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TAMPER-INDICATING ENCLOSURES WITH VISUALLY OBVIOUS TAMPER RESPONSE

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Abstract

Sandia National Laboratories is developing "bleeding" materials (analog of visually obvious bruised skin that doesn't heal) that provide inspectors the ability to *readily* recognize using simple visual observation that penetration into a material used as a tamper-indicating enclosure has been attempted without providing adversaries the ability to repair damage. Such material can significantly enhance the current capability for tamper-indicating enclosures (TIEs), used to support treaty verification regimes. Current approaches rely on time-consuming and subjective visual assessment by an inspector, external equipment such as eddy current or cameras, or active approaches that may be limited due to application environment. The complexity of securing whole volumes includes (1) enclosures that are non-standard in size/shape, (2) enclosures that may be inspectorate *or* facility owned, (3) tamper attempts that are detectable and not difficult or timely for an inspector to locate, (4) solutions that are robust regarding reliability and environment (including facility handling), and (5) solutions that prevent adversaries from repairing penetrations. The approach is based on a sensor compound within a microcapsule that changes color irreversibly when the microcapsule is ruptured. 3D printing of the microcapsules are investigated as well as a spray coating formulation. The anticipated benefits of this work are passive, flexible, scalable, cost-effective TIEs with obvious and robust responses to tamper attempts. This results in more efficient and effective monitoring as inspectors will require little or no additional equipment, and will be able to detect tamper without extensive time-consuming visual examination. Note that if desired, an autonomous system with a spectrometer could also detect the color change. Applications can include custom TIEs (cabinets or equipment enclosures), spray-coating onto facility-owned items, spray-coating of walls or structures, spray-coatings of circuit boards, and 3D printed seal bodies. The paper describes prior internal Sandia National Laboratories research that provides the foundation, research of the sensor compound and research of the microcapsules.

1. INTRODUCTION

Sandia National Laboratories (SNL) is developing "bleeding" materials (analog of visually obvious bruised skin that doesn't heal) that provide inspectors the ability to readily recognize using simple visual observation that penetration into the material has been attempted without providing adversaries the ability to repair damage. Such material can significantly enhance the current capability for tamper-indicating enclosures (TIEs), used to support treaty verification regimes. In the case of the readily-accepted anodized aluminum enclosures used by the International Atomic Energy Agency (IAEA), an inspector may visually observe the enclosure and note any anomalous features. This time-consuming method is heavily reliant on judgment and can miss subtle tamper attempts. Active tamper-indication for enclosures may include conductive materials that are continuously monitored. These technologies may not be suitable for all applications, require power, and may have environmental limitations. Simple visual approaches capable of high detection sensitivity have not received adequate R&D attention although applications already exist that could benefit from such a capability.

The complexity of securing whole volumes includes (1) enclosures that are non-standard in size/shape, (2) enclosures that are both inspectorate and facility owned, (3) tamper attempts that are detectable and not difficult or timely for an inspector to locate, (4) solutions that are robust in regard to reliability and environment (including facility handling), and (5) solutions that prevent adversaries from repairing penetrations. The existing toolkit for TIEs is extremely limited with respect to the complex issues involved.

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Our work comprises the following tasks: (1) sensor optimization regarding intensity of the response and subsurface “bleeding” area, (2) integration of microcapsules into 3D-printed and spray-coated geometries including optimization of microcapsule wall thickness and mechanical properties, and (3) testing and evaluation of prototypes, including environmental and industrial.

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2. FOUNDATIONAL RESEARCH

SNL internal research (unpublished) has demonstrated the feasibility of tamper-indicating materials based upon a turn-on fluorescence mechanism. Note that research on turn-on fluorophores and microcapsules occurs in a variety of fields; however, research on using these materials and techniques specifically for the unique application of TIEs is limited. Key results included the preparation of fluorophore compounds in liquid organic matrices that were encapsulated in copolymer microspheres. The different components of the sensor system were investigated in isolation and in combination.

The ideal turn-on fluorophore is one that undergoes a change from fully non-fluorescent to highly fluorescent following exposure to the analyte, or microcapsule breakage in this case. Three such compounds were prepared and investigated, although all were found to be unstable over a time period of several months. Following those results, the investigation turned to an exciplex turn-on fluorescence mechanism that provided very high environmental stability but reduced sensitivity with respect to the aforementioned true turn-on fluorophore compounds. This was due to lower quantum efficiency of the exciplex emission.

A second component of the research was the organic material that serves as a matrix for the fluorescent sensor compound. Different polymerizable ‘self-healing’ materials and aliphatic oils were investigated in this work. While the most promising results were obtained for the organic oils due to favorable flow and mass-transport characteristics, there is still a compelling case for self-healing monomers due to the permanence of their response following polymerization.

The third component for this system involved optimization of the tamper-indicating device architecture. The development involved 3D printing using dispersed microcapsules in a UV-curable resin. While this was successful as a proof-of-concept, there are considerations related to long-term compatibility of the microcapsule/resin mixture, the mechanical characteristics/detection sensitivity of the corresponding tamper-indicating device design, protection against routine facility handling (accidental bumps or drops), and CONOPs such as repair of the material if necessary. Fig. 1 displays the results of the prior work, for a co-polymer based microcapsule filled with an aliphatic oil and exciplex-based sensor material.

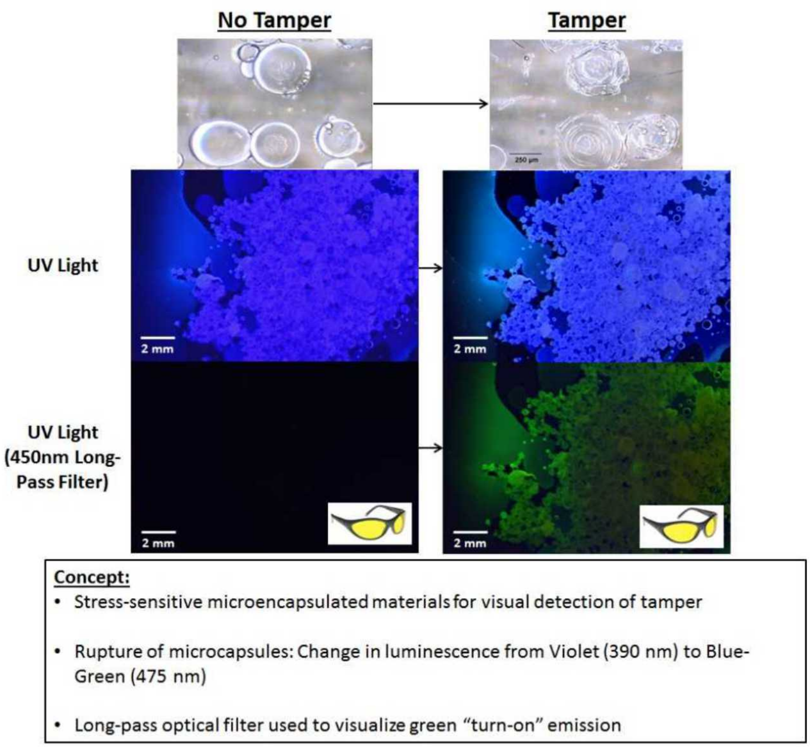

FIG. 1. Summary of the tamper-indicating material concept. Pressure-induced microcapsule breakage is visualized by the presence of green luminescence when viewed through a long-pass optical filter (bottom right image). An example of such a filter is the yellow-tinted sunglasses shown in the inset. No luminescence is evident in the undamaged system when viewed through the same filter (bottom left image).

3. CURRENT RESEARCH INTO SENSOR COMPOUNDS AND MICROCAPSULES

3.1. Sensor compounds

A two-part sensor mechanism is in development for visual tamper indication. The mechanism of this approach relies on a synthesized organic molecule binding to a transition metal cation, causing a dramatic and irreversible visible color change. These two components will be dispersed within a 3D-printable polymer matrix or sprayable polymeric solution to achieve the tamper-indicating properties. This approach is more advantageous and efficient than the fluorophore-based method described in Section 2 as the sensor requires no UV light excitation, and thus no instrumentation is required for visualization and confirmation of mechanically-based tampering.

The incorporation of the sensing organic molecule has three potential synthetic pathways toward the development of a functional material: the sensing molecule can simply be dispersed within a polymer, chemically attached to the end groups of commercial polymer, or used as a starting material to build polymer systems. Though the first method is the simplest approach, the final approach allows tunability of both chemical composition and molecular weight of the polymer system, which permits chemical and physical property manipulation. The second component of the sensing mechanism relies on a microencapsulated 3d transition metal solution dispersed throughout the polymer matrix. Upon mechanical damage the microcapsules break and the dispersed metal solution reacts with the sensing molecule in the polymer causing the irreversible dark color change. The concept is shown in Fig. 2 below.

FIG. 1. Colorimetric sensor mechanism using 3d transition metal solutions (TM) with sensing organic molecule (A) to irreversibly form molecular (TM-2A) complex.

3.2. Microcapsules

Microencapsulation provides a protective barrier between the dye-endcapped polymer and transition metal ion pair required for the colorimetric force response. Ideally, upon loading with a specific amount of force, the encapsulation will rupture and release transition metal ions to the surrounding environment, containing the dye-endcapped polymer, and thus produce a colorimetric response. As such, optimizing the microencapsulant properties, including shell material, shell thickness and diameter, and environmental stability, are important to developing the ideal response of minimal rupture under normal processing and handling of the fabricated part, and maximum rupture upon application of tamper force.

Previous microencapsulation research focused on emulsion-based, urea-formaldehyde polymer shells encapsulating hydrophilic dye compounds. When released, the dye compound would encounter either transition metal ions or form a charge transfer complex, which would alter the optical absorbance or fluorescence profile of the dye, and create a readable signal. While proof-of-concept demonstrations of cargo encapsulation and release in mineral oil dispersions were successful (Fig. 1) significant background colorimetric response present during synthesis and purification, and degradation of encapsulated material during storage precluded further exploration of urea-formaldehyde polymers as an encapsulating shell.

Encapsulation using silica (SiO_2 network) is a strategy successfully employed to contain hydrophilic dye compounds and biomolecules [1-2], as well as hydrophobic cargo such as hexadecane [3]. Compared to the polymer shells previously explored, silica shells are more resistant to premature breakage, and less permeable. To this end, silica microcapsules are being synthesized, for encapsulation of aqueous transition metal ion solutions as shown in Fig. 3. The route uses the well-known Stöber method to create solid, spherical SiO_2 seed particles of variable size, generally 100-1000 nm in diameter, followed by assembly of the seed particles into a spherical microcapsule containing transition metal ions *via* an inverse Pickering emulsion using controlled concentrations of an emulsifier and the transition metal solution. The walls of the microcapsule are solidified through crosslinking of the seed particles using additional $Si(OEt)_4$. By varying the seed particle and microcapsule sizes, and size distributions, the rupture profile will be tuned to match the tamper force. The identity and concentration of encapsulated metal ion can be varied, as shown in Section 3.1, to produce the most appropriate colorimetric response.

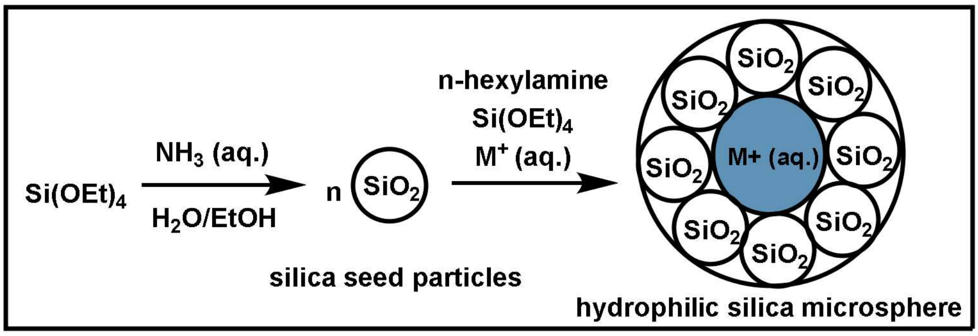

FIG. 3. Strategy employed for hydrophilic silica microcapsule synthesis. First, silica seed particles are created through the Stöber method, then the seed particles are assembled into a microcapsule using an inverse Pickering emulsion, and the sphere is solidified using additional $Si(OEt)_4$.

4. FUTURE WORK

The team continues research and development on sensor compounds and microcapsules. Sensor compounds and microcapsules will eventually be integrated and fabricated as 3D printed prototypes and spray coated prototypes. The prototypes will undergo environmental testing.

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