44th International SAMPE Symposium
May 23-27, 1999

MICROSTRUCTURAL CHARACTERIZATION FOR POLYMER COMPOSITES

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ABSTRACT

Characterization of composite microstructure is a crucial area since such features play a major role in processability, performance, damage tolerance, and service life. Moreover, since the reinforcement geometries are becoming more complex, the need to know and understand microstructure has increased significantly. One example is hybrid composites where the use of two or more fiber types add new complexity to the microstructure. In response to this need, NIST is developing or modifying test methods for characterizing local structure at a variety of size scales. Four examples will be briefly discussed. The first is the single fiber fragmentation test which examines the micromechanics of the fiber-matrix interface region. Continued improvement of this test in recent years has made it more reliable and versatile. The second example is a fiber optics method which can study the cure behavior of resins in the fiber-matrix interfacial region. The third example applies microscopy methods to characterize the microstructural features in hybrid composites. Finally, a new technique called optical coherence tomography is applied to composites and permits nondestructive generation of three dimensional images with internal structure and damage. The images can be obtained rapidly and cost effectively with resolution down to 10 μm.

KEY WORDS: Fiber-Matrix Interface, Hybrid Composites, Microstructure

INTRODUCTION

The importance of microstructure in determining the properties of composites is well known (1,2). Moreover, since most of this microstructure is generated during processing, variations in such features have long been used to explain why the same materials processed in different ways can yield final products with widely varying properties. As a result, the development of new techniques to characterize microstructure is an ongoing challenge. What makes this need particularly acute now is the dramatic increase in complexity of the reinforcement materials. The implementation of fabrics made by weaving, stitching, knitting, and braiding has produced reinforcement geometries that can be incredibly complicated in all three dimensions. Moreover, the geometry of the reinforcement can be quite different during processing and in the final composite, than it is in the dry fabric because

of preform compression and fiber wash. Knowing the microstructure is obviously important for prediction of performance since the position and orientation of the reinforcement directly controls many properties. Moreover, processing is also affected since complex reinforcements can be difficult to infiltrate with resin. Consequently, information on microstructure is very valuable in optimizing the process to minimize voids and achieve good fiber wetting.

Another recent development that produces more complex reinforcements is the expanded interest in hybrid composites. These materials combine different fiber types in an effort to get synergistic effects. The various fibers can be mixed in individual layers (plies), within layers as separate tows, or within the same tow. When fabrics are involved, the mix patterns can be even more complex. Each variation can have its own properties and processing problems. To establish a firm basis for fabrication and design with such materials, a connection between microstructure and performance is required. Characterization tools are an important part of this challenge.

The purpose of this paper is to briefly summarize four new or refined techniques to examine microstructure and related features. The first two methods focus on the fiber-matrix interface region looking in one case at micro-mechanics and in the other case at cure behavior during processing. The other two focus on microstructure and damage. The first is concerned with hybrid composites and the unique features associated with such materials. The second permits nondestructive observation of internal structure and damage through 3D imaging.

SINGLE FIBER FRAGMENTATION TEST FOR INTERFACE MICRO-MECHANICS

The importance of the fiber-matrix interface region is well recognized (1,2), and the last decade has seen intense interest in test methods to assess the strength of the interface (3). The most popular measurement method is the single fiber fragmentation test (SFFT). The method involves a dogbone sample with a single fiber along the central axis. The dogbone is loaded in tension and since the resin is chosen to have a higher extension to failure than the fiber, the fiber will break at some point. If the load is increased further, more fiber breaks will occur. Eventually, the fiber fragments become so short that the interface is no longer able to transfer sufficient stress into the fragment to cause it to reach its failure load. At this point, termed saturation, further loading of the dogbone does not cause additional fiber breaks. The fragment lengths at saturation are then measured and combined with an appropriate model to calculate τ which is sometimes called the shear strength of the interface, but might be better described as a coefficient characterizing the stress transfer capability of the interface.

The SFFT has been utilized for many years, but a number of questions have been raised about its validity. These questions were reinforced in the early 90's when an international round robin found that different laboratories were unable to get the same answer when testing a common material system (4). Unfortunately, the round robin provided the materials but did not specify exactly how the samples were to be made and how the test was to be performed. When large differences were found in the data from the various laboratories, the leaders of the round robin suggested that much of this variation might be the result of differences in specimen preparation and testing procedures. They recommended that the round robin be repeated with these issues addressed. Subsequent experiments (5) have clearly shown that sample preparation and testing procedure can dramatically affect test results so the suggestions and recommendation were quite reasonable.

Round Robin To address this issue, an international round robin has been organized by NIST and Michigan State University (MSU) and is now underway. A recommended test procedure has been developed with input from all of the participants. A large number of specimens were prepared by MSU following a predetermined procedure. These will be distributed to each participant who will then test the specimens using the recommended procedure. In addition, a number of laboratories are conducting general characterization tests on the resin, fiber, and test specimen. This will provide an extensive database for this model system, and such information will be very helpful for evaluating the various models currently available for calculating τ from the experimental data. Once completed, the program should provide a clear answer to the question of repeatability of the test in different laboratories.

Analysis Method Even if the round robin finds that the test provides equivalent results in different laboratories, there are still concerns about how to analyze the data. Two questions often ask have been the subject of recent work in this program and other laboratories. The first concerns the fiber strength. In order to calculate τ from the fragment lengths, all models require a knowledge of the statistics for fiber strength. This is usually obtained through separate experiments on the fiber itself. In recent years, however, SFFT has been applied in situations like durability studies on glass fiber composites where the fiber strength changes during the experiment. It is not possible to study this effect separately since the environment seen by the fiber inside the resin dogbone cannot be duplicated with just the fiber itself. Work in this program and other laboratories has now developed procedures for measuring both the fiber strength and τ from the same SFFT (see ref. 6,7 for details).

The second question that has been addressed in recent years is the effect of the resin modulus on the measurement. In the original Kelly-Tyson equation, the resin modulus does not appear. Experiments suggest, however, that modulus does have an effect (5). Many studies involve comparisons where the only change is the fiber surface treatment. As a result, the effect of resin modulus is a constant that cancels out. In experiments with different resins, however, or durability studies where the resin is plasticized by water uptake, the modulus effect must be included before meaningful results can be obtained. One of the most popular models now in use, the Cox equation, does contain the modulus, but it assumes linear elastic behavior for the resin, and there are questions about the validity of this assumption (5).

To investigate the effect of resin modulus, the apparatus for the SFFT was augmented with a load cell so both load and strain could be measured. The typical SFFT experiment is conducted by loading the specimen with a series of strain steps. After each step, there is a hold period during which the number of fiber breaks is monitored. Figure 1 shows the loading profile for such an experiment. The sample is an E-glass fiber in a common epoxy (see ref. 5,8,9

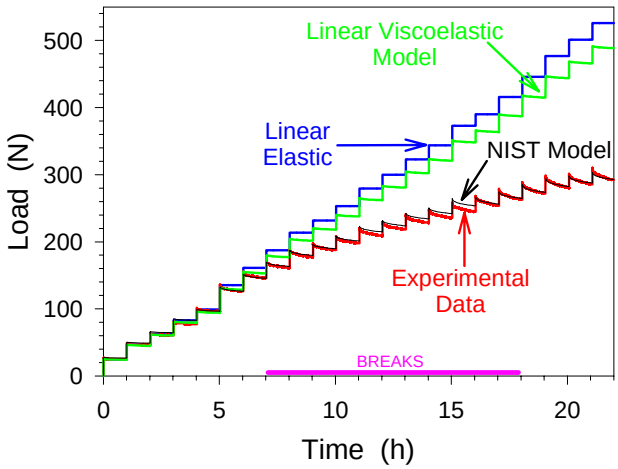

Figure 1*: Loading curves for SFFT. Region where fiber breaks occur is indicated with line just over the time axis. Standard uncertainty in the load measurement is 2 N.*

for details). For comparison, the predicted loading curves for a linear elastic material and a linear viscoelastic material are included. The parameters for these predictions were obtained from low strain measurements on the test sample (see ref. 8). Consequently, all the curves agree at low strains. The first fiber break occurs at just above 1 % strain, and by this point the curves are beginning to diverge. Over the range of loads where the breaks occur (see Figure 1) the curves are very different. Consequently, not only is the linear elastic assumption incorrect, but even the linear viscoelastic model is inadequate.

Table 1: Values of τ for Different Analysis Methods

Analysis Method	τ (MPa)
Kelly-Tyson Model	30 ± 5
NIST Model	93 ± 13
Cox Model	116 ± 17

Based on this result, a non-linear viscoelastic model was proposed. Details of the model are published elsewhere (8), but the ability of this model to correctly predict the loading curve is demonstrated in Figure 1. By using this relationship, a new analysis method was developed for the SFFT. It requires only one measurement of modulus made at the end of the experiment where the fiber break pattern is established. Table 1 shows the results for data on the same material used for Figure 1 analyzed with the Kelly-Tyson relationship, the Cox equation, and the new NIST model (9) (In the table and elsewhere in this paper, data ranges correspond to standard uncertainties). The values of τ produced by the various analyses are quite different, which indicates the importance of including modulus in the model.

Although questions still exist about the SFFT, the results cited above indicate that research is making progress in refining the test and expanding its range of applicability. Similar research is underway for other test methods that study the micro-mechanics of the fiber-matrix interface. As these tests become more established, they will have a useful impact on composite design and optimization.

FLUORESCENCE SPECTROSCOPY USING FIBER OPTICS FOR INTERFACE CURE

As discussed above, the nature of the fiber-resin interface can dramatically affect the final properties of the composite material. The interface, however, does not exist until the composite is fabricated so processing is critical to interface behavior. The type of coupling agent used to coat the fiber, the properties of the coupling agent layer, and the interaction between the resin and coupling agent, all affect the interfacial region. In addition, different cure conditions may exist near the interface due to the presence of this coupling agent layer, or the preferential diffusion of reactants to the surface (10). These effects can lead to a resin structure near the interface which is different from that of the bulk resin. Because it is difficult to relate the bulk resin structure to the interfacial properties, and since the fiber-resin interface is critical to the mechanical properties of the final composite part, it is advantageous to directly study this interfacial region.

Sensor System The approach used here is to conduct fluorescence spectroscopy via fiber optics. The challenge is to be sure that the fluorescence signal comes from the interface region, and to achieve this goal, a fluorescently labeled silane coupling agent (DMSCA) was chemically graft to surfaces of the optical fiber. In this way, the fluorescence response could be used to study the changes that occur in the fiber-resin interfacial region during cure. The molecule used, DMSCA,

was dimethylaminonitrostilbene fluorophore tethered to a triethoxy silane coupling agent as illustrated in Figure 2. In order to graft the fluorophore to the glass, the ethoxy functionalities on the silane end of DMSCA must be converted to hydroxyl groups. These hydroxyl groups can then condense with hydroxyl groups already present on the glass surface, forming covalent siloxane bonds (1). Coupling agents are widely used in industry to promote interface adhesion and durability, but to assure that the modified coupling agent does not change the nature of the interface region, a trace amount of DMSCA is mixed with a common epoxy functional coupling agent, glycidoxypropyltrimethoxysilane (GPS). The mixture, which contains less than one molecule of DMSCA for every 500 GPS molecules, is then grafted to the glass surface.

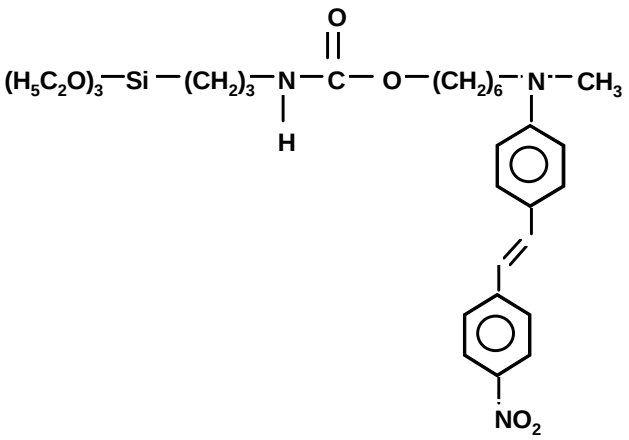

***Figure 2**: The dimethylaminonitrostilbene fluorophore is tethered to a triethoxy silane coupling agent, giving the DMSCA molecule shown here. This entire molecule is then grafted to the glass surface, immobilizing the fluorophore at the interface.*

A schematic of the measurement system is shown in Figure 3. The coupling agent mixture is bonded to a glass fiber optic. Laser light guided through the fiber creates an evanescent wave in the region adjacent to the fiber and excites the DMSCA molecule. Some fluorescence response from the dye is collected by the fiber and guided back to a detector. Because the dye is immobilized at the interface, the fluorescence response will only be sensitive to structural changes that occur at the interface region during processing. For example, the dye may be sensitive to local viscosity which increases as the resin cures, to penetration of the resin into the coupling agent network, and to dissolution of the coupling agent layer into the resin. If the changes in fluorescence during cure are sufficiently large for the grafted material and the fluorescence response of DMSCA can be calibrated against these structural changes, the grafted fiber optic sensor can be used for monitoring the interfacial region during the actual processing of a composite part.

Model System To address these questions, experiments were first conducted to characterize the coupling agent layer using glass microscope cover slips. After grafting the coupling agent mixture to the surface using an ethanol-water based deposition procedure, the coated cover slip was immersed in uncured epoxy resin. In this uncured system, the DMSCA fluoresces with maximum intensity, λ_m, at a wavelength of (632 ± 1) nm with an intensity of (2.0 ± 0.3) x10^6 counts per second (cps). While still immersed in the uncured resin, the same cover slip was then put in the oven for 4 hours at 100 °C to cure the epoxy resin over the coupling agent layer. The sample was removed from the oven and cooled to

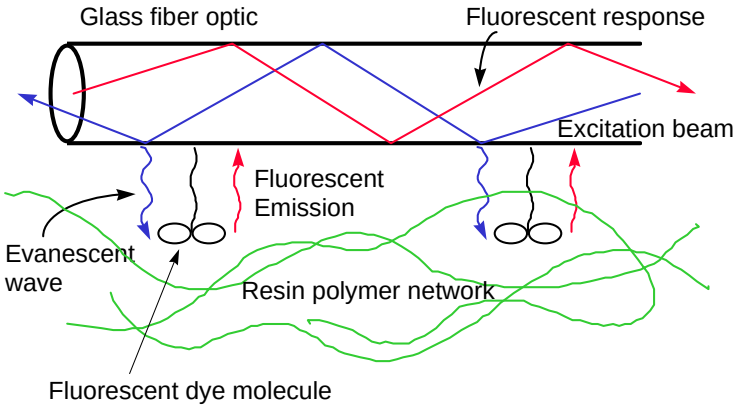

***Figure 3**: A schematic of the fluorescence based fiber optic sensor.*

room temperature. When the DMSCA fluorescence was measured in the cured epoxy, λ_m had shifted to (579 ± 4) nm and the intensity had increased to (7.0 ± 1.1) x 10^6 cps. To be sure these changes reflect interaction with the curing epoxy, two control experiments were performed. First a GPS/DMSCA coated cover slip was subjected to the same 4 hour 100 °C heat treatment but with no epoxy present. The fluorescence from this control showed no spectral shift or intensity change after the heat treatment; therefore, the epoxy was needed to see the changes. The second control used a cover slip coated with GPS containing no DMSCA. Although the coated cover slip itself had no fluorescence, after immersion in epoxy, a small peak was observed (Figure 4). This background fluorescence is probably due to small amounts of fluorescent impurities in the industrial grade epoxy resin that was used in this study. Fluorescent impurities are often present in such materials (11). This peak intensity is quite small compared to that for the DMSCA/GPS sample. When the GPS control immersed in epoxy was subjected to the heat treatment, the peak intensity remained very low and there was no spectral shift. Consequently, the results in Figure 4 show that both the blue shift in the fluorescence and increase in intensity can be used to monitor changes in a composite fiber-resin interface during processing.

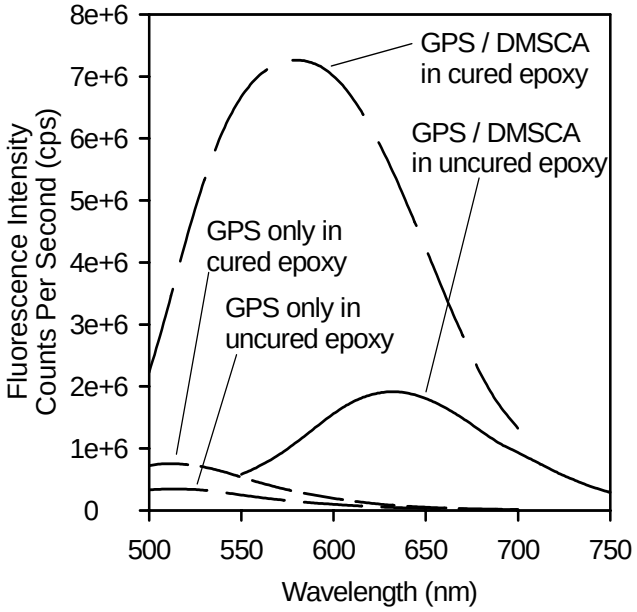

***Figure 4**: Both a blue shift and intensity increase can be monitored from the grafted DMSCA molecule, during cure of an epoxy above the coupling agent layer. This gives the technique potential to monitor the properties of the fiber-resin interface during processing.*

Next, it is useful to ask what these changes might indicate about the interface region. A likely explanation is that the blue shift and intensity changes observed in Figure 4 are a result of the fluorophore's response to changes in the dielectric constant and viscosity of the local environment. The effect of local dielectric constant on the emission position is given by the Lippert equation discussed in other work (12), and is manifested by the changes in emission relative to that of absorption. Increasing viscosity of the resin during cure can have an analogous effect. As the molecular mass and cross-link density of the resin increase near the interface during cure, the grafted DMSCA molecules become constrained. Rotational and vibrational mechanisms which dissipate the excited state energy are lost. This results in increasing fluorescence intensities because more molecules release energy through fluorescent pathways. Also the fluorescence occurs from higher energy levels, leading to a blue shift (13).

The next step in the work is to utilize a fiber optic as the substrate for grafting. Previous experiments (14) have shown that fluorescence monitoring of cure can be accomplished utilizing fiber optics with probe molecules dissolved in the resin. Extending the studies to grafted DMSCA will assure that

the data correspond to signals from the region very close to the interface. This will permit the comparison of interface and non-interface events during processing.

MICROSCOPY FOR HYBRID COMPOSITES

One of the most exciting areas in current composites research is hybrids. By combining the advantageous features of two or more different fiber types (carbon, glass, polymeric, etc.), the fabricator can achieve significantly better trade-offs among various properties and between properties and costs. Although this is an old idea (15-17), modern processing technology has enabled these materials to become viable candidates for many applications, and industries as divergent as oil production, infrastructure, alternative fuel vehicles, and aerospace are actively pursuing hybrids. The extraordinary variety of fiber mix patterns and reinforcement forms that are available provide an almost unlimited flexibility for tailoring these materials, but current design methodologies for hybrids is not capable of dealing with this potential (18). Consequently, the designs now being considered are achieved by trial-and-error, and far from optimum. The problem with current design methodology is that the properties and failure modes of hybrids depend on the detailed microstructure in ways that we do not yet understand. Important microstructural features include voids, flaws, fiber orientation and distribution, and the mix pattern of the different fibers. As a result, there is a real need for test methods that can characterize these features. A wide variety of measurement tools are available to examine the microstructure of composites, and many can be adapted to the study of hybrids. One of these is microscopy, and that is the focus of the work reported here.

Types of Hybrids There are many possible hybrid compositions, but one of the most popular choices combines glass and carbon fibers. This takes advantage of the low cost of glass and the high performance and light weight of carbon. Such hybrids are currently being considered for infrastructure applications. A common geometry is a glass reinforced beam with a small amount of uni-directional carbon fiber added to the flanges. The cost penalty for addition of a little carbon is small, and yet placing these fibers in the high load area of the part provides a big increase in stiffness which is often the design criterion for such structures. Such hybrids are termed interply because the carbon fiber are placed in layers near the outside surfaces of the flange. Although very effective for stiffness, such a design can creates a weak interface between the carbon and glass layers. As a result, some researchers are exploring intraply hybrids where carbon and glass fiber tows are mixed within each ply. This type of hybrid is under intense study by the off-shore oil industry. Failure modes in such designs can be quite complex so the need to characterize microstructure and understand its role in properties is even greater. The samples examined here have this mix pattern.

Microscopy To explore the use of microscopy to characterize hybrid composites, unidirectional samples were obtained with a mixture of glass and carbon tows in an epoxy matrix. The specimens were cut and polished in a plane perpendicular to the fiber direction using conventional methods. Both optical and scanning electron microscopy (SEM) were utilized, and typical micrographs from this work are shown in Figure 5. The most important result is that the two microscopies tend to enhance different features so combining both measurements significantly expands the utility of the approach. This is illustrated in Figure 5. In the optical microscopy, the carbon fibers stand out clearly while the glass fibers can be seen but are much less distinct. In the SEM, however, the situation is the reverse. The glass fibers are easily distinguished while the carbon fibers are more difficult to see. By combining the two techniques it is possible to characterize both fiber types for distribution of fibers within the tows, the size and shape of the tows, the arrangement of the tows in

the mix pattern, the interface between tows, and the flaws or voids that are present. Note that the void pattern is sometimes easier to see in regions where the individual fibers are less distinct. On the other hand, the position of the voids relative to the fibers and tows can be more easily defined when the fibers are distinct. From pictures such as those shown in Figure 5, the fiber diameters, fiber contents in the tows, fiber volume fraction, and fiber mix can be calculated. This makes microscopy a very useful tool for examining hybrid materials.

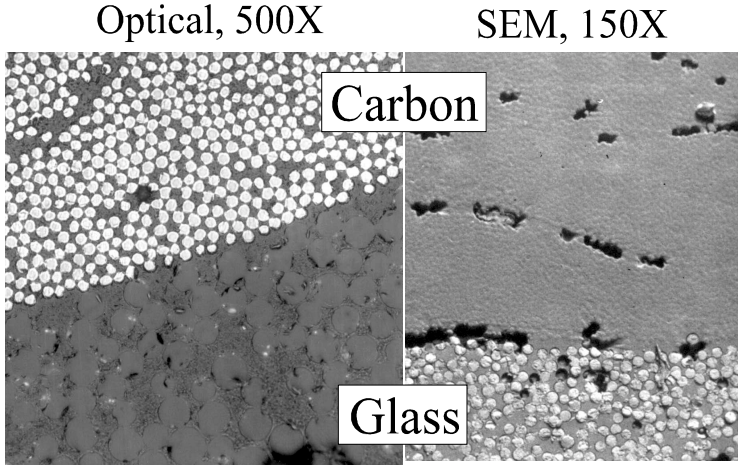

Figure 5*: Optical and scanning electron microscope (SEM) micrographs at indicated magnification. Carbon tows are at the top of each picture while glass tows are at the bottom. Voids can also be seen within the glass tows and between adjacent carbon tows.*

OPTICAL COHERENCE TOMOGRAPHY FOR 3D IMAGING OF INTERNAL STRUCTURE

In the past, microstructure and damage have often been characterized using destructive techniques such as microscopy on sectioned samples which provides detailed information on a small size scale. The capability to measure these features non-destructively, however, is very desirable since that permits monitoring of damage evolution and correlation of the results with microstructural features that can initiate, influence, or even control the damage. It is even more advantageous if these measurements are performed with a single technique because this eliminates the complications involved in combining data from different sources. Optical coherence tomography (OCT) is a new measurement method that can characterize both microstructure and damage with high resolution and good penetration depth.

Experimental Setup Optical coherence tomography is a non-invasive, non-contact, optical imaging technique that allows the visualization of microstructure within scattering media (19-21). OCT as a non-destructive evaluation (NDE) tool compares very favorably to more established composite NDE techniques (22). OCT uses light in a manner analogous to the way ultrasound imaging uses sound, providing significantly higher spatial resolution (10 to 20) μm albeit with shallower penetration depth. OCT is based upon low-coherence optical ranging techniques where the optical distance to individual sites within the sample is determined by the difference in time, relative to a reference light beam, for an incident light beam to penetrate and back-scatter within the sample. This temporal delay is probed using a fiber optic interferometer and a broadband laser light source (Figure 6). The fiber optic interferometer consists of single-mode optical fiber coupled with a 50/50 fiber optic splitter that illuminates both the sample and a linearly translating reference mirror. Light reflected from the reference mirror recombines with light back-scattered and reflected from the sample at the 50/50 splitter to create a temporal interference pattern which is measured with a photodiode detector. The resulting interference patterns are present only when the optical path of

the reference arm matches that of the sample arm to within the coherence length of the source. The incident light beam is scanned, and repeated measurements are performed at different transverse positions to generate a two dimensional array which represents the back scattering or back reflection of a cross sectional plane in the material. This data can be displayed as a gray scale or false color image.

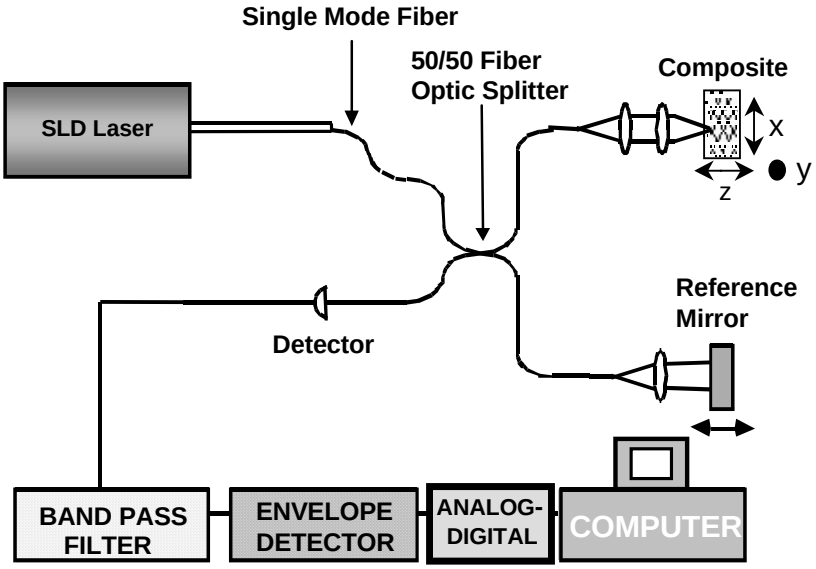

***Figure 6**: Schematic representation of the solid state laser and OCT system layout.*

The axial, or z, spatial resolution that can be obtained with OCT is determined by the coherence length, or inverse spectral width, of the light source and is typically (10 to 20) μm. The light source is typically a superluminescent diode laser, with a resolution as low as (10 to 15) μm. The transverse, or x, spatial resolution of OCT is determined by the focal spot size on the sample, which is typically (10 to 30) μm. The ultimate limitation on the depth of penetration within the sample is the attenuation of light caused by scattering and is nominally a few millimeters. Three-dimensional images of the sample are obtained by rastering the sample in the x direction between successive OCT measurements along the y axis. The standard uncertainty for the measurements in the x and y directions is 1.5 μm and 2 μm in the z direction.

Examples To illustrate the potential of OCT for imaging both microstructure and damage, an epoxy/unidirectional E-glass composite specimen is examined here. The characterization of fiber architecture is shown through volumetric imaging. The effect of the microstructure on permeability and mechanical performance predictions is discussed. Finally, OCT imaging of composite damage is shown by a tomographic reconstruction and re-slicing of impact damage along the thickness of the composite. This re-slicing of the image data reveals the progression of cracking and delamination within the composite.

Microstructure A volumetric reconstruction of the test specimen is shown in Figure 7. The composite cross-section is shown along the x-z plane. The image dimensions are 6.00 mm along the x axis, 1.48 mm along the z axis, and 3.85 mm axis the y axis. The gray ellipses are the fiber tows which are approximately 2 mm wide and

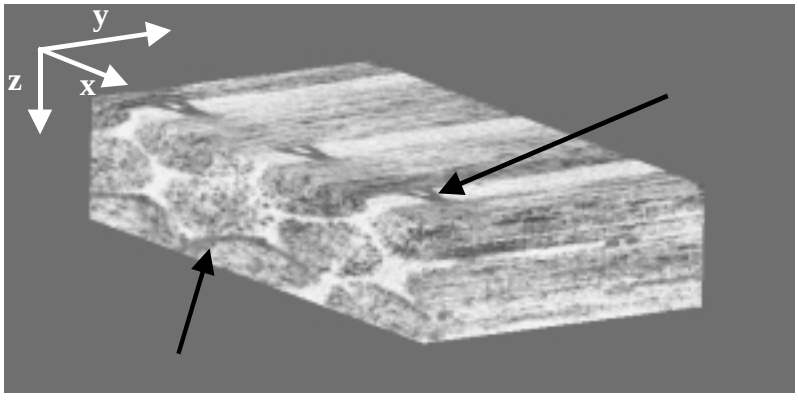

***Figure 7**: OCT volumetric reconstruction of an epoxy/unidirectional E-glass composite.*

750 μm thick and consist of about two thousand, (10 to 20) μm diameter glass fibers (23). The long axis of the tows is shown on the x-y plane. The polyester stitching that holds a single layer of tows together during processing is indicated by the black arrows. Upon closer inspection, small dark areas are evident inside the fiber tows. These dark areas are high reflectivity regions indicative of individual voids. During the molding process, air can become entrapped as channels in tows if there is insufficient driving pressure, high resin viscosity or low reinforcement permeability (24). Re-slicing of the volumetric information along an x-y plane at various depth in the z direction revealed these voids in the fiber tows (22). Also, the OCT images provide important information about the permeability of the reinforcement since the stacking of the layers has a large influence on the infiltration of the reinforcement by the resin. A preform in which the tows are nested has about half the permeability of the same material with the tows in a stacked configuration (23,25).

Damage OCT has also been used for non-destructive evaluation of damage in the composites. To illustrate this, the epoxy/uni-directional E-glass composite was subjected to impact damage, and imaging was performed along a crack that was produced by the impact. Figure 8A shows the damage along the x-y plane through the first layer of composite which is 652 μm along the z axis. This image is 5.50 mm wide (x axis), and 1.98 mm high (y axis). Figure 8B is a y-z image showing the position of the tows designated by the dark colored crossing thread and is 1.98 mm wide (y axis) and 2.23 mm high (z axis). The arrow on the left of these figures indicates the position of the image in Figure 8A with respect to the tow placement.

A delamination zone is shown by the white arrow in Figure 8A at the interface between the bottom of the first tow layer and resin (Figure 8B). The delamination is about 1.9 mm wide and 0.50 mm high and 652 μm from the surface. This is just one particular depth of interest. In fact, multiple slices though the composite thickness have been reconstructed to show a crack that begins at the surface of the sample, propagates along the fiber tow interface at 460 mm into the sample, evolves into a delamination zone 650 mm down, and then continues as a crack in the second layer of reinforcement (26). Another delamination area was found at 1.66 mm below the surface.

The above examples illustrate the potential of the OCT method. One limitation is that carbon fiber reinforced composites cannot be examined since the technique requires light penetration. Composites reinforced with glass or polymeric fibers as well as hybrids with a small amount of carbon are strong candidates for study, however. A second limitation is the penetration depth of the measurement. For those composite structures that involve thicknesses of several mm or where the important features are near the surface, the technique offers great potential.

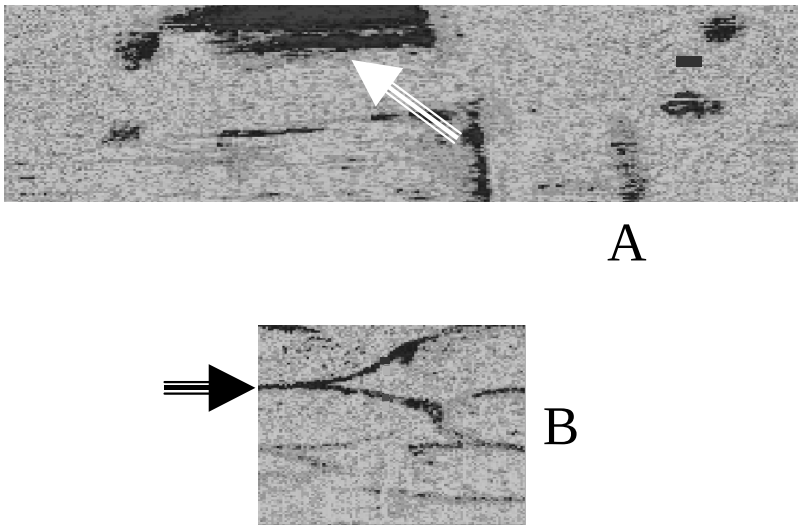

Figure 8*: OCT image of impact damage epoxy/unidirectional E-glass composite. Picture A is (652 ± 1.5) μm from surface along the x-z plane. Picture B is along the y-z plane showing placement of tows via polyester stitching.*

CONCLUSIONS

The paper briefly reviews four new measurement tools that are being developed or improved. They characterize internal damage and structure, interface mechanics, cure behavior near the interface, and microstructure for hybrid composites. With the current trend toward more complex systems with fabric and 3D reinforcement, some containing more than one type of fiber, characterization is becoming increasingly important. Moreover, since the unit cell for such complex reinforcements can be quite large, the range of size scale over which such measurements must be made continues to increase. As a result, further development of these and other techniques will continue to be a priority.

ACKNOWLEDGMENTS

Parts of this work were done in collaboration with the Advanced Technology Program at NIST. The authors wish to thank Dr. Felix Wu for his support and contributions to the research.

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