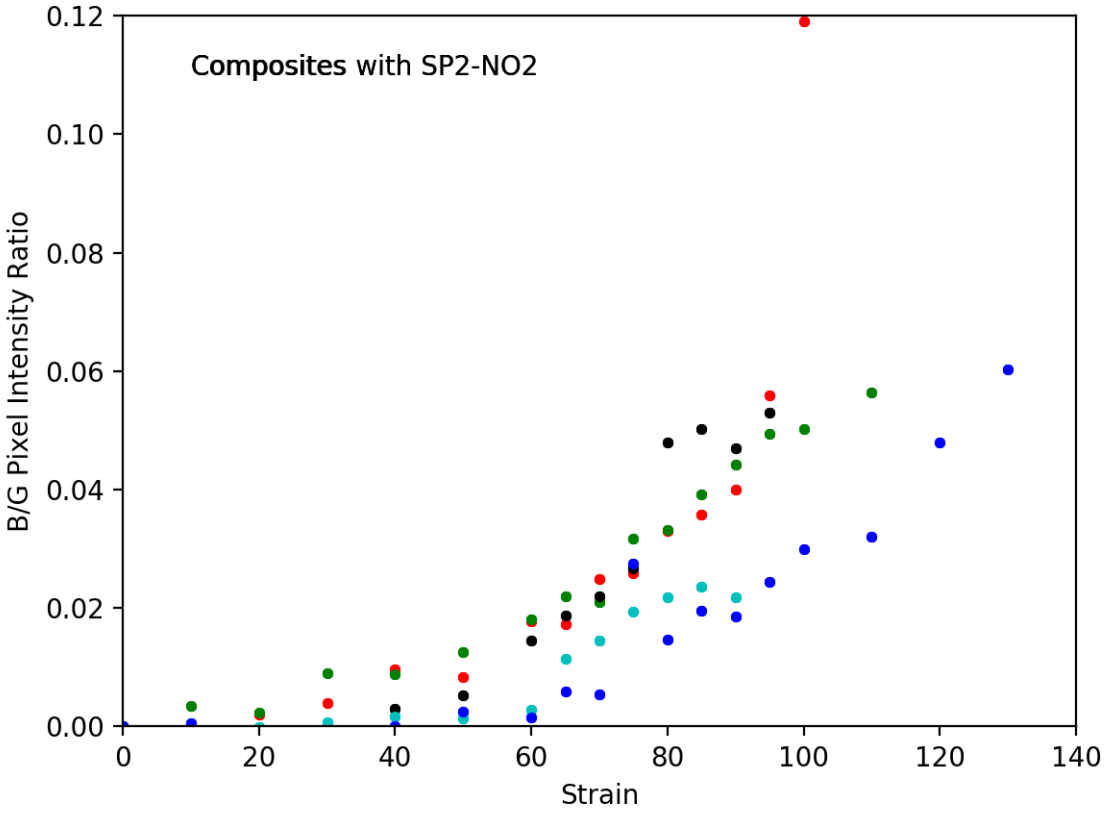
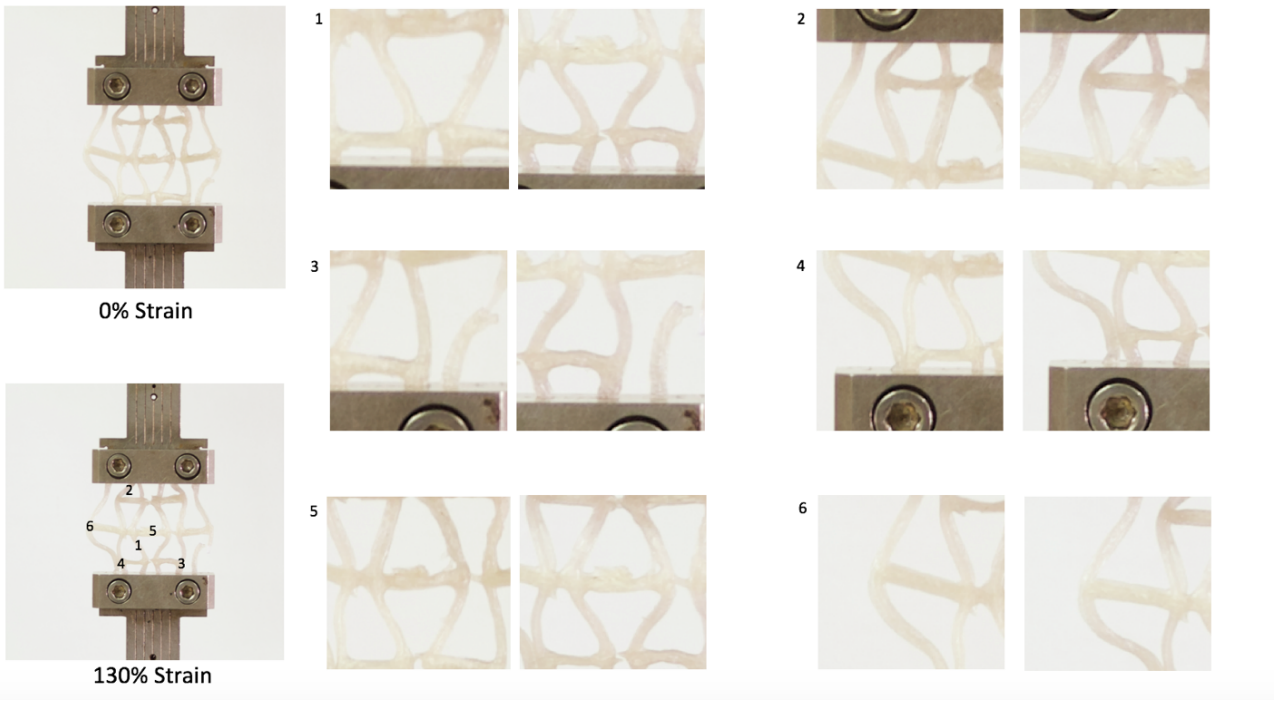


Figure S8: Figure of normalized B/G pixel intensity ratio for all tested specimens

a)



b)

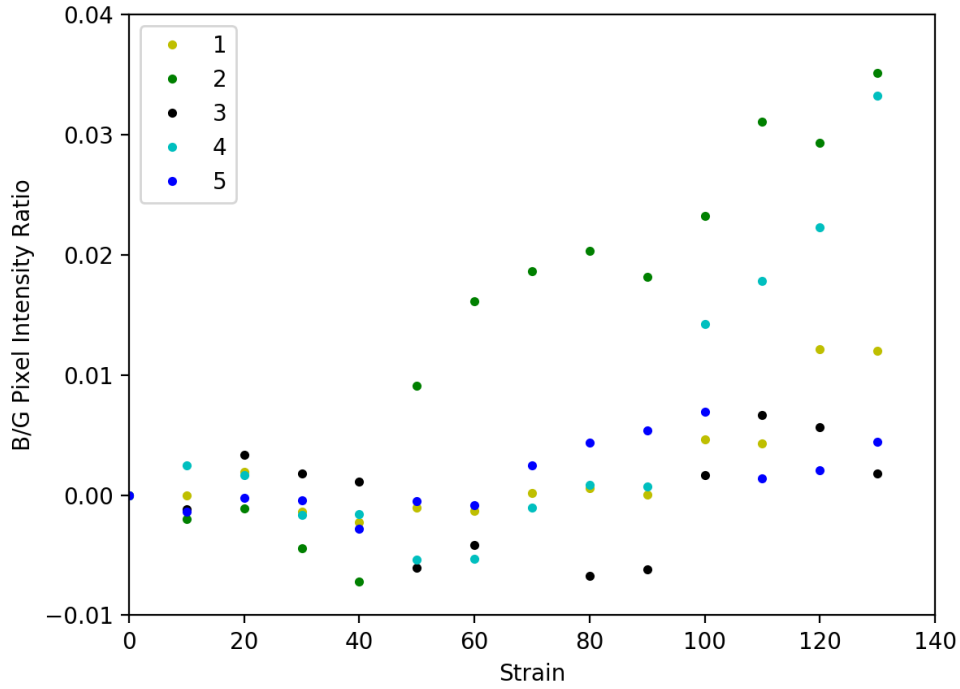


Fig. S9: 3D printed mesh like structures showing activation under tensile forces. **(a)** pictures of regionalized activation in mesh strucctures. **(b)** B/G Pinxel intensity Ratio of areas selected above. Mechanochromic activation appears to be most significant in areas close to the clamp.

1 M. H. Barbee, T. Kouznetsova, S. L. Barrett, G. R. Gossweiler, Y. Lin, S. K. Rastogi, W. J. Brittain and S. L. Craig, *J. Am. Chem. Soc.*, 2018, **140**, 12746–12750.