Technology and Innovation, Vol. 22, pp. 95-103, 2021
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ISSN 1949-8241 • E-ISSN 1949-825X
http://dx.doi.org/10.21300/21.4.2021.10
www.technologyandinnovation.org

FUNCTIONAL COATINGS FOR DAMAGE DETECTION IN AEROSPACE STRUCTURES

Agathe Demay, Johnathan Hernandez, Perla Latorre, Remelisa Esteves, Seetha Raghavan

University of Central Florida, Orlando, FL, USA

The future of aerospace structures is highly dependent on the advancement of reliable and high-performance materials, such as composite materials and metals. Innovation in high resolution non-invasive evaluation of these materials is needed for their qualification and monitoring for structural integrity. Aluminum oxide (or α-alumina) nanoparticles present photoluminescent properties that allow stress and damage sensing via photoluminescence piezospectroscopy. This work describes how these nanoparticles are added into a polymer matrix to create functional coatings that monitor the damage of the underlying composite or metallic substrates. Different volume fractions of α-alumina nanoparticles in the piezospectroscopic coatings were studied for determining the sensitivity of the coatings and successful damage detection was demonstrated for an open-hole tension composite substrate as well as 2024 aluminum tensile substrates with a subsurface notch.

Key words: Functional Coating; Piezospectroscopy; Non-Destructive Evaluation

INTRODUCTION

The aerospace industry is a distinct example of high value manufacturing where intensive, yet appropriate regulations for testing and validation before release to the market, contribute to challenges in commercialization. Despite the stringent and often costly validation, however, the outcomes from investments, such as the "integrated composite wing" and "next generation composite wing", have demonstrated some of the most significant impacts over the years in revolutionizing several other industries (1).

Aerospace structures are composed mainly of metal and composite materials. Metals are highly reliable, but with usage, they become susceptible to damage caused by fatigue, creep, and corrosion. Composites have gained significance in aerospace structures because of their high strength-to-weight ratio. However, damage caused by matrix cracking, impact and moisture ingression is of concern specifically because they are not as easily detectable before the failure of the structure ensues. This article highlights our development efforts, which utilize piezospectroscopic (PS) properties of ceramic nanoparticles, to create functional coatings applied to both metallic and composite substrates for stress and damage sensing. The results, summarized here, demonstrate innovative concepts that can be applied to qualification testing as well as structural integrity monitoring in the aerospace industry and beyond it.

BACKGROUND

Non-Destructive Evaluation

Non-destructive testing plays a critical role in flight and structural safety as well as material

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Accepted: March 1, 2021.
Address correspondence to Dr. Seetha Raghavan, University of Central Florida, 4000 Central Florida Blvd., P.O. Box 162450, Orlando, FL 32816-2450
Tel:+1(407) 823-1737. Email: seetha.raghavan@ucf.edu

qualification in aerospace structures. The standards for a variety of non-invasive technologies that exist today are driven by the stringent requirements for safety. While ultrasonic techniques are the primary source for structural integrity monitoring of disbonds and voids, these methods are limited in their ability to identify the localized weakening that occurs prior to the onset of debonding (2,3). The ability to detect weak bonds preceding failure is of significance, with new and promising laser-based and thermographic methods currently being researched to address this (4). Active thermography is based on differences in heat diffusion in the presence of air gaps due to voids or delamination (5,6) but this is limited in its ability to detect weak bonds due to low diffusion response and resolution. Laser bond inspection uses a shock wave generated by plasma originating from a high power laser with short pulse on the front surface. The laser propagates through the inspected structure in compression and its reflection on the back surface provokes a tensile strength (7). Such a technique is based on the principle that a weak bond would experience debonding whereas a good bond would not be damaged by determined tensile stress induced by the shock wave. Current needs in damage detection of aerospace structures include non-invasive techniques as well as quantitative measurements that can relate to the integrity of a structure prior to weakening and failure.

Photoluminescence (PL) spectroscopy can be used with materials that provide stress-sensitive emissions to enable the PS effect. For chromium (Cr^{3+}) doped α-alumina, the shift in the characteristic R-lines that appear when the material is excited by a laser, occurs when stress is applied (8). This shift results when the crystal field that encompasses the chromium ions within the alumina distorts due to the applied stress, causing a change in the energy of the electronic transfers. This property, known as piezospectroscopy, has been exploited in our work where stress-induced shifts of the characteristic R-lines present in the emission spectrum of chromium-doped alumina can be directly correlated to variations in stress. When they are excited by a laser, chromium ions Cr^{3+} ions impurities contained in these molecules release photons. They are distributed in the shape of the characteristic R-lines doublet, which is two peaks at 14403 cm^{-1} and 14433 cm^{-1}. This radiation, from the Cr^{3+} ions, occurs as a transition from the lowest energy excited state to the ground state of the ion.

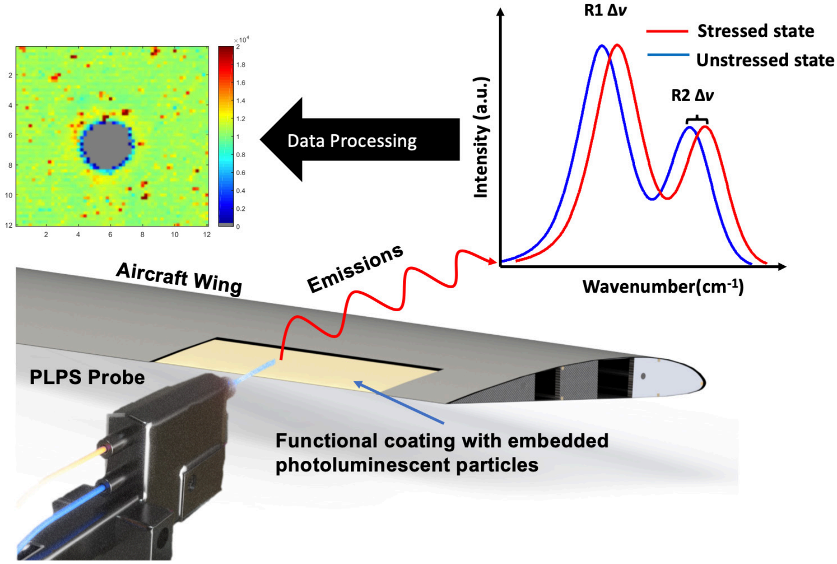

Figure 1. A schematic of photo-luminescent coating for stress sensing

The measurement of stress using the luminescence spectra of Cr^{3+} doped alumina or piezospectroscopy has been developed and advanced by scientists over the last five decades for new applications. Early use was in the form of ruby pressure gages in Diamond Anvil Cells (9) that aided high pressure experiments for stresses in the range of 30 GPa to 500 GPa with sensitivity in the range of 8 GPa. A significant achievement in sensing capability was demonstrated through thermally grown oxide (TGO) stress measurements for life prediction of turbine blade coatings (10). Capturing subsurface TGO stresses in the range of 4 GPa with microscale resolution and damage sensing in the form of bimodal peaks have been demonstrated over time (11). In general, for these applications, the sensitivity of measurements was in a range of less than 1 GPa. The next significant effort in taking this measurement method forward was achieved through our work on stress sensing composites developed with embedded alumina nanoparticles in a polymer matrix (12). Compression tests on alumina-epoxy composites of various volume fractions demonstrated tailorability and improved sensitivity thereby opening up new applications in stress and damage detection.

Designing Functional Materials with a Sensing Property

The concept of designing functional coatings that provide a sensing feature by utilizing intrinsic stress-sensitive properties of filler particles has been explored in a few studies. Strain sensing has been investigated by researchers using Raman peaks of carbon nanotubes (CNT), which have strain-sensitive bands (13). However, this technology needs to address the well-known issues related to the orientation and agglomeration of carbon nanotubes, which affect the accuracy of strain measurements. In another effort, Mechano-Luminescent-Optoelectronic (MLO) composites were developed as flexible materials that glow and produce an electric current when damaged (14,15) thereby producing a warning when a structure is at risk of damage. These efforts demonstrate the need for sensor materials that are light, passive, easily implementable and that can detect damage on an extensional area without altering the properties of the structure being monitored.

The following sections demonstrate how we have developed tailored coatings using nanoparticles of α-alumina that enable the capture of stress variations and damage initiation with sufficient sensitivity and at high spatial resolution for both composite and metallic structural substrates. These innovative functional coatings are anticipated for use in both qualification testing of new materials in a laboratory environment and the monitoring of the state of structures for integrity assessment.

Benefits of Piezospectoscopic Coatings for Damage Detection

The use of stress sensing photo-luminescent particles within a coating provides benefits of advanced non-invasive integrity monitoring through the detection of stress variations of the underlying substrate. Besides offering non-destructive and high spatial resolution data, the approach allows for sensing surface and subsurface damage prior to failure. This is made possible through the capture of variations in stress in the particles within the coating exhibited by shifts in the spectral peaks. In addition, alumina nanoparticles are accessible and produce strong photoluminescence emission for high sensitivity and accuracy. The coating can be extended over an area where structural integrity is critical and measurement efficiency is limited only by the imaging capability of the spectral collection device. Since the particles on the coating rely on the transfer of stresses to effectively detect changes, it is essential that the coating strongly bonds to the substrate. It is also critical that the coating does not fail or delaminate within the intended loading range. The coating's thickness and stiffness should also be low enough to have a negligible impact on the overall substrate behavior. As technologies for new, particle or fiber-reinforced composites continue to be developed, there is a need in the market for high spatial resolution testing and monitoring methods that can accurately show variations in stress leading to the failure of these materials. Most current methods do not have the ability to detect both surface and subsurface stress propagation within a composite or metallic. This early onset detection of this type of damage could prevent external damage in the form of delamination or cracking non-invasively with high spatial resolution. The PS coating offers a more effective method of sensing stress and structural failure prior to the appearance of visual signs. This would allow for a more precise understanding of newly developed composites for structural use in addition to more informative and reliable preventative maintenance on structures composed of composites or metals.

METHODS

Instrumentation

The instrumentation developed by our team to observe and exploit the PS effect is a Portable Piezospectroscopy System (PPS) (16), shown in Figure 2. It is composed of a spectrograph (Raman, variation in frequency, analyze diffuse light), a charge-coupled device, as well as a laser source (a green laser that operates at a wavelength of 532 nm and exerts a maximum output power of 200mW) and X-Y-Z stages that provide mapping capabilities.

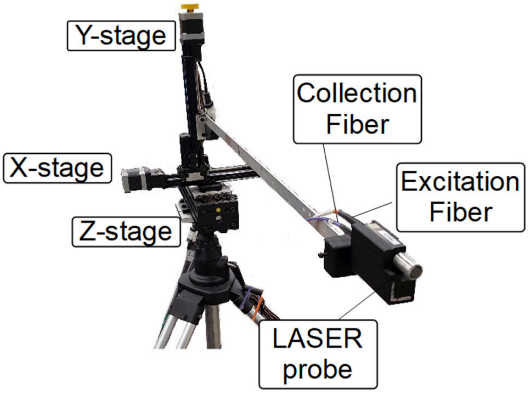

Figure 2. Portable Piezospectroscopy System experimental setup

Additionally, this portable system has a computer that is used for data collection and analysis. Analysis algorithms were developed to fit and deconvolute the R-lines from the raw data (17). With these algorithms, we have been able to obtain intensity maps to visualize the dispersion of α-alumina particles (18) and R-lines peak shifts to determine the condition of the substrate. Digital Image Correlation (DIC) has been used in conjunction with the PPS to provide displacement fields to correlate with the peak shifts measured.

Data Collection

In standard data collection with the instrumentation, the laser dot is initially focused on the specimen by incrementally moving the probe in the z-direction (toward or away from the sample), while simultaneously collecting spectral data. The optimal focal distance is achieved when the intensity of the R1 peak is observed at a maximum value. This focus distance is generally kept constant for all data collection areas on that specimen surface. The maximum R1 intensity value ensures greater certainty in the R1 peak position, which is needed for reliable piezospectroscopic measurements during load tests. Once the laser has reached its focal point, a zero position is determined as the start for all scans. The probe scans the sample point-by-point by a preset "snake scan pattern", after which it will automatically return to the zero position. Consequently, all the scans will show the same area, which allows for the study of the peak shift for each pixel.

PPS provides surface maps with a high spatial resolution of a few microns, which is dependent upon both the number of spectral collection points and the objective magnification.

PS maps of these samples with the stress-sensing coating, when subjected to load, will display a shift in peak position, as shown in Figure 3. The ability to observe these micro-mechanics of coating deformation under mechanical loading with high resolution highlights the advantages of the manufacturing of these stress sensing coating systems (19). In the following sections, the application of the instrumentation and the data analysis is described for both metallic and composite samples.

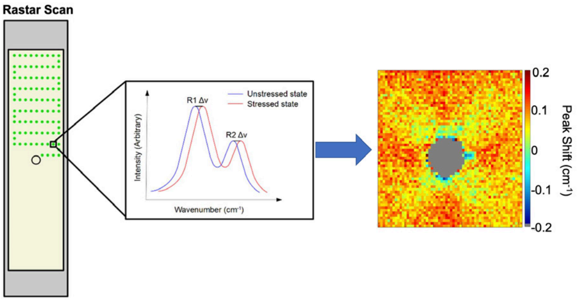

Figure 3. Scan pattern and R-lines

PIEZOSPECTROSCOPIC COATINGS ON OPEN-HOLE TENSION COMPOSITE SUBSTRATES

Materials

The PS nanocoating investigated in this part was manufactured by Elantas PDG Inc. by mixing 150 nm α-alumina nanoparticles (Inframat Corp.) with 99.8% purity in epoxy to achieve 5%, 10% and 20% volume fraction (VF) of particles. The coating was applied to an open-hole tension composite substrate consisting of laminated IM7-8552 unidirectional tape (20). The PS coating on the OHT CFRP sample had a film thickness of approximately 300 μm (21).

Volume Fraction

A challenge in the coating fabrication process is ensuring uniform particle dispersion and accurately controlling the volume fraction or weight percentages of the fillers during manufacturing (18). For optimal mechanical properties of the composite, a homogeneous dispersion of particles is needed with minimal inclusions, agglomerations, or aggregates.

One of the important parameters to determine is the appropriate volume fraction of α-alumina particles in the coating for damage detection. There should be sufficient particles to produce significant R-line intensities in order to observe the PS effect. However, with larger content areas of agglomeration will be more prevalent. Dispersion studies were conducted using PL spectroscopy to identify regions of increased agglomeration, and this demonstrated that the volume fractions used in this work had acceptable dispersion (22). The results from transmission electron microscopy and scanning emission microscopy validated these findings (22). Studies conducted show that beyond 20% VF of α-alumina in the coating (22,23), aggregates were visible. That is why only 5%, 10%, and 20% VF coatings are studied in this work. Figure 4 shows the results obtained for these samples with the data acquisition method, as previously explained. Each map has dimensions of 25.4 mm × 25.4 mm

As can be seen in this figure, the dispersion for the 5% VF coating seems to present the lowest intensity. We can also notice a small agglomerations even with

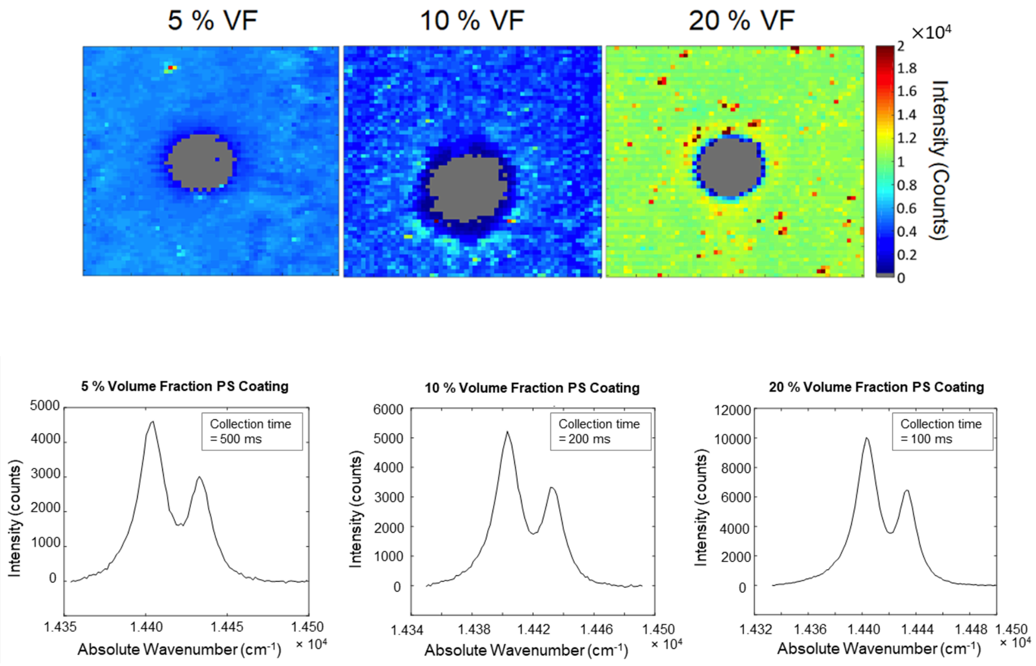

Figure 4. (Top) Contour maps showing α-alumina nanoparticle dispersion for 5%, 10%, and 20% VF PS coatings. (Bottom) Representative R-lines for each PS coating with corresponding collection times (23). The left peak shows R1 and the right peak R2.

low volume fraction. For 10% VF, the map shows a non-uniform dispersion of α-alumina nanoparticles, which is most likely due to the application method of this coating. This may have led to a greater amount of agglomerations of nanoparticles. Furthermore, we notice a ring around the hole where the intensity is lower than the rest of the sample. Both are not reliable enough for the damage detection test. Representative R-lines that correspond to each intensity map are shown in Figure 4 as well. Each intensity corresponds to the R1 peak at approximately 14403 cm^{-1}, which confirms the PL signal response coming from the PS coatings. Higher R1 peak intensity correlates with higher signal-to-noise ratio and, consequently, more distinctive, and greater certainty in peak shifts. These R1 peak characteristics are exhibited in the PS coating with 20% VF α-alumina nanoparticles. Despite some agglomerated areas, the 20% VF coating was shown to be the best option. It shows higher intensity readings in comparison to the dispersion maps for the 5% and 10% PS coatings. This sample demonstrated successful damage detection test as described in the following section.

Damage Detection

DIC and PS were used on either side of the open hole tension sample simultaneously in a loading test with both methods providing complementary data. With loading, the PS coating demonstrated stress patterns over the sample that corresponded well with the DIC strain distribution. As the load increased further, the PS coating started displaying a distinct area of significant peak relaxation at the corner of the hole, which was observable when 76% of the failure load was reached (Figure 5). At this point, the sample did not exhibit visible damage. However, in the peak shift map, it can be observed that, at 76% failure load, greater downshifts are shown near the hole compared to the rest of the sample. Typically, open-hole composite laminates tend to begin cracking prior to failure (24), especially near the hole, due to interlaminar failure. Thus, the downshifts observed near the hole indicate that strain energy was being released at the crack tip (19). Consequently, the higher stresses are redistributed throughout the larger area around the hole (21,23). As the load increased, the DIC measurements showed an increase in the intensity of the strain distribution around the open hole, and loss of signal at the same corner indicated damage emerging at the surface at 92% of the failure load that was also visually observable. The results showed the coating's ability to capture the variation in stress caused by subsurface damage initiation at the edge of the hole in the composite substrate prior to its emergence on the surface.

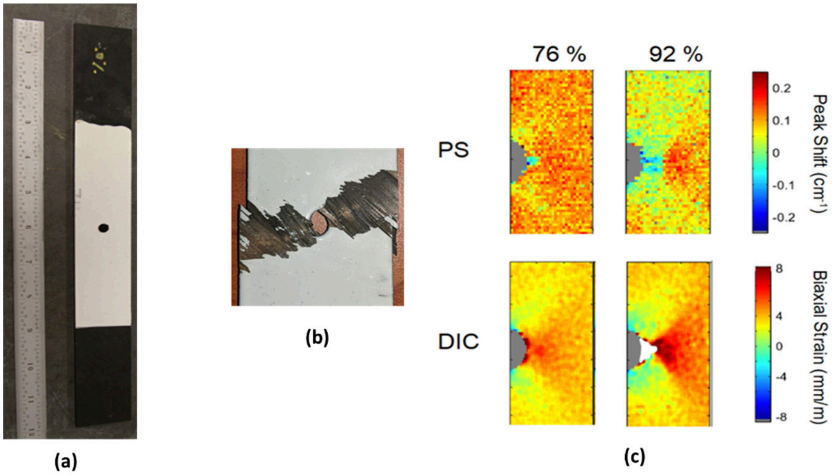

Figure 5. (a) Open-hole tension composite sample before testing, (b) open-hole tension composite sample after testing, and (c) PS shift and biaxial strain (DIC) maps for half of the open hole tension sample for 76% and 92% failure loads (19).

PIEZOSPECTROSCOPIC COATINGS ON METAL SUBSTRATES WITH A SUB-SURFACE NOTCH

Materials

Typical aircraft metallic coupons of 2024 aluminum were used as substrates in this test. Two samples were coated with PS coatings consisting of 1% VF and 10% VF α-alumina nanoparticles, with an average particle size of 150 nm, in the epoxy matrix. The substrates were machined and prepared in accordance with ASTM E8-0. In order to capture and monitor the development of the subsurface damage, a 0.25” × 0.16” × 0.08” notch was introduced in both substrates on the face opposite of where the coatings had been applied (25). The film thickness was in the range of 40 microns for the coatings with 1% and 10% volume fractions of alumina, respectively.

Damage Detection

The metallic samples were loaded in a tension test to demonstrate the evolution of the defects. For this material, an 18 mm × 30 mm area of the sample was scanned to give a 90 points × 150 points map, with a spatial resolution of 200 μm. The coupons were loaded from 0 kN to 20 kN, which is the anticipated failure load of the coupon, with an increment load of 4 kN. The peak shift maps obtained from the PL scans on the coated surface, opposite of the notch on each sample, are shown in Figure 6.

The peak shift map from the 10% VF PS coating better captured the stress concentration associated with the subsurface notch compared to the 1% VF PS coating. Downshifts were shown in the peak shift maps until post-failure due to the stress concentration arising from the subsurface notch, which caused the stresses to be redistributed around the notch as the load is applied. This observation indicated that the PS coating is capable of detecting the location of subsurface damage. Furthermore, the size of the stress concentration due to the subsurface damage showed more prominently on the peak shift maps from the 10% VF PS coating than the maps from the 1% VF PS coating.

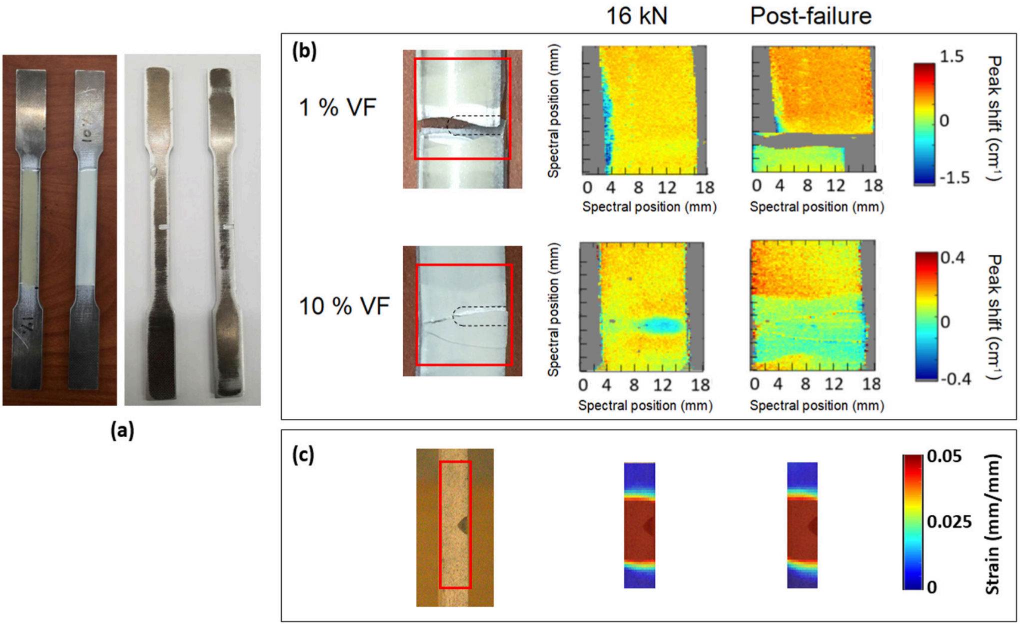

Figure 6. (a) Coated and uncoated sides of aluminum samples before testing; (b) Images of aluminum samples after testing with corresponding R1 peak shift maps for 16 kN and post-failure for 1% and 10% VF; (c) side view of the sample where DIC measurements were taken along with corresponding strain maps at 16 kN and post-failure (25).

CONCLUSION

In this study, functional coatings utilizing piezospectroscopy of embedded alumina nanoparticles demonstrated the capability of providing high spatial resolution images of peak shifts that correlate with substrate stress and detected the location of subsurface damage both in composite and metallic substrates. Comparing the volume fraction of the tailored PS coatings on the composite substrates, it can be concluded that the greater the volume fraction of α-alumina in the coating (up to 20% VF), the more sensitive to stress the coating is. In concurrent methods using PS and DIC, the PS coating demonstrated the ability to detect the subsurface damage at 76% of the failure load ahead of the damage becoming visual at 92% of the failure load. For the stress-sensing coatings on metal substrate testing, the 10% VF PS coating captured better the location and the extent of the subsurface notch compared with the 1% VF PS coating.

An ideal coating configuration that is sensitive to changes into stress without any negative impacts on the mechanical properties of the coating was demonstrated here. The functional coating innovation has successfully shown the ability to detect damage before any failure occurs. Therefore, the application of the functional coatings based on PS measurements can provide potentially valuable information to monitor the structural integrity of aerospace structures and allows for preventive measures to be taken before failure.

ACKNOWLEDGMENTS

The Boeing Company is acknowledged for their assistance with experiments. This work was supported by the National Science Foundation under Grant Nos. IIP 1701983 and CMMI 1130837.

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