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Polydiacetylene Sensor Arrays as Multimodal Tamper Indicators

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ABSTRACT

Treaty verification regimes rely on tamper-indicating technologies to maintain continuity of knowledge in between inspections. These technologies must indicate that tamper into equipment enclosures, material containers, or other items of interest has occurred, and indicate evidence of attempted repair. We are developing a novel and unique sensing concept based on the visual color change of polydiacetylene (PDA) materials that will indicate tamper and respond uniquely to multiple attack methods, including thermal, mechanical, solvent, and acid/base attack vectors. These materials benefit treaty verification regimes as well as other applications that require sensing phenomena or efficient and accurate indication of tampering.

Diacetylene (DA) monomers have a structure similar to lipids, with a customizable chemical headgroup and a long carbon-based tail. In the polymerized form, intramolecular interactions with neighboring headgroups, and how those headgroups interact with other molecules during solvent-based attacks, dictate the quantitative color changes and reversibility. Typically, literature has shown how specific PDA systems react for some types of stimuli, but no R&D has been performed evaluating how a PDA responds to all types of stimuli, which could be utilized for improved tamper indication. At a qualitative level an inspector could easily differentiate an attacked PDA system from an intact version due to the blue-to-red transition. The more-detailed color change would be verified via red-green-blue (RGB) analysis post-mortem to better understand the attack methodology. This talk will highlight the preparation, processing, and characterization of PDA materials and their associated colorimetric response to select stimuli relevant to tamper. Results on color variability, response repeatability, and principal component analysis (PCA), will also be discussed, as this is something that typically lacks in the current chemistry-base literature.

INTRODUCTION

Tamper-indicating technologies that alert authorities to prohibited or nefarious access to sensitive materials are used in many applications including pharmaceutical products, food and beverage products, and security seals. Particularly, tamper-indicating technologies are crucial for the monitoring of sensitive materials and are utilized in global treaty verification regimes to maintain continuity of knowledge in between inspections. While tamper-indicating devices (TIDs) do not necessarily prevent or inhibit illicit access to monitored items, they serve to indicate occurrences of possible tamper attempts such as attack to equipment enclosures, material containers, or other sensitive items. There are many varieties of TIDs that are actively employed, but it is important for the technology of TIDs to continually advance to keep up with advancements of adversaries. Furthermore, many of the currently existing TID technologies function by alerting to mechanical attacks and are not typically successful at indicating occurrences of chemical or thermal attacks.[1,2] The development of a tamper-indicating system that is capable of signaling a range of attack vectors, including a range of thermal and chemical exposures, would greatly advance the toolbox of TIDs and maintain their effectiveness towards thwarting adversarial efforts.

Our goal is to develop a novel and unique sensing system based on the colorimetric response of polydiacetylene (PDA) materials. Diacetylene (DA) monomers containing a pair of C≡C units (Figure 1) are colorless, but upon self-assembly in solution, they polymerize into corresponding polydiacetylenes (PDAs) with exposure to UV radiation.[3,4] The resulting PDAs are visibly blue due to the long-range conjugation among polymerized DA units; exposure to various types of stimuli (e.g., thermal, chemical, mechanical, electrical) disturbs the long-range conjugation of the PDA backbone and induces a visible color change along the blue-to-red spectrum (Figure 1).[4-11] The extent of color change depends on the molecular structure of the PDA (i.e., the chain length and headgroup of the DA monomeric units) and the stimulus (i.e., higher temperatures generally induce stronger blue-to-red transitions).

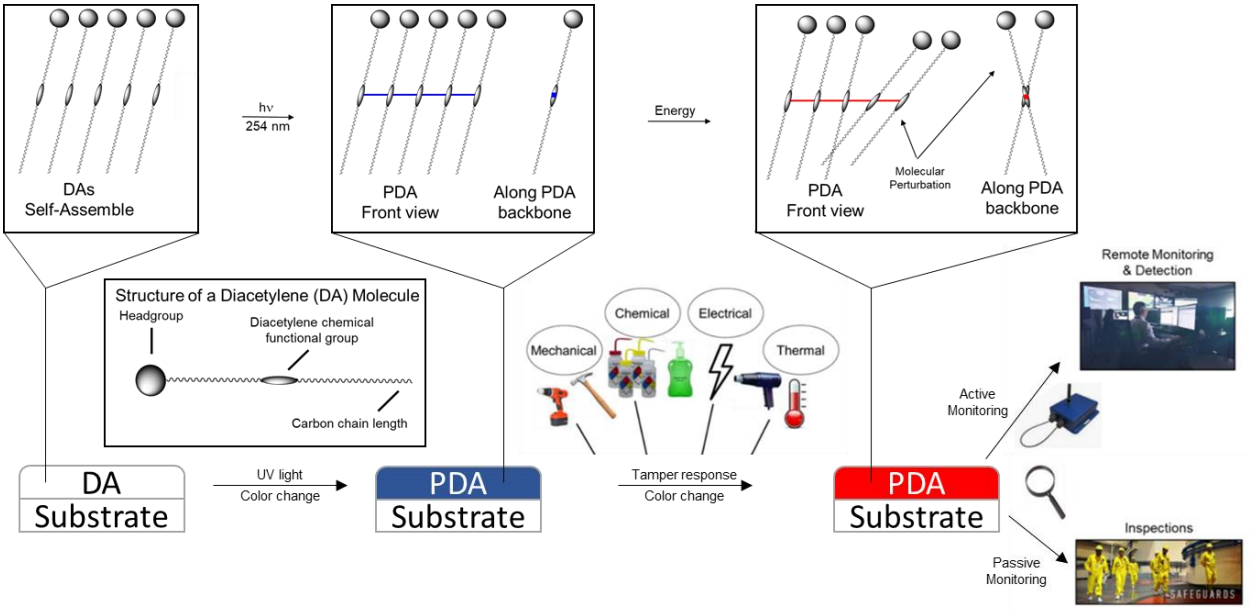

Figure 1. Generic structure of a diacetylene (DA) molecule (middle left); molecular view of the conversion of self-assembled DAs to polydiacetylenes (PDAs) (top left), which coincides with a visual color change from colorless to blue; molecular view of the kinking of PDA chains upon stimulus (top right), which coincides with a visual color change from blue to red. Overall concept, goal, and representative use-case for utilization of PDAs as tamper-indicating materials (bottom); the response can be evaluated by inspectors passively (right bottom) or actively monitored with appropriate engineering and equipment (right middle).

Since the colorimetric response to a given stimulus is different for different PDAs, our sensing concept is to utilize multiple PDA compounds as an array of sensors, where the combined patterned color of the post-exposure array would be unique for a given stimulus (Figure 2). This type of PDA-based array sensor would represent a unique and novel sensing concept utilizing a visibly obvious color change that can also be quantified by RGB colorimetric analysis to diagnose a tamper event among multiple possible attack methods. Furthermore, PDAs can be incorporated within a variety of composite matrices, with literature examples ranging from 3D printing to processing into packaging materials,[4] which makes PDAs uniquely well-suited for our envisioned application as an enhanced tamper-indicating technology.

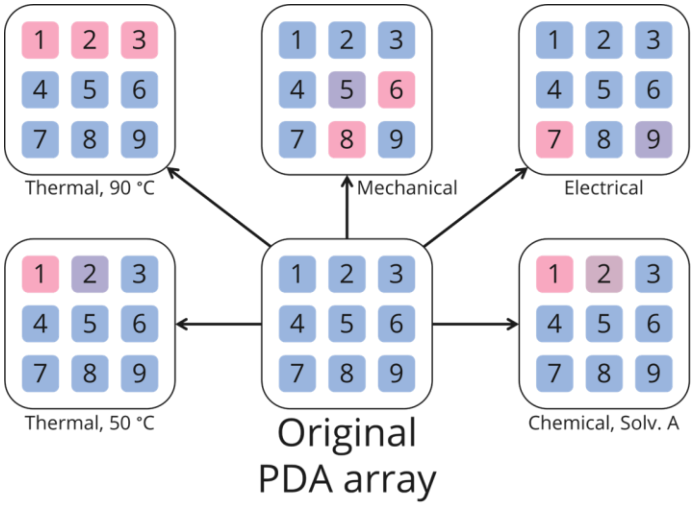

Figure 2. An unused PDA array (bottom middle) composed of nine different PDA compounds produces a variety of colorimetric responses when exposed to different stimuli (thermal, mechanical, electrical, chemical). If each stimulus produces a unique patterned response, the stimulus can be identified by post-mortem colorimetric analysis.

This report will focus on our preliminary efforts towards developing PDA-based arrays for tamper indication. We started with paper-based PDA arrays, as this sample type allowed for rapid and extensive data collection to screen PDAs for stimuli responses. Later, we progressed to arrays composed of PDA-silicone composites, which would be more resilient than paper-based samples towards adversary efforts to counterfeit or repair the tamper-indicating sensors.

PAPER-BASED PDA ARRAYS

We began by evaluating individual PDAs and their colorimetric responses to stimuli using a paper-based substrate due to ease of use. Approximately 20 PDA compounds were initially selected from literature precedent[10-13] and systematically screened by depositing solutions of the DA monomer onto commercial paper notecards; notecards were then exposed to UV radiation to polymerize DAs into corresponding PDAs, and then exposed to a selection of approximately 40 stimuli in order to collect preliminary data and investigate which selection of PDAs would be appropriate for a tamper-indicating PDA array system.

Our list of initially targeted PDAs was derived from commercially available DAs, DAs that were synthesized in-house, composite mixtures of DAs with other materials (i.e. ZnO, PEI, amines), and combinations of multiple DA monomers that co-polymerize to form a uniquely responsive material. These targets were chosen based on literature examples of irreversible colorimetric responses to a range of thermal and chemical stimuli. We quickly found that some of the literature procedures did not translate to our paper-based deposition methods (i.e., literature reports that studied PDA responses in solution), and work with many of these PDAs was halted due to success with many of the other targeted materials. Ultimately, we chose 10 PDA-based sensors to explore further as an array system (Figure 3); these PDAs were found in our initial screening process to provide varied colorimetric response to each stimulus such that an array composed of all 10 components should provide a unique pattern. Our aim was for the colorimetric responses of all 10 PDA sensors to be unique enough that the tamper type (i.e., thermal versus organic solvent versus

acid/base) or the actual stimulus (i.e., specific temperature, specific solvent, specific acid/base) could be identified by analysis of the array's post-exposure RGB values. The DAs used in this array included four commercially available monomers (PCDA, TCDA, DCDA, and DPHD), two monomers synthesized in-house (EAE-PCDA and EAE-PCDA-Br), and four combinations of these (PCDA+TCDA, PCDA+DCDA, TCDA+DCDA, and EAE-PCDA+EAE-PCDA-Br). Trial-and-error optimization for each of these resulted in determination of appropriate DA solutions using solvents that allowed self-assembly of the monomer, could be dried relatively quickly after drop-casting spots of the solution onto paper substrates, and afforded post-UV-exposure PDA spots that were visually appropriately colored (not too light, not too dark, for the same amount of UV exposure time for each PDA spot, with consistent coloration throughout the surface area of the spot).

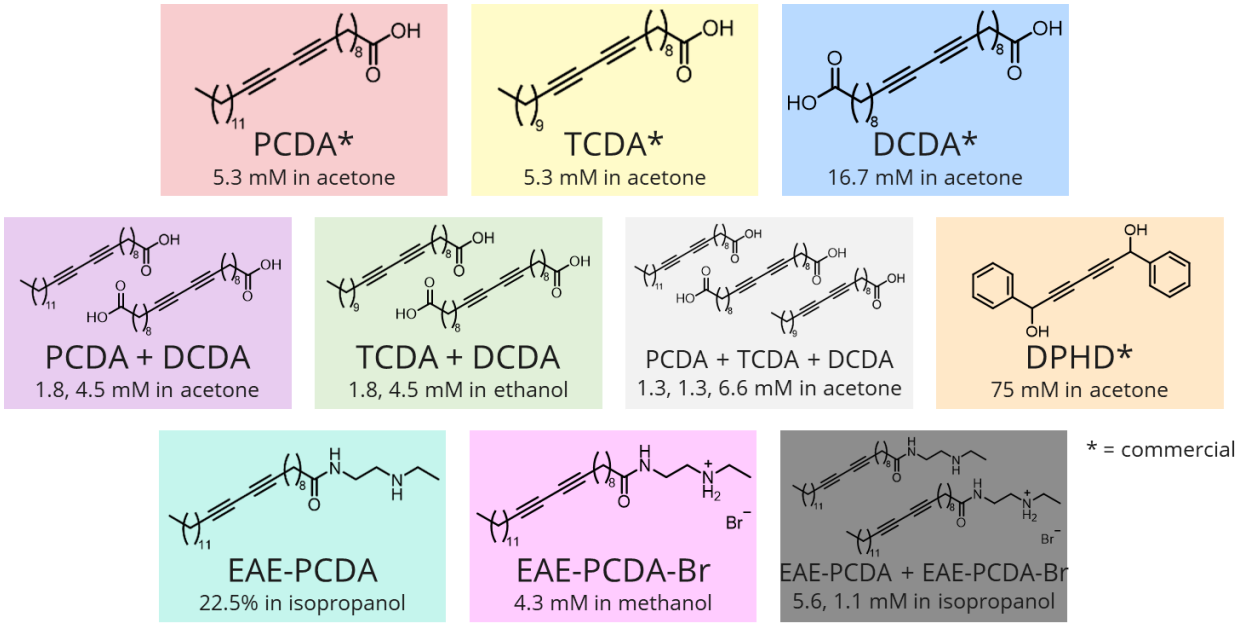

Figure 3. DA monomers and their concentrations/solvents used for drop-casted solutions for paper-based PDA arrays.

An assortment of 40 thermal and chemical stimuli were selected based on what could be reasonably accessible to an adversary, but all testing was performed in a laboratory environment using high purity chemicals (i.e., instead of commercial brand-name store-bought products) for consistency of results at this early stage of sensor development. To evaluate thermal responses, we chose six temperatures between 50 and 150 °C (with 20 °C increments); to evaluate chemical responses, we chose 19 organic solvents with a range of functional groups including alcohols (methanol, ethanol, isopropanol), halogenated solvents (chloroform, dichloromethane, dichloroethane), aromatics (toluene, xylenes), polar solvents (acetone, acetonitrile, ethyl acetate, methyl tert-butyl ether, dimethylformamide, dimethylsulfoxide, tetrahydrofuran) and nonpolar solvents (pentane, hexane, heptane, cyclohexane); we also included water, which we left in its own category due to its relationship to acidic and basic solutions; to evaluate acid/base responses, we chose three concentrations of HCl and NaOH (0.1 M, 0.01 M, and 0.001 M), in addition to three other acidic solutions (glacial acetic acid, 5% acetic acid, 1 M oxalic acid, 3% H_2O_2) and three other basic solutions (0.1 M KOH, aqueous ammonia, 0.5 M Na_2CO_3, 0.5 M $NaHCO_3$).

To conduct stimulus testing, notecard array samples were prepared with 1 drop of each of the 10 DA sensor solutions (Figure 3); notecards were exposed to 240 s UV radiation (254 nm) to polymerize DAs into corresponding PDAs. For thermal stimuli, notecards were placed inside a conduction oven pre-set to the given temperature and removed after 5 minutes. For all liquid stimuli, notecards were submerged in a glass Petri dish filled with the appropriate solution and removed after 1 min, then allowed to dry inside a fume hood. Each notecard was scanned using a commercial feed-through scanner both before and after stimulus exposure, and RGB values were extracted from each PDA sensing spot using the eyedropper tool in Adobe Photoshop (101x101 pixel average). 12 replicate notecard samples were tested for each stimulus to provide sufficient sample data for reliable results, and furthermore, the consistency/variability of colorimetric responses could be compared between stimuli. To demonstrate the visual range of colorimetric responses for the 10 PDA sensing spots after exposure to each of the 40 stimuli, one notecard for each stimulus is provided in Figure 4.

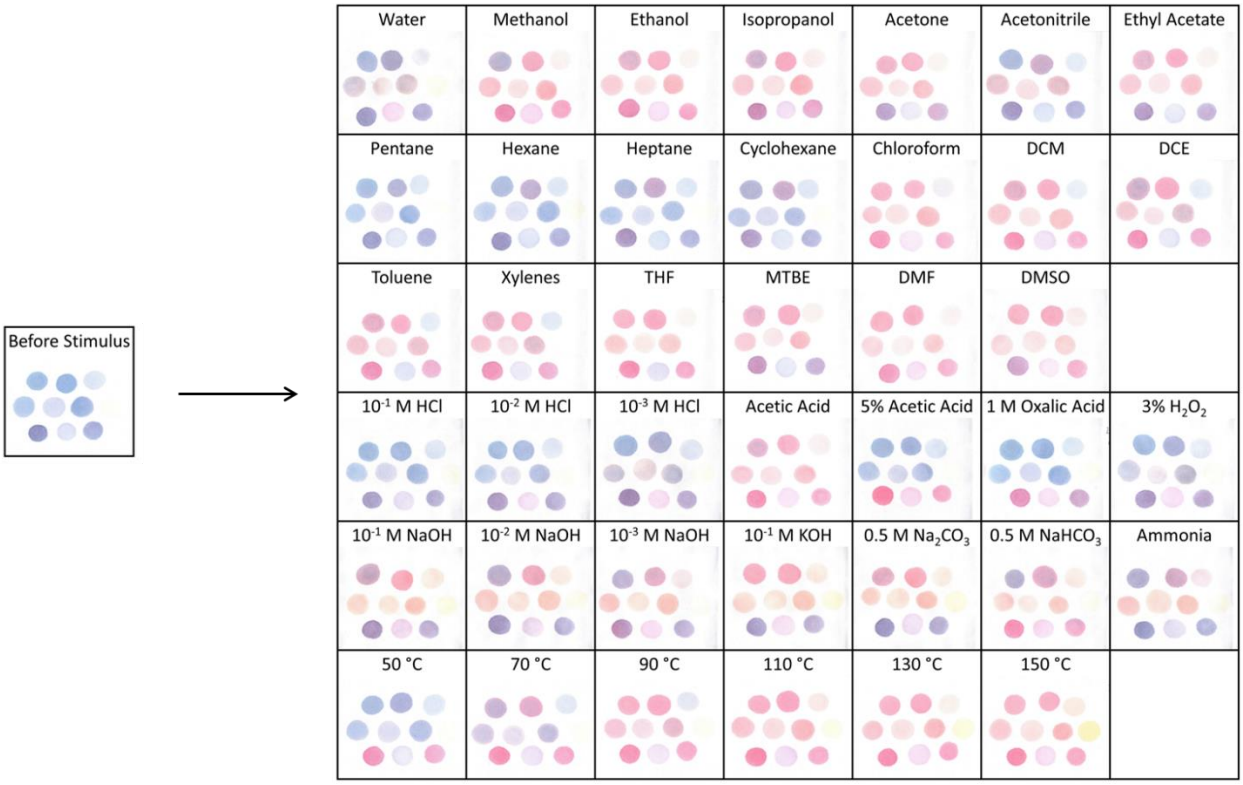

Figure 4. Paper-based PDA arrays before (left) and after (right) stimulus exposures. The order of PDA sensing spots matches Figure 3: top row, left-to-right: PCDA, TCDA, DCDA; middle row, left-to right: PCDA+DCDA, TCDA+DCDA, PCDA+TCDA+DCDA, DPHD; bottom row, left-to-right: EAE-PCDA, EAE-PCDA-Br, EAE-PCDA+EAE-PCDA-Br.

Overall, there is a stark and dramatic range in patterned responses. There is a noticeable trend among samples exposed to thermal conditions – each PDA sensing spot has a transition temperature below which it is blue or purple and above which it is red; higher temperatures show more sensing spots converted to red colors. There is less of an obvious trend among acid/base exposures, although the PDAs with amine-based headgroups respond more strongly to acidic solutions, whereas the PDAs with carboxylic acid-based headgroups respond more strongly to

basic solutions. Colorimetric responses to organic solvents are even less predictable or more difficult to rationalize. Solvents that are structurally similar (i.e., methanol/ethanol/isopropanol, pentane/hexane/heptane/cyclohexane, toluene/xylenes) provide similar patterned responses. Close inspection can reveal slight visual differences, even in these cases, but our main interest was to determine whether the differences between each stimulus's patterned response is statistically significant (or, alternatively, is the difference in response to similar stimuli different enough to be able to identify each stimulus in a hypothetical situation when the attack or stimulus exposure is unknown). Although we were interested to determine whether each of the 40 individual stimuli could be uniquely identified by post-exposure RGB analysis, it is important to note that even identification of tamper type (i.e. thermal versus chemical versus acid/base) would still represent an extreme advancement in the capabilities of tamper-indicating technologies.

We evaluated several different classification algorithms (e.g. principal component analysis, random forest, k-nearest neighbors, support vector machine, multinomial logistic regression) for their ability to identify tamper type and exact stimulus based on the collected RGB data of PDA sensing spots before and after stimulus exposure. Of these, a model utilizing a random forest algorithm was the most successful, which correctly identified 97% of notecard samples as the correct tamper type, and correctly identified 80% of notecard samples as the correct specific stimulus. This algorithm is still being optimized, but the current level of success is extremely promising for correctly identifying tamper type and stimulus exposures based on post-mortem analysis of PDA paper-based arrays, which represents a completely new and unique capability for broad-spectrum tamper indication and tamper diagnostics. We have also developed an automated process for extracting RGB values from images of array samples to greatly decrease the burden of previously time extensive data analysis.

SILICONE-BASED PDA ARRAYS

After collecting a plethora of colorimetric data from paper-based PDA arrays, we were interested in incorporating PDAs within polymeric host matrices to afford a more robust array or tamper-indicating device that would be more difficult to replicate, counterfeit, or repair. Initial experiments with PDA composites using polyvinyl alcohol (PVA), polyvinylpyrrolidone (PVP), and Sylgard (silicone) suggested that the silicone-based composites were the most successful in producing consistent, uniform, evenly colored hybrid materials. Due to relatively low yields of the DA monomers that were synthesized in-house (EAE-PCDA and EAE-PCDA-Br), we transitioned to using only commercial PDAs in silicone composite samples. For each PDA sensor, the PDA/silicone composite was optimized so that each sensing material (using different PDAs) would have relatively similar blue coloring after the same amount of UV exposure time. We selected six PDA/silicone sensors to move forward with array testing (Figure 5): PCDA, TCDA, DCDA, PCDA+TCDA, PCDA+DCDA, TCDA+DCDA; the TCDA/silicone sensor had an error in sample preparation, so it did not turn blue after UV exposure (i.e., the TCDA monomer did not polymerize into a PDA), so that sensor essentially became an accidental control, showing that the silicone material on its own does not change color with UV exposure or thermal exposure. 3D printed trays made out of polycarbonate-based material were used to house each PDA/silicone sensor in an individualized compartment (2x2 cm) such that each tray (7.2x4.8 cm) acts as a 6-membered array.

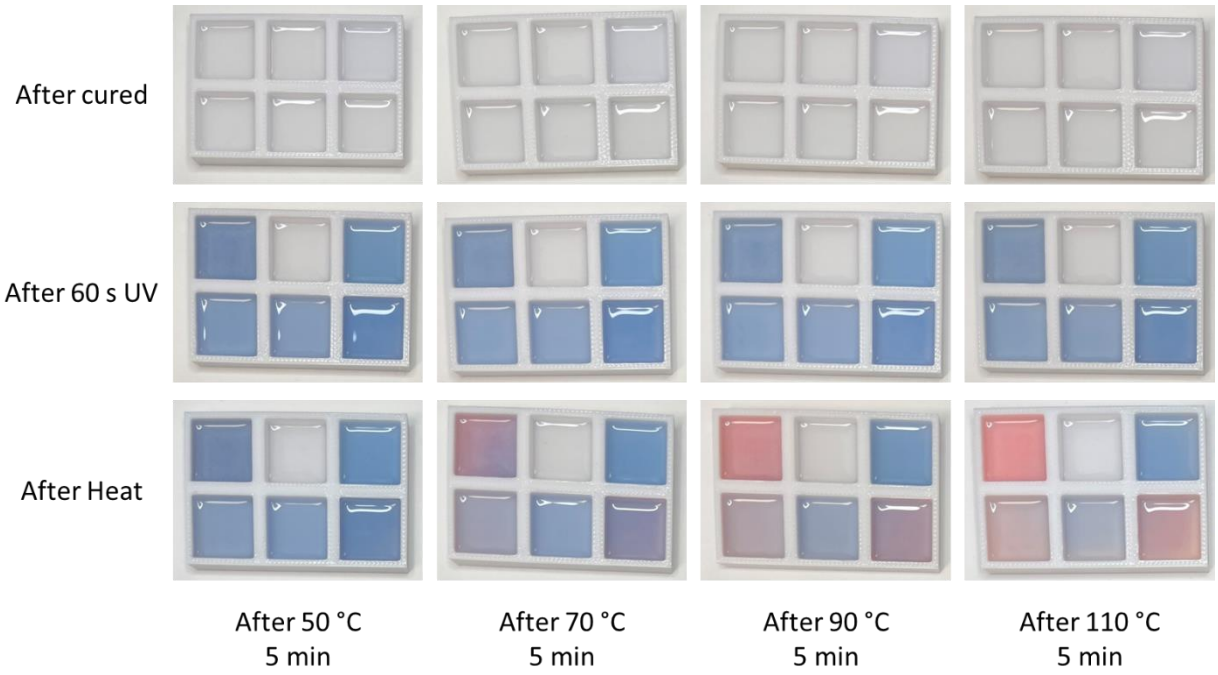

Figure 5. Silicone-based PDA arrays after silicone curing (top row), after UV exposure (middle row) and after thermal exposure (bottom row). The order of PDA/silicone sensing spots is (top row, left-to-right) PCDA, TCDA, DCDA, (bottom row, left-to right) PCDA+TCDA, PCDA+DCDA, TCDA+DCDA. Arrays were exposed to 50, 70, 90, or 110 °C for 5 min each.

SUMMARY AND NEXT STEPS

Current tamper-indicating technologies that are critical in the containment and surveillance of sensitive materials are majorly limited to detection of mechanical attack. The development of a tamper-indicating technology that could be used to diagnose the type of tamper that occurred, for example, by identifying a thermal, chemical, or acid/base attack would greatly enhance the toolkit of tamper-indicating capabilities. We have demonstrated a 10-membered paper-based PDA array that undergoes a visibly obvious colorimetric change that is unique in response to a variety of thermal, chemical, and acid/base stimuli; among 40 different stimuli, a random forest classification algorithm was able to correctly identify 97% of samples by tamper type (i.e. thermal versus chemical versus acid/base) and 80% of samples by exact stimulus. We are currently developing a silicone-based PDA array that would be harder for an adversary to counterfeit or repair compared to a paper-based system. We have shown that a 6-membered silicone-based PDA array responds uniquely to a range of temperatures between 50 and 110 °C. Next steps include more extensive sample preparation and stimulus exposure with silicone-based PDA arrays; we plan to apply the previously developed random forest algorithm to the post-mortem RGB data analysis of silicone-based PDA arrays and assess the ability to identify tamper type and stimulus. Furthermore, we plan to perform stability testing with a range of humidity exposures as well as long-term exposure to ambient temperature and lighting both before and after stimulus exposures.

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