

CONF-9610100-1

**LASER INDUCED FLUORESCENCE IMAGING OF
THERMAL DAMAGE IN POLYMER MATRIX COMPOSITES***

E.A. Wachter, W.G. Fisher, and K.E. Meyer
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6113

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

RECEIVED
NOV 21 1996
OSTI

MASTER

*Research sponsored by U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

"The submitted manuscript has been authored by a contractor of the U.S. Government under contract No. DE-AC05-96OR22464. Accordingly, the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U.S. Government purposes."

rf

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LASER INDUCED FLUORESCENCE IMAGING OF THERMAL DAMAGE IN POLYMER MATRIX COMPOSITES[†]

E.A. Wachter[‡], W.G. Fisher, and K.E. Meyer
Oak Ridge National Laboratory, Oak Ridge, TN 37831-6113

ABSTRACT

A simple, fluorescence based imaging system has been developed which is capable of identifying regions of thermal damage in polymer-matrix composites (PMC's). PMC's are playing an increasingly important role in applications where low weight and high mechanical strength are important. A particular concern in the aerospace industry is the tendency of some PMC materials to become irreversibly damaged when exposed to elevated temperatures. Traditional non-destructive evaluation (NDE) techniques are capable of detecting physical flaws, such as cracks and delaminations, but have not proven effective for detecting initial heat damage, which occurs on a molecular scale. Spectroscopic techniques such as laser-induced fluorescence (LIF) provide an attractive means for detecting thermal damage on large, irregularly shaped surfaces. In this paper we describe instrumentation capable of rapidly detecting thermal damage in graphite/epoxy components.

INTRODUCTION

The excellent mechanical properties combined with low weight of fiber-reinforced polymer matrix composites (PMC's) have resulted in their widespread use in high-performance aircraft. They also show promise for automotive (Lynn, 1990) and various industrial applications. Diaminodiphenyl sulfone (DDS)-cured tetraglycidyl-4,4'-diaminodiphenyl methane (TGDDM) epoxy-resin is the basis for most commercially available pre-preg resins. However, a drawback to this class of epoxy-resins is a serious degradation, embrittlement, and loss of strength that can occur upon exposure to elevated temperatures (Haskins, 1989; Luoma and Powland, 1986). In fact, these materials can loose up to 60% of their original strength while exhibiting no visual or microscopic evidence of degradation (Frame et. al., 1990).

We have recently shown that laser-induced fluorescence (LIF) can be used to quantify and image heat-induced damage in PMC specimens (Fisher et al., 1995). LIF is a rapid, non-invasive spectroscopic method which offers the potential for portable, sensitive evaluation of large areas. A laser is used to optically excite resin molecules exposed at the surface of a PMC specimen. This exposed resin then fluoresces (re-emitting a portion of this absorbed energy in the form of light at longer wavelengths). The properties of this laser-induced fluorescent emission can be correlated with the local environment and integrity of the resin, and are thus sensitive to changes in the PMC specimen at a molecular level.

[†]Research supported by the U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp.

[‡]Author to whom correspondence should be sent.

LIF MEASUREMENT AND CALIBRATION

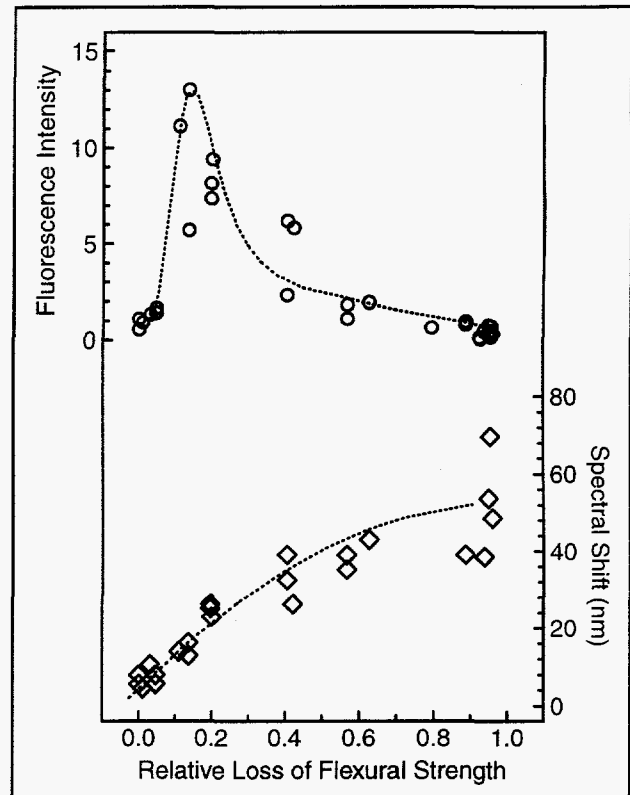
In an earlier publication we described methods for performing fluorescence measurements of damaged PMC samples using laser excitation at wavelengths ranging from 325 nm to 785 nm (Fisher et. al., 1995). In short, excitation light from a pump laser is focused onto a sample using a beamsplitter and microscope objective in a confocal epi-illumination configuration. The fluorescence emission thereby produced is collected by the microscope objective, focussed into an imaging spectrograph, and detected using a low-noise CCD camera. Appropriate optical filters placed upstream from the spectrograph reject scattered excitation light, permitting spectral analysis at wavelengths greater than about 15 nm above the laser line and extending beyond 900 nm in the near infrared. This arrangement proves very convenient for examining small locations (from $< 0.01 \text{ mm}^2$ areas) on the surface of a specimen.

To quantify the relationship between thermally-induced damage and key spectroscopic parameters, we collected fluorescence spectra from a series of 29 PMC coupons (prepared from Hercules IM6/3501-6 pre-preg tape, each of which were $2.5 \text{ cm} \times 7.6 \text{ cm} \times 0.3 \text{ cm}$ thick) that had been exposed to elevated temperatures for various durations. Wet and dry pre-treatments were used for subsets of these samples. Damage was independently quantified in terms of loss of flexural strength using standard ASTM flexure tests. When spectral properties of this test set are plotted relative to mechanical properties, several interesting correlations are noted (Figure 1). First, fluorescence intensity is found to increase sharply at the onset of thermal damage, reach a maximum value, and finally to drop off with further increases in damage. This sharp increase in fluorescence intensity can be useful for identifying the boundaries of a damaged area. Second, a dramatic monotonic shift occurs in the wavelength of peak fluorescence intensity, which moves towards longer wavelengths with increasing damage. This second factor may be useful in quantifying the degree of damage within a damage zone. This basic trend was observed for all excitation wavelengths and did not depend on the sample pre-treatment.

CHEMICAL BASIS OF FLUORESCENCE RESPONSE

The results shown in Figure 1 raise a fundamental question – what is being measured in the LIF method? We believe that laser-induced fluorescence provides a sensitive means for probing the structure of the epoxy-resin polymer at a molecular level. When cured at 175°C , three parallel reactions take place in the DDS-TGDDM epoxy-resin system that result in inter-molecular cross-linking and the formation of intra-molecular ring matrices. These complex macro-molecular structures exhibit optical absorption and fluorescence emission over an extremely wide range of wavelengths, spanning ultraviolet to near infrared optical wavelengths. But if this material is heated to temperatures above the service limit, the matrix degrades as a consequence of various oxidation, hydrolysis, and dehydration reactions. As a consequence, the fluorescence spectrum of a heat-damaged specimen consists of a superposition of fluorescence signatures from the original cure products and features attributable to these degradation products. Changes in this “spectral fingerprint” occur as the polymer is irreversibly heat damaged. These changes include variations in total emission intensity and in wavelength of maximum fluorescence intensity. Monitoring these spectroscopic parameters allows both qualitative identification of damage location as well as quantitative measurement of the severity of damage.

Figure 1. Relationship between damage and LIF response for thermally-damaged PMC coupons (fabricated from DDS-TGDDM epoxy-resin) excited using laser radiation at 633 nm. Upper curve, fluorescence intensity as a function of thermal damage. Lower curve, wavelength of peak fluorescence intensity as a function of damage. Damage was independently quantified using standard ASTM flexure tests.



IMAGING OF HEAT-INDUCED DAMAGE

The data in Figure 1 can serve as the basis for interpretation of LIF-based imaging. Two-dimensional LIF imaging of heat-induced damage can be achieved using flood illumination of a sample and photographic or videographic collection of the fluorescence emitted from the surface of the sample (Figure 2). We have found it convenient to couple laser excitation light into a multi-mode optical fiber, the divergent output of which is then positioned so as to evenly illuminate the composite specimen. Fluorescence emission from the surface of the specimen can then be collected using a standard 35-mm SLR camera lens, and detected by a high sensitivity video camera. Optical filters mounted on the front of the camera lens facilitate rejection of scattered excitation light. Images thereby produced are easily captured by a personal computer, which can be used to subsequently process image data to improve contrast or to determine emission wavelength characteristics. Using this general approach, images of areas in excess of 1 m² can be easily acquired in approximately one second.

To evaluate imaging performance, an additional set of test specimens were prepared, again using IM6G/3501-6 unidirectional pre-preg tape. These large specimens (measuring 30 cm x 30 cm x 0.2 cm thick) were assembled by laying a series of tape plies at the desired orientations, then vacuum-bag curing the laminate in an autoclave. The panels thereby produced were exposed to localized elevated temperatures by contact heating using a heated metal disk. This 5-cm diameter disk was placed into contact with the center of a panel for various times, producing a burn mark of varying severity. Thermocouples in contact with various locations on the panel surface were used to assure that material surrounding the contact area did not exceed the service limit. The pattern of LIF emission was then recorded for each specimen to determine whether imaging of this burn mark could be correlated with location and severity of damage.

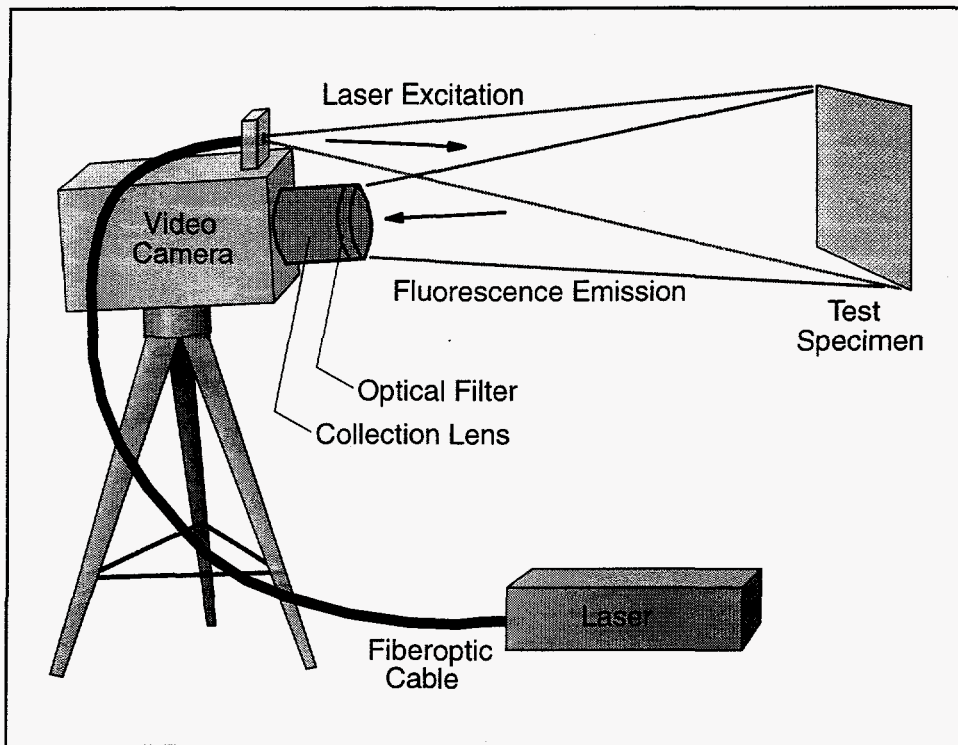


Figure 2. Instrumentation for LIF imaging of PMC's. For intensity imaging, a single image is collected using one bandpass optical filter. For wavelength shift imaging, multiple images are collected using different filters that cover a range of bandpasses.

Typical imaging data is shown in Figure 3, which shows the central region of a panel exposed to 250°C for 30 minutes. The small images on the left show intensity images taken in 10 nm wide bands spaced 20 nm apart (spanning emission wavelength bands from 550 nm to 650 nm, obtained using excitation at 514.5 nm). The large image on the right is a processed image showing wavelength shift (this will be discussed in detail below). Note that each of the individual intensity images in Figure 3 is characterized by a uniform field of resin surrounding a central burn area. Small variations in LIF intensity are observed in this unburned zone (for example, parallel diagonal lines are noted that correspond to the direction of the fiber plies in the top-most layer, while various ink marks on the surface are visible as dark areas). These artifacts are attributable to variations in the amount of resin exposed at the surface, which in turn affects the observed intensity – ink on the surface of the panel masks the exposed resin, producing a dark artifact. In each intensity image, the burn area is surrounded by a ring of bright emission, while the central circle – the area exposed to the highest temperature and presumably experiencing the greatest thermal damage – exhibits a reduced intensity relative to this ring. This unusual pattern can be understood by examining Figure 1. If intensity of fluorescence is measured at a given emission wavelength, the maximum intensity will correspond to lightly damaged material (the condition representative of the maxima in the upper curve of Figure 1), while severely damaged areas will exhibit reduced emission intensity (corresponding to the right side of the upper curve in Figure 1). Since severely damaged areas will always be surrounded by a border of lesser damage (due to the thermal gradient that must exist around the point of thermal exposure), this ring pattern will often be observed in intensity images. Hence the zone of maximum fluorescence intensity can be used to indicate the border between damaged and undamaged material.

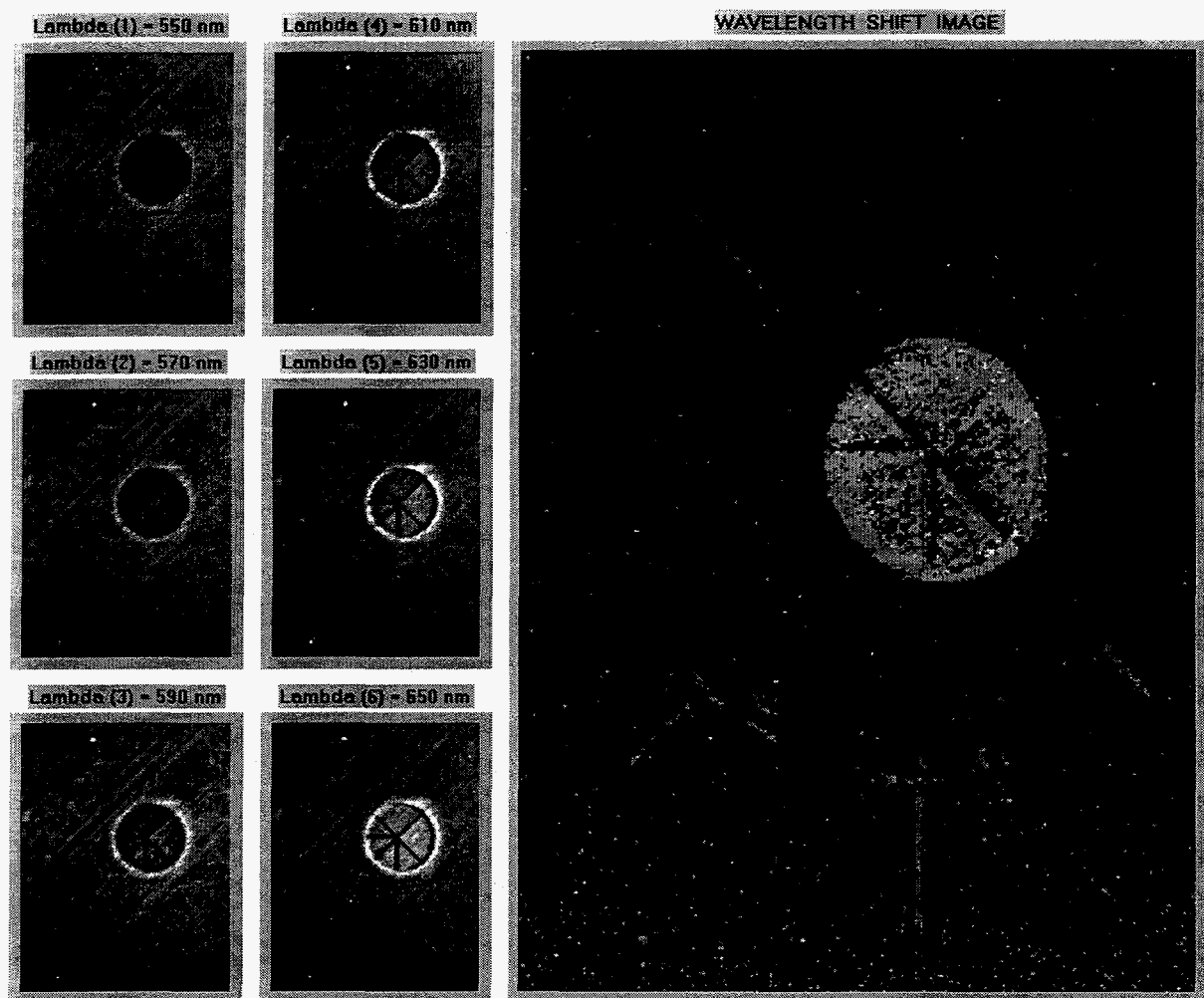


Figure 3. Intensity images (left) and resultant wavelength shift image for a PMC panel exposed to contact heating in the circular zone that is evident in all images.

To obtain quantified measurements of thermally-induced damage it is necessary to collect spectral data at multiple wavelengths so that the wavelength of maximum intensity (λ_{\max}) can be estimated. A calibration curve such as that shown in Figure 1 (lower curve) may then be used to convert λ_{\max} into an estimate of the degree of damage. It should be pointed out that no direct correlation to mechanical strength properties of a component can be made with this analysis, since the fluorescence measurement only evaluates the condition of the surface of the composite material, which may or may not be related to integrity of the underlying material – this is an important point since different damage scenarios, ranging from a short burst of extremely high temperature (fire) to gradual exposure to slightly elevated temperatures (thermal cycling), will determine the ultimate depth of damage. However, the relationship shown in Figure 1 implies that fluorescence response can serve as an accurate predictor of the extent of thermal damage. Imaging based on changes in wavelength of maximum fluorescence (or “wavelength shift imaging”) can be achieved by processing a series of images, such as those shown in the left portion of Figure 3, on a pixel-by-pixel basis to produce an image that plots estimates of λ_{\max} for each pixel. Such an image is shown on the right of Figure 3.

The wavelength shift image shown in Figure 3 demonstrates how the various artifacts observed in the individual intensity images are effectively compensated following processing. For example, the intensity artifacts observed in the undamaged zones of the panel essentially disappear in the wavelength image – this is as expected since these features should have no wavelength dependence. In fact, examination of these regions in the six individual intensity images confirms that no significant trends are noted from one emission band to another. The central burn pattern – which shows a progression in relative intensity from 550 nm to 650 nm – produces a uniform, high damage signature in the wavelength image. And the clearly defined ring observed in the intensity images disappears, confirming that this feature is actually indicative of only slightly damaged material relative to the bulk of the panel. Note that the grainy appearance of the wavelength image results from both the small number of wavelength bands used for processing – the small number of possible values for λ_{max} that are plotted (six levels), and that fact that the possible contrast is limited by the wavelength span covered by the intensity image set – to accurately detect extremely damaged material, intensity images further to the red are needed (ie, in the 650-750 nm region). Improved modeling and optimization of filter sets are expected to improve the resolution and accuracy of these wavelength shift images.

Figure 4 shows similar imaging results for a panel that was contact heated to 205°C for 120 minutes. The modest damage to this panel is characterized by a faint but clearly identifiable image in all intensity frames. Since the wavelength of fluorescence maxima for this lightly damaged resin is not appreciably shifted from that of undamaged resin, the wavelength image does not accentuate the damage feature. Hence, the wavelength method is shown to be successful at quantifying the level of damage, while the intensity images provide a very sensitive means for detecting the onset of damage.

In practice, the combination of fluorescence intensity and wavelength images can be used to detect and quantify the onset of thermally-induced damage. Since the required image processing is relatively simple, the entire sequence of images can be obtained in a matter of seconds. Note also that small, low-power solid-state diode lasers could be used for excitation. Hence, it is clear that this approach can be used to develop a portable system capable of scanning large surface areas and producing images of quantified surface damage in near-real time. Such a system could be operated by a single technician and would be sufficiently portable to access all but the most inaccessible surfaces of items undergoing characterization.

There are a number of remaining technical issues that must be addressed in order to fully specify the strengths and limitations of this method. For example, details of the thermal damage mechanisms and of the correlation between fluorescence signatures and specific cure reaction and degradation products are not well understood. Direct correlation between spectral properties and other bulk physical testing methods, such as glass transition temperature, t_g , must also be established. And factors such as environmental conditions and component age, along with the roles of surface coatings (such as paint) and surface conditioning (such as aerobic vs. anaerobic exposure) need to be evaluated. Finally, while applicability to other resin systems is anticipated, these need to be studied to determine the breadth of possible use for this technique.

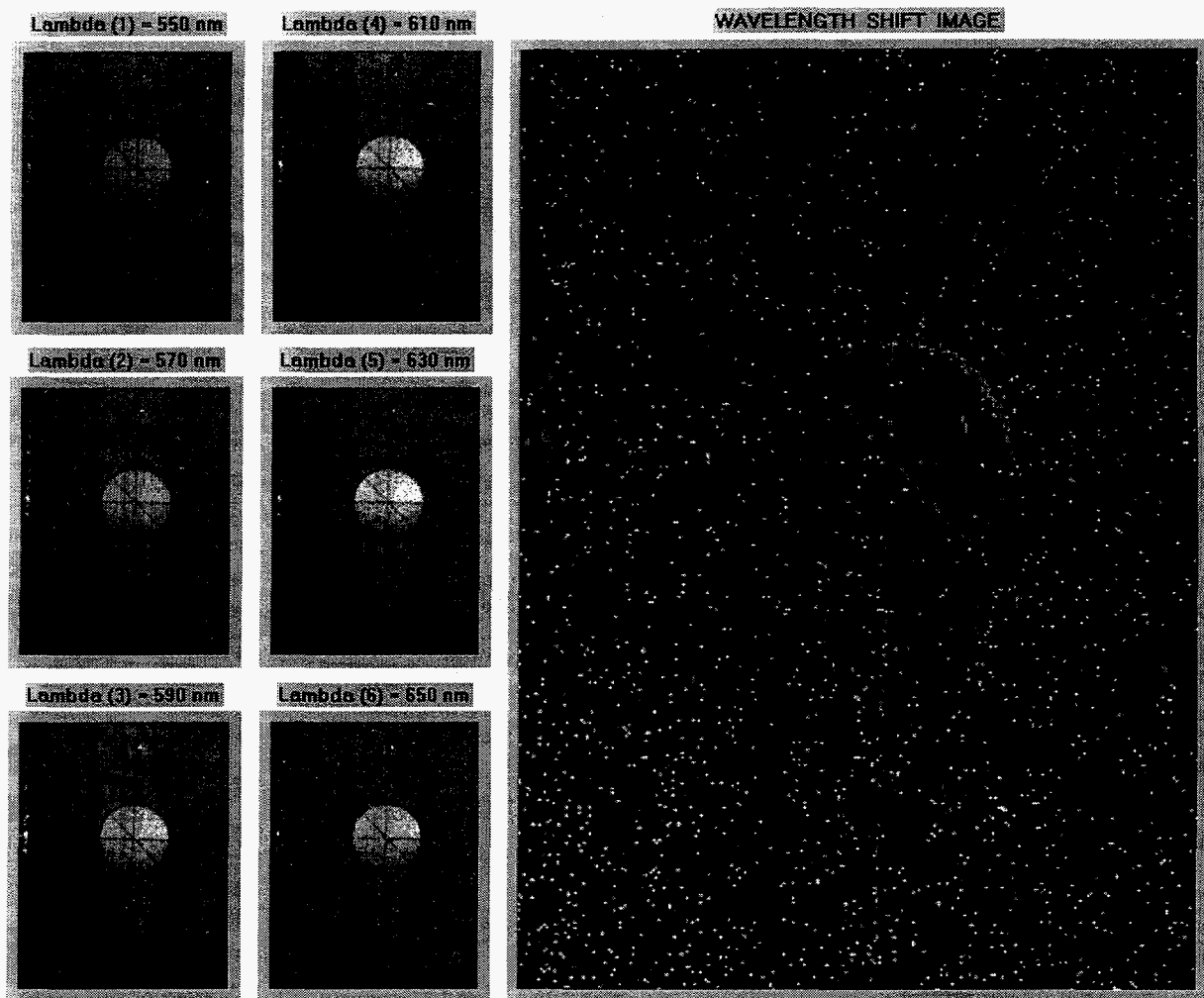


Figure 4. Intensity and wavelength shift images of panel contact heated to 205°C for 120 min.

CONCLUSIONS

Laser induced fluorescence has been demonstrated as a practical tool for imaging thermally induced damage in PMC's. The simplest configuration for accomplishing this involves acquiring fluorescence intensity images from the surface of the object under evaluation. The regions of highest intensity will correspond to areas that have suffered low to moderate damage. This mode is useful for identifying boundaries between undamaged and highly damaged material. An additional, more sophisticated mode of operation has also been demonstrated which combines measurements of intensity and wavelength. This yields quantitative information about thermally-induced damage over the measurement area.

ACKNOWLEDGMENTS

Research sponsored by U.S. Department of Energy under contract DE-AC05-96OR22464 with Lockheed Martin Energy Research Corp. W.G. Fisher and E.A. Wachter would like to acknowledge the Oak Ridge Center for Manufacturing Technology which was funded by the U.S. Air Force to conduct this investigation. Additional support was provided by the U.S. Air Force Wright Laboratory Materials Directorate, Dayton, OH, the Naval Air Systems Command, Washington, DC, and the Naval Aviation Depot in Cherry Point, NC. The authors are also grateful for the assistance of R.M. Collins of Grumman, M.G. Bradley of the GLCC/CECMT, J. Fuss and J. Elmore of NADEP, Cherry Point, D.R. Perl of NADEP, North Island, and P.J. Kulowitch of NAWC, Patuxent River, for their assistance with independent evaluation of the performance of the LIF method. The work of K.E. Meyer was supported in part by an appointment to the Oak Ridge National Laboratory Postdoctoral Research Associates Program administered jointly by the Oak Ridge National Laboratory and the Oak Ridge Institute for Science and Education.

REFERENCES

- Fisher, W. G., J. M. E. Story, S. L. Sharp, C. J. Janke, and E. A. Wachter, "Non-destructive Inspection of Graphite-Epoxy Composites for Heat Damage Using Laser Induced Fluorescence," *Applied Spectroscopy*, **49**, 1225-1231 (1995).
- Frame, B. J., C. J. Janke, W. A. Simpson, R. E. Ziegler, and H. E. Philpot, "Composite Heat Damage, Part I. Mechanical Testing of IM6/3501-06 Laminates, Part 2. Nondestructive Evaluation Studies of IM6/3501-06 Laminates," ORNL/ATD-33 (Oak Ridge National Laboratory, Oak Ridge, TN, 1990).
- Haskins, J. F., "Thermal Aging," *SAMPE Journal*, **25**, 29-33 (1989).
- Luoma, G. A., and R. D. Powland, "Environmental Degradation of an Epoxy Resin Matrix," *Journal of Applied Polymer Science*, **32**, 5777-5790 (1986).
- Lynn, J. C., "Polymer Composite Characterization for Automotive Structural Applications," *Journal of Composites Technology & Research*, **12**, 229-231 (1990).