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Toward a Diagnostic Helmet Impact Testing Method Utilizing Spiropyran Mechanophore-Embedded PDMS

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14. ABSTRACT

In this study, we demonstrate that mechanophore-embedded materials can potentially be helpful with diagnostics in helmet research studies to understand the load transfer from the source to the brain through the head protection system, to generate validation data for computational modeling, and ultimately to help design better head protection systems. Versions of this concept can be further developed in the future to be implemented into in-theater head protection systems for immediate assessment of Soldier health and functionality.

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1. Introduction

The predominant threats that cause brain injuries are: 1) fragmentation and ballistic threats from explosions, artillery, and small-arms fire, and 2) blunt trauma caused by translation from blast, falls, vehicle crashes, and impact with vehicle interiors and from parachute drops. Brain injuries, whether acute or mild, severely impede military operational capabilities. Most severe injuries result in death, whereas less severe and moderate injuries result in loss of function. Symptoms due to mild injuries can surface in the long term and reduce the quality of life for the Soldier. As head protection technologies are further developed, there is a need to diagnose and assess impact loads that can result in mild to moderate levels of injuries associated with the brain. Loss of brain function, the type of function compromised, as well as potential long-term effects, can be better predicted and treated if the transfer of loads through the head protection system to the brain are better understood, and if the brain physiological tolerance can be linked to the magnitude and location of the impact force as it gets transferred through the head protection system into the brain (Fig. 1).[1]

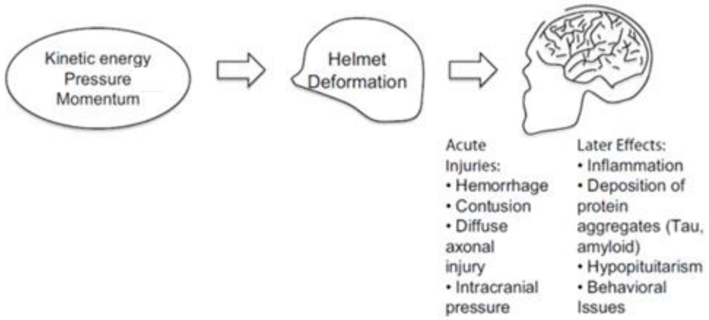


Fig. 1 Linkage between impact force transferred through the helmet to the human skull and brain, and potential brain injuries as a result (Image adapted/modified from National Research Council[1])

It is desired to have embedded diagnostics to indicate if previously determined critical loads are exceeded, and where (which region of the head/brain) they are exceeded. To do this, we first need to define and determine the critical loads. Systematic studies are required to establish the links between the force, location, rate, duration, and direction of impact to physiological tolerances and/or negative outcomes so that these critical loads are also well defined in a correlated manner for the head protection system. In parallel, we need to investigate diagnostic mechanisms that can be incorporated into the testing protocol and/or to the in-theater head protection systems, and we need to figure out if we can tailor the response of the diagnostic systems to the critical loads as described.

Monitoring head impacts through environmental sensors is an active technology development goal for the Army. Various commercial and prototype environmental sensors were tested to assess accuracy and usefulness of collected data, and to assess if they introduce an additional safety hazard to the Soldier.[2] To the best of our knowledge, all existing diagnostic options require power, adding parasitic mass (batteries), and have not been demonstrated so far to reliably collect accurate data. In contrast, the approach proposed herein is a passive system that relies on chemistry alone, where data do not need to be transmitted or collected but can be visually detected by the Soldier or the medical professional instantly after the event. In other words, a mechanochemistry-based sensor can add functionality to the existing mitigation/protection system without degrading its performance in any way.

In this study, we demonstrated that mechanophore-embedded materials can potentially be helpful with diagnostics in helmet research studies to understand the load transfer properly, to generate validation data for computational modeling, and ultimately to help design better head protection systems. Versions of this concept can be further developed in the future to be implemented into in-theater head protection systems for immediate assessment of Soldier health and functionality.

Our method uses mechanophore-embedded specimens between the helmet and the head form, in the space where the load transfer from the helmet to the head occurs. Mechanophores are force-sensitive chemical species that can be embedded into a host material. In our case, the host material is polydimethylsiloxane (PDMS); a silicone elastomer. When the host material (PDMS) is subjected to mechanical loading, the mechanophore gets “activated” (chemically reacts); that is, a specifically designed weak bond breaks at the molecular level that results in an altered chemical composition with different bulk properties. In this case, the changed bulk property is color. In other words, beyond a certain critical loading, the material changes color, clearly indicating at macroscopic level that the critical load for which it is designed is exceeded. Currently, the critical load of activation cannot be designed, and is still in discovery stage. There exists parallel research efforts toward improved understanding of the activation mechanisms[3–6] and the effect of various parameters on the critical loads of activation, toward manipulation of the critical loads of activation by design (work in progress by the authors Berry, Craig, Shannahan, and Fermen-Coker). If the critical load of mechanophore activation is tailored so that the mechanophore-embedded host materials can be utilized to implicate certain types and levels of injury, correlated with location and direction of impact loading, the levels and consequences of injuries can immediately be known. Soldier functionality as well as treatments can therefore be optimized to conduct operational missions without any further consequences to the safety of the Soldier.

Helmet impact tests using spiropyran-embedded PDMS (SP-PDMS) cylindrical specimens were conducted and the results are summarized. The objective of the experiments was to demonstrate that SP-PDMS placed between the helmet and the headform would get activated during a standard helmet impact test. Activation of PDMS is evidenced through a color change, which in turn is indicative of loading that exceeded a certain critical stress and strain value. Since SP-PDMS specimens are made using a mold, no attempt has been made to modify the shape of the SP-PDMS specimens to resemble any current mitigation mechanism within the helmet or as indicated by helmet testing protocols. Regardless of the lateral shape, the crucial information pertaining to the objectives of the current effort was whether the critical stress/strain for onset of activation of mechanochromic response in SP-PDMS specimens were going to be compatible and useful for helmet impact tests. Note that these critical values are not yet correlated to brain physiological tolerance/injury critical values. However, it is feasible that the critical stress/strain values of the diagnostic system can be calibrated in the future to reflect exceedance of critical values that would cause various levels of injuries in the brain. Computational models of the Advanced Combat Helmet (ACH) shell and its suspension system can be used to predict the stress levels experienced by the padding at various impact locations, relative to the headform acceleration, to guide this design.[7]

2. Helmet Impact Testing

There are various standardized tests to evaluate the impact attenuation performance of recreational helmets such as the National Operating Committee on Standards for Athletic Equipment (NOCSAE) performance standards (NOCSAE DOC (ND)002-17m19a),[8] Federal Motor Vehicle Safety Standard (FMVSS) No. 218,[9] ASTM F1446-13,[10] and ANSI/ISEA Z89.1-2014.[11] The blunt-impact protection requirements for helmets fielded by the US Army are listed in the purchase descriptions (PDs) for each helmet model. The ACH and Enhanced Combat Helmet (ECH) are both evaluated for blunt-impact performance using the Department of Transportation (DOT) FMVSS 218 format with specific modifications for military relevance.[12,13] This standard requires that helmets must limit headform acceleration to less than 150 g (g-force, 9.81 m/s^2) for impacts at 10 ft/s. The headform and helmet assembly is dropped from elevation, guided by a monorail, such that impact occurs onto a rigid, stationary anvil with hemispherical shape at a prescribed velocity (Fig. 2). The impacts can target specific areas of the helmet including the crown, front, rear sides, and nape regions.

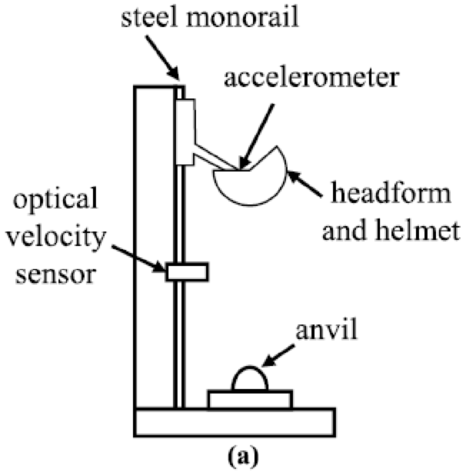


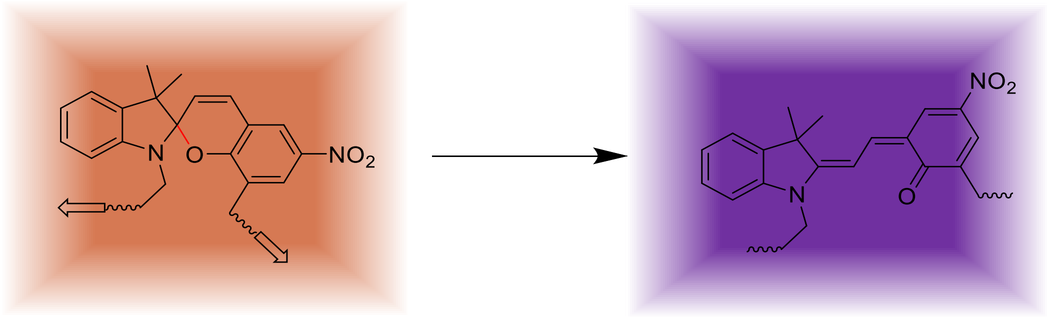
Fig. 2 Helmet impact test platform schematic[14]

For the purposes of this report, the impact speed considered was 10 ft/s. The point of testing at 10 ft/s was that even at the lowest required impact speed, the SP-PDMS would get activated, which would demonstrate its potential diagnostic function in helmet testing or applications. For comparison purposes, a fall from only 3 ft can generate an impact speed of 14 ft/s, and typical vehicle crashes can generate 50 ft/s impact speed on the head. Thus, the majority of general blunt-trauma threats are much higher than the 10 ft/s drop-test requirement.[1]

A clear helmet was fitted to a DOT size C headform and impacted at the crown and front locations as described in Section 4. Positioning of the DOT headform followed the specifications in the ACH PD and Army Test Center procedures.[15]

3. Mechanophore-Embedded PDMS Preparation

The spiropyran mechanophore is one of the most commonly used mechanophores in the literature.[3,16–22] The utility of this molecule arises from its relatively low activation threshold (240 pN for the nitro derivative adapted in the current study),[23] combined with a robust color change upon activation. When covalently embedded into a polymeric system and exposed to an external force, the accumulation of stress along the polymer backbone is concentrated[24] to the weak, spirocyclic C-O bond (red bond, Fig. 3a) of the mechanophore. This causes bond breakage, resulting in a molecular rearrangement that results in the purplish-colored merocyanine form (Fig. 3b).



(a) (b)

Fig. 3 Spiropyran (a) to merocyanine (b) transition due to mechanical force. Figure adapted from Li et al.[25]

The synthesis of the functionalized spiropyran used in this study was adapted from previous work,[26–28] and its specific chemical structure is shown in Fig. 4.

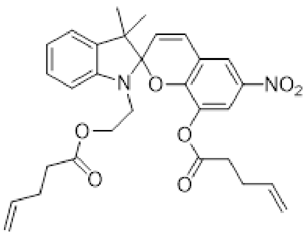


Fig. 4 Functionalized spiropyran used in this study

To incorporate the functionalized spiropyran mechanophore into PDMS and cast the proper size (0.25 inch diameter) cylindrical samples for testing, an aluminum mold was used to cure the samples. The details on the mold specifications and the curing process can be found in Shannahan et al.[28] Upon cooling, the material was gently removed from the mold with the aid of a small metal spatula to obtain the requisite cylinders. These SP-PDMS cylinders were then cut to an appropriate height to fit in the space between the headform and the helmet, making sure that the top and bottom surfaces were loosely in contact with the headform and the helmet. They were then glued onto the inner surface of the helmet using Skilcraft Spray Adhesive MMM-A-105-A (Part No. 0534-000).

4. Diagnostic Helmet Test Configuration using SP-PDMS Specimens and Results

A transparent helmet is used for the experiments to enable visual diagnostics of the SP-PDMS specimens that are placed between the helmet and the headform via a high-speed color camera. The specifics of the helmet used are shown in Fig. 5, including the internal webbing-based suspension system which was removed for the testing reported herein.

Portwest PV54 Peak View Polycarbonate Plus
Protective Work Ratchet Hard Hat ANSI, Clear

STANDARDS: ANSI/ISEA Z89 TYPE II (Class G)
100% Translucent Polycarbonate

Weight: 0.16 ounces = 4.5 grams = 1/100 lb

Fig. 5 Transparent helmet specifications

SP-PDMS specimens were cut to fit in the space between the headform and the clear helmet. Special care was taken to make sure that the specimens were in contact with both the headform and the inside surface of the helmet. Cylinders were glued in place on the inner surface of the helmet and lowered on top of the headform to visually confirm contact between the headform and the SP-PDMS specimens. The height of most of the cylinders used in the experiments discussed in this report approximated the thickness of the suspension system padding in the ACH, which are 3/4 inch thick. Depending on the spacing available in different locations inside the helmet, some cylinders were cut a little shorter to measure approximately 1/2 inch, so as to maintain contact with the helmet interior and the headform, without pre-stressing the specimens.

For the crown impact configuration, three SP-PDMS specimens were placed in the crown area as shown in Fig. 6.

Fig. 6 **SP-PDMS placement in initial configuration for crown impact testing**

A second test configuration was performed on the frontal location of the helmet. As shown in Fig. 7, two SP-PDMS specimens were placed on the front and one SP-PDMS specimen was placed on the back side of the helmet. The impact direction is aligned with one of the front specimens as indicated in Fig. 6.

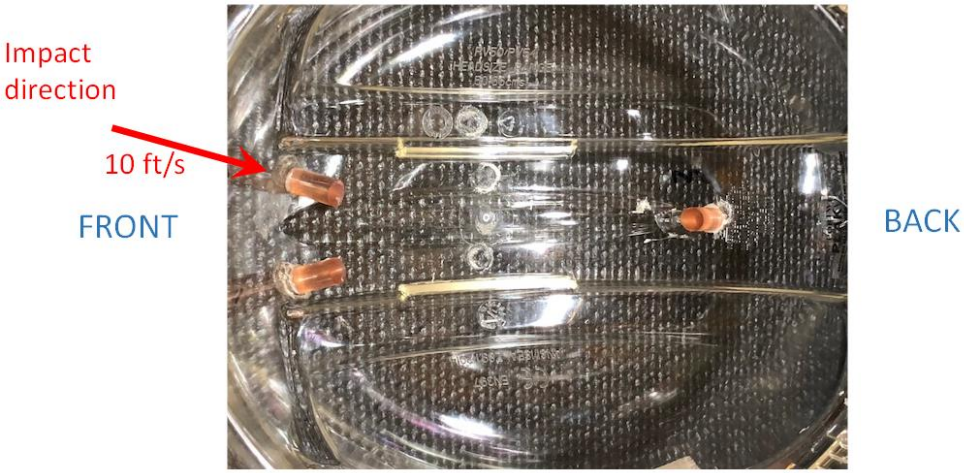


Fig. 7 **Front asymmetric impact initial configuration**

The experiments and the corresponding configuration is listed for readers' convenience in Table 1, and the results are discussed for each experiment in Section 5.

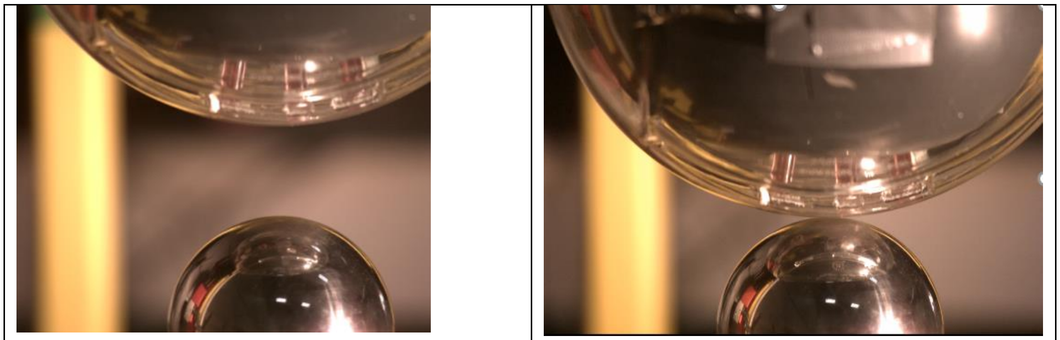
Table 1 **Experiments conducted to demonstrate load transfer and mechanophore activation during helmet impact**

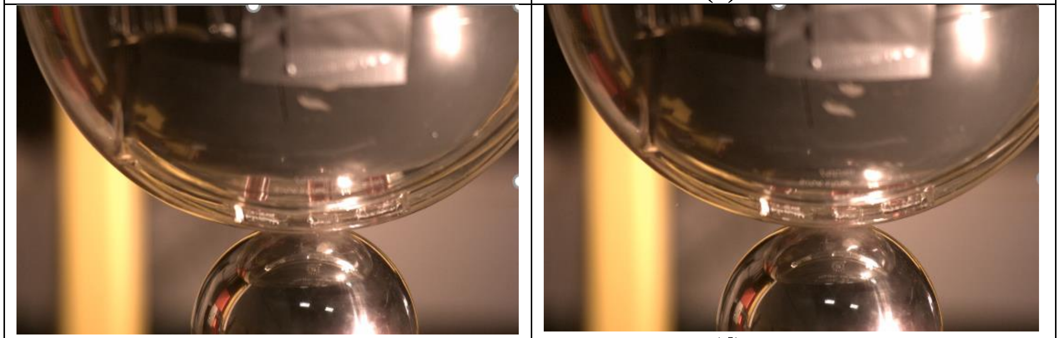
Experiment	Configuration
1	Crown impact (see Fig. 6)
2, 3	Asymmetric frontal impact (see Fig. 7)

5. Summary of Results and Discussion

For this preliminary assessment, a total of three experiments were performed for the two configurations described in the previous section. Mechanophore activation was captured using a Phantom V2012 high-speed color camera. The framing rate was 5000 fps and the resolution was 1280 × 800. The impact speed was 10 ft/s, as previously mentioned.

Progression of the crown impact experiment is captured for Experiment 1 in Fig. 8. The helmet and the headform are on top as depicted in the sketch shown in Fig. 2. Visible in Fig. 8a is the top of headform and the clear helmet with the three SP-PDMS specimens in between. The descent of the headform and the clear helmet toward the anvil shown at the bottom continues until Fig. 8e, and the headform–helmet assembly rebounds beginning in Fig. 8f. The view of the SP-PDMS specimens is somewhat obscured in these images because of the grooves on top of the helmet; however, one can still see that all three samples have changed color following the rapid compression event, indicating that the SP-PDMS specimens have endured stresses/strains that exceeded the critical onset of activation.


(a) Time = 0 (b) Time = 2.21 ms


(c) Time = 2.67 ms (d) Time = 2.9 ms


(e) Time = 4 ms (f) Time = 6.25 ms

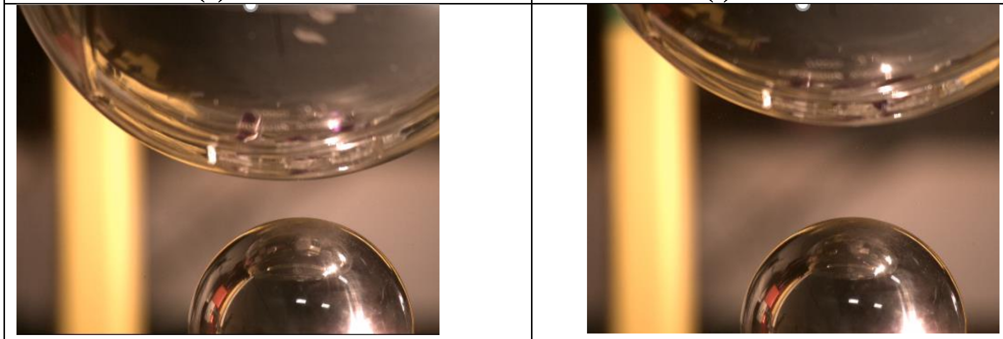
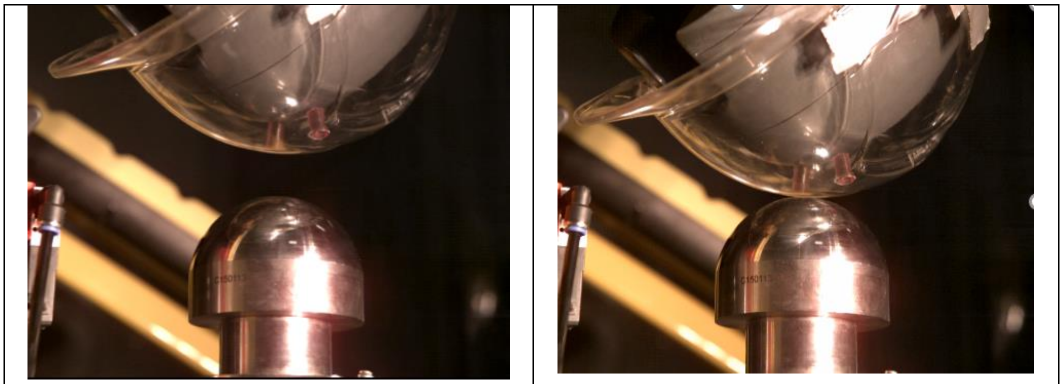

(g) Time = 9 ms (h) Time = 11.9 ms

Fig. 8 Results for crown impact test (Experiment 1) at 10 ft/s

The critical stress and strain values for SP-PDMS activation were obtained through Kolsky bar compression experiments in the manner described in Shannahan et al.[28] For the specific SP-PDMS used in this study, the critical stress and strain values are 7.8 ±1.0 and 0.65 ±0.04 MPa, respectively, where the corresponding strain rate was around 2200 /s. The activated state lasted several minutes. Figure 9 shows the three SP-PDMS specimens still in their activated state following the experiment.

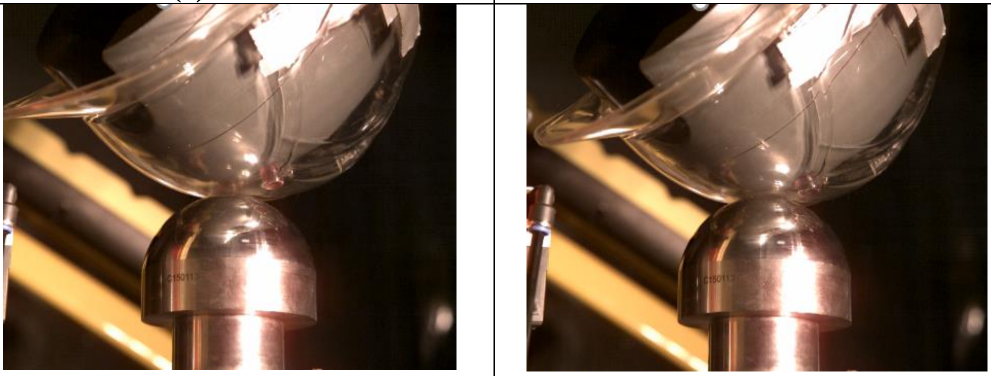
Fig. 9 Crown impact test (Experiment 1) posttest image of SP-PDMS

The second and third experiments utilized the helmet/SP-PDMS configuration shown in Fig. 7, where the asymmetric frontal impact was aligned with one of the two SP-PDMS specimens placed on the front side of the helmet as shown. The progression of impact event for the second experiment is shown in Fig. 10. The SP-PDMS specimen that is aligned with the impact direction is displaced after the event.



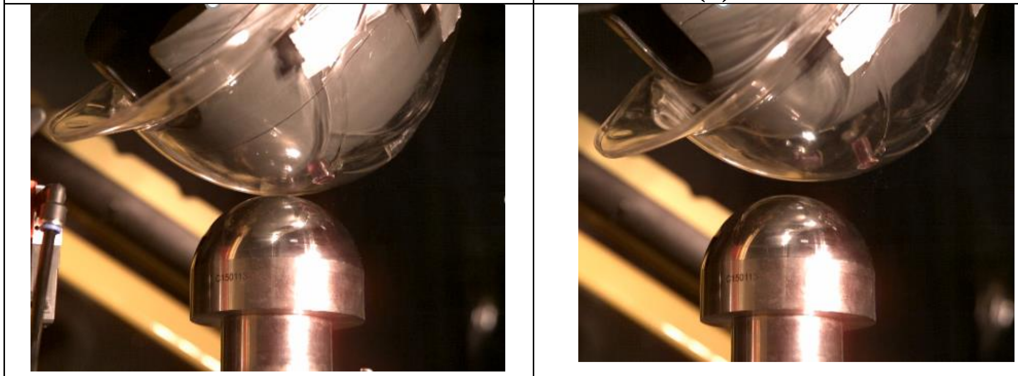
(a) Time = 0

(b) Time = 1.84 ms



(c) Time = 2.09 ms

(d) Time = 2.75 ms



(e) Time = 3.96 ms

(f) Time = 7.46 ms

Fig. 10 Results for asymmetric frontal impact test (Experiment 2) at 10 ft/s

All three specimens recovered after the experiment are shown in Fig. 11. The two specimens in the front indicate the severity of the loading. The specimen that was directly aligned with the impact direction indicates more intense activation, and the specimen that was located to the side of the impact direction indicates a less intense color change correlated with the less severe loading it experienced during the event. The specimen in the back did not receive much loading and shows no sign of reaction. These results indicate that if a continuous form of SP-PDMS were incorporated inside the helmet, the location and the severity of the impact could easily be determined.

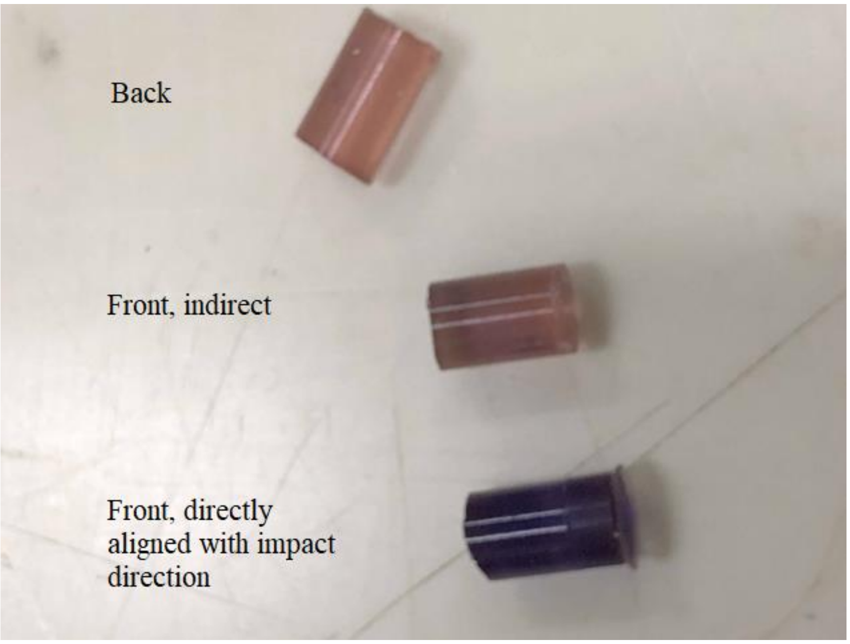
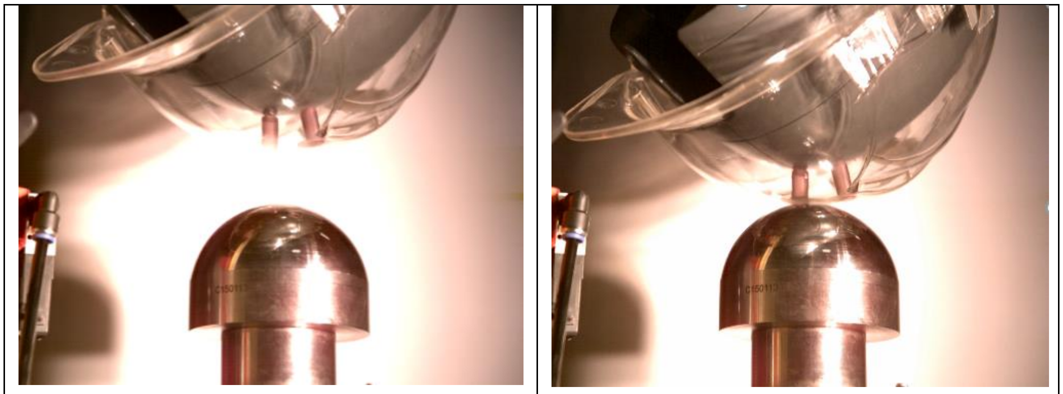


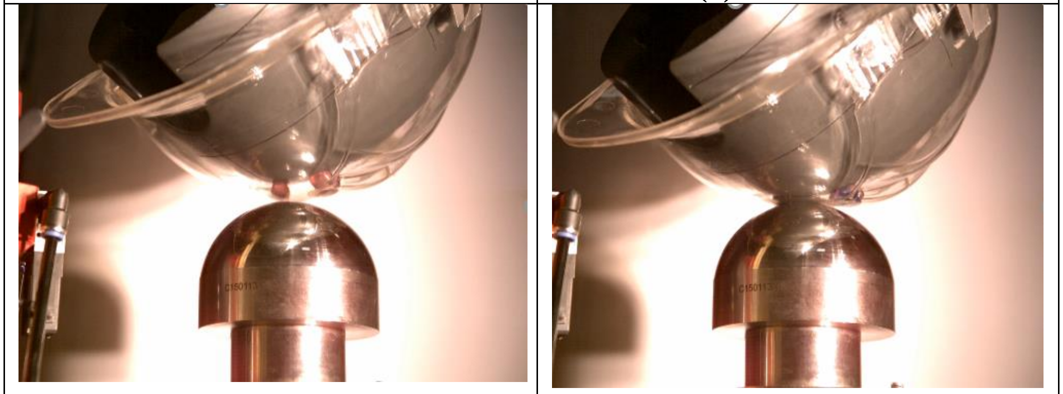
Fig. 11 Asymmetric frontal impact test (Experiment 2) posttest image of SP-PDMS

The third experiment was a simple repetition of Experiment 2 with light background for better imagery and for confirmation of the results of Experiment 2. The progression for Experiment 3 is shown in Fig. 12.



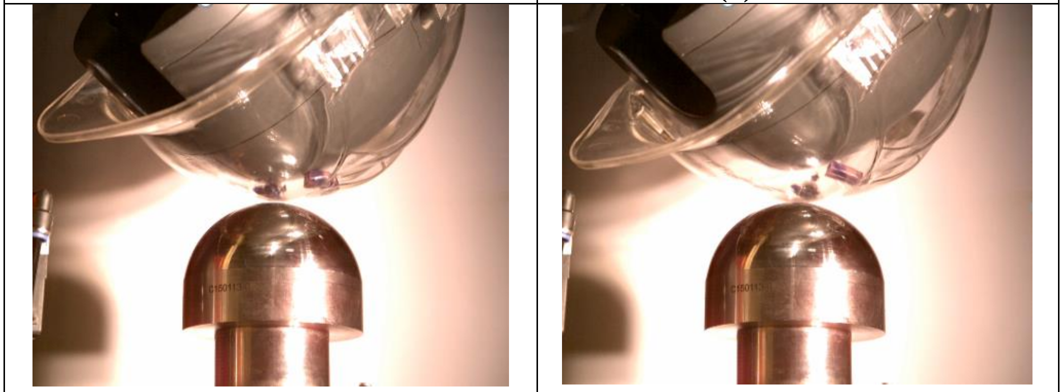
(a) Time = 0

(b) Time = 1.75 ms



(c) Time = 2.25 ms

(d) Time = 3 ms



(e) Time = 4.75 ms

(f) Time = 5.88 ms

Fig. 12 Results for asymmetric frontal impact test (Experiment 3) at 10 ft/s

Note that the specimen that receives the loading directly does not fully recover in this experiment and a piece is broken. The second specimen on the front side that indirectly receives the loading is buckled, and the outcome of this nonuniform loading is demonstrated in Fig. 12f, where only a portion of the SP-PDMS is activated fully. At the completion of the experiment, the recovered specimen indicates this nonuniform loading. The photograph of the three specimens is shown in Fig. 13.

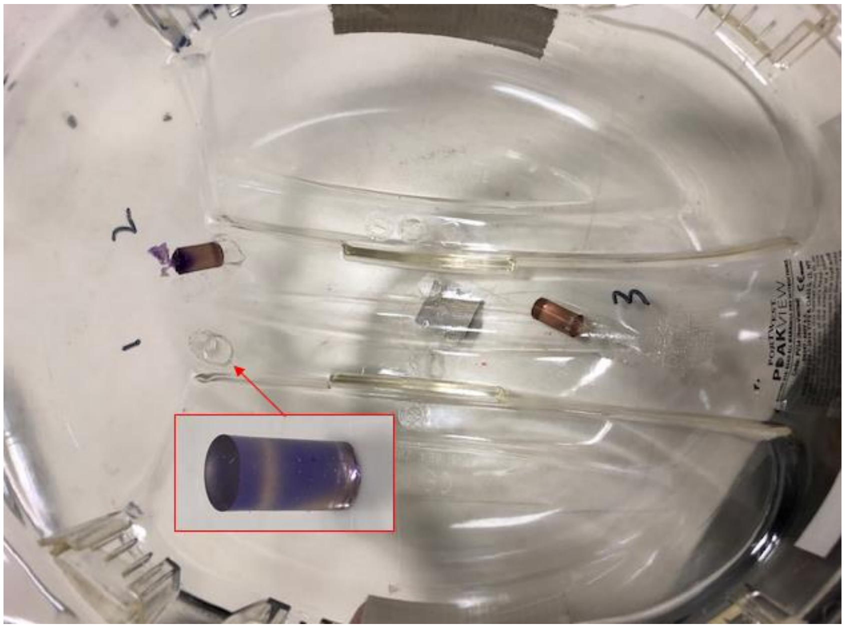


Fig. 13 Asymmetric frontal impact test (Experiment 3) posttest image of SP-PDMS shown inside the clear helmet in their original locations

6. Conclusions

Following are the conclusions of the experimental work discussed in this report:

- SP-PDMS is activated due to load transfer through the helmet, against a headform, during standard helmet impact testing at 10 ft/s impact speed. This makes SP-PDMS a good candidate to be potentially used as a stress-reporting material in helmet testing.
- SP-PDMS can be used to pinpoint loading/impact location and intensity effectively. Future studies can include tailoring of critical activation stress/strain to improve the functionality of the material for this application. Modeling efforts can enrich this pursuit. A follow-up study is underway to incorporate SP into a surrogate scalp cap that can be placed on headforms used in blunt and ballistic impact studies. The cap is to mimic the attenuation properties of the human scalp in simulated impact scenarios, but with an integrated mechanophore function, it could also provide valuable information on the location and magnitude of impact loading.
- Activated state (color) lasted for approximately 10 min, which is an acceptable duration for the function intended in the laboratory environment.

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List of Symbols, Abbreviations, and Acronyms

ACH	Advanced Combat Helmet
DOT	Department of Transportation
FMVSS	Federal Motor Vehicle Safety Standard
ft/s	feet per second
m/s^2	meters per second squared
ms	milliseconds
NO_2	nitrogen dioxide
NOCSAE	National Operating Committee on Standards for Athletic Equipment
O	oxygen
PD	purchase description
PDMS	polydimethylsiloxane
pN	piconewton
SP	spiropyran
SP-PDMS	spiropyran-embedded PDMS

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