Smart Mechanoluminochromic Coating for Impact Damage Detection in Composite Structures

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ABSTRACT

The susceptibility of composite materials to impact loads remains a critical challenge in aerospace applications. Conventional Structural Health Monitoring (SHM) systems employ embedded or adhesively bonded sensors, such as Bragg gratings or ceramic piezoelectrics, which compromise the mechanical integrity of the laminate and introduce complexities in signal acquisition due to optical, electrical, or wireless connections. Mechanoluminochromic (MLC) materials offer a transformative solution by exhibiting fluorescence emission spectrum changes under mechanical stimuli. This study presents a novel smart coating utilizing an MLC Cu-based Hybrid Coordination Polymer (HCP) dispersed into a thermoset epoxy-based paint. Applied via spray painting on a cross-ply carbon fiber reinforced plastic (CFRP) laminate, the coating enables full-field impact damage detection under UV illumination without altering the aesthetic appearance of the structure. Low-velocity impacts (LVI) were conducted at varying energy levels, and the resulting barely visible damage (BVD) was analyzed using smartphone-acquired images processed with Matlab algorithms. The green/blue fluorescence ratio demonstrated correlation with impact forces, while micrograph analysis of the laminate cross-section confirmed damage alignment with mechanoluminochromic responses. This innovative nondestructive inspection (NDI) technique offers cost-efficiency, reliability, and ease of implementation, establishing a promising avenue for SHM applications with potential real-time computer vision integration.

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INTRODUCTION

Composite materials have become indispensable in aerospace applications due to their superior mechanical properties and lightweight nature. However, their susceptibility to impact loads combined with a barely visible damage outside the laminate, poses significant challenges for maintaining structural integrity and ensuring safety. Structural Health Monitoring (SHM) systems have emerged as a pivotal solution to this issue, with embedded or adhesively bonded sensors such as Bragg gratings and ceramic piezoelectric transducers commonly employed for impact detection and damage assessment. While these sensors are effective, these systems present several limitations. he fragility of the sensors can degrade the mechanical properties of the host laminate [1], [2] while the need for intricate cabling or wireless connections introduces electromagnetic interference, weight penalties, and fabrication complexities [1].

In contrast, mechanocromic materials offer an innovative solution for impact detection by exhibiting a change in optical response when subjected to mechanical stress. This unique characteristic enables comprehensive damage assessment across the whole composite structures, while preserving their mechanical integrity and avoiding intricate cabling and fabrication process complexities [3], [4].

Among machancromic material category, mechanoluminocromic (MLC) stands out because operates through emission spectra change instead of absorption mechanism. Measurements based on changes in emission properties are less affected by disturbances caused by the ambient or dirt compared to those based on changes in absorption [5].

Despite these advantages, the direct application of MLC compounds is hindered by their insufficient mechanical characteristics. To address this limitation, they can be combined with a polymeric matrix by means of two different approaches: exploiting intrinsically luminochromic polymers or adding MLC additives into a neutral polymer matrix. The first method entails the covalent bonding of chromophoric units within macromolecular chains, producing a polymer with mechanoluminochromic characteristics. While this approach necessitates functional groups in both the polymer matrix and involves complex chemical reactions, it activates only with high loads and demonstrates reversible chromic behavior [5], [6]. The second method maintains the polymer matrix unaltered while introducing the MLC as a filler, creating a biphasic system. It offers flexibility in combining polymers and dyes for customized behaviors, leveraging dye interactions to produce optical and responsive properties. Its simplicity eliminates the need for hazardous solvents and complex reactions. However, weak interactions between the dye and polymer may lead to poor dispersion and low load transfer between the matrix and the mechanophore, leading another time to response only at high loads.

Researchers have developed mechanisms such as piezochromic pigments (e.g., CuMoO4) that change color under pressure and mechanochromic polymers that fluoresce upon stress-induced chemical bond rupture [7]. Applications include coatings and integration into composite matrices to enhance damage detection capabilities. While effective, limitations exist in activation thresholds, fluorescence decay, and fluorescence intensity relative to material strength [7], [8].

To address this limitation, this study explores the dispersion of MLC Cu-based Hybrid Coordination Polymer (HCP), characterized by low activation threshold and high tunability, in to a thermoset epoxy matrix to create a smart coating. The MLC coating was applied on a cross-ply carbon fiber reinforced plastic (CFRP) laminate.

Low-velocity impact (LVI) tests revealed the coating's capability to correlate fluorescence emission changes with impact forces through a custom image-processing algorithms. The preliminary results reported in this work demonstrate the potential of MLC coatings as a cost-effective, reliable, and implementable nondestructive inspection (NDI) technique.

MATERIALS AND METHOD

MLC SMART COATING

The MLC employed in this study is a copper iodide-based HCP with chemical formula [(CuI)3-Br-py]n, firstly synthetized by S. Masahara et al [9]. It was selected due to its high spectrum response under UV light and white color under natural light, which make it suitable for smart coating applications in terms of sensing and aesthetic performances. It was synthetized as polycrystalline powder via slurry, by the Molecular Crystal Engineering Group of the University of Bologna.

In Figure 1 it is shown the normalized spectral response under a UV light (365 nm wavelength) exposure of the MLC powder: pristine and after 10 minutes of grinding [10]. It can be observed that the emission maximum shift from blue (474 nm) to green (524 nm) upon grinding. The change in emission is associated with the introduction of defect that decrease the Cu-Cu interatomic distance [4].

The polymeric matrix in which the chromophores were added as a filler is two-component epoxy-water based paint with a slightly yellow color, supplied by Renner Italia. The MLC powder was dispersed in the in the pre-polymer by stirring for 10 minutes before adding the hardener. The mixing ratio of the prepolymer and hardener was 73-23 wt% respectively, while MLC % of the filler was respect to the total mass of the paint was 3.5%.

The MLC paint was deposited on the composite panels by spry coating, using a conventional spray gun. Three layers of paint were applied every10 minutes to ensure a uniform coat. It was then cured at 60° for 24° to maximize the glass transition temperature (Tg).

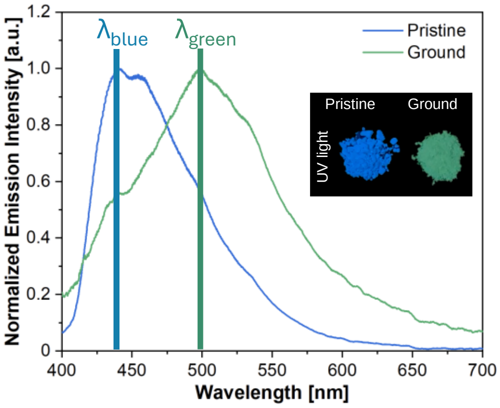

Figure 1 Emission spectra of [(CuI)3-Br-py]n in pristine and ground condition [11].

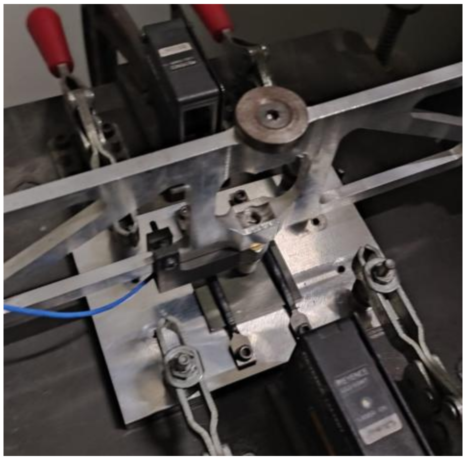

Figure 2 Low velocity impact drop-weight set-up.

CFRP LAMINATE & LOW VELOCITY IMPACT

The CFRP laminate stacking sequence, on which the MLC paint was applied, is a symmetric cross-ply $[(0°/90°)_2]_S$ made of 300 g/m^2 T700 carbon fiber unidirectional (UD) epoxy prepreg with a nominal Tg of 120 °C, supplied by DeltaPreg (UTS300 T700 -DT120). The laminate was cured in autoclave, under vacuum and a pressure of 6 bars, with an isotherm of 2 hours at 120 °C and relative heating and colling ramps of 2 °C/min. Resulting cured thickness was 2.5 mm. Two plates were fabricated: one was painted with the MLC coating (named MLC) and one was left as its (named Pristine). Specimens with a dimension of 50 x 50 mm were extracted from both CFRP plates by diamond sawing.

Low-velocity impact tests (LVI) were performed on both laminates, to investigate the ability to distinguish the damage on the top surface of the non-coated one and the mechancromic performance of the smart coating. The tests were conducted following the ASTM D7136 standard [11], using the drop-weight machine shown in

Figure 2, equipped with a 1.3 kg impactor mass and a load cell and a 12.7 mm hemispherical steel tip. To adapt to the small dimensions of the laminates, the specimens were leaned on a support plate with a cylindric hole with a diameter of 20 mm. Impacts were performed at energy levels of 0.5, 1 and 3 J and 3 samples were tested for each level. After impact and spectral response characterization of the top surface, laminate micrograph analysis of the cross section was performed.

SPECTRAL RESPONSE CHARACTERIZATION

The relationship between impact force and the MLC coating mechanocromic emission was evaluated by analyzing images captured by a digital camera sensor under UV light conditions to have a full field pressure analysis. The key factor in postprocessing was the ratio of green to blue light intensity, derived using MATLAB's image processing capabilities. This approach was suggested by the observation on the graph of Figure 1. in which the mechanical stimuli induce a shift of the emission spectra peak from blue to green color. The concept can be summarized in the following formula:

$$mechanical\ damege \propto \frac{I_{em}(\lambda_{green})}{I_{em}(\lambda_{blue})} \qquad (1)$$

On the contrary of the fluorometer employed to obtain the graph of Figure 1, for each pixel a digital camera sensor cannot give as information the full emission spectrum. It can only give the emission intensity of the red, blue and green colors, that are proportional to the number of photons that reach the relative 3 photodetectors with corresponding color filters. Therefore, the correlation between the impact force and the MLC coating emission spectra will be obtain directly through the red and green ratio (R/G) detected for each pixel.

The impacted specimens were illuminated with a 365 nm wavelength commercial UV torch (Darkbeam) in a dark ambient (inside a cardboard box) to enhance the photoluminescence response. The images were captured using a smartphone camera (Xiaomi Mi 11 Lite), maintaining consistent camera settings for all shots: format RAW; aperture f/1.79, shutter speed 1/15 s, ISO: 640, focal length: 4.74 mm (equivalent focal length 17 mm), WB: 0.604492, 1, 0.640625.

A MATLAB script was developed to post process the images and evaluate the optical response of the MLC coating after impact.

RESULTS AND DISCUSSION:

LOW VELOCITY IMPACT

The impact damage on the pristine and MLC laminate was induced by low velocity impact test, according to the procedure described in previous section. In Figure 3 the force vs time curves for the MLC coated specimens (the pristine behavior is comparable) are reported for the three impact energy levels. A force drop, which is usually linked to high energy damage events such as fiber brakeage [12], can be observed only for the highest energy level, corresponding to 3 J.

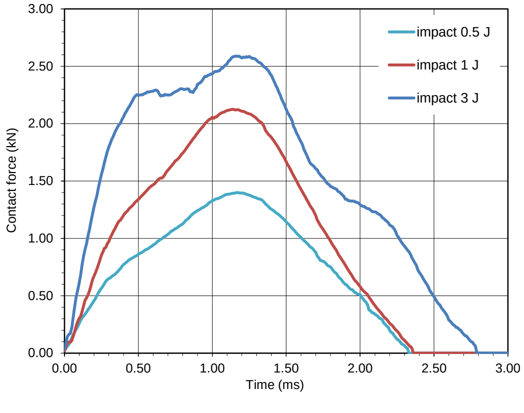

Figure 3 Low velocity impact test @ 0.5, 1, 3 J: Force vs time.

Differently, the cross-section micrograph analysis already shows matrix cracks propagation (low energy event) on the bottom side of the laminate, for the specimen impacted at only 1J. This can be ascribed to the tensile stress generated by bending load [12].

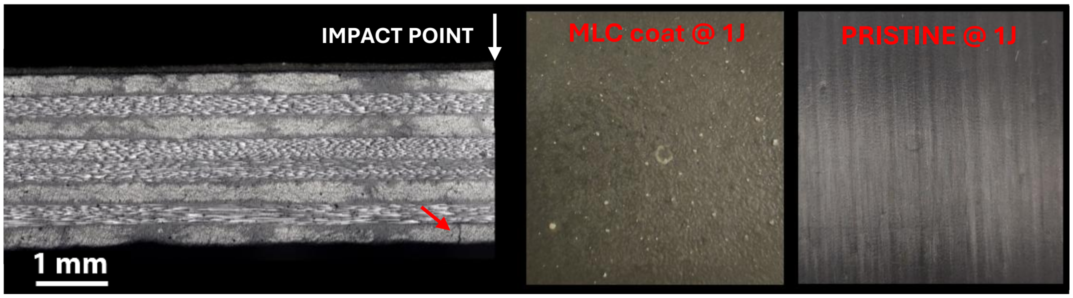

Figure 4 Cross-section micrograph of the MLC coated laminate impacted @ 1 J and top surface of the pristine and MLC laminates impacted @ 1J.

Nevertheless, as shown in Figure 4, only a barely visible impact damage (BVID) can be observed on the top surface of laminates impacted at the same energy levels of 1 J and illuminated by natural light. Considering that the mark dimension is smaller than 3 mm, it can be hardly identified during a general inspection of composite structures with dimension of an airplane.

LUMINESCENCE ANALYSIS

In Figure 5 from the left to the right, are summarized the image analysis steps performed, through the program developed in MATLAB, on the MLC coated laminate after impact: (1) RAW image of the impacted specimen illuminated by the UV torch and acquired by the digital camera; (2) G/B ratio calculated for each pixel and graphed in greyscale; (3) G/B ratio in greyscale after subtracting the background G/B ratio of the coating in the none impacted zone. As can be observed from first image, thanks to the UV light the impact point can now be easily identified. The third image shows a remarkably lighter area corresponding to the impact point which should be correlated to the contact pressure exerted by the impactor on the laminate. However some white dots are visible around the impacted zone, which could be ascribed to the sensor noise (amplified by the G/B ratio operation) and not perfectly uniform coating (caused by paint agglomerations of MLC crystals).

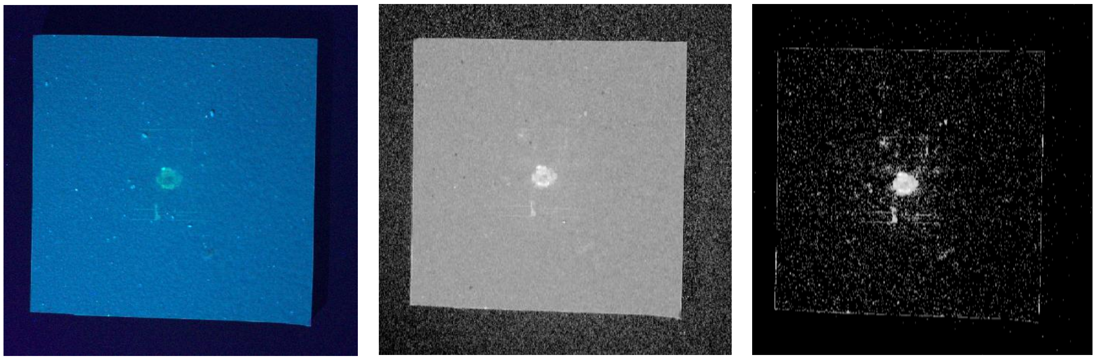

Figure 5 Image analysis steps performed on the impacted MLC coated laminate.

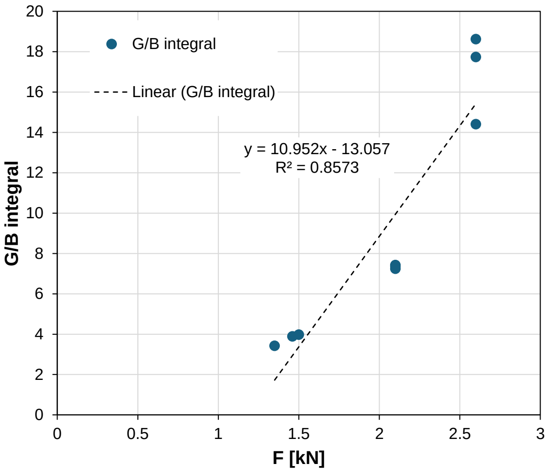

Figure 6 Integral of G/B pixel ratio on the impacted zone vs maximum impact force.

After scaling the third image to the real dimensions, it was possible to calculate the integral of the G/B pixel ratio on the impacted zone, which should correlated to the impact force (integral of the contact pressure). In

Figure 6 the G/B integral for each impact energy and repetition is reported as function of the corresponding maximum impact force. As can be observed there is a quasi-linear correlation (R^2= 0.85) between the maximum impact force and the integral of the emission spectra variation (G/B) of the MLC smart coating.

CONCLUSIONS:

A smart mechanoluminocromic coating has been developed by combining as a filler a MLC Cu-based Hybrid Coordination Polymer chromophore with an epoxy-based paint matrix. The coating was applied by spry gun on a CFRP cross ply composite laminate. Specimens were impacted at different energy levels ranging from 0.5J to 3 J. Micrograph analysis confirmed that for energy levels higher than 1 J damage develop inside the laminate, despite on the top surface of the laminate the damage is barely visible. However, by illuminating it with a UV torch the impact indentation can be identified.

A MATLAB image analysis program was developed to calculate the G/B ratio for each the pixels of a digital image acquired by a smartphone digital camera. The integral of the G/B pixel ratio on the impacted zone showed a quasi-linear correlation with the maximum impact force for different energy levels. These preliminary results demonstrate the correlations between the change in emission spectra of the MLC coating and the contact pressure developed between the indenter and the laminate during impact.

In conclusion, the developed smart MLC coating enables a highly efficient, cost-effective, and easily implementable nondestructive inspection (NDI) technique for detecting impact damage in composite structures. Furthermore, its potential integration with real-time computer vision positions it as a promising strategy for structural health monitoring (SHM).

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