Autonomous Indication of Mechanical Damage in Polymeric Coatings

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Polymers are susceptible to damage in the form of small cracks, which are often difficult to detect. Even at small scales, crack damage can significantly compromise the integrity and functionality of polymeric materials. Damage to protective polymer coatings on metal substrates initiates corrosion undercutting and other forms of environmental degradation.1,2 Barely visible impact damage of fiber-reinforced polymer composites leads to significant degradation in mechanical performance.2,3 Here we introduce a microcapsule-based system for autonomous indication of damage in polymers and polymer composites. The ability to detect damage early, before catastrophic failure, improves safety and has potential to reduce maintenance costs. Moreover, our damage indication strategy can be combined with other functions such as self-healing and corrosion protection.4,5 to both report and repair cracks.

A wide range of mechanisms for mechanically triggered color change and fluorescence in polymers have been reported, including single molecule turn-on/off fluorescence,6–8 mechanochromism,9–23 phase/morphology/defect evolution,24–26 and embedded capsules.27–33 Single molecule optical techniques enable force detection at very small length scales, such as studies of cell adhesion and interfaces in biological systems.24,25 Recently, biomolecules have also been exploited as mechanophores to reveal microscopic damage in bulk polymeric composites.36,37 However, these detection mechanisms are currently restricted to internal material interfaces and potential problems with false positive indications and long-term stability require further investigation. Mechanochromically induced color/fluorescence changes have been generated under large strains in bulk polymers. Many of these early mechanophores exhibit a reversible optical change,19,20 and therefore are not promising to detect permanent damage. Several mechanochemical systems have been developed to indicate damage,28–30 but performance is limited by low intensity and potential bleaching of fluorescence. An alternate strategy for damage detection is to store indicators in isolated capsules22–30 or hollow fibers31–33 in a polymer matrix. However, these encapsulated systems are currently limited by lack of a turn-on mechanism (i.e., the indicator is always “on,” fluorescent or colored), low contrast between the indicating color and the coating, and poor stability. The indication system reported previously by Vidinejevs et al.29,30 requires two different capsules, one containing crystal violet lactone leuco dye and a second containing methyl 4-hydroxybenzoate color developer, embedded in the coating with a solid silica gel color developer. This three-component system produces a very low contrast color indication for a significant amount of indentation damage to the coating. Also, there is no discussion of stability or controls (false positives).

For successful damage detection, high contrast between the “on” and “off” states and high stability both before and after damage are critical. In this work, we report a microcapsule-based strategy that provides in situ visual indication of damage as small as 10 µm in polymer coatings. We demonstrate that the indication mechanism is extremely stable and no degradation is observed over 8 months for both damaged and intact areas of polymer coatings. In great contrast to previous capsule-based systems,27–30 the chemical indicator we report here does not require additional components (e.g., color developer or catalyst) or activation (e.g., UV light). Instead, visual indication is triggered by the amine-cured epoxy coating. The removal of additional additives maintains the original coating properties and prevents potential indication voids due to inhomogeneous dispersion of components. Our robust microcapsules coupled with the availability of diverse amine-containing coatings create a versatile platform for self-reporting materials.

Our damage indication concept is illustrated in Figure 1. Microcapsules containing the indicator 2′,7′-dichlorofluorescein (DCF) dissolved in ethyl phenyl acetate (EPA) are homogeneously dispersed in an epoxy coating on a substrate. Mechanical damage (e.g., scratch, abrasion, or compression) causes the microcapsules to rupture and release the core materials. A dramatic color change from light yellow to bright red is generated when DCF species come in contact with the amine-cured epoxy matrix materials. Since the DCF provides strong photoluminous signals, only a dilute DCF/EPA solution (i.e., 5 × 10⁻³ M) is required. Due to the highly localized release mechanism and minimal absorption of core materials into the
polymer coating, the delivery of DCF species is restricted to the damaged region alone.

In prior work, DCF has been used for adsorption indicators and fluorescent biosensors. Here, DCF is selected as the indicating agent due to its high reactivity with a variety of amines to produce a vibrant color change. DCF is soluble in EPA, a nontoxic solvent that has previously been encapsulated. The DCF solution is initially light yellow in color, but changes into an opaque red suspension immediately after addition of 1 droplet of amine (i.e., polyoxypropylene triamine, EPIKURE 3233) (Figure 2a and Figure S1, Supporting Information). Molecular structures of DCF before and after the reaction were determined by nuclear magnetic resonance (NMR) analysis (Supporting Information) and are shown in Figure 2a. The addition of the amine causes DCF molecules to evolve into a base form and precipitate out of the EPA solution due to a dramatic drop in solubility.

We hypothesized that DCF would undergo a similar reaction with unreacted amines in an epoxy. Epoxy specimens were prepared with stoichiometric ratio EPON Resin 813 (bisphenol-A based epoxy resin diluted with cresyl) and curing agent...
EPIKURE 3233 (100:43) and subject to various cure cycles. The degree of cure was 96% after 48 h at 35 °C and 100% after additional 2 h at 100 °C (Figure S2, Supporting Information). The free amines and residual amines were detected by ninhydrin (2,2-dihydroxyindane-1,3-dione) reaction.45) Epoxy specimens were imaged after being soaked in a ninhydrin–ethanol solution for 1 h and then heated at 100 °C for 15 min. A strong purple color was observed in both samples cured at 35 °C and 100 °C (Figure S3, Supporting Information). Even though the epoxies were fully cured, unreacted amine groups were still present in the matrix. To examine the ability of DCF to react with the residual amines, cured epoxy samples were soaked in the core solution (i.e., 5 × 10^-3 M DCF/EPA solution). DCF precipitates were continuously generated and the entire epoxy specimen turned red when lifted from the solution after 1 h (Figures 2b,c and Figures S4, S5, Supporting Information). Fracture surfaces of the epoxy specimens were examined to exclude any possible surface effect, and the reacted red color species were found not only on the surface of the epoxy pieces, but also within the interior of the samples. The mass uptake of EPA by epoxy after a 1 h soaking was 2.9% for specimens cured at 35 °C and 1.4% for specimens cured at 100 °C (Figure S3, Supporting Information). The absorption of EPA into epoxy aids the transport of DCF species in to the matrix and the formation of red precipitates in the epoxy.

Stable microcapsules containing a 5 × 10^-3 M DCF/EPA solution as the core material (referred to as DCF microcapsules) were fabricated by adopting the method of Caruso et al.44) Representative images of dry capsules before and after rupture are shown in Figure 3a. The microcapsules are 48 ± 13 µm in diameter, and the shell wall is well formed with a characteristic rough surface46) and thickness of approximately 300 nm. Capsules were then submerged in the amine curing agent and some were ruptured in a similar fashion (Figure 3b). The damaged microcapsules immediately changed color while the intact microcapsules remained unchanged.

The stability of DCF microcapsules in amine curing agent was examined by immersing them in EPIKURE 3233 for 48 h (Figure S6, Supporting Information). Their thermal stability was also evaluated by isothermal gravimetric analysis at 120 °C for 200 min (Figure S7, Supporting Information). In both tests, the DCF microcapsules remained intact and no color change or significant weight loss was observed. After each of these stability tests, the microcapsules were crushed within amine and found to remain active indicators.

DCF capsules were mixed with epoxy and coated (approx. 350 µm thick) onto a steel substrate. Coatings were scribed with a stylus and imaged by digital camera (Canon EOS 7D) and stereomicroscope (Zeiss SteREO Discovery V20 Microscope). The scribed region immediately changed color and the intensity grew stronger.

Figure 3. DCF filled microcapsules before and after rupture. a) SEM images of as-prepared microcapsules and capsule ruptured by razor blade. b) Optical images of microcapsules immersed in curing agent (polyoxypropylene triamine). Color develops when the core materials are released by rupture of the capsule shell wall.
and stabilized within a period of ≈30 min. As shown in Figure 4a, the scratch in the self-reporting coating was highly visible in comparison to an identical scratch in a control epoxy coating that did not contain DCF microcapsules but was otherwise identical.

In order to better evaluate the performance of coatings and maximize color intensity, we carried out further experiments on transparent glass substrates. Shown in Figure 4b, a series of scratches with increasing depth were created in a specimen with 15 wt% DCF microcapsules. As the cutting depth increases, considerably more capsules are damaged and the color intensity is significantly enhanced (Figure S8, Supporting Information). The width of the scratch increases with cutting depth as well, leading to rupture of a greater number of microcapsules. In this specimen, scratch as small as 10 µm in width is clearly indicated. Further improvement in indication resolution can be achieved by utilizing smaller microcapsules, but would require magnified optical observations as this current self-reporting ability reaches the limit of non-equipment-aided visual detection.

Color intensity is also dependent on the concentration of DCF microcapsules in the coating (Figure 4c). As expected, color intensity increased with increasing microcapsule concentration due to higher number density per unit area of ruptured microcapsules for identical size scratches (Figure S9, Supporting Information). A minimum microcapsule concentration of 5 wt% was required to provide sufficient color intensity for significant visual indication.

Control experiments that were performed in coatings with (1) nonindicating microcapsules (EPA core) in amine-cured epoxy and (2) DCF microcapsules in amine-free polymers (polydymethylsiloxane, polyurethane) (Figure S10, Supporting Information) confirmed our proposed indicating mechanism. The simultaneous presence of both DCF species and free amine groups is required for the autonomous damage indication. We examined coatings that were cured at higher temperature (10 h at 100 °C) and found no degradation of indication performance (Figure S11, Supporting Information). DCF microcapsules were also added to a gray colored commercial epoxy coating (Intergard 251 Epoxy Primer, International Paint) and both scratch and impact damage were successfully indicated (Figure S12, Supporting Information).

The DCF indicating system is also highly stable. Scratched coatings stored for over 8 months were imaged again (Figure S13, Supporting Information) and no change in color intensity was observed at either damaged or intact regions. New scratches were then made to undamaged locations, and the autonomous indication was equivalent in intensity to those carried out 8 months previously.

As a final step, we investigated a dual-microcapsule system for damage indication, consisting of DCF microcapsules and...
microcapsules containing primary amines.\textsuperscript{[4,5]} The addition of amine microcapsules enabled damage indication in coatings without free amines available in the matrix polymer. The damage induced color change in a polydimethylsiloxane coating containing both DCF and amine microcapsules exhibits high indicating intensity and excellent stability (Figure S14, Supporting Information). Through the addition of microcapsules containing an epoxy monomer, we could enable coatings that not only indicate crack damage but also self-heal. In future generations of self-reporting coatings, we anticipate the ability to autonomously indicate a damage event, heal the damage and provide a secondary indication that the damage had healed.

We have demonstrated a self-reporting polymeric coating capable of indicating cracks as small as 10 µm in width. DCF was successfully encapsulated and dispersed into several types of polymeric coatings. In epoxy coatings, the DCF indicator released by mechanical damage was able to react with the residual free amines in the coating matrix, creating a highly localized red color in the cracked region. Through the addition of a second type of microcapsule containing liquid primary amines, autonomous damage indication was also achieved in nonepoxy coatings. In all coating systems, the indicating color change was vibrant, easy to detect and highly stable. Work is in progress to combine the ability to detect virgin damage with self-healing functionality and a secondary indication that reveals that crack healing has occurred.

**Experimental Section**

**Materials**: 2’,7’-Dichlorofluorescein (Sigma-Aldrich, St. Louis, MO) was used as a visual indicator for mechanical damage. Ethylene maleic anhydride copolymer (EMA, Zemic-400, average molecular weight = 400,000) from Vertellus (Indianapolis, IN), urea, ammonium chloride, resorcilon, 1-octanol, formaldehyde solution (37 wt% in H₂O), EPA, sodium hydroxide (NaOH) from Sigma-Aldrich, and triamine (Miller-Stephenson, Houston, TX) were selected as matrix materials. Ninhydrin (2,2-dihydroxyindane-1,3-dione) obtained from Sigma-Aldrich was used to detect the residual amines in epoxies. Specifically, epoxy samples were soaked in the ninhydrin–ethanol solution for 1 h, and then held at 100 °C for 15 min. Free amine groups were then indicated by a produced purple color. For comparison, parallel tests were conducted in 5 × 10⁻³ m DCF/EPA solution to demonstrate the ability of DCF to react with the residual amine groups in the epoxy. Molecular structures were determined by NMR spectra (Varian Unity 400 NB, Varian VXR 500, and Varian Unity 500 NB spectrometer). Visible spectra of DCF/EPA solution and soaked epoxy samples were obtained by ultraviolet-visible-near-infrared spectrophotometry (UV-vis-NIR, Varian/Vary S 5 G), Thermal behavior of DCF microcapsules and epoxy coatings were characterized by Thermogravimetric Analysis (TA Instrument Q50) and Differential Scanning Calorimetry (TA Instrument Q20). The heating rate was kept at 10 °C min⁻¹ and the purge gas was nitrogen.

**Fabrication of Coatings**: Epoxy EPON 813 and curing agent EPIKURE 3233 were mixed by stoichiometry (i.e., weight ratio of 100:43). Microcapsules were added into the mixture at various weight percentages. The well-mixed suspension was coated on glass slides or thin films. The final film thickness was 350 ± 50 µm.

**Supporting Information**

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

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