

## Effect of Matrix Resin Properties on Activity of a Mechanochromic Fluorescent Probe for use in a novel Non-Destructive Inspection Technique for Aerospace Polymer Matrices

Natalie M. LARSON<sup>1</sup>, Ryan E. TOIVOLA<sup>1</sup>, Zhengwei SHI<sup>1</sup>, Sei-Hum JANG<sup>1</sup>, Alex JEN<sup>1</sup>, Gary GEORGESON<sup>2</sup>, Brian D. FLINN<sup>1</sup>

<sup>1</sup> Materials Science and Engineering Department, University of Washington; Roberts Hall 302, Seattle, Washington, USA; Phone: +1 2069 148022; email: nmlarson2@gmail.com, toivolre@uw.edu, shizw@u.washington.edu, jangsh@u.washington.edu, ajen@uw.edu, bflinn@uw.edu

<sup>2</sup> The Boeing Company; 9725 East Marginal Way South, Tukwila, WA, USA; email: gary.e.georgeson@boeing.com

### Abstract

A non-destructive inspection (NDI) technique that integrates mechanochromic fluorescent probe molecules into aerospace matrix resins was investigated. This experiment was focused on determining the effect of the matrix resin mechanical properties on the activity of the fluorescent probe molecule. In the first step of this experiment, samples of epoxy (diglycidyl ether of bisphenol A (DGEBA)-diethylenetriamine (DETA)) functionalized with fluorescent probe molecules were fabricated. To change the mechanical properties of the epoxy samples, diglycidyl ether (polypropylene glycol) (DGE(PPG)) was added to the samples incrementally from 0-100 weight percent (wt%). To determine the effect of mechanical deformation on the probe in cured DGEBA/DGE(PPG)-DETA, fluorescence spectra were taken before and after incremental compression of the functionalized epoxy samples. The fluorescence testing revealed that the fluorescence activation increases with increasing compressive strain, strain energy, and stress, with a linear relation between fluorescence activation and strain. Furthermore, the fluorescence testing revealed that the fluorescence activation decreased as the modulus of the sample decreased, with the exception of the neat DGEBA-DETA sample. The fluorescence testing also revealed that, without exception, the fluorescence activation decreased as the glass transition temperature decreased and as the wt% DGE(PPG) increased, with no fluorescence activation for 40 wt% DGE(PPG) and above.

**Keywords:** Non-Destructive Inspection (NDI), mechanochromic, fluorescent probe, epoxy, diluent, DGEBA, elastic modulus, aerospace, carbon fiber reinforced polymer (CFRP)

### 1. Introduction

Fiber reinforced composites are being used increasingly in the aerospace industry because of their advantageous controlled anisotropic mechanical properties, primarily their high specific modulus and specific strength [1]. A significant problem with these composites, however, is their impact damage detectability. While metallic parts will dent to indicate significant impact damage, composites may suffer sub-surface fiber breakage, matrix cracking, fiber pullout and delamination without visible surface damage or indentation [1]. Such impact damage, termed barely visible impact damage (BVID), can propagate below the surface of the material to areas outside of the impact region and cause substantial reduction in mechanical properties [2].

A rapid large-area non-destructive inspection (NDI) method is needed to identify BVID in routine aircraft inspections. Current NDI methods for polymer composites include X-radiography and X-ray diffraction, thermography, ultrasonic NDI methods, and shearography [3-5]. While these methods may be useful in small-scale or out-of-service inspection, requirements in part geometry, part composition, or part preparation limit their use in inspecting in-service aircraft [3-5]. For example, ultrasonic C-scan, the most commonly applied NDI method for composite parts, generally requires that the aircraft be taken out of service for scanning thoroughly enough to detect BVID. Because current NDI methods would require prohibitive

aircraft down time to detect BVID, composite structures for aircraft are designed to allow the aircraft to stay in service with BVID present. This requirement sometimes adds significant weight to the aircraft, reducing its potential for improved fuel efficiency.

The current research aims to develop a novel technique for quick, accurate, and cost-effective NDI that can be used to detect BVID during routine aircraft service. The NDI technique under development integrates mechanochromic fluorescent damage probe molecules into matrix resins, functionalizing them to be sensitive to mechanical damage. Under stress, the fluorescence behavior of the probe molecules changes, allowing the use of fluorescence imaging technology to measure impact damage [6]. Such a technique could be used to quickly locate potential areas of concern and determine whether a more detailed inspection is necessary. With a consistent and accurate BVID detection system in place, composite structures engineers could lower their BVID tolerances and design lighter-weight airplane parts.

Prior to beginning the current study, a fluorescent damage probe (AJNDE17) had been developed that reliably changed its fluorescence emission upon deformation when incorporated into the matrix resin Di-glycidyl ether of Bisphenol-A (DGEBA)-Dithylenetriamine (DETA) [6]. While the fluorescent probe responds in DGEBA-DETA, matrix resins used in aerospace applications can have a variety of mechanical properties which may affect how AJNDE17 responds to compression. The purpose of this research was to determine how the fluorescent probe response depends on the strain, strain energy, and stress on the matrix resin, and how the mechanical properties of the matrix resin affect the response of the fluorescent probe.

## 2. Experimentation

To investigate how the mechanical properties of the matrix resin affect the probe response, diluted epoxy samples with lower elastic moduli were fabricated. The resulting bulk samples were characterized as cured and then subjected to probe response tests—as detailed below.

### 2.1. Materials and Sample Preparation

#### 2.1.1. Epoxy Resin and Curing Agent

Di-glycidyl ether of Bisphenol-A (DGEBA) is a basic epoxide commonly used in composite materials. The molecular structure of DGEBA is shown in Figure 1. In this experiment, DGEBA from Dow Chemical Company (trade name DER 330) was used [7].

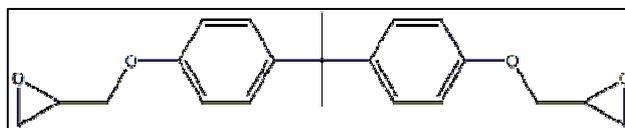


Figure 1: DGEBA Molecular Structure

Diethylenetriamine (DETA) from Sigma Aldrich was used as the curing agent (shown in Fig. 2).

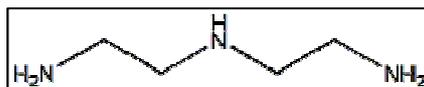


Figure 2: DETA Molecular Structure

### 2.1.2. Epoxide Functionalized Reactive Diluent

An epoxide functionalized reactive diluent was mixed into the DGEBA-DETA at a variety of weight fractions to manipulate the mechanical properties of the matrix resin. The diluent used was diglycidyl ether (polypropylene glycol) (DGE(PPG)), which is shown in Figure 3. In this experiment, DGE(PPG) from Dow Chemical Company (trade name DER 736) was used [8].

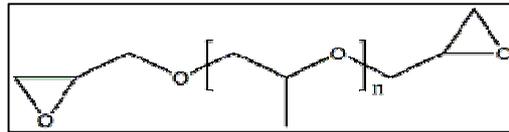


Figure 3: DGE(PPG) Molecular Structure

### 2.1.3. Fluorescent Probe Molecule AJNDE17

The fluorescent probe molecule AJNDE17 has two functional states, which are illustrated in Figure 4. In the “OFF” state, the probe molecule is bonded to the epoxy network, causing its backbone to be unconjugated. Mechanical force applied to the functionalized epoxy sample will cause some of the fluorescent probes to be ripped off of the epoxy network. After being ripped off the epoxy network, the probe backbone conjugates, changing the optical properties of the probe and hence turning the probe into the “ON” state.

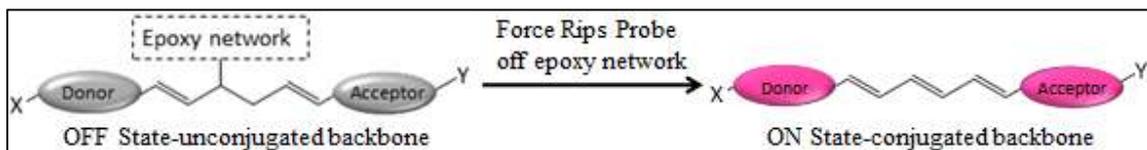


Figure 4: Schematic of AJNDE17 Mechanism

As AJNDE17 transitions from the “OFF” to “ON” state, it will show both color (UV Vis Absorbance) and fluorescent emission changes.

#### 2.1.3.1. Color Response of AJNDE17 in “ON” → “OFF” Transition

In the “ON” State, AJNDE17 exhibits an absorbance peak at ~535 nm. In the “OFF” state, no absorbance peak is observed (see Figure 5).

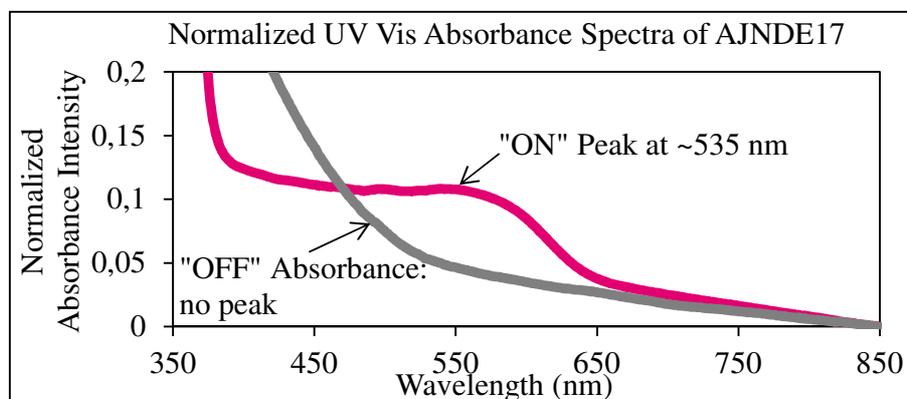


Figure 5: Normalized UV Vis Absorbance Spectra of AJNDE17 in “ON” and “OFF” States

### 2.1.3.2. Fluorescence Response of AJNDE17 in “ON” → “OFF” Transition

A representative fluorescence spectra (normalized to the intensity at the 505 nm peak) of AJNDE17 in its “ON” and “OFF” states is shown in Figure 6. In the “ON” state, AJNDE17 exhibits fluorescence emission peaks at 505 nm and 610 nm. In the “OFF” state, however, only the 505 nm fluorescence emission peak is present.

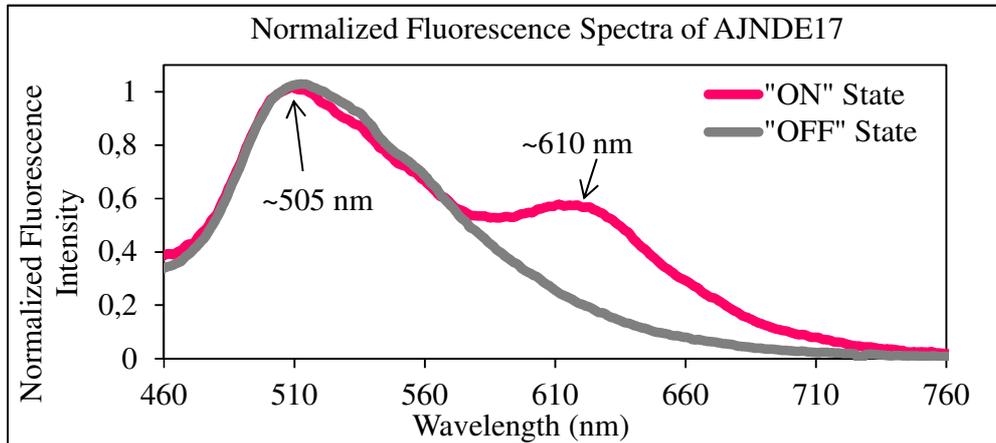


Figure 6: Normalized Fluorescence Spectra of AJNDE17 in “ON” and “OFF” States

### 2.1.4. Incorporation of AJNDE17 into DGEBA/DGE(PPG)-DETA

Eight different blends of DGE(PPG) + DGEBA were fabricated, varying the weight percent (wt%) of DGE(PPG) from 0 to 100 %. The DGE(PPG)/DGEBA samples used the DETA curing agent in a 1-1 stoichiometric ratio, and contained 0.05 wt% AJNDE17 with respect to the uncured DGE(PPG)/DGEBA-DETA mixture.

AJNDE17 was received in the “OFF” state in solution with 50 wt% DETA. Next, the AJNDE17 + DETA was diluted with DETA to a weight percent AJNDE17 that would give 0.05 wt% AJNDE17 in the final cured sample. The DGE(PPG)/DGEBA blends were mixed in separate beakers and degassed under house vacuum for 5-10 minutes. The AJNDE17 + DETA solution was then added in the 1-1 stoichiometric amount, mixed thoroughly, and degassed. Finally, the samples were cured for 24 hours at room temperature.

## 2.2. Sample Characterization

### 2.2.1. Fluorescent Emission Spectra of Samples

The fluorescent emission spectra of the functionalized epoxy samples were collected with a Stellarnet Blue-WAVE UVN spectrometer (Stellarnet US, Tampa, FL). 390 nm excitation light was sent through 7 optical fibers from an LED single-wavelength source to the sample surface. The resulting emission spectra were collected by one optical fiber.

### 2.2.2. UV Vis Absorbance Spectra of Samples

The UV Vis absorbance spectra of the functionalized epoxy samples were collected with a ThermoFisher EVO350 UV-Vis (ThermoFisher, USA, Madison, WI). Light ranging from 300 nm to 900 nm was sent through the sample and the resulting absorbance spectra were collected.

### 2.2.3. Measurement of the Elastic Modulus

The elastic modulus of the epoxy was determined by conducting a compressive loading/unloading mechanical test using an Instron 5500R Test Frame (Instron Worldwide Headquarters, Norwood, MA). The sample was of flat rectangular geometry (~10 mm \* 10 mm \* 1.5 mm) to allow for increased plastic deformation before fracture. The measured elastic modulus was taken as the slope of the linear portion of the unloading stress-strain curve. By using the unloading curve to determine the elastic modulus, “toe” issues due to sample shifting and settling on the loading curve are avoided.

### 2.2.4. Measurement of Glass Transition Temperature ( $T_g$ ) of Samples

The  $T_g$  of the samples was measured per ASTM E1640-09 Method #1 using a PerkinElmer 7e Dynamic Mechanical Analyzer (PerkinElmer, Waltham, MA) [9]. The samples were heated from as low as -40 °C to 90 °C at 5 °C/min. In addition, a static force of 20 mN, a dynamic force of 10 mN, and a frequency of 1 Hz were used. The  $T_g$  was calculated from the resulting Storage Modulus vs. Temperature curve, and the average  $T_g$  of five specimens was used for each sample.

## 2.3. Measurement of Probe Response to Compression

Fluorescence spectra of all samples were collected before compression testing. In compression testing (with the Instron 5500R), 5-8 specimens from each of the samples (0-100 wt% DGE(PPG)) were compressed to incremental levels of strain. From the stress-strain curves produced, the maximum true stress applied was determined. In addition, the strain energy was taken as the total area under the engineering stress-strain curve for each specimen. Furthermore, the true plastic strain was determined from measurements of the sample thickness before and after compression. Immediately after compression, the fluorescence spectra were measured.

## 3. Results

The results of the as-cured sample characterization and probe response testing are discussed in the following sections.

### 3.1. AJNDE17 Optical Responses in DGEBA/DGE(PPG)-DETA as cured

#### 3.1.1. Color Response of AJNDE17 in DGEBA/DGE(PPG)-DETA

The eight samples with increasing wt% DGE(PPG) are shown in Figure 7.

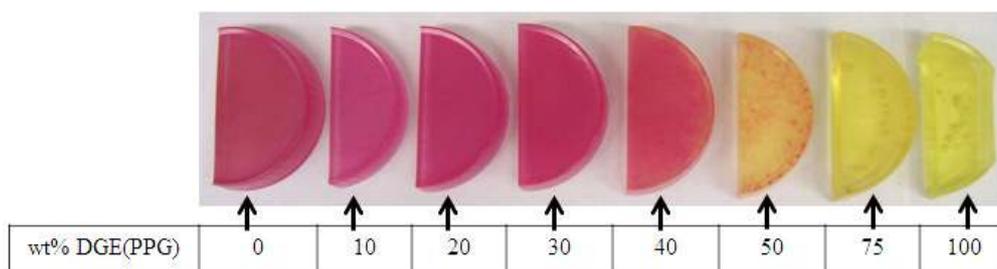


Figure 7: DGE(PPG)/DGEBA-DETA+AJNDE 17 Samples

The red-purple color of the 0-40 wt% DGE(PPG) samples corresponds to the increased absorbance at 535 nm as shown in the UV Vis absorbance spectra in Figure 8. The absorbance at

535 nm for the 10-40 wt% DGE(PPG) samples indicates that the probe turned on slightly during cure (Note: neat DGEBA-DETA was not measured in UV Vis tests). The yellow color of the 50-100 wt% DGE(PPG) samples corresponds to the UV Vis absorbance spectra shown in Figure 8. The lack of absorbance at 535 nm for the 50-100 wt% DGE(PPG) samples indicates that the probe was not turned on during the cure of those samples.

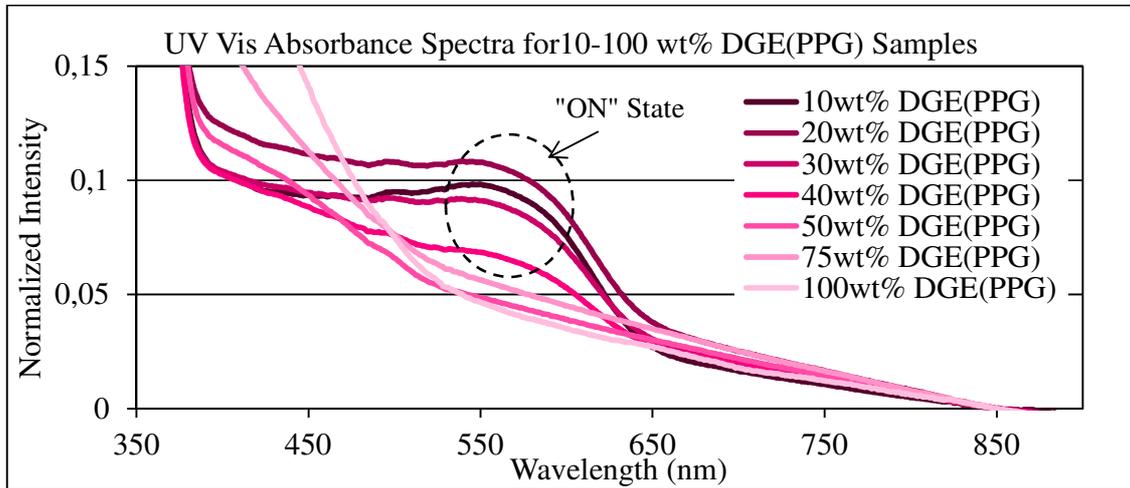


Figure 8: Normalized UV Vis Absorbance Spectra for 10-100 wt% DGE(PPG)

### 3.1.2. Fluorescence Response of AJNDE17 in DGEBA/DGE(PPG)-DETA

The fluorescence spectra (normalized to 505 nm peak) for the eight DGEBA/DGE(PPG)-DETA + AJNDE17 samples are shown in Fig. 9. Like the UV Vis absorbance spectra, the fluorescence spectra show that for 40 wt% DGE(PPG) and below, the fluorescent probe transitioned into the "ON" state during cure, exhibiting fluorescence emission peaks at 505 nm and 610 nm. In addition, the fluorescence spectra show that for 50-100 wt% DGE(PPG), the fluorescent probe did not turn on during cure, exhibiting a fluorescence emission peak only at 505 nm.

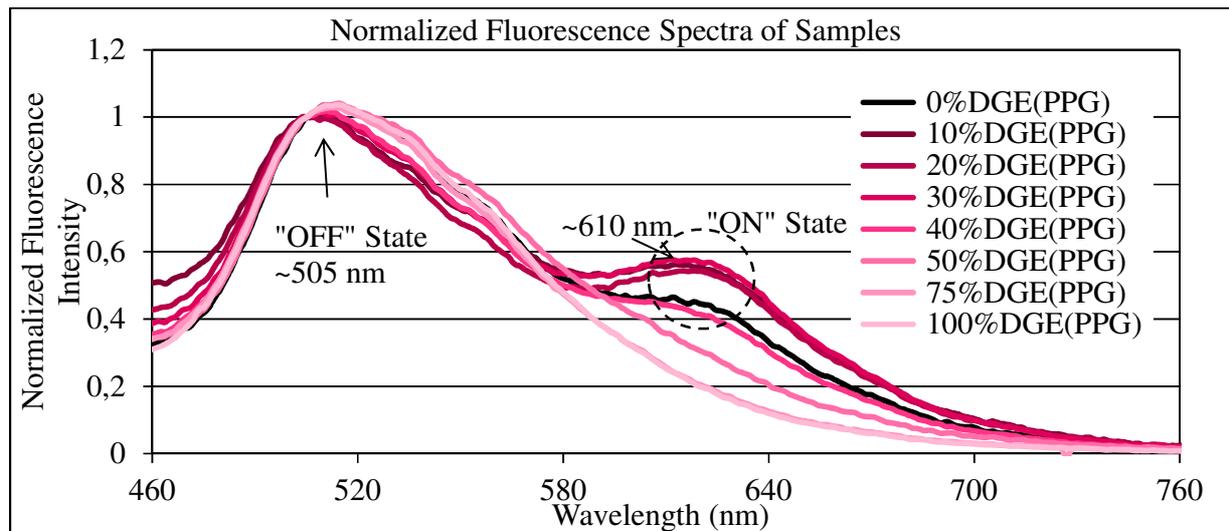


Figure 9: Normalized Fluorescence Spectra of Samples

### 3.2. Effect of Mechanical Deformation on AJNDE17 in cured DGEBA/DGE(PPG)-DETA

For each sample, 5-8 specimens were cut to the approximate dimensions of 10 mm\*10 mm\*1.5 mm. The fluorescence spectra before compression were collected for each specimen, and then the specimens were deformed in compression at 0.1 mm/min crosshead speed to varying final strains. A typical stress-strain curve representing the behavior of all of the samples is shown below in Figure 10.

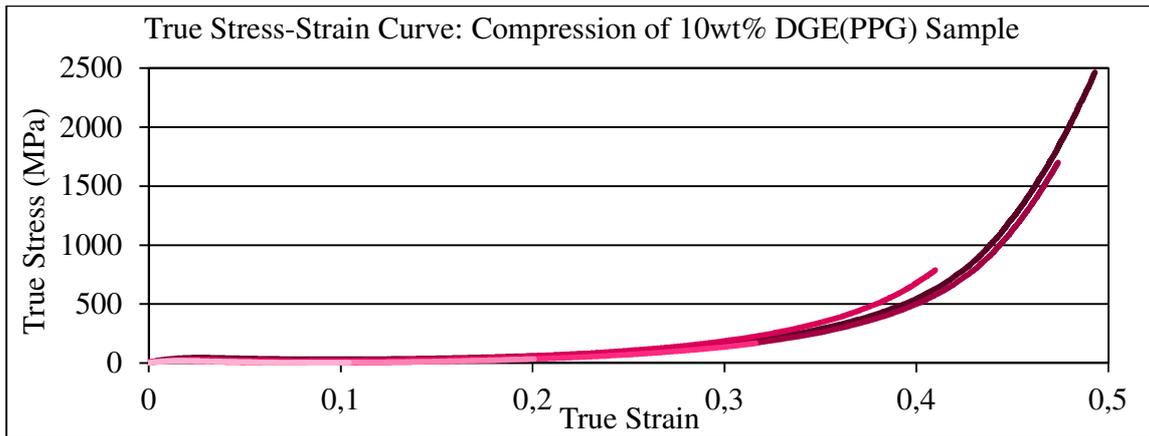


Figure 10: Representative Compressive Stress-Strain Curve for 10 wt% DGE(PPG) Sample

Following compression, the fluorescence spectra for each specimen were measured. During these tests, the fluorescence behavior of the 0-30 wt% DGE(PPG) samples differed significantly from that of the 40-100 wt% DGE(PPG) samples. Thus, a typical fluorescence spectra for both the 0-30 wt% DGE(PPG) sample behavior and the 40-100 wt% DGE(PPG) sample behavior are shown in Figures 11-12.

#### 3.2.1. Typical Fluorescence Spectra for 0-30 wt% DGE(PPG) samples

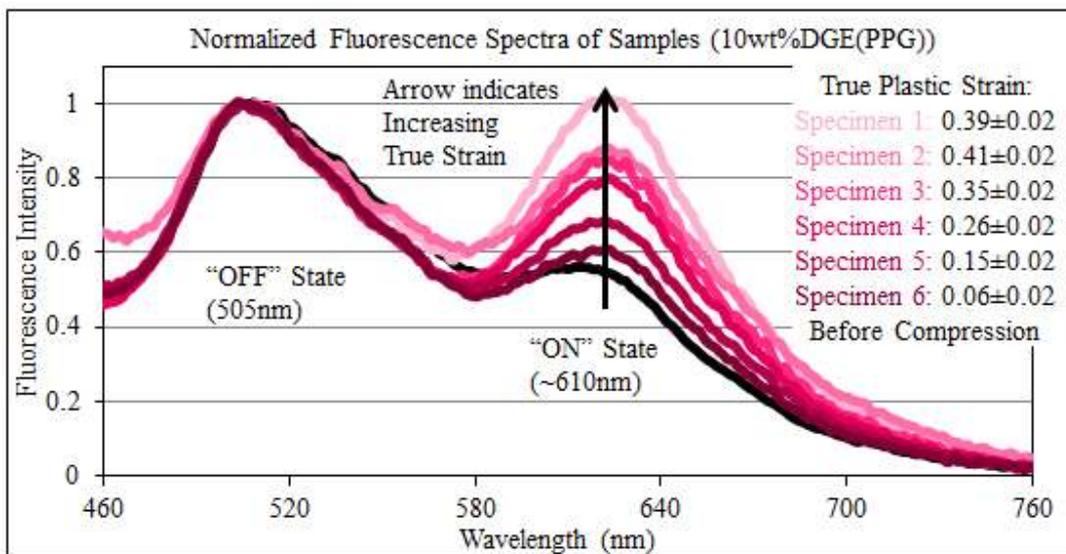


Figure 11: Normalized Fluorescence Spectra after Compression for 10wt% DGE(PPG) Sample

Figure 11 shows the fluorescence spectra of the 10 wt% DGE(PPG) sample after compression. The spectra are normalized to the 505 nm peak intensity to show that the emission ratio of the 610 nm peak to the 505 nm peak increases as the true strain on the specimen increases. These fluorescence results are indicative of the probe responding to compressive deformation.

### 3.2.2. Typical Fluorescence Spectra for 40-100 wt% DGE(PPG) samples

Figure 12 shows the fluorescence spectra after compression of the 40 wt% DGE(PPG) sample. The spectra are normalized to the 505 nm peak intensity to show that the emission ratio of the 610 nm peak to the 505 nm peak does not change as the true strain on the specimen increases. These fluorescence results are indicative of the probe not responding to deformation.

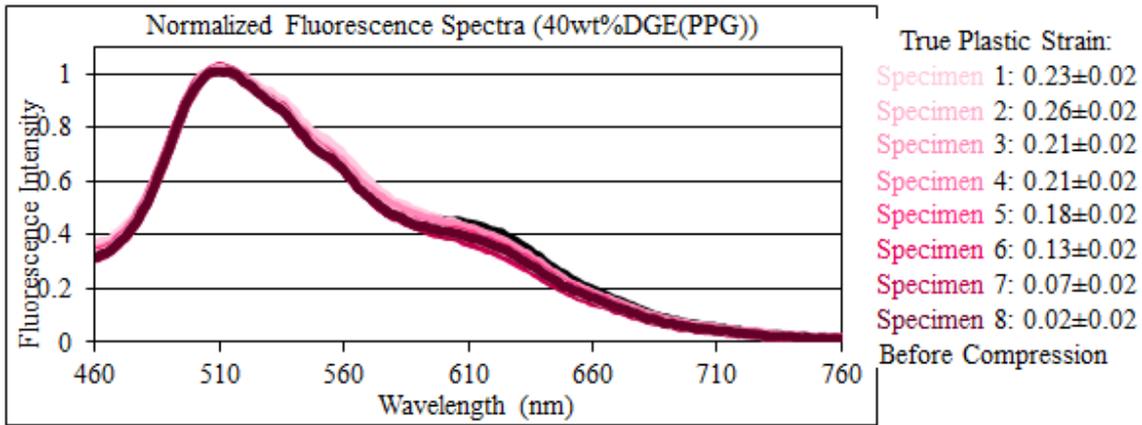


Figure 12: Normalized Fluorescence Spectra after Compression for 40 wt% DGE(PPG) Sample

### 3.2.3. Quantitative Method for Measuring Fluorescence Emission Ratio

Based on the observations of the emission ratio of the 610 nm peak to the 505 nm peak changing with strain if the probe responds to compressive damage, a quantitative measure of the probe response is defined. The ratio of the ON and OFF peaks before and after compression can be compared with the following relation, termed the Probe Response Index (or *PRI*):

$$PRI = \frac{I_{610nm}^{AC}/I_{505nm}^{AC} - I_{610nm}^{BC}/I_{505nm}^{BC}}{I_{610nm}^{BC}/I_{505nm}^{BC}} * 100 \% \quad (1)$$

where  $I_x^y$  is the fluorescence emission intensity of the peak of wavelength  $x$  under condition  $y$ , AC denotes the intensity after compression, and BC denotes the intensity before compression.

### 3.3. Effect of Mechanical Deformation on AJNDE17 in cured DGEBA/DGE(PPG)-DETA as a Function of True Strain

The *PRI* values were calculated for each specimen in each of the eight samples. A plot of the *PRI* against the final true plastic strain for 0-40 wt% DGE(PPG) is shown in Figure 13. For the 0-30 wt% DGE(PPG) samples, the *PRI* shows a linear dependence on true plastic strain, with  $R^2$  (coefficient of determination) values of 0.88 or above. Furthermore, the slope of the *PRI* versus true plastic strain decreases as the weight percent of DGE(PPG) in the sample increases, revealing that the probe becomes less responsive to damage with increasing diluent content in the

sample. For the 40-100 wt% DGE(PPG) samples, the *PRI* shows no dependence on the true plastic strain, and (as shown in section 2.2.2) does not respond to compressive damage.

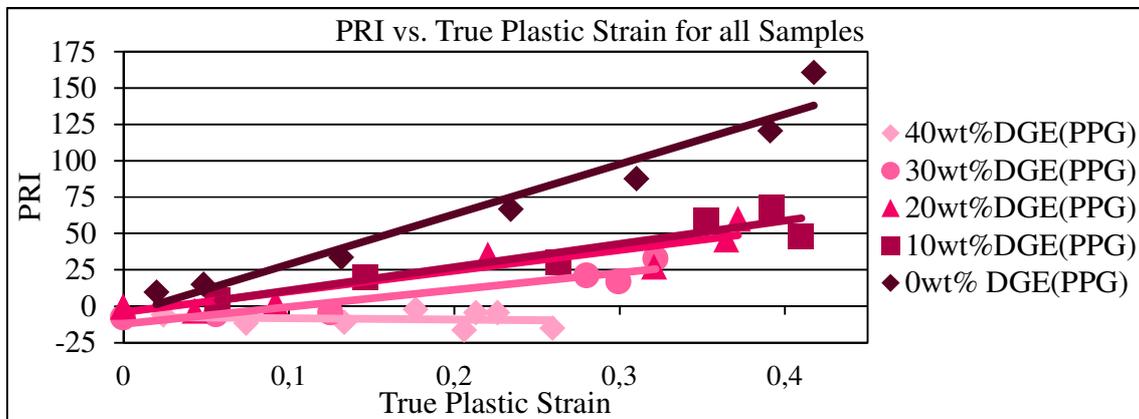


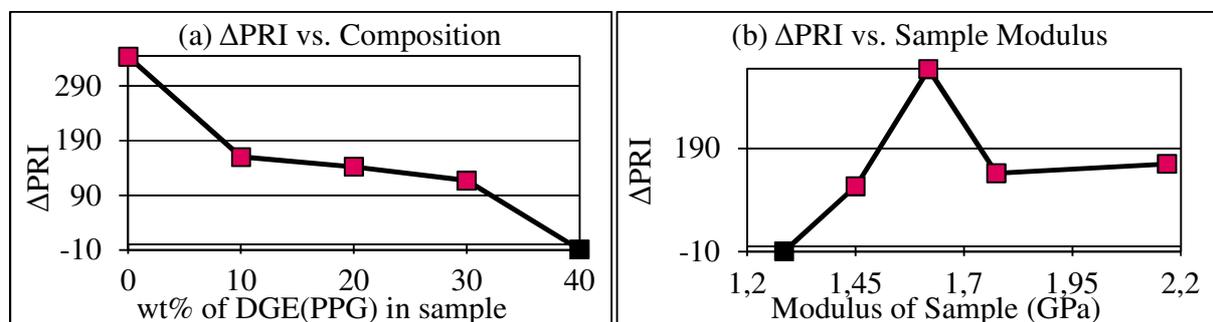
Figure 13: Plot of *PRI* vs. True Plastic Strain for 0-100 wt% DGE(PPG)

### 3.4. Effect of Mechanical Deformation on AJNDE17 in cured DGEBA/DGE(PPG)-DETA as a Function of Strain Energy and as a Function of Stress

In addition to plotting the *PRI* against true plastic strain, the *PRI* was plotted against the total strain energy and the maximum stress applied during incremental compression. Linear fits to the data from each of the samples were made. The  $R^2$  values for the *PRI* vs. true plastic strain fits were relatively high ( $>0.88$ ) and relatively constant ( $0.90 \pm 0.03$ ), indicating a strong linear dependence of the *PRI* on true plastic strain. Meanwhile, the  $R^2$  values for the *PRI* vs. strain energy and *PRI* vs. maximum stress applied linear fits decrease as the wt% DGE(PPG) increases, indicating that the *PRI* does not show a linear dependence on strain energy or maximum stress.

### 3.5. Effect of Sample Properties (Modulus, wt% DGE(PPG)) on Probe Response

As noted in section 3.3, the *PRI* plotted against true plastic strain shows a linear relationship. Thus, a slope for the best fit linear curve for each sample can be calculated. The slope of the *PRI* vs. true plastic strain for each sample shall be referred to as  $\Delta PRI$ . Figure 14 shows the  $\Delta PRI$  against the sample's wt% DGE(PPG) and elastic modulus.



■ =Probe Responded to Compression, ■ =Probe did not respond to compression

Figure 14: Plots of  $\Delta PRI$  vs. (a) the sample's wt% DGE(PPG) and (b) the sample's modulus

As shown by the plots in Figure 14, the  $\Delta PRI$  decreases as the wt% DGE(PPG) increases. However, the  $\Delta PRI$  shows no clear correlation with the elastic modulus of the samples. These results suggest that the sample's composition (wt% DGE(PPG)) is a more dominant factor affecting the probe's response than the sample modulus.

#### 4. Conclusions

The fluorescence testing revealed that the  $PRI$  increases with increasing compressive strain, strain energy, and stress, with a linear relation between fluorescence activation and strain. Furthermore, the fluorescence testing revealed that the  $\Delta PRI$  decreases monotonically as the wt%DGE(PPG) increases, but does not vary monotonically with the sample's elastic modulus. These results suggest that the experiment did not effectively isolate the effect of the elastic modulus on the fluorescent probe response. Rather, this experiment revealed that the local chemical environment (wt%DGE(PPG)) surrounding the fluorescent probe had a stronger effect on the  $PRI$  than the elastic modulus. Changes in the local chemical environment include changes in the polymer polarity, dielectric strength, and free volume—all of which could prevent the probe from attaching to the epoxy network during sample fabrication, reducing the  $\Delta PRI$ .

Future work will be aimed at determining why the probe response decreases with increasing wt% DGE(PPG). Such research will involve investigating how changes in the local chemical environment affect the interactions between the fluorescent probe and the epoxy network. Furthermore, to allow the initial research question to be answered, future research will aim to separate the effects of matrix stiffness from those of a changing local chemical environment—possibly via the use of DGEBA derivatives of varying molecular weights as reactive diluents.

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