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Self-sensing of Matrix Damage using Mechanophore-based Smart Polymer in Fiber Reinforced Composites

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KEYWORDS

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smart polymer

ABSTRACT

Polymer matrix composites (PMCs) are widespread in engineering applications due to their superior mechanical properties at low weight. However, they are susceptible to damage due to their low interlaminar mechanical properties and poor electrical and thermal conductivities in the transverse direction to the laminate. Moreover, methods to inspect the embedded damage and to ensure the reliability of composites are expensive and labor intensive. Recently, mechanophore-based smart polymer has attracted significant attention, especially for self-sensing of matrix damage in PMCs. A cyclobutane-based self-sensing approach using 1,1,1-tris (cinnamoyloxymethyl) ethane (TCE) and poly (vinyl cinnamate) (PVCi) has been studied in this paper. The developed TCE and PVCi based smart polymer blends were characterized to understand their thermal and mechanical properties. The self-sensing function was investigated at both the polymer level and composite laminate level. Fluorescence emissions from fiber reinforced composite laminate were observed on specimens subjected to low velocity impact load and low cycle fatigue load, indicating the presence of matrix cracks.

1. INTRODUCTION

The field of fiber reinforced composite materials has grown rapidly in the last decade such that over 20 million tons are now produced every year for a variety of applications including aerospace, civil, and mechanical infrastructures. However, concerns remain about the structural integrity of composite materials subject to fatigue and impact loading, as such materials are susceptible to cracks or delamination that form deep within the structure. In addition, the failure mechanisms of composite laminates are more complicated and damage detection is challenging. Damage accumulation in composites is progressive in nature, with damage initiation in the formation of microscale matrix cracks that lead to delamination and even fiber fracture. Matrix damage can cause significant reduction in load carrying capability of the laminate and early failure. The integrity of polymer matrices in composites is therefore critical for structural durability and operational safety.

Identification of matrix cracks and delamination in polymer composites is of significant importance so that preventative maintenance can be taken before catastrophic structural failure. Scientists and engineers have been developing damage detection technologies over many years, which are recognized as nondestructive evaluation (NDE) and structural health monitoring (SHM) techniques. Common NDE techniques include ultrasonics [1], acoustic emission [2,3], infrared thermography [4], etc. Although these techniques have been well validated in laboratory environments, in-field applications, especially real-time NDE (also referred to as SHM), are still difficult due to the bulky size of NDE equipment and the time-consuming data post-processing and decision making procedures. SHM techniques combining sensors and complex feature extraction algorithms have been well studied [5–8]. Piezoelectric ceramic sensors have been employed to record guided waves or impedance data for local and global damage awareness [9–11]. The application of

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advanced sensors, such as optic fibers [12,13] and wireless sensors [14], and vibration based diagnostic methodologies [15] have been reviewed and summarized in literature. However, current sensor based data driven SHM techniques are incapable of early damage detection.

Nanoscale materials and smart materials provide the potential solutions for real-time matrix crack detection in polymer composites. Multiple nanoscale materials, such as uniformly dispersed pristine carbon nanotubes and functionalized carbon nanotubes [16,17], aligned carbon nanotube forests [18], carbon nanotube thread [19,20], graphene [21], and nanoscale piezoelectric ceramics [22], have been integrated within polymer matrix systems. By measuring the tailored material properties, such as electrical impedance and resistance, the local strain field and damage conditions can be estimated for laminated composites under simple uniaxial load conditions [23]. However, it is still difficult to detect the matrix crack initiation at the early damage state under complex fatigue and impact load conditions.

Recently, mechanophore-based polymers have received increasing attention for damage detection in composites. Such materials are able to translate mechanical energy to a chemical transformation so that the damage can be detected by measuring a visible color change. Piermattei et al. reported an optic activated mechanophore-linked polymer, which could mechanically induce luminescence emission at low stress level [24]. Such polymers incorporating the bis(adamantly)-1,2-dioxetanes unit enabled the transduction of force into luminescence by opening the four-membered dioxetane ring with subsequent ketone product relaxation from its excited state to the ground state. However, the time for monitoring the mechanically induced luminescence was short, which restricted its use in practical applications. Pyran-based organic compounds, like spiropyrans, spirooxazines, and naphthopyrans, are well known chromogenic materials whose structure changes accompanied by a color change induced by temperature or light. Davis *et al.* synthesized spiropyran-linked elastomeric polymers which could act as force sensors in response to stress loading [25]. They applied tensile testing and simultaneous optical spectroscopy to examine force-induced scissile transformation. Force distribution was detected by monitoring the color change due to a mechanically induced 6-electrocyclic ring-opening reaction from colorless spiropyran to colored merocyanine conformations. Our research group recently reported a cyclobutane-based polymer for early damage detection in epoxy [26]. To our best knowledge, the color change mechanisms have not been applied for early damage detection in fiber reinforced composites.

Although mechanophore-linked polymers have provided tremendous new opportunities, especially in the areas of stress sensing and early crack/failure detection, many unknown fundamentals as well as unexplored applications remain. Current research gives greater emphasis to pure and bulk traditional polymers; synthesis relies solely on an individual chemistry/reaction mechanism that is often limited and complicated. In this paper we have designed and synthesized a mechanically responsive composite material system by integrating cyclobutane-containing polymer into an epoxy matrix and further extended this approach to identify low-cycle fatigue damage in glass fiber reinforced polymer composites through mechanically induced fluorescence generation.

2. CONCEPTS OF SELF-SENSING POLYMER MATERIALS

2.1. Self-sensing Concept using Fluorescence Based Smart Polymer

Integrating smart materials within conventional composite matrix systems is a practical way to monitor and detect the matrix crack damage in laminate composites. In particular, we applied cyclobutane as mechanophore functional group to epoxy; the matrix system in the composite. Both 1,1,1-tris(cinnamoyloxymethyl) ethane (TCE) and poly (vinyl cinnamate) (PVCi) were studied. TCE was dimerized into cyclobutane rings under photoirradiation. This cyclic product has been proved to efficiently generate fluorescence emission upon the cleavage of the cyclobutane ring [27]. TCE has trifunctional mer units on each molecule. It forms three-dimensional networks under UV photoirradiation. For comparison, a second polymer, poly (vinyl cinnamate) (PVCi) with the functional group as the side chain on the polymer to form a cross-linked polymer, was selected. PVCi is commercially available and very prominent in photochemistry with some attractive characteristics [28,29].

The cyclobutane-based polymer was produced by photodimerization of the C=C bond from the cinnamoyl function group of TCE and PVCi, respectively. Cyclobutane-based polymers were dispersed in the epoxy as self-sensing crack sensors. When the polymer blends undergo crack formation and propagation, the cyclobutane is mechanochemically cleaved to afford the chemicals that are capable of strong fluorescence emission, indicating the location of the crack in the epoxy, as shown in Figure 1. In this work, the effect of the functionalization of two different cyclobutane-based cross-linked polymers on the thermal and mechanical properties of new epoxy matrix composites was investigated and the relationship of the stress-spectroscopic signals of the composites was also studied.

2.2. Material Preparation and Characterization

In this work, all of the following listed materials and reagents were used as received. 1,1,1-tris(hydroxymethyl) ethane (99%), cinnamoyl chloride (98%), tetrahydrofuran (≥ 99.9%), 4-(dimethylamino)pyridine (≥ 99%), dichloromethane (≥ 99.8%), ethanol (≥ 99.5%), and poly(vinyl

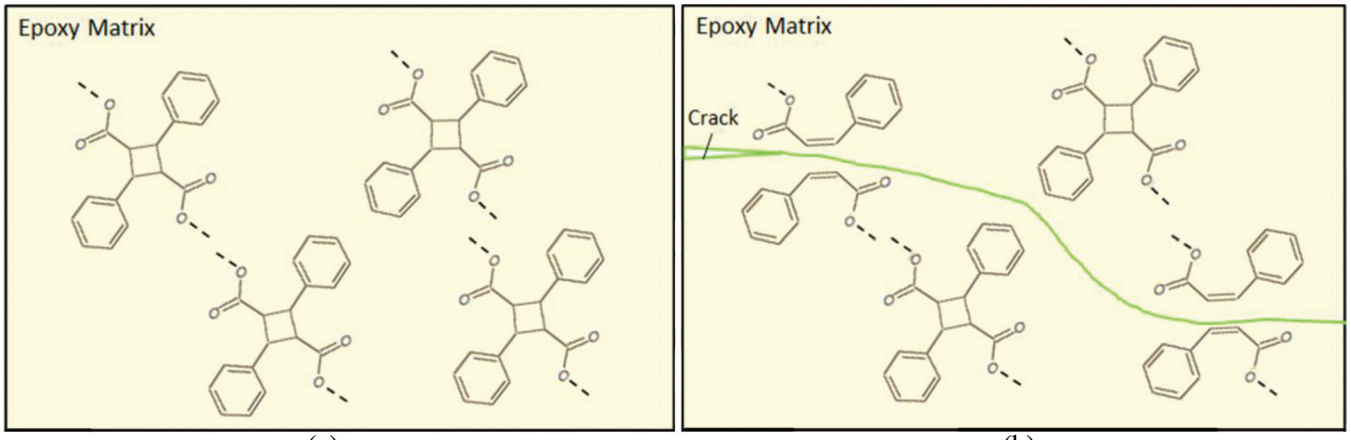

Figure 1. *Depiction of the blending approach to create a stress-sensitive material. (a) before crack formation; (b) after crack formation [23].*

cinnamate) (PVCi, average Mn 45,000–55,000) were purchased from Sigma-Aldrich. Sodium chloride (≥ 99%) and water (HPLC) were purchased from Fisher Scientific. Epoxy resin FS-A23 (digycidylether of bisphenol F, DGEBPF) and epoxy hardener FS-B412 (diethylenetriamine, DETA) were purchased from Epoxy System Inc.

The TCE polymers or PVCi polymers were prepared using the following procedure. Solid TCE or PVCi was first dissolved in CH_2Cl_2. The solution was then applied on a clean silicon mold to form a thin film and placed in a vacuum to evaporate the excess CH_2Cl_2. After the evaporation, the thin film was photoirradiated under a UV light source at 302 nm for 4 h. All of the silicon molds and glass slides used for preparation of samples were pretreated with a mold release agent.

To prepare polymer/epoxy polymer blends, the TCE or PVCi solution was added to DGEBPF and thoroughly dispersed by using an ultrasonic probe sonicator (Sonics VibraCell, 500W model) for 20 seconds. The mixture was then placed in a vacuum chamber at 50°C to evaporate the CH_2Cl_2 until the mass of the mixture remained unchanged, indicating that the excess CH_2Cl_2 had evaporated. The resin mixture was cooled to room temperature before DETA was added and mixed (M_{TCE} or M_{PVCi}: M_{Epoxy} = 1:10; M_{DGEBPF}: M_{DETA} = 100:27). The mixture was sonicated in an ice bath to prevent any premature curing. After the mixture became homogenous, the mixture was poured into the silicon molds and moved into a vacuum chamber to degas for 30 min, followed by photoirradiation conducted by a UV lamp of 302 nm wavelength (UVP, UVM-28). According to the manufacturer's data, the light density was approximately 1300 μWcm^{-2} at a distance of 3 cm. The sample was exposed to UV light for 4 hours and cured overnight at room temperature at atmospheric pressure. A neat epoxy sample followed a similar procedure for comparison. After simple machining, the sample was ready for testing. The average dimension of the cubic sample was 3 × 4 × 8 mm^3.

The glass fiber reinforced composites laminate was fabricated using the wet layup method. A polymer blend containing uncured epoxy and 10 w.t.% TCE was first mixed thoroughly. The uncured composite was cured under a load of 50 kg for 10 minutes and photoirradiation for four hours under UV light at 302 nm wavelength. In order to achieve further improved performance, the composites were posted-cured at 60°C overnight in an oven and allowed to cool gradually. The composite laminate sample size was 30 × 80 × 0.4 mm^3.

To characterize the mechanical and thermal properties of the proposed polymer matrix system, differential scanning calorimeter (DSC) thermal analysis, thermogravimetric analysis (TGA), and dynamic mechanical analysis (DMA) were conducted. The effect of the addition of the cross-linked polymer to the epoxy on glass transition temperature (T_g) was studied using DSC. The experiments were performed in a nitrogen atmosphere using TA Instruments Q20. TGA monitors the amount and rate of change in the mass of a sample as a function of temperature or time as a sample is heated at a programmed rate in a controlled atmosphere. The measurements are used primarily to determine the thermal stabilities of materials. DMA was used to measure the glass transition temperature, storage modulus, loss modulus. Cross-link density of the neat epoxy, the epoxy blended with TCE polymer, and the epoxy blended with PVCi polymer was calculated through DMA. Experiments were performed in a tension mode using a TA Instruments Q800. The detailed property characterization results have been reported in [26].

3. MECHANICAL STRESS INDUCTED SELF-SENSING POLYMER

The self-sensing capability of the proposed polymer was first investigated at the polymer level. The goal for the application of the cyclobutane-based polymer was to demonstrate mechanochemical cleavage of a covalent bond and investigate the use of these cyclobutane polymers blended with

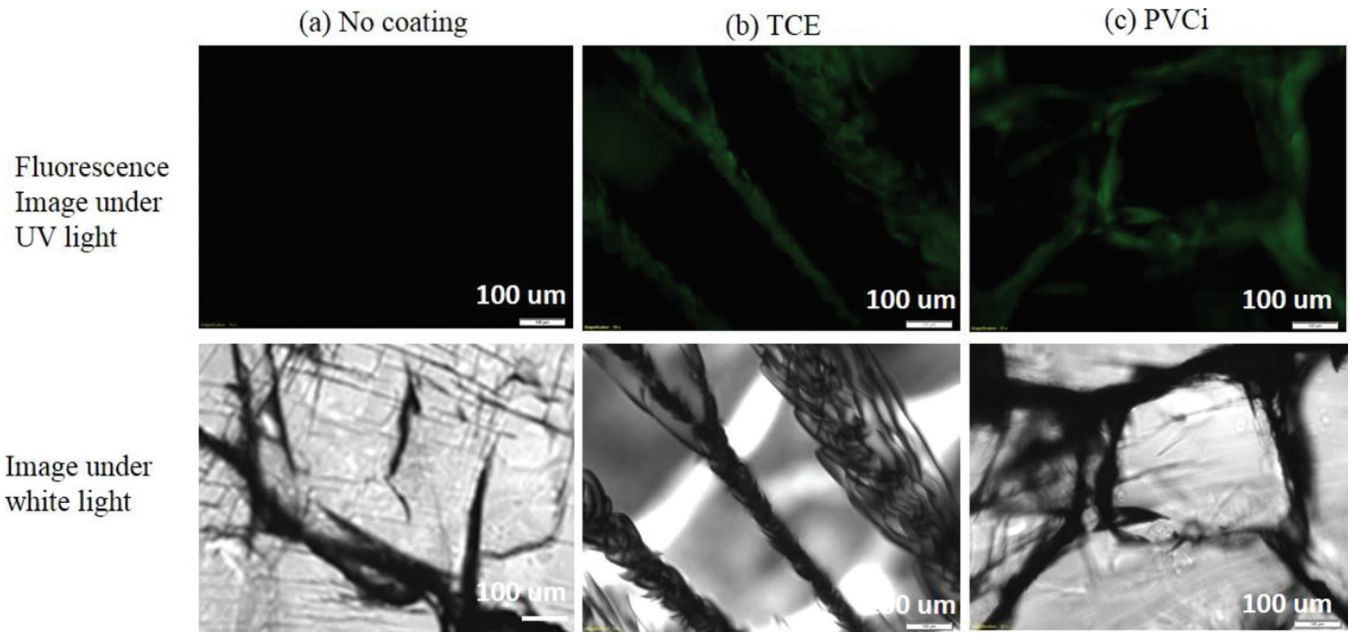

Figure 2. *Microscopic images of cracks generated by hammer hit on (a) a clean polystyrene substrate, (b) a polystyrene substrate coated with cross-linked TCE and (c) PVCi polymer under a UV light. Images in second row were the corresponding images under a white light.*

epoxy as damage sensors by visual detection for composite laminates. Here, we applied a simple and direct method for detecting mechanochemical reactions with UV microscopy. The fluorescence response was first confirmed by coating cross-linked TCE polymer film on a polystyrene substrate. The cracks were generated by low velocity impacts using a hammer and observed using UV microscopy, as shown in Figure 2. Under the microscope with white light, the cracks were observed both on the polystyrene and polystyrene with coating. But the fluorescent signal was only detected on the polystyrene coated with cross-linked TCE polymer exposed to UV light. Furthermore, the cross-linked PVCi polymer was coated on the polystyrene substrate. The fluorescence emission was observed along the crack as well. The results indicated that the mechanochemical cleavage of cyclobutane occurred along the crack propagation and induced the fluorescence generation.

To further understand the self-sensing capabilities of the proposed smart polymer system, experiments were conducted under a quasi-static compression load condition using polymer cubic samples fabricated by the following procedures in Section 2.2. When the cracks were generated by external force on the polymer blends with different amounts of the cross-linked TCE polymer, fluorescence emission from the cracks was clearly observed under UV and white light both, as shown in Figure 3. The fluorescent signal was

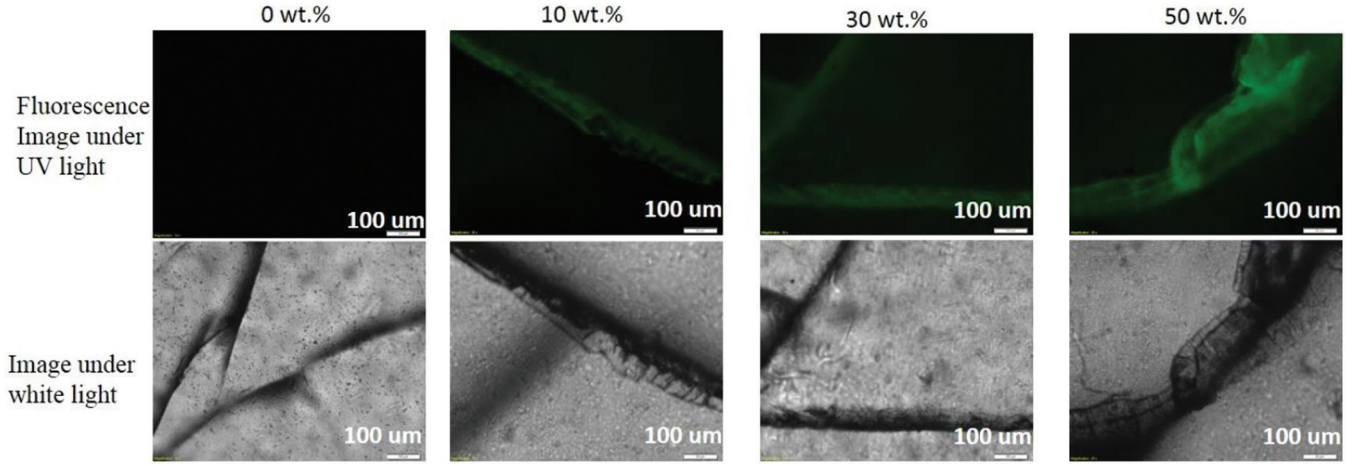

Figure 3. *Microscopic images of fluorescence emission along cracks generated by hammer hit on polymer blends (a) 0 wt.% (b) with 10 wt.% (c) 30 wt. % (d) 50 wt.% cross-linked TCE polymer. Images in the second row were the corresponding images under white light.*

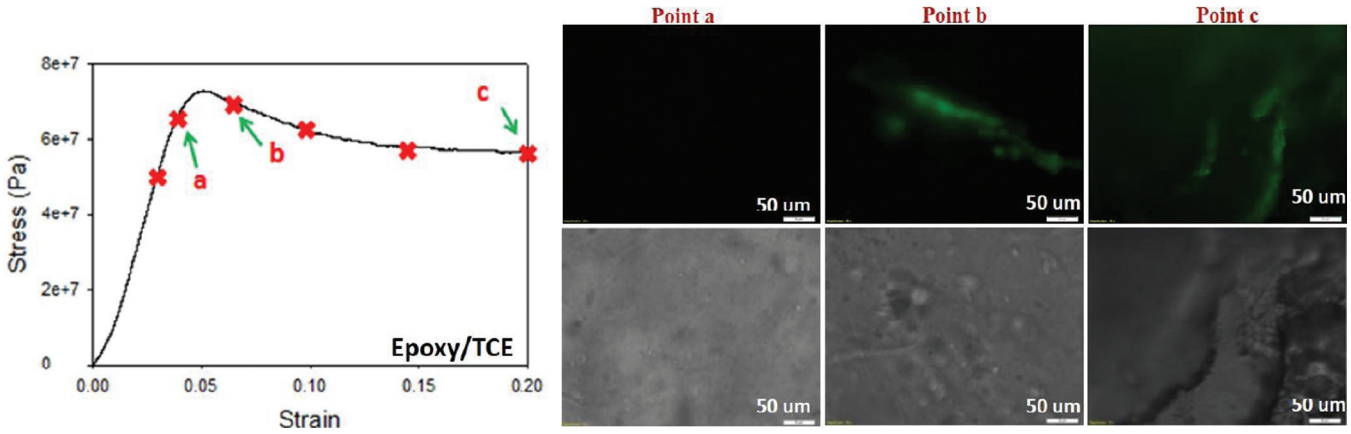

Figure 4. *Microscopic images of fluorescence emission in response to different strains of epoxy with 10 wt.% cross-linked TCE polymer blends.*

further augmented with increasing amounts of cross-linked TCE polymer (30 w.t.% and 50 w.t.%) blended with epoxy. No fluorescence emission was found on neat epoxy in the same experimental conditions. From the images, epoxy with 10 wt.% cross-linked TCE polymer gave strong enough fluorescent emission to detect the damage. Thus, the content of 10 wt.% was used for the following fluorescence tests. Comparing the images under white light and UV light, it is noted that the proposed cyclobutane-based smart polymers were able to clearly identify the existence of polymer cracks when mixed with structural epoxy. The detailed crack shape and crack depth were represented by the intensity of fluorescence lights. The green light intensity of fluorescence images became stronger as more cracks existed in the polymer matrix system.

Neat epoxy and smart polymer samples were compressed to different strains, respectively. As shown in Figure 3, no fluorescence was detected on the neat epoxy. The evolution of induced fluorescence emission on the epoxy samples mixed with 10 wt.% TCE is shown in Figure 4. For all the polymer samples, limited fluorescence was observed before the stress passing yield point. However, the intensity of fluorescence emission from the proposed polymer significantly increased right after stress passing the yield point and microcracks starting to form. Those cracks could not be clearly observed under white light, indicating that the fluorescence emission could provide a higher sensitivity and easier detection for the location of cracks, especially cracks at the micro scale. It is also notable that fluorescence emission along the crack intensified with strain after the yield point. Similar results were observed using epoxy samples mixed with 10 wt.% PVCi smart polymers, as shown in Figure 5. In addition, through characterization of both TCE and PVCi smart polymers, it is shown that PVCi based smart polymers have a higher glass transition temperature, which results in better thermal stability and more potentials for practical applications in fiber reinforced composites.

In order to further explore the relationship between the strains and their corresponding fluorescence response, ten fluorescent micrographs were processed by ImageJ. The average fluorescence densities and related deviation for each mechanical load state were calculated. The density change as a function of strain was plotted in Figure 6. As expected, the densities increased with the accumulation of strain, which indicates that the more cleavages of cyclobutane were activated as strained increased.

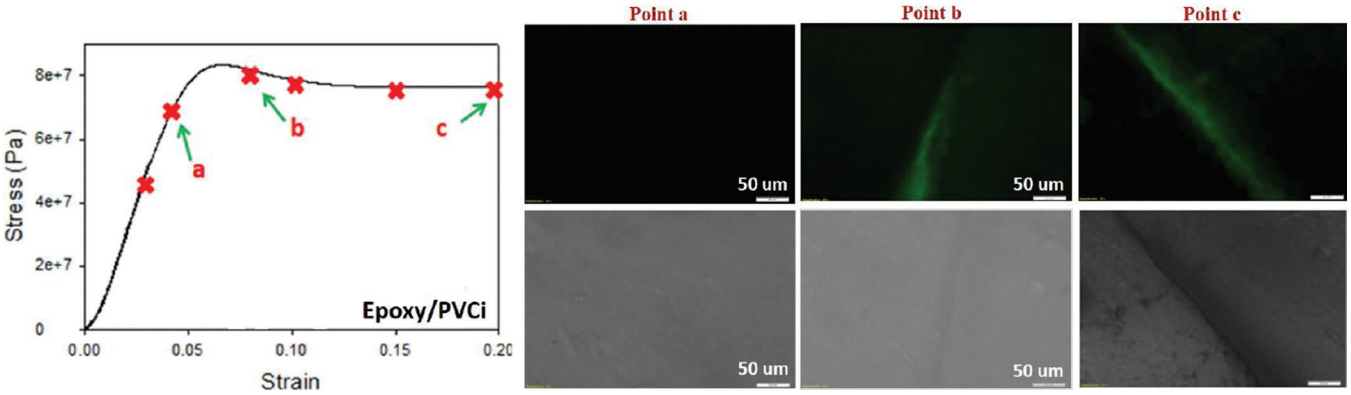

Figure 5. *Microscopic images of fluorescence emission in response to different strains of epoxy with 10 wt.% cross-linked PVCi polymer blends.*

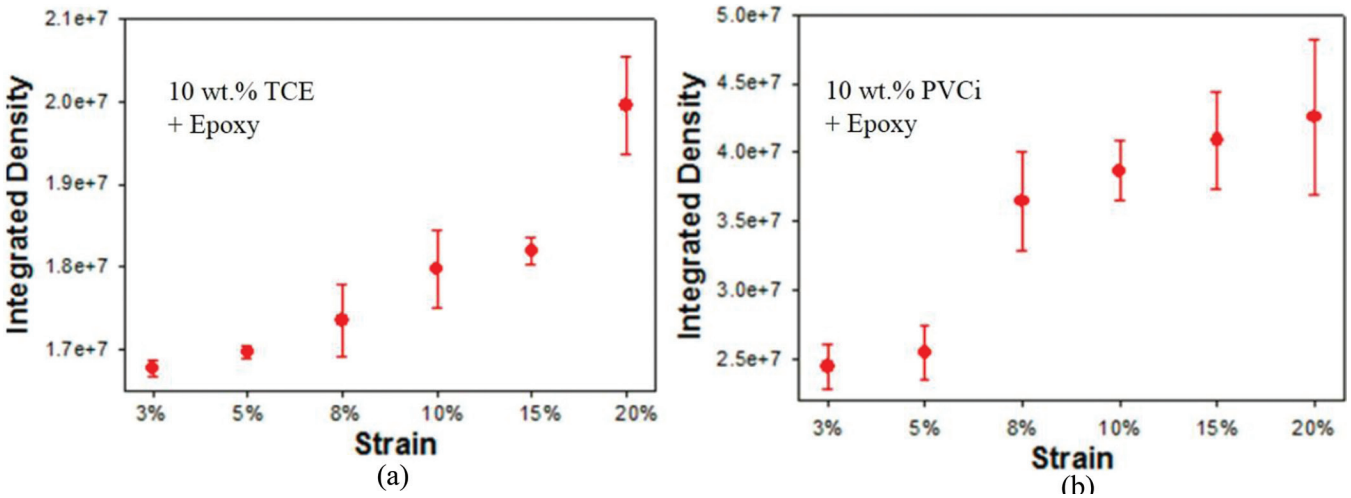

Figure 6. *Integrated density of fluorescence emission in response to different strains of epoxy w/ 10 wt.% cross-linked (a) TCE and (b) PVCi polymer blends.*

4. SELF-SENSING OF LOW CYCLE FATIGUE DAMAGE IN COMPOSITE LAMINATE

In general, fatigue of fiber reinforced composite materials is a complex phenomenon. Multiple parameters, including fiber type, matrix type, load conditions, and boundary conditions, can significantly influence the fatigue performance of composites. Fatigue damage starts very early and the extent of the damage zones grows steadily, but the damage type in these zones can change. For example, small matrix cracks can lead to large size delamination as damage accumulates. Therefore, being able to efficiently detect early matrix cracks in composite laminates are critical for the structural safety and reliability of composites. The proposed self-sensing method using cyclobutane based smart polymers was further studied under low fatigue cycle load conditions.

The fluorescence response on the glass fiber reinforced composite (GFRC) was first validated by the damage applied with a hammer. A circle was marked and the damage was made by the hammer impacted on one side of the single sheet within the circle, as seen in Figure 7 (right). The images within the circle before and after the damage were collected and compared. Obviously, the fluorescence was observed along the fiber after the damage was applied, as seen in Figure 7 (left).

The fatigue tests were performed on a glass fiber reinforced composite (GFRC) sheet under uniaxial tensile load conditions. A 4 mm wide hole in the center of the specimen

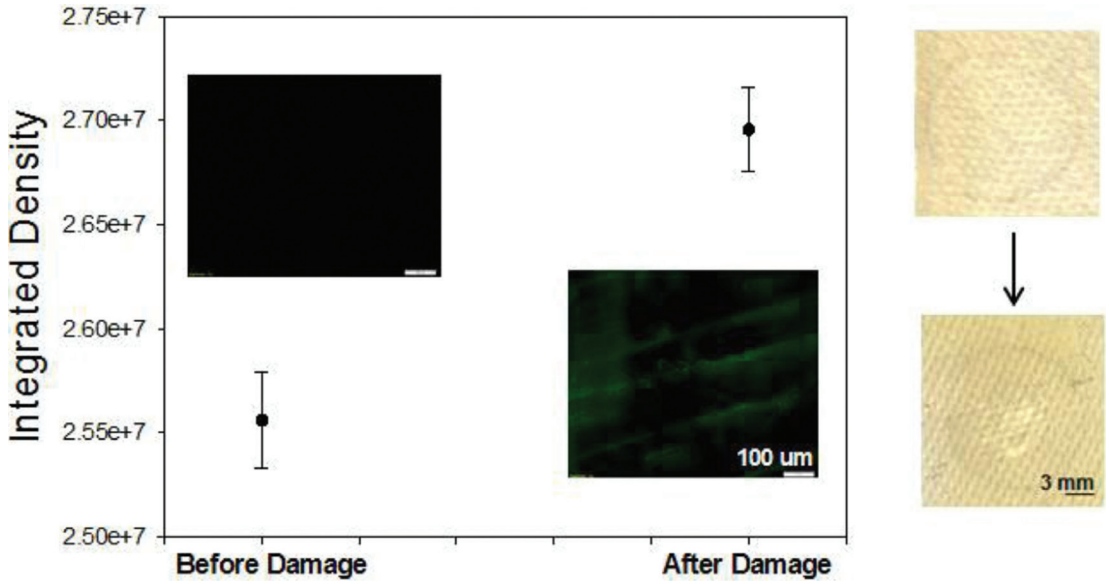

Figure 7. *(Left) Fluorescence density of fiberglass epoxy composite with 10% TCE before and after damage was applied. (right) GFRC specimen under a white light.*

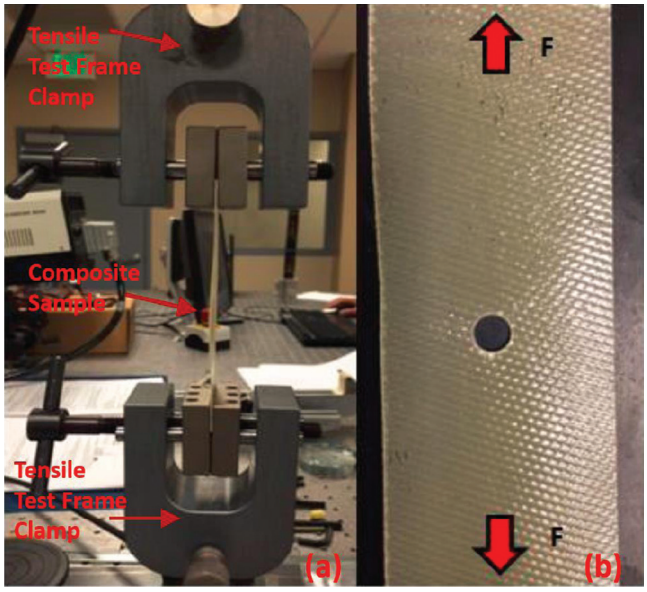

Figure 8. *(Left) Experimental setup of the unidirectional tensile fatigue test using GFRC sample; (Right) GFRC sample with tensile load.*

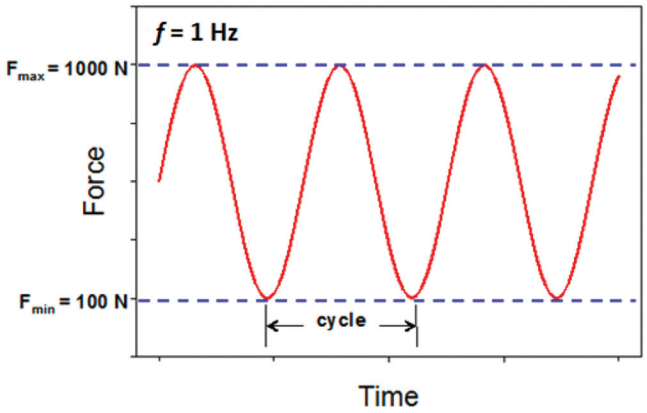

Figure 9. *Low cycle fatigue load history applied in the experiment.*

was introduced before the fatigue test to create a stress concentrate area and the fatigue damage was expected to initiate around the hole. A TestResource 800L mechanical testing system was used in the experiment, as shown in Figure 8. The specimen was cycled in a load-controlled mode at stress ratio (R), $\sigma_{min}/\sigma_{max} = 0.1$ on a uniaxial fatigue frame operating with a sinusoidal waveform at a frequency of 2 Hz, as seen in Figure 9. Maximum stress (1000 N) and minimum stress (100 N) was constant for each cycle of a test. The number of fatigue cycles was recorded. After the application of a certain number of load cycles, the test was stopped. The specimen was removed from the fatigue frame and photographed under white light and a UV microscope. Then the specimen was remounted and fatigue cycles continued. The fluorescent intensity at each fatigue cycle loading was calculated through ImageJ. The average data against cycles are shown in Figure 9. The fatigue fracture surface of the specimen was sputter coated with a thin layer of gold to observe the fatigue crack growth under the scanning electron microscope (SEM). The specimens for SEM were sputter coated with gold and viewed by SEM-XL30 (FEI). The specimens for SEM experiments were prepared by placing a piece of GFRC sheet onto a newly cleaved mica substrate and applying Au coating of 10–15 nm thick using a sputter coater.

In order to monitor the crack growth on the GFRC specimen, SEM characterization of the specimen was carried out. Figure 10 shows the matrix cracks, matrix crack and fiber breakage on the GFRP specimen surface. Figure 10 (left) shows micro-cracks on the matrix after 500 cycles. The exposure of glass fibers after 1,000 cycles in Figure 10 (middle) shows interface debonding. These exposed glass fibers tend to fracture under cyclic tensile force. After 1350 fatigue cycles, more breakage of glass fibers was observed as well as matrix cracks, causing a noticeable propagation along the longitudinal direction, as shown in Figure 10 (right). The corresponding macroscopic images are shown in Figure 10 (inset). With increasing fatigue cycles, the cracks developed in the 0° direction and became visible. The higher the number of fatigue cycles, the more cracks formed. UV microscopic images of fluorescence emission at different fatigue stages are shown in Figure 11. The damages were first formed

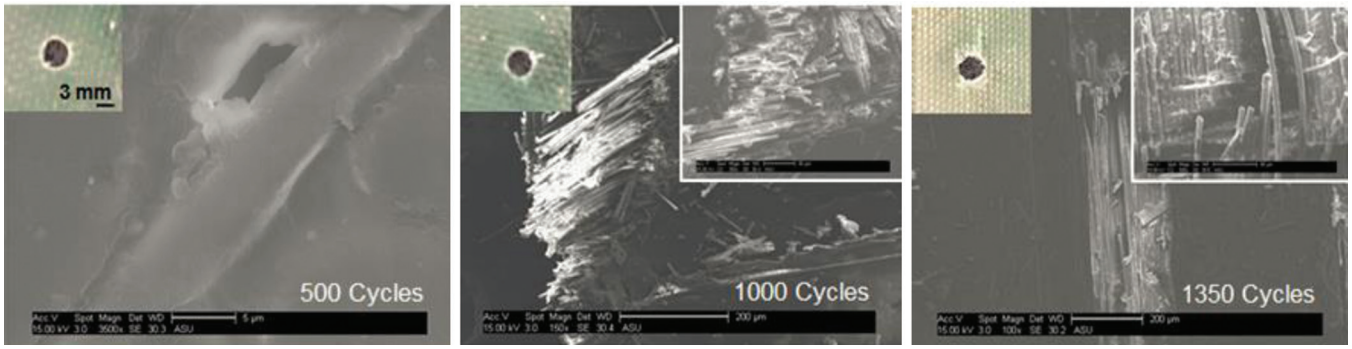

Figure 10. *SEM micrographs of glass fiber reinforced epoxy composite with 10% TCE at different fatigue cycle stages. insets are the images under white light.*

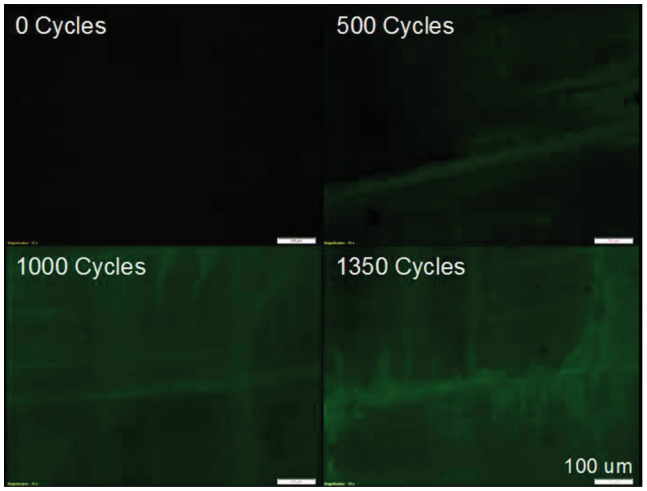

Figure 11. *Microscopic images of fluorescence emission on GFRC in response to different fatigue cycle stages.*

along the glass fibers in the 0° direction. With cycles, the fluorescence emission became more obvious and the cracks along the glass fibers at 90° direction grew as well. Fluorescent micrographs at different fatigue cycles were processed through ImageJ and the average fluorescence densities were calculated. The corresponding fluorescence density change was plotted in Figure 12. As expected, the density intensified as cycles increased, indicating that there were more cyclobutane molecules cleaved into cinnamate molecules due to the weaker bond strength on the cyclobutane ring than on the other bonds.

5. CONCLUSION

In this paper, a novel self-sensing approach is developed to detect the matrix cracking in composite laminates. The cyclobutane based smart polymers were synthesized and integrated within conventional epoxies. Once external forces were applied on the smart polymer and composites, fluorescence emissions were observed under UV microscope. Both TCE and PVCi based smart polymers were investigated. Compared to smart polymers with TCE, polymers integrated with PVCi showed stronger fluorescence intensity at the same stress level, which lead to stronger sensing capabilities to stress and matrix crack damage. The smart polymers were further applied to GFRP composites to detect the low cyclic fatigue damage. Significant fluorescence emissions were measured as the damage accumulated during the experiments. The developed self-sensing approach provided a new method to efficiently detect matrix cracks in composites without using any bulky NDE equipment or complicated SHM sensors. This developed self-sensing method provides a practical approach to identify structural damage in composites under complex load conditions.

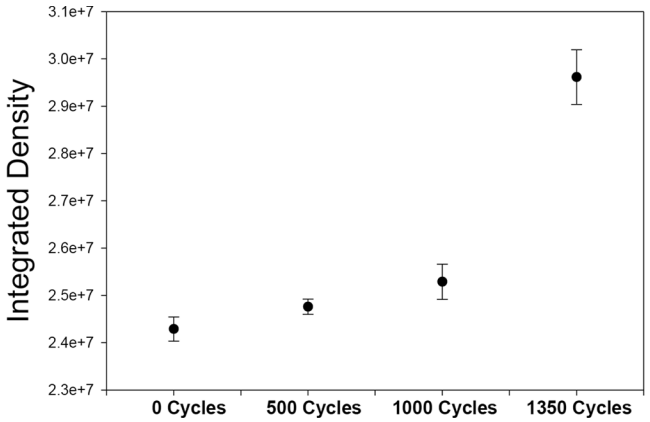

Figure 12. *Microscopic images of fluorescence emission on GFRC in response to different fatigue cycle stages.*

6. ACKNOWLEDGEMENT

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