Activation of Mechanophores in a Thermoset Matrix by Instrumented Scratch

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ABSTRACT: Scratches in polymer coatings and barrier layers negatively impact optical properties (haze, light transmission, etc.), initiate routes of degradation or corrosion (moisture permeability), and nucleate delamination of the coating. Detecting scratches in coatings on advanced materials systems is an important component of structural health monitoring but can be difficult if the defects are too small to be detected by the naked eye. The primary focus of the present work is to investigate scratch damage using fluorescence lifetime imaging microscopy (FLIM) and mechanical activation of a mechanophore (MP)-containing transparent epoxy coating. The approach utilizes a Berkovich tip to scratch MP-epoxy coatings under a linearly increasing normal load. The goal is to utilize the fluorescent behavior of activated MPs to enable the detection of microscale scratches and molecular scale changes in polymeric systems. Taking advantage of the amine functionality present in a polyetheramine/bisphenol A epoxy network, a modified rhodamine dye is covalently bonded into a transparent, thermoset polymer network. Following instrumented scratch application, subsequent fluorescence imaging of the scratched MP-epoxy reveals the extent of fluorescence activation induced by the mechanical deformation. In this work, the rhodamine-based mechanophore is used to identify both ductile and fracture-dominated processes during the scratch application. The fluorescence intensity increases linearly with the applied normal load and is sensitive to fracture dominated processes. Fluorescence lifetime and hyperspectral imaging of damage zones provide additional insight into the local (nanoscopic) environment and molecular structure of the MP around the fracture process zone, respectively. The mechanophore/ scratch deformation approach allows a fluorescence microscope to probe local yielding and fracture events in a powerful way that enhances the optical characterization of damage zones formed by standard scratch test methods and leads to novel defect detection strategies.

KEYWORDS: instrumented scratch, epoxy, mechanophore, damage sensing, strain sensor, polymer, organic coating

1. INTRODUCTION

Structural health monitoring (SHM) is required for the discovery, development, and deployment of advanced materials such as fiber reinforced polymer composites in aerospace, infrastructure, and renewable energy applications. An important aspect of SHM is the detection of scratches on surface coatings that create delamination points, initiate points of degradation, and diminish optical properties. One promising approach for monitoring in situ mechanical degradation in polymers is to utilize mechano-responsive materials, that is, to leverage the mechanochemistry inherent to molecules that change their properties and chemical structure upon

mechanical deformation.^{1,2} The study of the chemical response of polymers to mechanical strain has been ongoing for decades.^{3,4} Here, we report on furthering our understanding of the mechanochemistry of polymers by applying selfreporting damage sensor molecules coupled with fluorescence

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Figure 1. (a) Spirolactam-based MP transition catalyzed by strain or ultraviolet irradiation in the presence of water. (b) Schematic of progressiveloading scratch-testing experiment illustrating direction of trigonal pyramid-shaped tip along and into surface of MP-loaded epoxy. (c) Chemical reaction of MP (top circle) or control dye (bottom circle) with DGEBA epoxy network during thermal cross-linking reaction. (d) Shape and angle of high angle Berkovich tip utilized in all scratch experiments. Sideview (left) and top view (right) shown.

lifetime imaging. This approach provides researchers with a new tool for evaluating the long-term effects of complex mechanical loading scenarios, coupled with environmental stressors like temperature, ultraviolet (UV) exposure, and humidity, on polymers.⁵⁻⁷

Mechanoresponsive molecules that exhibit a chemical change in their response to mechanical deformation are referred to as mechanophores (MP).⁸⁻¹¹ In soft material systems, a MP is covalently bound along the backbone of a polymer chain^{12,13} or reacted into a cross-linked network.¹ This direct attachment is essential to ensure that the mechanical energy applied to the bulk component is transferred through the polymer system and applied to the MP.¹⁵ As the bulk polymer specimen is loaded, the MP is subjected to mechanical loading. This loading typically stimulates a structural and/or chemical rearrangement within the MP, leading to a distinct change in the resulting optical properties.¹⁶ In most cases, the MP within the polymer system will exhibit a visible color change upon deformation. The ensemble activation of many mechanophores indicates the location and magnitude of the applied stress.^{9,17} As the magnitude of the applied stress increases on a MP-containing material, more MP functional groups undergo structural changes, and if the activated form of the mechanophore is fluorescent the resulting fluorescence intensity increases. These self-reporting damage sensing materials could potentially be used to observe and monitor the durability and wear of polymers, allowing for the optimization of fatigue life estimates. For example, using such an approach in MPcontaining fiber reinforced composites would prevent premature retirement of wind turbine blades, aircraft, and bridge deckings,¹⁸ ensuring that necessary repairs are completed, and each costly component is deployed for its full useful lifetime.¹¹ Additionally, MPs could be utilized to detect microcracking in glassy epoxy systems. Early detection

of microcrack propagation would highlight areas requiring maintenance thereby increasing the safety of the parts in use.¹⁹

An overarching goal of this work is to experimentally measure the extent of fluorescence activation of a mechanophore covalently attached to a cross-linked polymer network as a function of mechanical damage. A more extensively studied mechanophore, spiropyran,²⁰ has been reported to require approximately 2 nN to 3 nN of force to activate a single molecule.⁹ In this study, a modified spirolactam-based MP is utilized, and given the relative robustness of the spirolactam MP, a higher stress concentration in the epoxy network was required to mechanically activate the MP.

By utilizing mechanophores in a glassy epoxy, a methodology for the detection of microscale scratches is presented here to further our understanding of MP technologies toward the development of self-reporting damage sensors. Thus far, several novel mechanochemistries have been developed that qualitatively indicate the magnitude of a load with an increased color change or fluorescence intensity response (i.e., higher force leads to higher intensity).^{9,10,21,22} However, for MPs to be useful as damage sensors, a quantitative relationship between bulk deformation and MP activation must be determined.¹¹ Single molecule force experiments such as those performed by Wang et al. are an important step toward developing this relationship.²³ Building on existing MP studies, a methodology and technique to relate mechanically induced damage to MP fluorescence activation are presented here to further understand MP technology for self-reporting damage sensing applications.

The mechanical deformation technique selected for the present study is instrumented progressive-load scratch testing. Instrumented scratch testing is a proven tool to evaluate the damage mechanisms in materials subjected to a sliding tip.^{24–26} The deformation of the polymer surface can be controlled by modifying the shape of the sliding tip (sphere,

cone, pyramidal), angle of attack, sliding speed, and the normal load.^{27,28} By inducing the scratch with a linearly increasing normal load, referred to here as a "progressive" load, a wide range of failure conditions can be observed within the same sample.^{29,30}

In this paper, MPs covalently bound in a polyetherdiamine and bisphenol A diglycidyl ether (DGEBA) network are activated by progressive-loading instrumented scratch deformation to quantify the relationship between applied scratch load and MP activation via fluorescence intensity. Maximum normal loads are varied while the tip shape and lateral scratch velocity are held constant. These constraints mean that the normal loading rate per length of scratch increases proportionally with the maximum load. The penetration depth during scratch, lateral force, and residual groove depth are recorded during each test. After the application of scratches, laser scanning confocal microscopy (LSCM) is used to image each scratch and quantify fluorescence intensity. Bright field optical microscopy (BF) is also utilized to measure scratch width along each scratch. Fluorescence lifetime imaging microscopy (FLIM) is used to qualitatively observe changes in the local chain mobility near the mechanophore resulting from the applied deformation. Hyperspectral (HS) imaging provides additional insight into the molecular structure of the MP. A time lapse LSCM experiment is conducted over many hours to determine the thermal relaxation of the MP. The overarching goal of this work is to develop a methodology to highlight the utilization of MPs as self-reporting damage sensors for microscale scratch detection.

2. MATERIAL AND METHODS

2.1. Synthesis of Rhodamine B Spiroamide and 110 **Spiroamide.** The synthesis of the rhodamine B spiroamide compound was performed as reported previously.³¹ The synthesis of rhodamine 110 spiroamide is similar to that for rhodamine B spiroamide. Approximately 518 mg of rhodamine 110 HCl (1.41 mmol) and about 1.76 g of ethylenediamine were refluxed in anhydrous ethanol for 24 h until the initial dark red color faded and the reaction appeared yellow. After the solvent was removed in vacuo, the solids were resuspended in 50 mL of dicholoromethane, washed twice with 25 mL of water, and then dried over anhydrous sodium sulfate. The solids were removed by vacuum filtration, and the compound was recovered from the filtrate by removing the solvent in vacuo. The yield was approximately 285 mg, 0.765 mmol, 54%. ¹H NMR (600 MHz, DMSO-d⁶): δ = 2.18 (t, 2H, N-CH₂-), 2.96 (t, 2H, C(O)-N-CH2-), 5.3-6.4 (m, 6H, xanthene Ar-H), 7.00 (d, 1H, Ar-H ortho to xanthene), 7.49 (m, 2H, Ar-H meta and para to xanthene), 7.76 (d, 1H, Ar-H ortho to carbonyl).

2.2. Sample Preparation. Fully cured MP-containing epoxy samples were prepared for progressive-loading scratch testing experiments. The glassy, cross-linked polymer samples were composed of a commonly employed epoxy/polyetherdiamine system. Rhodamine 110 (MP, Sigma-Aldrich) was chemically modified by replacing the hydroxyl group on the pendant carboxylic acid with an amine functionality (Figure 1a).

The resulting MP was then dissolved in a curing agent mixture containing two polyetherdiamines (Jeffamine D-230 and Jeffamine D-2000, Huntsman), selected to enhance epoxy toughness. The MP was added to the Jeffamine mixture (mass fraction of 90% D-230, mass fraction of 10% D-2000) to achieve a final stoichiometric epoxy formulation that contained a nominal mass fraction of 0.2% MP. An epoxy-functionalized monomer of bisphenol A diglycidyl ether (DGEBA, D.E.R. 332, Sigma Life Science, St. Louis, MO) was then added to the MP/curing agent solution and mixed by hand (Figure 1b). After degassing at 50 °C for approximately 10 min, the liquid MP epoxy was poured between two fluorosilane functionalized glass slides

separated by a nominaly 100 μ m thick polytetrafluoroethylene shim. The glass/MP-epoxy/glass sandwich structure was placed in an oven at approximately 80 °C for 8 h to cure. The resulting solid epoxy film was carefully removed from the glass mold after cooling to room temperature. Care was taken to avoid exposing the samples to visible or UV light during preparation. The same procedure was followed to fabricate the control samples, with the rhodamine 110 replaced by rhodamine B (Sigma-Aldrich) (Supporting Information (SI) Figure S1a). Tensile testing of epoxy dog bone samples was conducted according to ASTM 638.³² The moduli for all samples tested was 1.45 \pm 0.05 GPa with a yield stress of 44 \pm 5 MPa with a combined standard uncertainty determined from n = 4 samples indicating that the addition of the MP into the network did not affect the mechanical properties within the uncertainty of the ASTM measurement.

2.3. Instrumented Scratch Experiments. A nominal 10 mm by 10 mm section was cut from the MP-epoxy sample with a razor blade, soaked in deionized water for about 12 h, and then carefully conditioned in air at a nominal relative humidity of 50%. The sample was mounted with a clear epoxy to a glass slide which was subsequently mounted to the nanoindenter (MTS Nanoindenter XP) stage with double-sided tape. Scratches were applied at a constant scratch velocity of 10 μ m/s and a linearly increasing normal load from about 20 μ N to the maximum prescribed normal load, $P_{\rm m}$. The scratch length was held constant at 1000 μ m, as illustrated schematically in Figure 1c. A diamond Berkovich tip with a face angle of $\theta_{\rm B} \approx 42.3^{\circ}$, a semiapical angle of 120.05°, and an equivalent cone angle of 49.5° was used for all experiments (dimensions reported by manufacturer). The scratches were conducted with the flat triangular face of the Berkovich tip facing forward (in the direction of lateral displacement). Two scratches, about 90 μ m apart, were applied at each of the maximum normal loads ($P_{\rm m} = 5 \text{ mN}$, $P_{\rm m} = 10 \text{ mN}$, $P_{\rm m} =$ 25 mN) tested. These maximum loads resulted in loading rates of 0.05 mN/s, 0.10 mN/s, and 0.25 mN/s, respectively. The normal and lateral loads and displacements of the probe were recorded during each scratch.

Over the course of a scratch experiment, the indenter tip acts as a profilometer on the surface by moving at a low constant normal load of 20 μ N, called the preprofile, to account for sample tilt. The tip then moves across the surface at the programmed loading rate and velocity called the scratch. Finally, a postprofile is conducted where the tip again acts as a profilometer, at a low constant normal load of 20 μ N, to determine the residual scratch depth and the onset of cracking. The prescratch profiles measured the average surface roughness of the undeformed MP-epoxy films to be 50 nm ± 25 nm.

2.4. Optical Imaging. After the application of the scratches, the damaged samples were removed from the nanoindenter stage and optically imaged with laser scanning confocal microscopy, fluorescence lifetime imaging microscopy, and hyperspectral imaging microscopy.

2.4.1. Laser Scanning Confocal Microscopy. Each scratch was imaged with LSCM (Leica SP5). An argon, continuous wave laser (λ = 488 nm) excited the sample and a dichroic (DD488/561) was used to filter the emission, captured with a photo multiplying tube monitoring the band between λ = 520 nm and λ = 600 nm. This emission band was well outside of the known autofluorescence peak emission (λ = 300 nm) of bisphenol A (the monomer in the epoxy).³³ Eight scans (155 μ m by 155 μ m at 512 px by 512 px) were taken along each pair of scratches with an infinity corrected 100× air objective (numerical aperture, NA = 0.9). Confocal z-slices of 0.25 μ m thick were taken of each field of view with the number of slices determined by the depth of the scratches. Using image analysis software (ImageJ, National Institutes of Health), these slices were then collapsed to develop a 2D max intensity projection to show the "top view" of each scratch.

2.4.2. Advanced Imaging: Fluorescence Lifetime and Hyperspectral Imaging Microscopy. The fluorescence lifetime is the decay time of an electron from the excited state to the ground state in the molecule. Repeated measurements of decay time allow for a histogram of decay times to be built-up at each spatial location. This distribution of decay time measurements can subsequently be fit to determine the

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Figure 2. Penetration depth versus scratch distance for maximum loads of (a) $P_m = 5$ mN, (b) $P_m = 10$ mN, and (c) $P_m = 25$ mN. Each plot presents both the vertical penetration depth during the scratch (black) as well as the postscratch profile (orange), which reveals information regarding permanent, plastic deformation and elastic recovery. The oscillating penetration depth in (c) indicates that fracture occurred in that region. For reference, the applied load is indicated by the pink dashed line with values given on the right *y*-axis. The label and values on the left *y*-axis and the legend in (a) and the right *y*-axis in (c) apply to all plots.

characteristic lifetime, τ , of the molecule. A FLIM image is achieved by measuring τ at each position as the sample is moved beneath the field of view of the microscope.

The FLIM setup used for this experiment is described in detail in Woodcock et al.²¹ The pulses from a femtosecond Ti:sapphire laser were frequency doubled, temporally stretched, and spectrally narrowed to produce picosecond pulses at 488 nm to excite the molecules. A high numerical aperture (0.95 NA) objective was used to excite the molecules and collect the fluorescence in an epiconfiguration. The sample was raster-scanned through the focus to build up images. The resulting fluorescence was sent to a single photon counting module (SPCM) to produce lifetime images. An excitation power of 100 nW into the back aperture was used for these experiments. The FLIM images were acquired within 12 h of the application of the instrumented scratches. The images were 256×256 px.

HS imaging used the same pulsed laser system as the FLIM acquisition to obtain a complete emission spectrum at each point on a sample and then rastering across the region of interest to produce a complete image. The same experimental setup and conditions for the FLIM measurements were used for HS imaging. In this case, the signal was sent to a spectrometer and charge coupled device (CCD). The integration time per pixel was 3 s and the images were 128×128 px.

3. RESULTS AND DISCUSSION

3.1. Instrumented Scratch Mechanics. The effect the instrumented scratch has on the epoxy network is evaluated by quantifying the elastic-plastic response of the epoxy. A quick estimate is the rheological factor, X, which represents the ratio of the deformation strain imposed by the indenter to the elastic component of the total deformation:^{34,35}

$$X = \frac{E}{\sigma_y} \cot \theta \tag{1}$$

where *E* is Young's modulus, σ_y is the yield stress determined from tensile testing, and θ is the angle of the equivalent cone.³⁵ Low values of the rheological factor represent a predominately elastic response and high values represent a plastic response. For the control epoxy (MP covalently incorporated into the network at only one site) and the MP-epoxy, the rheological factor was 30 ± 2.2, indicating that both materials exhibit a similar elastic-plastic response to deformation by the tip.

Figure 2 contains representative plots of the penetration depth of the indenter tip as a function of lateral position

(scratch length) for each of the three maximum loads. Each plot shows the scratch and postscratch traces (the prescratch trace is omitted as the samples were relatively flat). The elastic recovery is defined as the difference between the penetration depth of the indenter tip during scratching and the residual scratch depth normalized by the penetration depth of the indenter tip during scratching.³⁰ The elastic recovery immediately after scratching was approximately 65% \pm 3% for all scratches, which indicates an elastic-plastic deformation.

There were two scratch damage mechanisms observed optically and from the nanoindenter profilometry. At low normal loads, the epoxy exhibited a ductile groove with material pile-up on the edges of the scratch. The MP activated along the length of the scratch for $P_{\rm m} = 5$ mN and $P_{\rm m} = 10$ mN. The $P_{\rm m}$ = 25 mN scratch exhibited ductile grooving at low normal loads. At higher normal loads, fractures in the epoxy were observed in the bottom of the scratch and a pile-up of material was observed on the outer edge. The onset of fracture is identified from the optical image and nanoindenter profilometry as initiating at a normal load of $P = 13 \text{ mN} \pm$ 2 mN and a scratch distance of 729 μ m \pm 94 μ m (see Figure 2). The onset of fracture identified both optically and via fluorescence, allows for the ranking of coating scratch performance. Linking this behavior to a macroscale engineering property is required to determine how the coating performance may be improved.

Akono et al. have developed a variety of analysis techniques to relate the deformation imposed by the indenter tip to the fracture toughness of the material.³⁶⁻³⁹ Application of Akono's methods to the present study is described in detail in SI Figure S2 and the results are highlighted here.

Two important results are gleaned from this analysis of scratching with a self-similar tip geometry. The total pressure on the tip scales exponentially with the penetration depth, indicating a potential constant of proportionality for fluorescence intensity with increasing damage. Second, beyond a scratch load of approximately $P_{\rm N} \geq 13$ mN, the scratch damage was fracture dominated and governed by the fracture toughness of the epoxy. The plane strain fracture toughness of the epoxy, K_c , using SI Figure S3 was estimated to be $K_c = 0.60 \pm 0.08$ MPa·m^{1/2}, which is in excellent agreement with literature values of similar epoxy-amine blended thermosets with $K_c = 0.61 \pm 0.10$ MPa·m^{1/2}.⁴⁰



Figure 3. Fluorescence activation of MP after progressive scratch loading. Each set of three images on the left are max intensity projections obtained from LSCM imaging in bright-field, fluorescence, and overlaid bright-field and fluorescence (from left to right) for scratches with maximum loads of (a) 5 mN, (b) 10 mN, and (c) 25 mN. The scale bar to the right of (c) applies to a, b, and c. Higher magnification images of the deepest end of each scratch are shown in (d1–d3) fluorescence and (e1–e3) overlaid bright-field and fluorescence for each maximum load ((d1, e1) 5 mN, (d2, e2) 10 mN, and (d3, e3) 25 mN). The scale bar in (d1) applies to d1-e3). (f) The resulting intensity of each fluorescence image as a function of position along the scratch reveals increasing fluorescence intensity with increasing load.



Figure 4. Mechanophore activation (measured with fluorescence intensity) as a function of mechanical deformation with varying maximum normal loads. Intensity versus (a) normal load and (b) area of contact. The values on the *y*-axis in (a) apply to both plots.

3.2. Fluorescence Intensity as Indicator of the Extent of MP Activation. After all scratches were applied, the damaged MP-epoxy films were observed with several optical imaging techniques to evaluate the extent of fluorescence activation of the MP and further understand the optical properties of the activated MP as a function of position. Specifically, BF, LSCM, FLIM, and HS imaging microscopy

were utilized. To ensure the occurrence of MP activation was from the instrumented scratch, a control sample and MP functionalized sample were compared (SI Figure S1). The control sample had no fluorescence response while the MP functionalized sample elicited a fluorescence response. Additionally, mechanical activation and photoactivation are compared in SI Figure S1.

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Figure 5. Optical imaging of activated scratches. Images of the deep end of the $P_m = 25$ mN scratches (a1–a4). Images were obtained with (a1) BF, (a2) LSCM, (a3) FLIM, and (a4) HS imaging. The color-coded legends beneath the images apply to the FLIM (a3 lifetime) and HS (a4 peak emission) images. (b) Histogram of fluorescence lifetime distribution over the entire region of interest for $P_m = 25$ mN (light blue) scratches as well as an undeformed MP-epoxy sample that was photoactivated (black). (c) Schematic of FLIM and HS imaging light path.

To determine the fluorescence intensity of the activated MP, a confocal microscope was operated simultaneously in transmitted bright field mode and laser scanning confocal fluorescence mode (Figure 3). This imaging approach allowed the physical shape of the scratch to be captured along with the fluorescence emission intensity of the activated mechanophore. Small regions of each scratch were imaged at a high magnification (100×) and then stitched together to achieve a high-resolution image of the entire length of the scratch. To verify that the MP activation occurred in the damaged regions of the scratch, the stitched BF and LSCM images were then overlaid with image processing software (ImageJ MosaicJ, National Institutes of Health).⁴¹

Significant fluorescence activation was observed only in the trenches or bottom of the grooves in the center of each scratch with less intense activation observed along the sides of each scratch. The width and intensity of the fluorescent region increased, as expected, as the depth of the scratch into the MP-epoxy surface increased. At higher loadings ($P \approx 15$ mN), the stress in the scratched material exceeds the fracture toughness and periodic fractures along the groove of the scratch occur. This accounts for the distinctive pattern in the deepest 400 μ m of the P = 25 mN scratch (Figure 3d3). A line trace was placed on each scratch from the shallow end (about P = 0.02 mN) to the deep end ($P = P_m$) on the LSCM images and the resulting fluorescence intensity is plotted as a function of lateral position in Figure 3f.

To further quantify the relationship between MP activation with mechanical deformation, Figure 4a compares the normal load to the resulting fluorescence intensity. The activated MP intensity increases linearly as a function of normal load. Since the lateral translation velocity of the probe was held constant at $V = 10 \ \mu m/s$ and each scratch was 1000 μm long, the overlapping curves in Figure 4a indicate that the extent of the MP activation does not have a strong dependence on loading rate over the narrow range of strain rentes measured here. Figure 4b shows the fluorescence intensity as a function of scratch probe contact area $(A = h_{c,f}^{2*} \tan \theta_B)^{42}$ The linear relationship suggests that for a self-similar Berkovich tip, the intensity of MP activation is proportional to the area of material that is displaced during the scratch along with the presence of a fracture-dominated damage mode.

3.3. Advanced Optical Microscopy. To better understand the physical environment of the MP molecules in the damaged zones of the scratches, FLIM and HS microscopy were used to image specific regions of interest in the scratched samples. A custom-built microscope (illustrated schematically in Figure 5c) was used to acquire these FLIM and HS images. The resulting images of the "deep end" of a $P_m = 25$ mN scratch are shown in Figure 5a3,a4.

The characteristic fluorescence lifetime (τ) can be affected by several different factors. One factor of interest in this study is the local mobility of the dye molecule. In solution, organic dyes have short τ while a dye that is fully immobilized and fixed in a glassy polymer network has a much longer τ .^{43,44} In the FLIM image in Figure 5a3, the lifetime of the activated MP in the deep groove is shorter than in the fractured material near the scratch edges (triangular portions) that propagated away

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Figure 6. Fluorescence activation persistence over 1200 h. (a) Time lapse LSCM images of the same $P_m = 25$ mN scratch captured 1, 100, and 1200 h after instrumented scratch. (b) Mechanophore fluorescence intensity along scratch for the three different times demonstrating approximately a 50% decrease in fluorescence intensity with time. (c) Higher magnification images of the deep end of the same scratch at the three different times illustrating relaxation and reversion of a fraction of the mechanophore to the "closed" or nonfluorescent form.

from the scratch probe edge. This result can be interpreted by considering that as the crack propagated away from the tip, the polymer chains in the deepest part of the groove where the strain energy is highest have been stretched and likely fractured. This fracture alleviates residual stress and results in increased molecular mobility of the dye molecules that is evident in the decrease in τ within the groove region.

Alternatively, the material farther away from the tip during the scratch application experienced sufficient stress to activate the MP, yet, the lifetime is longer than in the groove, indicating that the cross-linked polymer network surrounding the MP away from the tip apex remains largely intact. By plotting the distribution of lifetimes for the FLIM image in Figure 5b, a bimodal distribution that further highlights the two regions (deep grooves and fractured chips) in the center and edges of each scratch can be observed. As a reference, the lifetime distribution plot in Figure 5b also shows the narrow τ distribution at longer characteristic lifetimes for an undeformed area on the same sample that was photoactivated rather than mechanically activated. Further discussion of fluorescence lifetime distributions can be found in SI Figure S5.

Just as the FLIM provides a semiquantitative measure of the damage to the polymer network near the MP, HS imaging can indicate changes to the molecular structure of the MP itself. Small changes in the molecular structure of a dye molecule can result in significant changes in the characteristic emission wavelength (λ_{em}).⁴⁵ For example, the structure of the MP and control dye molecules differ only in the dialkyl amines versus the amine groups attached to the conjugated ring system as seen in Figure 1c. However, for the MP, $\lambda_{em} = 510$ nm in solution, while for the control, $\lambda_{em} = 550$ nm, a difference of 40 nm.

3.4. Temporal Stability of MP Activation. Several mechanophores have been developed which are suitable indicators of mechanical strain for in situ or cyclic deformation. These mechanophores revert to their quenched or "closed" form shortly after activation with activation times ranging from several seconds to minutes. Depending on the electronegativity of the electron-withdrawing groups attached to the mechano-

phore.^{13,46} While this short-lived fluorescence can be attractive for some applications, a longer sustained fluorescence response is of interest for structural health monitoring and damage sensing where monitoring occurs on a less frequent basis. To determine the persistence of the fluorescence activation of the spirolactam MP discussed in the present work, the fluorescence intensity of the same scratch was measured by LSCM for 7 weeks. Figure 6 highlights the results of this time study. While a decrease in fluorescence intensity was observed, it is clear that the persistence of the mechanoactivation of the spirolactam is much longer than that reported for other similar mechanophores.^{47,48}

4. CONCLUSIONS

A mechanically responsive rhodamine-spirolactam was covalently bound into the cross-linked network of a glassy thermoset epoxy. Progressive load scratches were applied to the MP-epoxy and MP activation of the spirolactam in the damaged regions was observed with several optical imaging techniques. The fluorescence intensity increased monotonically with mechanical deformation. The fluorescence lifetime of the activated MP decreased significantly in the more heavily damaged regions of each scratch. HS imaging indicated that the molecular structure of the activated MP was unaffected by the application of deformation. Finally, an approximate 50% decrease in the fluorescence intensity was observed after more than a month under ambient conditions.

The methodology and system described here is a straightforward technique that demonstrates how MPs perform as self-reporting damage sensing technologies for both haze and scratch detection and assessment. As mechanophores move from invention and synthesis to applications, MP technologies that can detect a wide variety of deformation modes (viscoplastic–plastic-fracture shown here) will be required for various loading scenarios. The relatively long half-life and high activation forces required for spirolactam are ideal for detecting highly localized stresses, like surface cracks and scratches, as demonstrated here, which demonstrates the potential of using this MP system for SHM.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.1c15004.

Control experiments for photoactivation and covalent attachment of the mechanophore into the matrix, scratch mechanics analysis, fluorescence lifetime imaging phasor analysis, MP, and control spectral emission (PDF)

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Notes

The authors declare no competing financial interest.

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