Cephalopod-Inspired High Dynamic Range Mechano-Imaging in Polymeric Materials

Jess M. Clough, Jasper van der Gucht, Thomas E. Kodger, and Joris Sprakel*

Cephalopods, such as squid, cuttlefish, and octopuses, use an array of responsive absorptive and photonic dermal structures to achieve rapid and reversible color changes for spectacular camouflage and signaling displays. Challenges remain in designing synthetic soft materials with similar multiple and dynamic responsivity for the development of optical sensors for the sensitive detection of mechanical stresses and strains. Here, a high dynamic range mechano-imaging (HDR-MI) polymeric material integrating physical and chemical mechanochromism is designed providing a continuous optical read-out of strain upon mechanical deformation. By combining a colloidal photonic array with a mechanically responsive dye, the material architecture significantly improves the mechanochromic sensitivity, which is moreover readily tuned, and expands the range of detectable strains and stresses at both microscopic and nanoscopic length scales. This multi-functional material is highlight by creating detailed HDR mechanographs of membrane deformation and around defects using a low-cost hyperspectral camera, which is found to be in excellent agreement with the results of finite element simulations. This multi-scale approach to mechano-sensing and -imaging provides a platform to develop mechanochromic composites with high sensitivity and high dynamic mechanical range.

1. Introduction

Stress and strain localization perform crucial roles in diverse processes across a wide range of fields, with both productive and destructive results. For instance, in nature, the metastasis of cancer cells is sensitive to local mechanical cues,[1] and pathogenetic fungi generate high local stresses in order to penetrate plant leaves.[2] In the field of polymeric materials, reinforced polymer composites derive their enhanced toughness from interfacial stress localization[3]; however, stress-concentrators in other situations can accelerate material failure - for example, microscale defects nucleate macroscale cracks. Such local mechanics often dictate how materials respond to deformation, yet remain difficult to study in detail by conventional bulk mechanical analysis. Optical mechano-sensing has emerged as a powerful tool for quantifying how such local phenomena govern the failure of polymeric materials and more broadly for monitoring bulk material integrity. Materials capable of revealing spatial distributions of stresses and strains by optical means incorporate structures which activate mechanically to produce distinctive optical signatures, such as color change (mechanochromism),[4–7] the onset of or change in fluorescence (mechanofluorochromism),[8–10] or the emission of a photon (mechanoluminescence).[11,12] The mechanisms resulting in this responsivity operate on length scales ranging from 10 µm to the molecular level, including periodicity changes in photonic elastomers and gels,[5,11,14] nanoparticle rearrangement in plasmonic materials,[15] disruption of aggregochromic dyes,[6,16] stretching of conjugated polymers,[10] and the scission of weak covalent bonds (as in mechanophores).[4,8,11,12] Compared to other mechanical detection methods, such as electrical read-outs,[17] optically based approaches offer excellent spectral, spatial, and temporal resolution. For example, molecular probes containing scissile covalent bonds where the weak bond of a mechanophore undergoes mechanically induced rupture, resulting in activation of a constructive function, such as the turn-on of fluorescence.[18] These probes offer key advantages that their incorporation has on a relatively small effect other properties of the material, and the synthetic ease with which they can be covalently incorporated.

However, this information can be lacking in key detail. The single mode of action of almost all covalent mechanophores is to switch “on” above a certain critical force threshold, producing unsatisfactory binary mechanographs. Furthermore, the force threshold, being dictated by scissile bond energy, is not amenable to chemical tuning and often the material has already sustained considerable permanent damage when the mechanophore activates,[18] although recent work has demonstrated that it is possible to lower the strain and stress of activation...
by incorporating stress-concentrators in the material, such as voids[19] or silica nanoparticles.[20] Mechanochromic photonic materials such as colloidal photonic elastomers are inherently more tunable and provide continuous mechano-sensing output, yielding grayscale mechanographs. However, such materials have limited dynamic range restricted to imaging only small strains, and cannot give any insights on the mechanical processes at molecular length scales, where mechanical damage initiates. Yet, in a real material, a single applied bulk strain produces a broad distribution of local strains and stresses, particularly in the vicinity of heterogeneities, where stresses are often orders of magnitude higher than in the bulk of the material.[3] A fully functioning mechano-sensor must be able to report the locations of stress or strain concentrations and the magnitudes of the stress or strain in a continuous or grayscale output, as well as the sub-critical conditions in the surrounding bulk material, thereby permitting a quantitative relation between the two.

Through natural evolution, many elegant and highly responsive display strategies combine multiple optical elements producing spectacular feats of coloration that are variously bewildering, attractive, deceptive, or informative to other animals, depending on the intended purpose.[21] For instance, cephalopods such as octopuses, squid, and cuttlefish have the ability to drastically and dynamically alter their appearance for camouflage and signaling thanks to an array of responsive dermal structures that modulate the animal’s appearance via two distinct mechanisms.[22–24] These structures include pigment-containing chromatophores in the uppermost layer of their skin, which absorb light of certain wavelengths; alongside these, there are structural color organs, iridophores, which reflect light of certain wavelengths by constructive or destructive interference. Scientists have been inspired by these biological coloration strategies to create electrically responsive polymeric materials for displays[25] and mechanochromic devices for encryption,[26] but these materials have not yet been utilized for mechanical localisation and are limited to visualising small strains or in an on/off binary fashion.

In this work, we present a high dynamic range mechano-imaging (HDR-MI) polymeric composite, which is able to report on a wide range of stresses and strains as a result of a multiscale mechano-sensing architecture. Comparable to the skin of a cephalopod, the material integrates two responsive pigment structures: one absorptive, indicating forces at the molecular level, and the other photonic (or structural), reporting on strain-induced changes at microscopic length scales. Specifically, the mechano-responsive absorptive structure is spiropyran, which contains a weak bond that reversibly opens under mechanical force resulting in the purple fluorophore, merocyanine,[4] and the mechanically-responsive structural component is a photonic colloidal array, which undergoes deformation-induced shifts in its photonic bandgap. The two mechanochromisms dovetail in strain, the photonic array responding to lower strains and spiropyran to greater strains, affording a reversible high dynamic range mechanochromatic (HDR-MI) material. Our control over the structure of the photonic elastomer grants enables further tuning of the strain sensitivity of the material, which can be further enhanced by the photochromic properties of the spiropyran. Furthermore, by combining mechanical testing of our sensors with finite element simulations, we demonstrate that the dual mechanochromic responsivity of the material records high local stresses around a defect and directly relates them to the local strain fields.

2. Results and Discussion

2.1. Material Design

The remarkable combination of absorptive and structural coloration enables cephalopods to achieve their impressive repertoire of optical effects. The chromatophores have a central, flexible sac, containing yellow, red, or brown pigment, which expands or shrinks in area as the muscles attached to its periphery contract or relax. From a retracted size of 0.1 mm, the sacs can expand 10–20 times in diameter; the concerted action of thousands of chromatophores dramatically reveals the color of the pigment sacs, often in intricate patterns.[27] Below the chromatophores, there are iridophores, which are formed from aligned arrays of thin, colorless platelets that have a higher refractive index than the medium in between them, generating color from thin-film interference that the animal can control by varying the distance between the platelets.[28] These two coloration strategies are frequently deployed in a concerted fashion: for example, by using the absorptively colored chromatophore layer as a dynamic filter to modulate the color reflected by the structurally colored iridophores below.[27,28]

Our high dynamic range mechano-imaging (HDR-MI) elastomer mimics this highly functional, dual mode coloration strategy by integrating two responsive, pigmentary structures: one absorptive, the other photonic (Figure 1). The absorptive, responsive constituent is a silicone elastomer containing spiropyran (SP), a mechanochemically active group or mechanophore, that is coupled covalently into the elastomer as a cross-linker. The spiropyran is initially colorless, but at sufficiently large deformations of the material, the macroscopic forces on the polymer transfer to the spiropyran groups, transforming them to purple-colored and fluorescent merocyanine (MC) via scission of the weak, spiro C–O bond. Underneath, there is a photonic, non-close packed array of rigid, silica particles set in a flexible, poly(ethylene glycol) (PEG)-based elastomeric matrix, which undergoes deformation-induced changes to the periodicity of the array of silica particles, altering the position of the photonic bandgap of the material. The most important feature of this composite dual mechanismochromic design is the complementarity of the two mechanoresponsivities: the photonic array provides a continuous colorimetric response at lower strains (0–80%) while spiropyran activates at higher strains (>80%), revealing the sites of high stress concentration. Overlaying the two permits the two mechanochromic read-outs to be monitored simultaneously; alternatively, the fluorescence signal of merocyanine offers the possibility to track the two strain regions in separate optical channels. While some mechanochromic hydrogels have recently been reported with large strain-sensing ranges,[29,30] such materials tend to be soft or may have other limitations, such as a dependence of the optical response on the sample dimensions. Furthermore, the chemical mechanophore in the HDR-MI system provides a snapshot of the molecular level stresses in the material.

To make the photonic array of the HDR-MI material, silica particles (200 or 250 nm in diameter, <10% polydispersity by DLS
or SEM, Figure S2, Supporting Information) are dispersed in a liquid precursor to the elastomer, poly(ethylene glycol) phenyl ether acrylate (PEGPEA), together with a small amount of cross-linker and photo-initiator (see Experimental Section). PEGPEA is chosen to provide enhanced refractive index contrast between silica \((n = 1.45 – 1.46)\) and the matrix (PEGPEA, \(n = 1.50)\). The PEG chains bound to the surface of the silica particles, coupled with the surface charge of the particles, provide the electrosteric stabilisation which allows the particles to crystallize into a non-closed packed array above a certain critical volume fraction of silica (20 vol%).\(^5,13,31\) These films can be stretched to high extensional strains, relative to other photonic polymeric materials such as mechanochromic gels or inverse opals,\(^32\) and in a reversible manner. Separately, spiropyran cross-linker is incorporated in a PDMS elastomer (see Experimental Section and Supporting Information); the spiropyran is functionalized with two alkene groups, which allow it to be covalently coupled into the PDMS network via hydrosilylation.\(^{33–36}\) The photonic film is then positioned on top of the cured spiropyran-PDMS. To reduce diffuse scattering from the photonic film which makes the color appear pale, a separately cured film of PDMS containing 5 wt% carbon black nanoparticles is placed on top of the photonic film; alternatively, 0.5 wt% carbon black nanoparticles can be added to the PEGPEA/silica pre-polymer mixture prior to photo-curing. Sylgard 184 pre-polymer mixture, without spiropyran or carbon black, is then poured on top and cured, encapsulating the photonic film entirely in PDMS elastomer. The PEGPEA matrix adheres to PDMS, remaining flat against the PDMS during the final curing step. The two components also have similar Young’s moduli, in the range of 0.5–1 MPa.\(^5,37\)

The striking multiple mechano- and photo-responsivities of the HDR-MI elastomers are readily observed by eye. Exposing the films briefly (5 s) to UV light converts the spiropyran groups to merocyanine photochemically, generating an intense purple coloration that acts as a color filter for the photonic array as it is stretched or indented. The photo-responsivity of the spiropyran and the mechaioresponsivity of the photonic array are essentially orthogonal in this situation, as the mechanochromic spiropyran-merocyanine conversion is undetectable when the spiropyran has already been activated photochemically. In parallel, the photonic array and spiropyran also produce distinct responses to mechanical deformation. For example, on approaching an indentation site, the reflected light from the photonic array blue-shifts, as the thickness of the film perpendicular to the axis of the applied strain is reduced, as described in the Poisson relation, and the periodicity of the array is decreased. Where the stress is most concentrated, the second mechanochromism comes into play: spiropyran converts to merocyanine, as indicated by the strong purple coloration there, demonstrating that the two mechanochromisms work in tandem to provide a high dynamic range mechano-imaging system. Ultimately, the transformations of both mechanochromic motifs are reversible: the photonic array relaxes back immediately by eye, while the merocyanine switches back to spiropyran within 30 min, permitting the mechanoactivated area to be characterized post mortem (following removal of the deformation).

2.2. Orthogonal Photo- and Mechaioresponsivity

The color-filtering effect of the merocyanine when photo-activated can be used to tailor the mechaioresponsivity of the HDR-MI material, as demonstrated in Figure 2. To quantify the orthogonal photo- and mechaioresponses, the HDR-MI
material was indented and the spectral output recorded with a reflectance spectrometer (force-indentation depth data, Figure S4, Supporting Information). Figure 2A,B show the spectra of light reflected from the photonic array when under either spiropyran or photo-activated merocyanine, respectively. The effect on the mechanoresponsivity of the HDR-MI material is quantified in Figure 2D. In Figure 2A, the wavelength of peak intensity reflected from the photonic array decreases approximately linearly over the measured range, shifting from deep red to green-yellow, with increasing normalized indentation depth, \( h = d/t \) where \( t = \) sample thickness and \( d = \) indentation depth. Throughout this experiment, the strains are insufficient to activate the spiropyran groups mechanochemically, so no color-filtering is observed. The intensity of the photonic reflection also decreases gradually as the film is indented, which has been attributed to a reduction in refractive index contrast upon compression.[5]

Following a brief exposure of the material to UV light, the material gains an intense purple coloration from merocyanine. Repeating the same indentation experiment as in Figure 2A under spiropyran or photo-activated merocyanine respectively, the effect on the mechanoresponsivity of the HDR-MI material is quantified in Figure 2D. In Figure 2A, the wavelength of peak intensity reflected from the photonic array decreases approximately linearly over the measured range, shifting from deep red to green-yellow, with increasing normalized indentation depth, \( h = d/t \) where \( t = \) sample thickness and \( d = \) indentation depth. Throughout this experiment, the strains are insufficient to activate the spiropyran groups mechanochemically, so no color-filtering is observed. The intensity of the photonic reflection also decreases gradually as the film is indented, which has been attributed to a reduction in refractive index contrast upon compression.[5]

Following a brief exposure of the material to UV light, the material gains an intense purple coloration from merocyanine. Repeating the same indentation experiment as in Figure 2A on this photo-activated material gives a very different set of spectra, shown in Figure 2B. The spectra in Figure 2B undergo a blue-shift in the position of the peak photonic wavelength, but more remarkably, the intensity of the photonic reflection decreases sharply to zero at \( h = 0.6 \), with an intensity drop-off \( (\Delta I/\Delta h) \) 1.6 times as steep as under unactivated spiropyran. At this level of deformation, the photonic array would reflect in the green-yellow part of the visible spectrum; however, the merocyanine absorbs this light strongly, preventing incident light with those wavelengths from reaching the photonic array. In this photo-activated mode, the material is a highly sensitive, tunable threshold mechano-sensor: the photonic reflection read-out switches off at a well-defined strain, which can furthermore be selected as desired by altering the colloidal volume fraction of the photonic array. Increasing the volume fraction of silica from 35 vol% as in the material indented in Figure 2A,B, to 40 vol% shifts the critical threshold for switching “off” the photonic reflection to considerably lower strains, \( h = 0.2 \). The intensity also decreases to essentially zero at this point, while a sample with the same colloidal fraction under spiropyran continues to display a photonic reflection even at much greater indentation depths (Figure S5, Supporting Information); \( \Delta I/\Delta h \) increased by factor of 1.4, similar to the 35 vol% sample. At zero

**Figure 2.** Absorptive filtering: photo-activation of spiropyran alters the apparent mechanical response of the photonic array to indentation with a plate (silicon wafer), which provides uniform deformation over an area \( \approx 5 \times 5 \) mm. A) Under spiropyran, the reflectance spectra shift to shorter wavelengths as the periodicity of the photonic elastomer (35 vol% silica) decreases with increasing indentation depth, \( h \). B) Under photo-activated merocyanine, the reflectance spectra undergo a similar shift in wavelength, but the intensity of the reflectance signal also drops to zero. C) Increasing the colloidal density of the photonic elastomer to 40 vol% silica, the intensity of the reflectance peak from the photonic array drops to zero after a smaller blue-shift. D) The mechano-sensor is made sensitive to particular strain ranges by varying the colloidal volume fraction of the photonic elastomer: 40 vol% silica under photo-activated merocyanine (filled triangles); 35 vol% silica under photo-activated merocyanine (filled circles); 35 vol% silica under unactivated spiropyran (open squares). All reflectance spectra corrected against PTFE as a white control.
strain, a photonic array with a greater colloidal volume fraction reflects light at shorter wavelengths, closer to the absorption maximum of the merocyanine: the threshold for this absorptive switch is therefore readily tuneable in a predictable fashion.

2.3. Parallel Mechanoresponsivity

Spiropyran also responds to mechanical deformation, which when combined with the photonic array grants parallel, complementary mechanoresponsivity. To gain spatial information, we use a hyperspectral camera, which records a spectrum in every pixel of the image (FWHM 10 nm), in contrast to the spatial average of the spectral reflectometer. Every single pixel in the mechanograph contains a spectrum of light reflected from the photonic array, minus the light absorbed by the merocyanine, taken under a white light source. The fluorescence emission from the merocyanine under green light excitation (peak 525 nm) can also be used for greatly improved sensitivity in monitoring the spiropyran to merocyanine conversion, given here at a single wavelength (650 or 680 nm).[35]

Figure 3A,B show a typical series of mechanographs obtained upon indenting the HDR-MI material with a steel sphere from below, while imaging the material’s response through a glass plate from above (force-indentation depth data, Figure S6, Supporting Information). In the direction along which the sample is imaged (z-axis), the colloidal close-packed planes in the photonic array are compressed together as the sample is further compressed.

![Mechanograph of HDR-MI material](image)

**Figure 3.** Indentation of HDR-MI material with a steel sphere (diameter 1 mm). Photonic array contains silica colloids, diameter 250 nm at 40 vol%.
A) Local strain in z-direction, εz, at smaller normalized indentation depths, h, from photonic array response (recorded under white light). Scale-bar 4 mm.
B) Spiropyran to merocyanine mechanooactivation at greater h over same indentation site (fluorescence intensity at 650 nm, excitation with green light).
C) Fraction of indented area with a photonic reflection in one of four εz bands: 0.05–0.08 (red squares); 0.11–0.15 (orange squares); 0.18–0.22 (green squares); 0.25–0.29 (teal squares). Total mechanooactivated merocyanine fluorescence intensity over indentation area (purple squares).
D) Spectra in individual pixels marked with crosses along a white bar corresponding to a length of 4 mm in the mechanograph taken at h = 0.17; each pixel of the mechanograph is color-coded according to the wavelength of peak intensity in these spectra.
E) Local εz across the indentation site, marked with a white stripe in the mechanograph at h = 0.17. Contact area of the indenting sphere at this h indicated by gray shading.
F) The merocyanine fluorescence intensity along a line across the indentation site, as shown by a white bar corresponding to a length of 4 mm in the mechanograph at h = 0.9.
The photonic array in the HDR-MI material in Figure 3 has a maximum dynamic range of \( a = 150 \) nm, from 650 to 500 nm (red to blue-green), dictated by the silica volume fraction of the photonic elastomer (40 vol%). At the central point, the photonic array reaches this maximum blue-shift at a normalized indentation depth of \( h = 0.3 \) (Figure S7, Supporting Information). At even greater \( h \), the area reporting the maximum \( \varepsilon_z \) value of the photonic array continues to increase, as shown in the graph Figure 3C. These plots show how the area of the indentation site with a value of \( \varepsilon_z \) within a particular \( \varepsilon_z \)-range changes with indentation depth: the proportion of the indentation area indicating higher local \( \varepsilon_z \) peaks at progressively greater indentation depths. Spiropyran mechanoactivates in a similar fashion to the photonic array, first at the center of the indentation site, with activation spreading radially outward at progressively greater \( h \) as a greater proportion of the area experiences a stress that is equal to or greater than the critical threshold value (Figure 3B,F).

In Figure 3C, the sum of the activated fluorescence intensity at 650 nm becomes detectable at \( h = 0.7 \), and increases sharply after an initial induction period. As can be seen from Figure 3C, the two mechanochromic responses dovetail in this representation, as the photonic array ceases to respond to the increasing applied strain just as the spiropyran begins to activate mechanochromically. The HDR-MI material provides a mechanochromic read-out of the local stresses and strains in the material across the full range in \( h \), up to material failure.

### 2.4. HDR Mechano-Imaging of Defects

In polymeric materials, damage at the macroscopic level must initiate from defects on microscopic or even nanoscopic length scales as a result of stress and strain amplification around those defects.\(^{[40-42]}\) HDR mechano-imaging can allow the complex strain and stress distributions around such defects to be visualized and probed in greater detail than before, as demonstrated in Figure 4 for an idealized defect: a circular hole cut in a material. When placed under uniaxial tension, the material around the hole is under-strained with respect to the bulk in lobes adjacent to the hole along the axis perpendicular to the axis of applied
strain, and conversely over-strained with respect to the bulk, in lobes adjacent to the hole along the axis of applied strain. The two responsive pigmented structures of the HDR-MI material provide complementary insights on the predicted stress and strain distributions. The photonic array displays regions of under-strain and over-strain as red-shifted and blue-shifted respectively with respect to the bulk: the close-packed layers of colloids are progressively compressed together with increasing strain in the direction along which the sample is imaged (z-axis). Moreover, by performing a simple calibration experiment relating the applied tensile strain $\varepsilon_x$ to the wavelength shift, the spectra in every pixel of these mechanographs can be converted to local values of $\varepsilon_x$ (Figure 4B, calibration Figure S9, Supporting Information), which are further supported by the results of finite element simulations (Figure 4A). However, by a bulk strain of 0.3, the limited dynamic mechano-imaging range of the photonic array alone is already becoming apparent: the over-strained lobes become progressively more difficult to distinguish from the bulk at bulk strains of 0.3 and above.

The higher strains are instead addressed with spiropyran, which also reveals the distinctive stress profile around the hole. Spiropyran activates to merocyanine at the sites of greatest stress concentration close to the hole along the axis of applied strain, as seen from the lobes of increased fluorescence intensity with respect to the bulk signal away from the hole. As under indentation, the photonic array and spiropyran respond to distinct extents of deformation under tension. After returning to zero strain, the merocyanine fluorescence in these high stress lobes remains visible for approximately an hour, as the back conversion of merocyanine to colorless spiropyran is slow in the polymeric matrix, requiring approximately an hour for the color to disappear by eye under white light. The local strain values and merocyanine fluorescence intensities along an ellipse at a constant distance from the edge of the hole are plotted for the different applied bulk strains in Figure 4C.

### 2.5. HDR Mechanographs

To demonstrate that the extended mechanical visualisation range of the HDR-MI material is broadly applicable to different mechanical situations, we apply it to membrane indentation (Figure 5), in which the material is clamped along its periphery and indented from below while imaging from above. Thin, elastic films spanning large areas are found in diverse engineering contexts, in which they are expected to resist puncture: for example, when stones become embedded in tyres, or needles come into contact with protective gloves. Additionally, membrane indentation in biology has served as a model system for seed germination.[43] These mechanical situations present a wide range of local stresses and strains: The positive curvature in the part of the membrane in contact with the indenter promotes stretching of the membrane, leading to high local tensile strains, facilitating the mechanoactivation of spiropyran to merocyanine; close to the clamped edges, the strains and stresses are close to zero.[43,44] Indenting the HDR-MI material with a sphere, a single indentation depth invokes the full dynamic mechanical range of the HDR-MI material. The responses of the photonic array and spiropyran to the deformation are recorded consecutively (Figure 5A,B, respectively), then combined to make the high dynamic range mechanograph (Figure 5C). At low strains, the pixels are colored according to the wavelength reflected most strongly from the photonic array (Figure 5A); where the local strain exceeds the dynamic range of the photonic array, the pixels contain instead fluorescence intensity information from the mechanoactivation of merocyanine. The HDR mechanograph is analogous to a HDR photograph composed of two photographs taken with different exposure times (Figure 5C): one at a longer exposure time to image the regions of low light intensity (shadows) and the second at a shorter exposure time to capture regions of greater light intensity (highlights). The HDR mechanograph demonstrates that the part of the membrane in contact with the indenter becomes strongly fluorescent upon spiropyran activation, while the film close to the edges remains relatively unstrained, as indicated by the red-orange color of the photonic array. The sharp decrease in strain from the central top part down the free sides of the membrane is clearly visualized in rings of photonic color in the HDR mechanograph (Figure 5C), and in the steep slope of peak wavelength versus position in profiles across the indentation site (Figure 5D).

![Figure 5](image-url)
2.6. Conclusions

This study demonstrates that the multiscale architecture in photonic-absorptive mechanochromic composites offers both expanded dynamic mechano-sensing range and tunable mechano-sensitivity. General design principles emerge from the absorptive filtering experiments: at an optimum spectral separation of the photonic reflection at zero strain and the absorption of the mechanochemical dye, both strain sensitivity (the smallest detectable strain) and signal sensitivity (as defined by signal-to-noise ratio) are achieved. In chemically mechanochromic materials, the onset of mechanochromism is limited by the ability of polymer chains to reach their maximum extensions, and in physically mechanochromic materials the maximum visualizable strain is constrained by, for example, the minimum separation distance between colloidal layers. By contrast, the multiscale architecture of the photonic-absorptive composite structure in this study simultaneously reduces the onset for mechanochromism and expands the dynamic mechano-sensing range, whilst retaining the mechanical properties of the matrix. In situations where the distribution of local strains was especially wide, as in membrane indentation, the photonic-absorptive architecture reported on a wide range of local strains from the site of puncture to the clamped edges in a continuous, grayscale fashion at the same bulk indentation depth, leading to the creation of a HDR mechanograph, the first to our knowledge. This advance will allow us to probe a much broader range of strain conditions with mechanochromism, from very small to large deformations, as well as provide intriguing insights on the process of mechanotransduction, by which force is transferred from the macroscopic to microscopic and nanoscopic length scales. We envision that this system or similar materials could also find application as laminate mechano-reporters for a wider range of polymeric materials, moreover, while the work here has focused on tension and indentation, other modes of mechanical deformation, such as shear, perhaps could conceivably be imaged with these materials. Future developments of an even more deformable photonic array with a wider dynamic mechanical range, as well as a mechanochemical component responsive to smaller forces such as a supramolecular mechanophore, would enable the creation of more detailed mechanographs, with both local stress and strain information in a single deformation state. In addition, the underlying principles of this multi-scale approach are readily transferred to other types of matrices; developing dispersible spheres or fibres of HDR-MI material which can be incorporated in other polymeric or even biological matrices would undoubtedly extend its applicability, not only in the context of structural integrity monitoring, but to electronic inks and biodiagnostics.

3. Experimental Section

Preparation of Photonic Mechanochromic Films: Monodisperse silica particles were obtained from Angstrom spheres (diameter 100 and 250 nm). Where necessary, 100 nm particles were used as seeds for the Stöber method to generate particles with larger diameters. In an example of a seeded Stöber reaction to generate particles 210 nm in diameter by DLS, 2 mL of a 50 mg mL$^{-1}$ dispersion of silica seed colloids was mixed with 30 mL ethanol, 7 mL water, and 1 mL 28–30% ammonium hydroxide, then 1.4 mL TEOS was added at a rate of 0.8 mL/h while stirring at room temperature. Following TEOS addition, the dispersion was stirred at room temperature for a further 60 min, then the colloids were washed with ethanol and dried at 70°C for 18 h. The dry, silica powders were dispersed in ethanol at a concentration of 50 mg mL$^{-1}$ with sonication (Qsonica500, 1 h pulsed protocol 1 s on and 1 s off, with ice cooling, 50% maximum amplitude, 500 W, 20 kHz). The silica dispersion was then mixed with poly(ethylene glycol) phenyl ether acrylate, PEGPEA (Mn 324, Sigma-Aldrich) containing 1 w w% photoinitiator of 2-hydroxy-2-methyl-1-phenyl-1-propanone and 1 mol% poly(ethylene glycol) diacrylate, PEGDA (Mn 575, Sigma-Aldrich), where the amount of PEGPEA is determined from the weight of silica powder necessary for a target volume fraction of silica particles once the ethanol is removed; the densities of silica particles and PEGPEA were approximated as 2.0 and 1.127 g mL$^{-1}$, respectively (densities provided by suppliers). For example, 0.18 mL PEGPEA mixture was added to 4.7 mL of the ethanolic silica dispersion, to give a final volume fraction of silica of 0.4 following the removal of ethanol. Where necessary, 0.1 mL of a 1 w w% dispersion of carbon black nanoparticles in ethanol was added to the PEGPEA-based mixture. Ethanol was removed under a gentle flow of air to produce a somewhat iridescent dispersion of silica in PEGPEA (with photo-initiator); this protocol has been adapted from literature. A few drops (50–100 μL) of the dispersion was placed on a clean glass slide, and a second glass slide placed on top, with the two slides held apart by Parafilm spacers (thickness 130 μm). The high degree of ordering is evidenced by the color and slight iridescence even in the fluid state. The dispersion was irradiated by UV light (Omninicure LX300, maximum intensity 8 W cm$^{-2}$) for 5 min. The polymerized photonic film was released carefully from the glass slides with a blade.

Fabrication of Dually Mechanochromic Films: The photonic film was placed on top of the spiropyran-PDMS where the photonic film does not already contain carbon black nanoparticles, a pre-cured film of PDMS containing 5 wt% carbon black nanoparticles, large enough to cover the photonic film, is placed on top of the photonic film. The weight of the spiropyran-PDMS and photonic film were on a glass slide, this slide was placed in a petri dish and covered with 10 g Sylgard 184 prepolymer mixture (10:1 base:curing agent) that had been centrifuged to remove air bubbles was poured over the top; where the spiropyran-PDMS and photonic film were already in a petri dish, 10 g Sylgard prepolymer mixture was directly poured on top. The PDMS was further degassed under vacuum in a desiccator to remove air bubbles, and cured at 70°C under vacuum for 18 h, producing layers 0.2 mm in thickness.
Hyperspectral Imaging: Samples undergoing indentation or tensile testing were illuminated with either a broadband white LED (Thorlabs MCWHL5) or a green LED (Thorlabs LIU525B). The reflected light was recorded on a hyperspectral camera consisting of a Kurios liquid-crystal tunable band-pass filter mounted onto an Andor Zyla 5.5 sCMOS camera. The tunable band-pass filter can be tuned to wavelengths in the range of 420–730 nm. Triggering between camera and tunable band-pass filter enabled sequential acquisition of image stacks, in which every frame in the stack corresponds to the image taken at a different wavelength, at typical exposure times of 20–100 ms per frame, at 10 fps, giving a total acquisition time for each hyperspectral image stack of ~30 s. The obtained spectra were corrected against Teflon as a white standard using MATLAB. To visualize the fluorescence of spiropyran, the sample was illuminated with a green LED (Thorlabs LIU525B), and the intensity of the fluorescence recorded at 650 or 680 nm.

Mechanical Characterization: For indentation, the translation stage (Thorlabs MTS500/M-28) was connected to a control box (C-663.12 Mercury Step Stepper MotorController) that was controlled on a computer with Kinesis software. A load sensor (Futek FSH03871, 250-lb limit) measures the forces upon indentation, which are read out via an analog amplifier (SG-3016, ICP DAS) connected to a computer via a digital acquisition device (USB-6001, National Instruments). The load cell was sampled every millisecond, and an average was taken over a thousand samplings. The filtered voltage signal was then converted to the measured force, after calibration with standard weights.

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

Acknowledgements
This work was financially supported by the Nederlandse Organisatie voor Wetenschappelijk Onderzoek (NWO) (VENI 722.016.001, VIDI 723.016.001) and the European Research Council (ERC Consolidator Grant Softbreak). This research forms part of the research programme of DPI (731.015.501).

Conflict of Interest
The authors declare no conflict of interest.

Author Contributions
J.M.C. and J.S. conceived the idea. J.M.C. synthesized the materials, performed the mechanical characterization, and analyzed the data. T.E.K. assisted in the design of the mechanical testing set-ups and the analysis of the data. J.S. also participated in analyzing the data. J.G. performed the simulations. All authors participated in writing the manuscript.

Keywords
colloids, mechanochemistry, mechanochromism, photonics, polymers

Received: March 26, 2020
Revised: May 28, 2020
Published online: July 23, 2020

[1] J. M. Northcott, I. S. Dean, J. K. Mouw, V. M. Weaver, Front. Cell Dev. Biol. 2018, 6, 17.
[2] A. Goriely, M. Tabo, Mycol. Res. 2006, 110, 755.
[3] J. Schiwe, Fatigue of Structures and Materials, Springer, Berlin 2009.
[4] D. A. Davis, A. Hamilton, J. Yang, L. D. Cremar, D. Van Gough, S. L. Potisek, M. T. Ong, P. V. Braun, T. J. Martinez, S. R. White, J. S. Moore, N. R. Sottos, Nature 2009, 459, 68.
[5] G. H. Lee, T. M. Choi, B. Kim, S. H. Han, J. M. Lee, S. H. Kim, ACS Nano 2017, 11, 11350.
[6] A. Lavrenova, D. W. Balkenende, Y. Sagara, S. Schrettl, Y. C. Simon, C. Weder, J. Am. Chem. Soc. 2017, 139, 4302.
[7] M. E. McFadden, M. J. Robb, J. Am. Chem. Soc. 2019, 141, 11388.
[8] R. Gölstl, R. P. Sibbesma, Chem. Sci. 2016, 7, 370.
[9] T. Wang, N. Zhang, J. Dai, Z. Li, W. Bai, R. Bai, ACS Appl. Mater. Interfaces 2017, 9, 11874.
[10] T. van de Laar, H. Schuurman, P. van der Scheer, J. Maarten van Doorn, J. van der Gucht, J. Sprakel, Chem 2018, 4, 269.
[11] Y. Chen, A. J. Spiering, S. Karthikeyan, G. W. Peters, E. W. Meijer, R. P. Sibbesma, Nat. Chem. 2012, 4, 559.
[12] J. M. Clough, A. Balani, T. L. Van Daal, R. P. Sibesma, Angew. Chem., Int. Ed. 2016, 55, 1445.
[13] S. Ye, Q. Fu, J. Ge, Adv. Funct. Mater. 2014, 24, 6430.
[14] Y. Yue, T. Kurokawa, M. A. Haque, T. Nakajima, T. Nonoyama, X. Li, I. Kajiwara, J. P. Gong, Nat. Commun. 2014, 5, 1.
[15] C. A. Burel, A. Alsayed, L. Malassis, C. B. Murray, B. Donnio, R. Dreyfus, Small 2017, 13, 1.
[16] A. Pucci, G. Ruggeri, J. Mater. Chem. 2011, 21, 8232.
[17] S. N. Raja, X. Ye, M. R. Jones, L. Lin, S. Govindjee, R. O. Ritchie, Nat. Commun. 2018, 9, 1155.
[18] A. S. Jabbar, S. Akbulatov, R. Boulou, ChemPhysChem 2017, 18, 1418.
[19] J. Park, Y. Lee, M. H. Barbee, S. Cho, S. Cho, R. Shanker, J. Kim, J. Myoung, M. P. Kim, C. Baig, S. L. Craig, H. Ko, Adv. Mater. 2019, 31, 1.
[20] T. A. Kim, C. Lamuta, H. Kim, C. Leal, N. R. Sottos, Adv. Sci. 2020, 7, 1903464.
[21] J. Teyssier, S. V. Saenko, D. Van Der Marel, M. C. Milinkovitch, Nat. Commun. 2015, 6, 1.
[22] W. J. Crookes, L.-L. Ding, Q. L. Huang, J. R. Kimbell, J. Horwitz, M. J. Mcfall-Ngai, Science 2004, 303, 235.
[23] D. G. DeMartini, D. V. Krogsstad, D. E. Morse, Proc. Natl. Acad. Sci. U. S. A. 2013, 110, 2552.
[24] A. Ghoshal, D. G. DeMartini, E. Eck, D. E. Morse, J. R. Soc. Interface 2014, 11, 20140106.
[25] Q. Wang, G. C. Gossweiler, S. L. Craig, X. Zhao, Nat. Commun. 2014, 5, 4899.
[26] S. Zeng, D. Zhang, W. Huang, Z. Wang, S. G. Freire, X. Yu, A. T. Smith, E. Y. Huang, H. Nguon, L. Sun, Nat. Commun. 2016, 7, 11802.
[27] L. M. Mäthinger, E. J. Denton, N. J. Marshall, R. T. Hanlon, J. R. Soc. Interface 2009, 6, S149.
[28] T. L. Williams, S. L. Senft, J. Yeo, F. J. Martín-Martínez, A. M. Kuzirian, C. A. Martin, C. W. DiBona, C. T. Chen, S. R. Dinneen, H. T. Nguyen, C. M. Gomes, J. J. Rosenthal, M. D. MacManes, F. Chu, M. J. Buehler, R. T. Hanlon, L. F. Deravi, Nat. Commun. 2019, 10, 1004.

[29] J. Chen, L. Xu, M. Yang, X. Chen, X. Chen, W. Hong, Chem. Mater. 2019, 31, 8918.

[30] Q. Zhu, K. Van Vliet, N. Holten-Andersen, A. Miserez, Adv. Funct. Mater. 2019, 29, 1808191.

[31] H. Nakamura, M. Ishii, Langmuir 2005, 21, 11578.

[32] E. P. Chan, J. J. Walish, A. M. Urban, E. L. Thomas, Adv. Mater. 2013, 25, 3934.

[33] Z. Xia, V. D. Alphonse, D. B. Trigg, T. P. Harrigan, J. M. Paulson, Q. T. Luong, E. P. Lloyd, M. H. Barbee, S. L. Craig, Molecules 2019, 24, 542.

[34] Y. Lin, M. H. Barbee, C. C. Chang, S. L. Craig, J. Am. Chem. Soc. 2018, 140, 15969.

[35] J. B. Kim, S. Y. Lee, J. M. Lee, S. H. Kim, ACS Appl. Mater. Interfaces 2019, 11, 14485.

[36] I. D. Johnston, D. K. McCluskey, C. K. Tan, M. C. Tracey, J. Micromech. Microeng. 2014, 24, 035017.

[37] Y. Yu, D. Sanchez, N. Lu, J. Mater. Res. 2015, 30, 2702.

[38] J. N. Boots, R. Fokkink, J. Van der Gucht, T. E. Kodger, Rev. Sci. Instrum. 2019, 90, 015108.

[39] R. W. Style, C. Hyland, R. Boltianskiy, J. S. Wetlaufer, E. R. Dufresne, Nat. Commun. 2013, 4, 1.

[40] C. Creton, M. Ciccotti, Rep. Prog. Phys. 2016, 79, 46601.

[41] A. Vespignani, H. E. Stanley, S. Zapperi, Nature 1997, 388, 659.

[42] C. J. Norris, G. J. Meadway, M. J. O’Sullivan, I. P. Bond, R. S. Trask, Adv. Funct. Mater. 2011, 21, 3624.

[43] S. P. Pearce, J. R. King, M. J. Holdsworth, Int. J. Nonlin. Mech. 2011, 46, 1128.

[44] W. H. Yang, K. H. Hsu, J. Appl. Mech. 1971, 38, 227.

[45] Y. Vidavsky, S. J. Yang, B. A. Abel, I. Agami, C. E. Diesendruck, G. W. Coates, M. N. Silberstein, J. Am. Chem. Soc. 2019, 141, 10060.

[46] H. Fudouzi, K. Tsuchiya, S.-I. Todoroki, T. Hyakutake, H. Nitta, I. Nishizaki, Y. Tanaka, T. Ohya, in Sensors and Smart Structures Technologies for Civil Mechanical and Aerospace Systems, SPIE, Bellingham, WA 2017, p. 1016820.

[47] C. M. Kingsbury, P. A. May, D. A. Davis, S. R. White, J. S. Moore, N. R. Sottos, J. Mater. Chem. 2011, 21, 8381.

[48] M. N. Silberstein, K. Min, L. D. Cremar, C. M. Degen, T. J. Martinez, N. R. Aluru, S. R. White, N. R. Sottos, J. Appl. Phys. 2013, 114, 023504.

[49] K. J. Bathe, Finite Element Procedures, Prentice Hall, Upper Saddle River, NJ 1996.