

**MECHANISMS OF PROCESSING-RELATED
DEFECTS IN PMR-15/CARBON
COMPOSITE MATERIAL LAMINATES**

THESIS

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By

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CHAPTER 1

INTRODUCTION

Advanced Composite Materials

In the last thirty years, the field of Materials Science has contributed some remarkable new materials to the world. Among this new generation of materials are high temperature superconductors, shape memory alloys, ceramic alloys, and advanced composite materials. Advanced composite materials are one of the most revolutionary materials because they are fast becoming excellent replacements for many metals.

A composite material can be defined several different ways. Composite refers to something that has two or more associated, constituent parts. A composite material can therefore further be defined as a material that is made up of two or more component materials. This is a highly general definition of what is referred to as a composite material. Some examples of general composite materials are metal alloys, ceramic alloys, concrete and fiberglass reinforced plastic.

More specifically, there is a subclass of general composite materials which are often referred to as advanced composite materials. An advanced

composite material (ACM) is defined by Casate and Gilchrist as " A composite material made by imbedding high-strength, high-modulus fibers within an essentially homogeneous matrix." [1] An example of an advanced composite material is the above mentioned fiberglass reinforced plastic.

Today many types of fibers and matrices are used to constitute advanced composite materials. The term fiber refers to a homogeneous strand of filaments which exhibit a high tensile strength. A matrix can be defined as the material in which the fibers are imbedded.

Examples of fiber materials include glass, carbon, graphite, boron, etc.. It is an extremely important consideration when selecting the fiber component of an ACM to meet the material's design specifications. The fibers need to be compatible with the matrix in order to ensure good bonding along the fiber-matrix interface. Another consideration of major importance is that the fiber component of an ACM will be the primary load carrying member of a fiber-reinforced composite structure during tensile loading situations.

In advanced composite materials there are three general groups of materials used as matrices, these include polymers, metals, and ceramics. As stated by Mallick [2]; " The role of the matrix in a fiber-reinforced composite material is (1) to transfer stresses between the fibers,(2) to provide a barrier against an adverse environment, and (3) to protect the surface of the fibers from mechanical abrasion." These provisions demonstrate the importance that matrix selection will have in designing an ACM.

The polymer matrix composites (PMCs) make up a large portion of advanced composite materials today. "A polymer is defined as a long-chain molecule containing one or more repeating units of atoms joined together by strong covalent bonds."^[2] A relevant subclass of polymers called plastics can also be broken into two even more basic classes, thermoplastics and thermosetting plastics. Both thermoplastic and thermoset polymers are used in PMCs, however, thermosets are used most commonly. Thermoset polymer resins are used primarily because they exhibit good fiber-matrix bonding to optimize the mechanical properties of the PMC.

Another important property that both thermoset and thermoplastic polymers have in common is a quantity known as the glass transition temperature. Glass transition temperature (T_g) is defined as the temperature at which a thermoplastic or thermoset polymeric solid may lose a large portion of the material's tensile modulus. Figure 1.1a illustrates the general behavior of a thermoplastic solid where near the glass transition temperature its tensile modulus begins to rapidly decline.^[2] This transition is a result of weak intermolecular bonds (Van der Waals bonds) being broken within the solid. The intermolecular bonds exist between the polymer chains of the amorphous thermoplastic polymer. If temperature is further increased, the solid will reach its melting point and become a viscous liquid with an entirely different set of physical properties.

A thermoset polymer solid does not follow the same behavior as that of

Tensile Mod vs. Temp. (Thermoplastic)

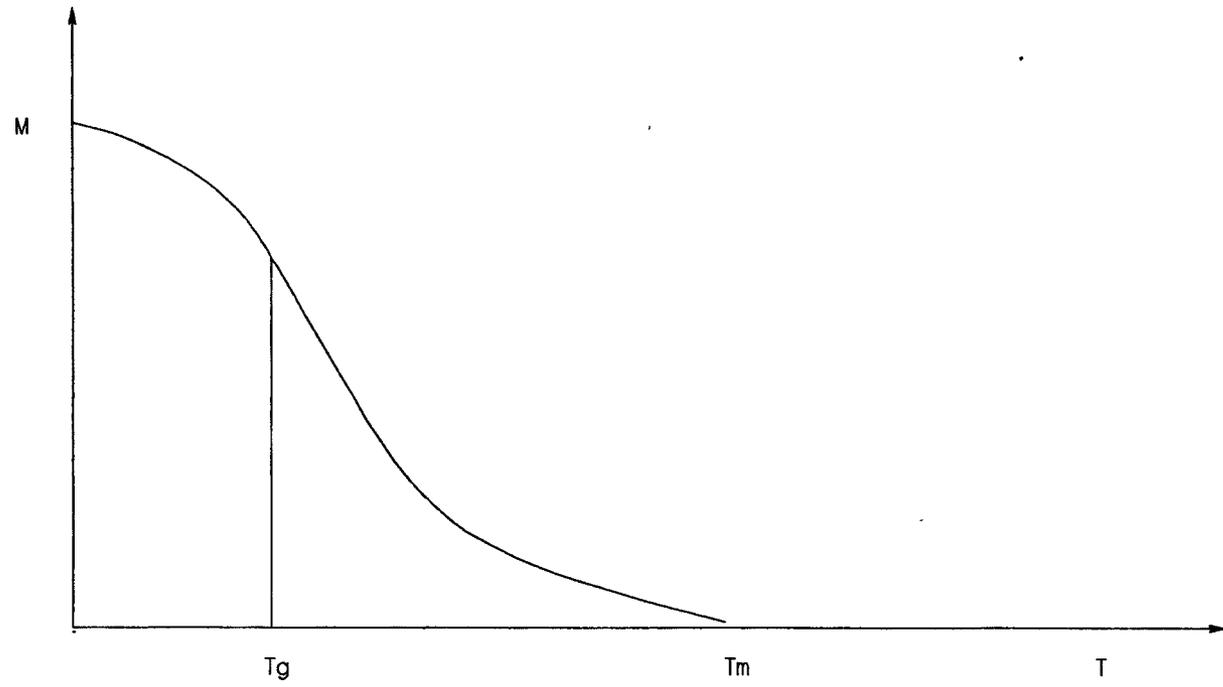


Figure 1.1 a

Tensile Mod vs Temp (Thermoset)

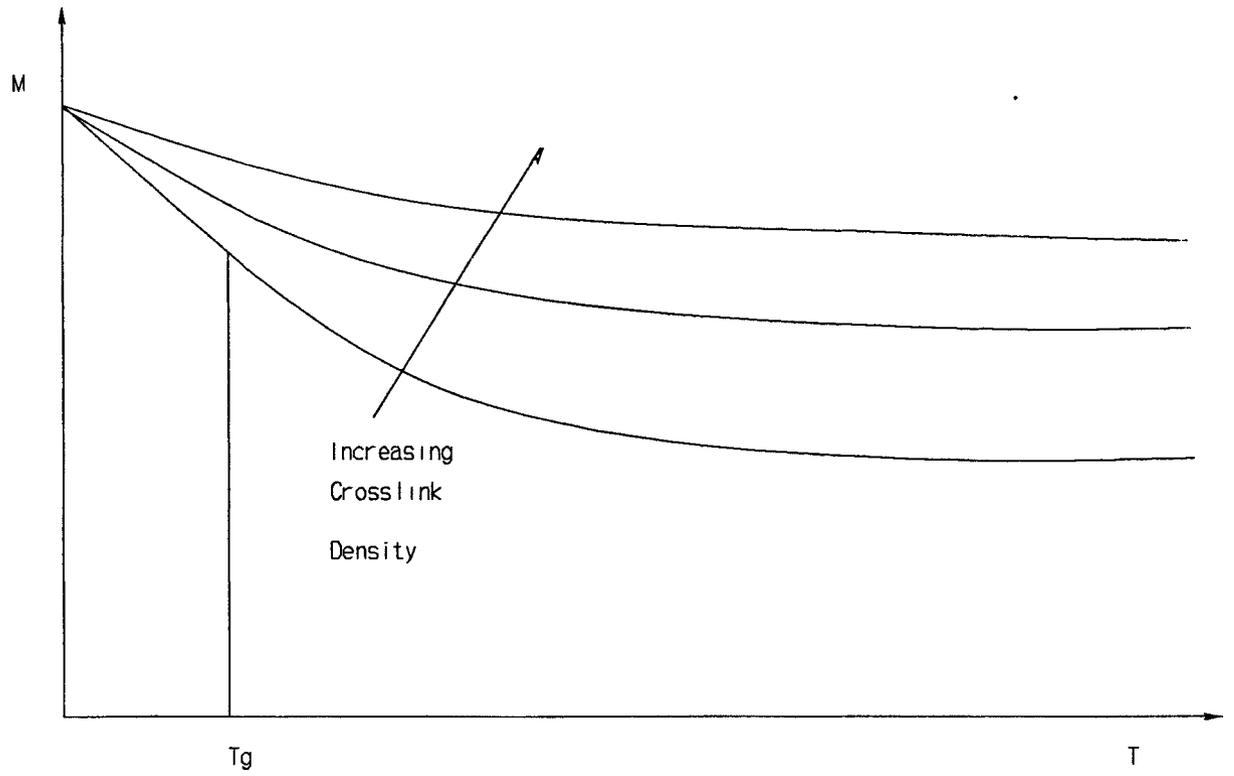


Figure 1.1 b

the thermoplastic solid under conditions similar to those described above. Figure 1.1b more closely approximates the behavior of a thermoset polymer's tensile modulus as a function of temperature.[2] For thermoset solids, the tensile modulus does not decrease as rapidly as for thermoplastic solids when heated to the material's glass transition temperature. This is because a solid thermoset material is not an amorphous solid like the thermoplastic polymer. The thermoset polymer is different in that covalent bonds are formed between molecules of adjacent polymer chains. These bonds are referred to as crosslinks within a thermoset polymer. Crosslinking gives thermoset polymers a semicrystalline structure which makes thermosets more rigid than thermoplastics. Also, the number of crosslinks within a thermoset polymer determines its characteristic glass transition temperature and can be varied by how long the polymerization reaction is allowed to continue.

With sufficient crosslink density (Number of crosslinks/Unit volume of material), a high strength PMC will exhibit a high degree of rigidity and a high glass transition temperature.

The glass transition temperature of a thermoplastic or a thermoset polymer can be measured by a method called Thermomechanical Analysis (Appendix A). Although there are other methods of measuring a material's T_g, Thermomechanical Analysis is one of the most widely used methods in industry.

PMR-15/Carbon Composites

In certain applications, composite structures are required to retain their mechanical properties at high temperatures. These temperatures span a range from 450 to 600 degrees Fahrenheit. One might assume that a metal matrix composite would be the best and most logical choice of ACM to be used. However, this is not always the case, since a composite structure's weight may also be a concern.

There is a class of thermosetting polymer matrix materials called polyimides which are commonly used in many high temperature applications. One such application is the fabrication of components for jet engines that endure high operating temperatures. PMR-15 is a polyimide that is widely used as the matrix material for many composite aerospace structures. PMR is an acronym which stands for in-situ polymerization of monomer reactants.[3] The 15 refers to the formulated molecular weight (1500 grams/mole) of the PMR-15 polymer.[3] PMR-15 was developed at the NASA/Lewis Research Center and is made from a mixture of three monomer reactants which can be chemically combined to yield the PMR-15 polymer. The three above mentioned monomer reactants are the dimethyl ester of benzophenone tetracarboxylic diester (BTDE), the monomethyl ester of norborene anhydride (NE) and 4,4'-methylene dianiline (MDA).[3] These three compounds are all soluble in methanol and are

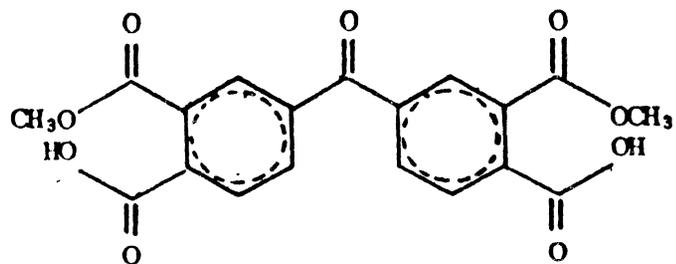
generally combined in a methanolic solution. The molecular structures for these molecules are shown in figure 1.2a.[3]

"Achieving the 1500 formulated molecular weight is based on combining the BTDE, MDA, and NE in molar ratios of $n: (n+1): 2$ where $n = 2.087$."[3] The computed percent by weight of the respective monomeric reactants is 44.54% BTDE, 33.79% MDA, and 21.67% NE.

During the production stage of PMCs containing PMR-15, methanol constitutes a large portion of the condensation volatile products yielded. The details of the processing scheme for a PMR-15 PMC will be discussed in section 1.3.

The material investigated in this study employs a carbon fiber reinforcement. The carbon fiber reinforcement of PMR-15/Carbon is in the form of a fabric. In other words it consists of many carbon fibers woven into a cloth. The cloth can be woven one of several different ways. In this study, the carbon fiber reinforcement was woven in a style referred to as an eight harness satin weave. This style of weaving is described by one fiber (3000 Carbon filaments) woven over eight fibers, then woven under one and over eight again as in figure 1.2b.[1] The eight harness satin type of weave has several advantages. One is its ability to conform to a molding surface. Another is that it requires the least number of plies for a given part thickness. A third is that it yields a smooth cured surface.[1]

Carbon fibers can be of two different varieties. One variety consists of



ABBREVIATION

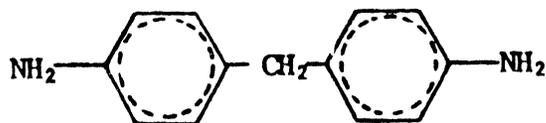
MOLES

PERCENT
BY WEIGHT

BTDE

2.087

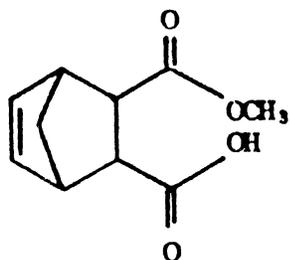
44.54



MDA

3.087

33.79



NE

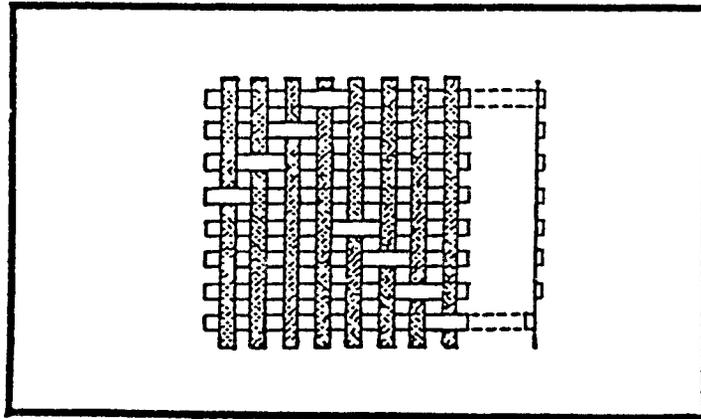
2.000

21.67

Figure 1.2 a PMR-15 Components

pure graphite and the other is a mixture of amorphous carbon and graphite.

Figure 1.2 b



8 Harness Satin Weave

The material in this study employ's fiber of the second type. These fibers are chosen for the fact that they provide adequate strength and are less expensive than pure graphite fibers.

Processing PMR-15/Carbon Materials

The processing technique for a PMC often requires a long period of development to produce high quality components. Therefore much careful consideration is placed into designing a scheme for production of ACM components. Advanced composite materials are generally processed in three stages. The first stage (A stage) is the time at which the initial ingredients of a thermoset resin mixture are combined. An example of this is when the PMR-15 resin is created from the mixture of BTDE, MDA, an NE. The second stage (B stage) is the point at which a fiber reinforced composite material is referred to as a prepreg. In other words, a thermosetting (PMR-15) resin has been prepared to impregnate a cloth woven from the fiber component of a PMC. It can also be said that the B stage is the point at which the material is ready to be molded. From the B stage, the material is usually cooked in some manner in order to chemically combine the fibers and the resin components of the material. Cooking the material is sometimes referred to as a curing cycle. The final stage (C stage) is the time at which the material is a fully cured composite material, ready for further processing if needed.

PMR-15/Carbon is generally received by a composite material manufacturer in the form of a prepreg. The prepreg material is purchased in large rolls and is normally chemically inspected before and after shipment from

the prepreg manufacturer. The purpose of the chemical inspection is to ensure that the resin component of a prepreg roll is suitable for quality processing.

Rolls of PMR-15/Carbon prepreg material must be stored in a freezer which is kept at a temperature -15° F. The material is stored in this manner to retard premature polymerization of the PMR-15 resin. Since the actual part manufacture takes place at room temperature (75° F), each roll of PMR-15/Carbon prepreg has its own time log to keep track of how long the roll spends in an unrefrigerated state. In practice, a prepreg roll is allowed to spend no more than 240 hours outside of the storage freezer. If a roll were to exceed this limit, the polymerization reaction sequence of the PMR-15 resin could proceed and render the roll unusable.

Creating a PMR-15/Carbon component begins while the material is in the B-stage. PMR-15/Carbon is generally processed using either a compression molding or autoclave molding technique. In this study only the autoclave molding process will be considered.

Initially, the prepreg material is taken from the freezer and cut into sheets of desired area to be molded. Additional methanol solvent may be sprayed on the prepreg in order to make the material more ductile. In the molding process the sheets are layered to produce a laminated type structure. The procedure for molding a laminate begins by placing a specified number of prepreg sheets onto the mold surface. The prepreg layers are then covered with a perforated teflon sheet, a breather cloth, and a Kapton vacuum bag.

The vacuum bag is then sealed with an adhesive tape around the edges of the mold. Vacuum lines are then attached to the vacuum ports on the mold. A low vacuum is pulled within the bag between 23 - 27in. of Hg to draw excess methanol from the prepreg and to adhere the specified number of plies under the bag. The bag is then removed from the molded plies and more plies are added. The above steps are subsequently repeated until the laminate has reached its desired thickness.

A typical lay-up scheme for a PMR-15/Carbon laminate is illustrated in fig.1.3a. When the prepreg laminate reaches this stage of production, it is ready to be placed in an autoclave to endure the curing cycle.

As mentioned earlier, the technique employed for curing PMR-15/Carbon in this study is an autoclave modeling process. The autoclave process offers several advantages. These include isothermal heating of the laminates, an isostatic distribution of pressure over the laminate surface areas and the ability to cure several large components at once. The purpose of heating the material is to add energy such that the chemical reaction responsible for combining the fibers and the resin proceeds as quickly as possible. It is also important to understand that full consolidation of the laminates requires the application of pressure during the cure process.

Additionally, PMR-15/Carbon laminates are covered with a vacuum bag as shown in fig. 1.3a.. This is because vacuum lines are attached to each laminate mold within the autoclave before curing. The purpose for the vacuum

PMR-15/Carbon Layup Scheme

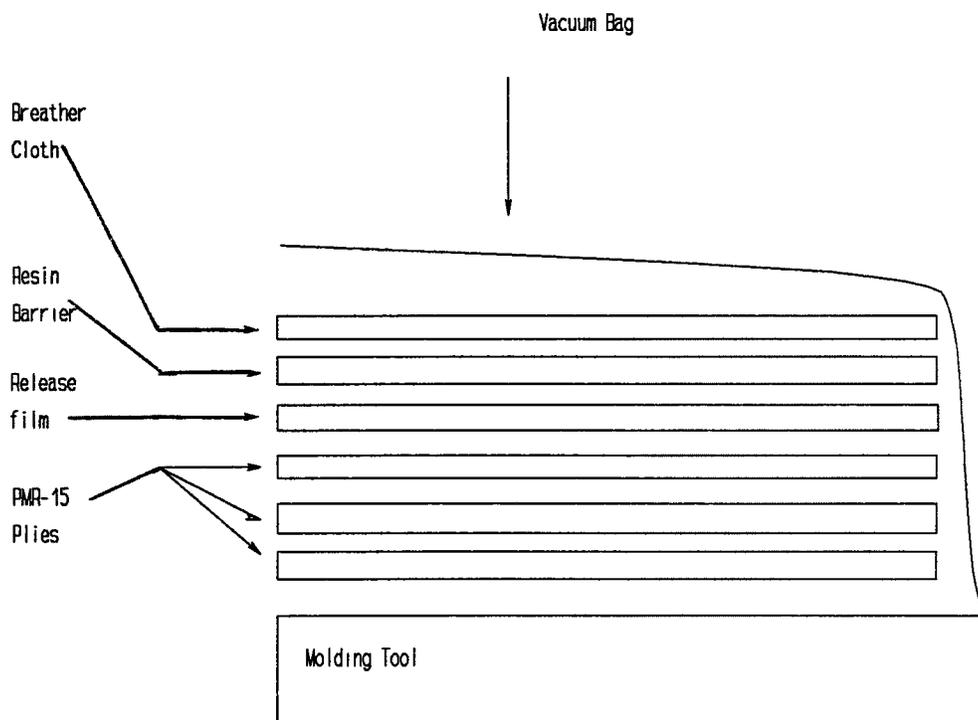


Figure 1 3 a

lines is similar to the one described in the lay-up procedure. PMR-15/Carbon laminates expel large volumes of volatile reaction products during the cure cycle necessitating the use of the vacuum bag.

A time vs. temperature plot of a typical PMR-15/Carbon composite cure cycle is illustrated in fig. 1.3b. The superimposed curve is a plot of viscosity vs. temperature of the PMR-15 resin during the cure process.

The laminates are heated slowly to maintain a minimal temperature difference between the molds and the autoclave. At the end of the first heating ramp, the laminates are held at constant temperature (soaked) to begin the combination of the PMR-15 resin components. At this point, the material begins to produce a large amount of methanol vapor. A low vacuum is applied during this soak to draw the methanol vapor from the prepreg and to adhere the plies of the laminate to one another. At the end of the first soak, a sharp rise in the resin viscosity can be observed. During this period, low temperature oligomers are being formed in the resin system which results in the yield of large volumes of condensation volatile products. For this reason, the full vacuum is applied near the midpoint of the second heating stage. As the viscosity curve reaches its first peak, the liquid resin begins to gel and transcend to a solid state. The soak during this period is to assure that the majority of condensation volatile products are removed from the laminates. Following this soak, a drastic decrease in the PMR-15 viscosity occurs. This is prompted by a melt flow of the low density prepolymer formed at the gel

Typical PMR-15 cure cycle (—) and superimposed complex viscosity (---) vs. temperature.

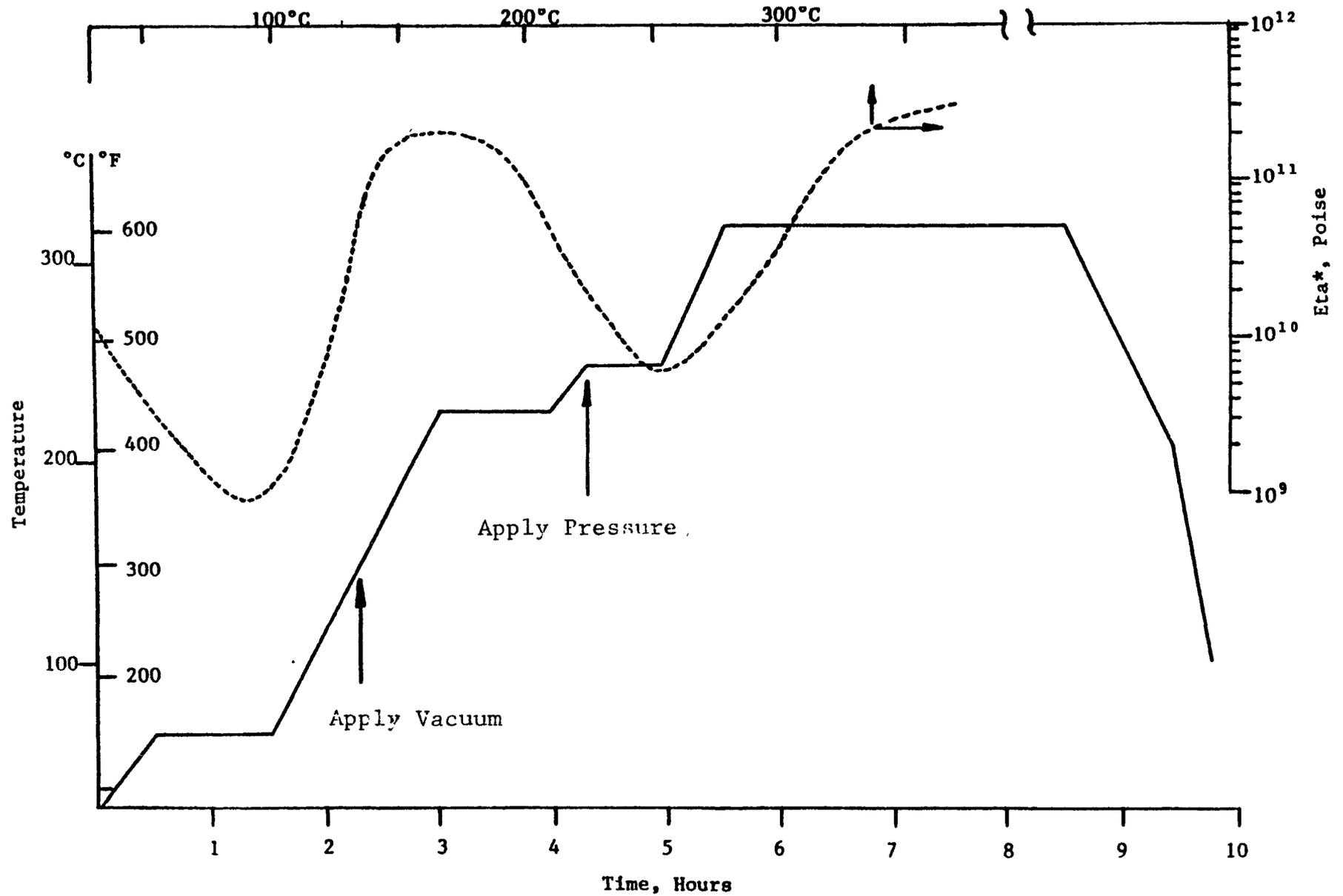


Figure 1.3 b

time. Along the declining viscosity curve, the autoclave becomes pressurized to begin uniform compression of the laminates. From the second knee of the viscosity curve, crosslinking reactions begin to occur within the laminates and give the PMR-15/Carbon material its rigid semicrystalline structure. The sharp increase in the viscosity indicates an increasing crosslink density within the material. During this increase, the laminates are brought to a final isothermal hold and cooled slowly to avoid induced microcracking from thermal shock.

After the laminates are removed from the autoclave they are placed in a conventional air circulating oven to be further cured. This portion of the PMR-15/Carbon processing scheme is referred to as postcuring. The purpose of postcuring is to increase the crosslink density of the material. With sufficient postcuring, a PMR-15/Carbon laminate can obtain a high T_g and optimum mechanical properties.

A typical postcuring process is similar in design to the autoclave curing process with the absence of the applications of pressure and vacuum. To elaborate, the laminates are slowly heated and kept at isothermal holds for reasons mentioned above.

The final steps of processing are generally machining and testing of the laminates to meet the desired component specifications. There are several widely accepted means of Non Destructive Testing (NDT) used to inspect composite materials for defects. These include a variety of ultrasonic analyses, radiographic and thermographic testing. Radiographic testing includes X-ray,

gamma ray, and neutron analysis of the laminates.

Common defects associated with PMR-15/Carbon composite materials are voids and delaminations. A void can be defined as a bubble of trapped gas or air within an ACM laminate. Formation of voids may stem from several factors. These include the entrapment of air in a prepreg, the introduction of foreign particulates in a prepreg, or the inability of volatile contents to escape from the prepreg during the cure process.

Delaminations can be defined as the absence of interlaminar bonding between the plies of a composite material laminate. The development of delaminations in the cure process of PMR-15/Carbon is a primary concern of this study and will be addressed in the experimental analysis chapter.

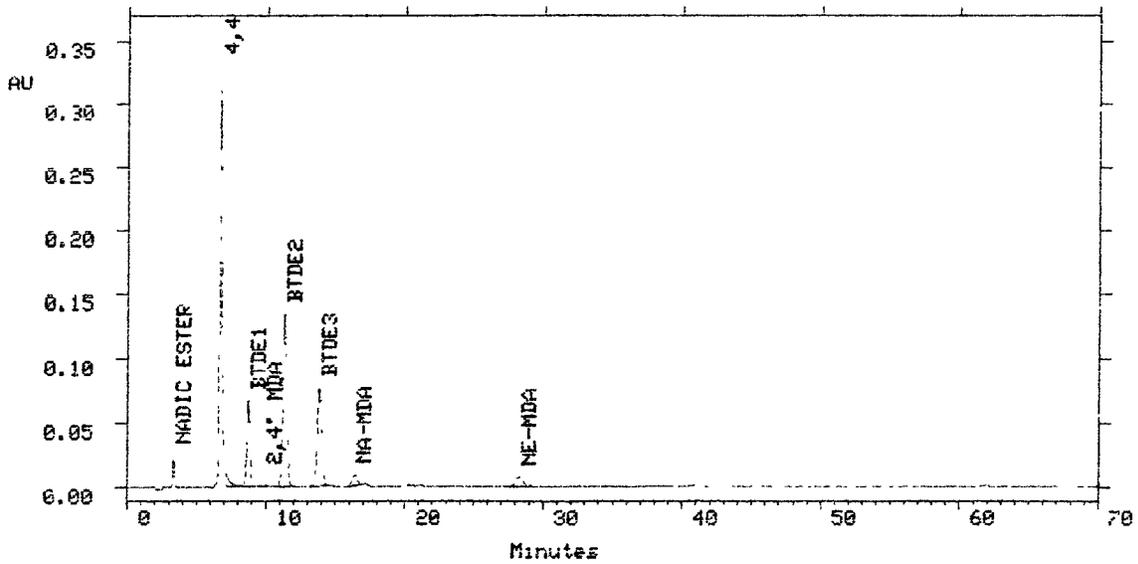
Processing Quality Control of PMR-15/Carbon

Quality control is a very important aspect of an ACM production scheme. This is because the production of ACMs can be a very expensive process depending on the nature of the components produced. Hence, an ACM production scheme requires that quality control measures be instituted during certain portions of the scheme.

PMR-15/Carbon prepreg rolls are generally inspected by the prepreg manufacturer before they are shipped to the customer. The rolls are inspected by chemical and physical means. Some types of chemical analyses typically employed are high performance liquid chromatography (HPLC), gel permeation chromatography (GPC), and infrared (IR) spectroscopy. The HPLC method is most frequently used to analyze PMR-15 and will be discussed further here.

The HPLC chromatogram in fig. 1.4a was made with a sample of PMR-15 resin from a PMR-15/Carbon prepreg. It is a plot of the chromatograph detector response on the ordinate versus elution time of the sample on the abscissa.[4] This plot is used to determine the exact chemical content of the PMR-15 resin in a prepreg sample. "The area of each peak in the chromatogram is proportional to the concentration of the peak's component." [4] Included under the chromatogram is a list of percentages of the components in the PMR-15 resin system. Notice that BTDE, NE, and MDA comprise the

Figure 1.4 a HPLC Chromatogram PMR-15/Carbon



NE WEIGHT % IS	20.13
BTDE WEIGHT % IS	44.17
MDA WEIGHT % IS	31.26
TRIESTER WEIGHT % IS	0.00
NA-MDA WEIGHT % IS	1.82
MONOESTER WEIGHT % IS	0.21
NE-MDA WEIGHT % IS	2.40
BIS-NADIMIDE WEIGHT % IS	0.00
TETRAESTER WEIGHT % IS	0.00
.	
TOTAL NE WEIGHT % IS	22.36
TOTAL BTDE WEIGHT % IS	44.15
TOTAL MDA WEIGHT % IS	33.48
SIMPLE FORMULATED MOLECULAR WEIGHT =	1453

majority of the resin's chemical composition. The other components listed within the resin system are a result of chemical reactions that take place even at the refrigerated temperature of -15° F. If certain specifications are not followed, the resin could produce PMR-14 or PMR-16 during the cure. If PMR-15 is not the result of the cure, the composite structure will not exhibit its desired structural properties.

Prepreg rolls of PMR-15/Carbon are also subjected to physical testing which includes a test for resin content and fiber volume. In a typical PMR-15/Carbon prepreg, the resin content is 40% and the average fiber volume is 60% by weight.

Recall from the end of chapter one that after a laminate is created from a molded prepreg, it may be subjected to various types of NDT analyses. Although many other types of NDT are used in industry, only two means of inspection will be discussed. These methods of inspection are C-Scan and A-Scan ultrasonic testing. C-Scan analysis is commonly used to determine the existence and location of discontinuities in composite material laminates. It is also used to analyze other solid materials for similar defects. A-Scan analysis is used to resolve the details of discontinuities, for example the depth and size of a defect.

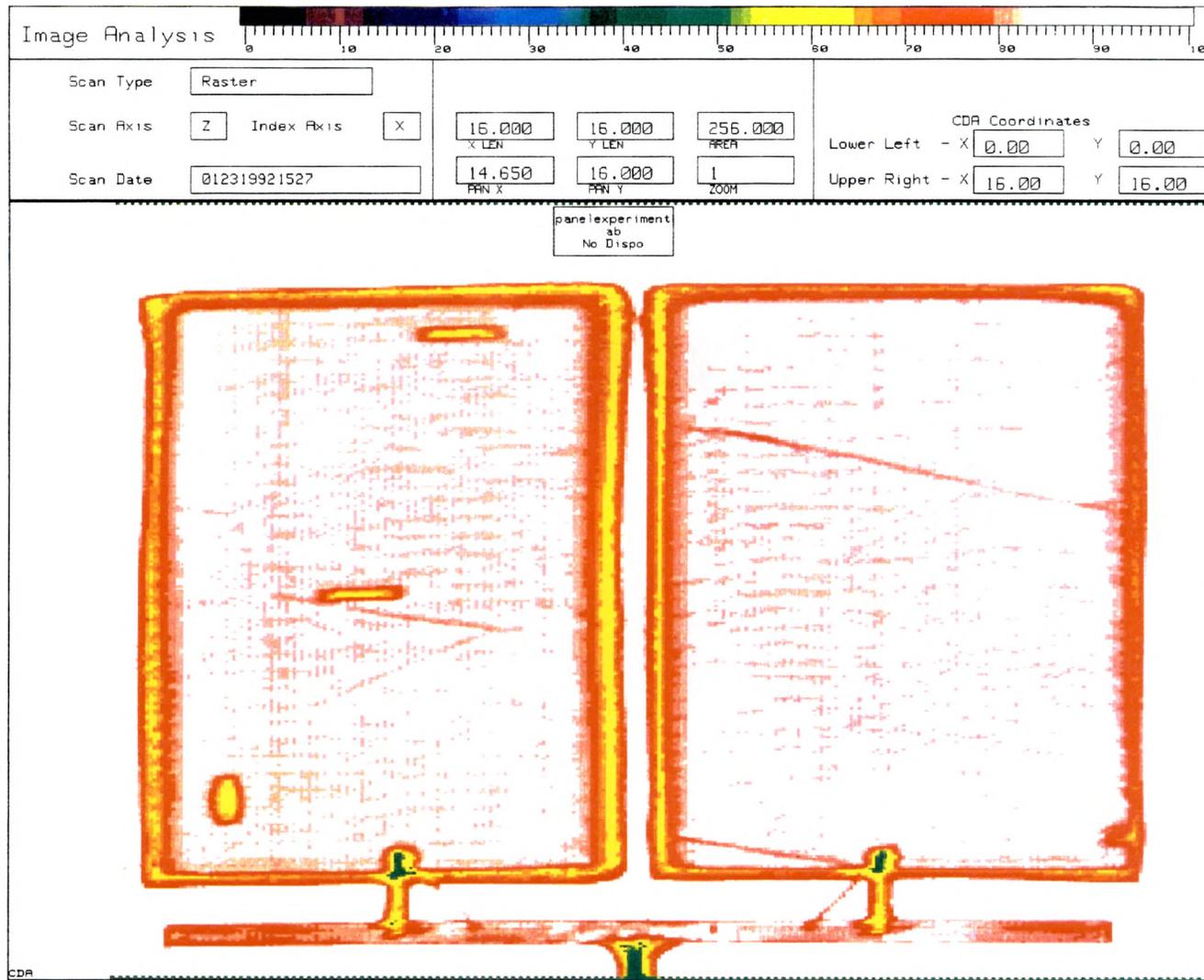
The C-Scan inspection method can be discussed at great length and therefore deserves a more detailed explanation. The C-Scan method employs a pair of ultrasonic transducers to examine a given specimen. The specimen

is placed between the transducers in a water tank and an ultrasound signal is transmitted through the specimen by the transmitting transducer. The other transducer is used to recover the remaining portion of the transmitted signal. The specimen and transducers are immersed in water to promote good sound transmission and recovery. Water acts as a transducer-specimen couplant to more closely match the acoustic impedances at the water-specimen interface.

C-Scan testing uses a constant frequency transmitting transducer to scan the specimen under analysis. Scanning frequencies can range from 0.2 to 25 mhz and vary based on the application need. High frequency signals tend to be attenuated more rapidly through a specimen but exhibit less beam divergence meaning more sensitivity. With low frequency scanning, the signal is attenuated less rapidly but suffers a larger beam divergence implying reduced sensitivity.

An example of a C-Scan sonogram is given in fig. 1.4b. This is a sonogram of two PMR-15/Carbon panels mounted on a t-shaped holder at the bottom of the figure. The sonogram reveals a color display of the specimen under consideration. The color designations have great significance in the interpretation of the figure. Note the colored scale at the top of fig. 1.4b which displays the numbers 0 to 100 above which are the color designations that pertain to those numbers. The numbers represent the percent transmission of the original signal strength through the specimen depending on how the system

Figure 1.4 b C-Scan PMR-15/Carbon Panels



is calibrated. The colors above the percent transmission scale are the respective colors on the sonogram. In other words, the green areas in fig. 1.4b represent a signal recovery by the receiving transducer of between 39 and 51 percent of the transmitting transducer's original signal.

The major percentage of figure 1.4b is represented by the red to pink regions of the transmission scale. This implies that through the majority of the panels good sound transmission was achieved. Also note the three distinct yellow regions on the left panel. These areas indicate poor transmission of sound through the specimen as denoted by the transmission scale. From this indication, one can surmise the presence of discontinuities in the materials under analysis.

Research Objective

The primary focus of this study will be to understand the means by which processing-related defects occur in PMR-15/Carbon Composite material laminates. It will also demonstrate the fracture mechanism that is responsible for a stress induced failure in PMR-15/Carbon composite material laminates.

The processing-related defects of major concern in this study are voids and delaminations. The objective in the experimental portion of the study will be to investigate several PMR-15/Carbon manufactured products and conduct two experiments with the PMR-15/Carbon material. The first experiment will be designed to initiate conditions that may cause the material to incur voids and or delaminations during the curing stage of processing.

A second experiment will be conducted to determine what part of the material is responsible for failure when a laminate suffers an interlaminar fracture.

CHAPTER 2

EXPERIMENTAL ANALYSIS OF PMR-15/CARBON MATERIALS AND PRODUCTS

Failure Analysis of PMR-15/Carbon Engine Duct

PMR-15/Carbon is a unique material with a wide range of applications. It was mentioned previously that this material is quite often used to fabricate jet engine components because it exhibits good thermal stability. Some example products are fan blades, stator vanes, fan frames, fan ducting, cowlings and shrouds.[5]

The component under study is a jet engine duct used on a military fighter jet engine product. The purpose of this duct is to shroud the combustion chamber of the engine. Originally, the duct was made from a titanium alloy which weighed fourteen pounds more than a similar duct made from PMR-15/Carbon. PMR-15/Carbon was chosen because it displays very similar mechanical strength properties to those of the originally used titanium alloy. These considerations are important to fighter aircraft employing the engine duct may endure long missions where the weight reduction is a definite advantage.

Occasionally, engine ducts made from PMR-15/Carbon will incur

processing defects such as excessive voids or delaminations. Defects of this nature can justify the rejection of a processed duct component. This requires that such components must be subjected to some form of non destructive evaluation (NDE) during processing such as the C-scan method.

In general, there is a defined void content level that is acceptable in the duct component. As the void content grows, there will be a significant reduction in the laminate's short beam shear strength. If a high void content were to be present in a duct component, it would seriously endanger the operator of the aircraft employing this structure.

Voids in a PMR-15/Carbon engine duct tend to coalesce near differing ply buildups. To elaborate, the duct thickness varies because there are a different number of plies in certain areas of the duct from other areas. The areas of differing thickness are located where the boss plies are situated. Figure 2.1a illustrates an engine duct structure where the bosses are clearly marked.[3] When this duct is molded, the boss plies are located in a recessed portion of the mold. These portions of the mold are also the locations of the vacuum port attachments on the mold. If the boss plies are not completely compressed or purged of air in the recessed areas, this may initiate ideal conditions for void growth. For this reason, it is very important to make sure that the prepreg laminate is fully purged in these areas of the mold before autoclave curing.

Delaminations in a PMR-15/Carbon duct are also a major quality

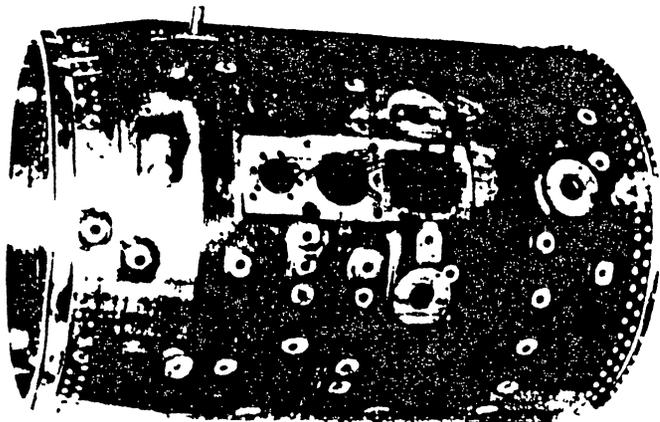
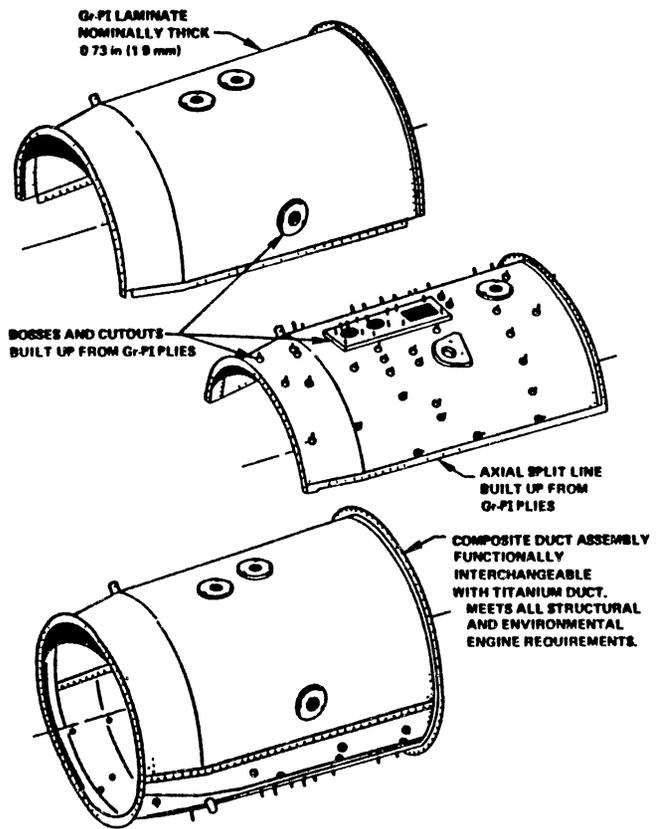


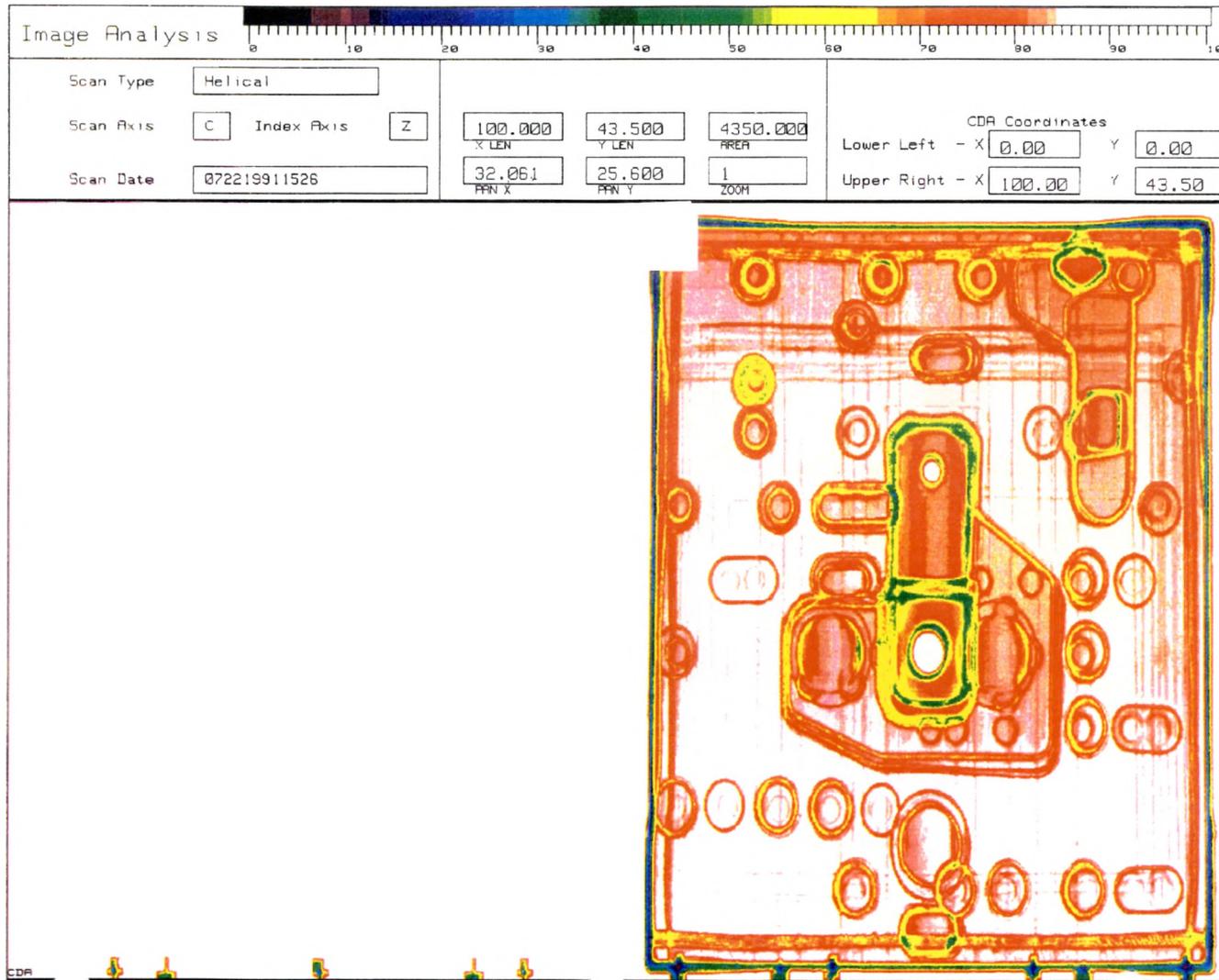
Figure 2.1 a PMR-15/Carbon Engine Duct Component

concern associated with production of this component. This type of defect can jeopardize the structural integrity of the duct component. Delaminations may be found along both the radial and axial flanges of the structure. If delaminations exist along the flanges, the component may not be rejected from the production process. However, if delaminations are noted along the axial body of the duct, the component must be rejected based on its risk of failure when in use. The failure will occur as a result of in-flight exterior forces, causing the delamination to grow into a larger defect.

In this portion of the experimental study, three PMR-15/Carbon engine ducts were examined to determine their exact mode of failure. The three ducts are labeled duct A, B, and C respectively. These ducts were rejected based on the results of their respective C-Scan analyses.

Duct A is a classic example of both types of failures discussed above. It was noted after cross sectioning the duct that a large delamination was present along one of the axial flanges of the duct and gross voids were present around some of the boss plies. The duct originally failed its C-Scan inspection stage of processing. The C-Scan (Fig. 2.1b) clearly shows that duct A exhibits many discontinuities around the middle boss plies. These discontinuities are characterized by the green color near the boss ply areas on the C-Scan. The cross sections were also further analyzed by cutting the sections into small pieces. The pieces were mounted in Lucite disks and the surfaces were polished using a Leco metallographic polishing instrument. The polished

Figure 2.1 b DUCT A



surfaces were examined with a reflection metallurgy microscope. The results of the microscopic examination are shown in fig. 2.1c.

Figure 2.1c(i) is a micrograph of a piece of the cross section taken from the radial flange of duct A taken at 50X magnification. The elliptical shaped bundles of dots in the micrograph represent a cross sectional view of fiber tows. The white lines are fiber tows running transverse to the fiber tows represented by the elliptical shaped groups of dots. Also note the gray areas intermixed with the dot groups and the lines. These represent pools of the PMR-15 matrix material that have been produced by the resin bleeding through the prepreg.

A special feature of fig. 2.1c(i) is the dark line across the middle of the micrograph. This line is a classic case of delamination between adjacent plies within a laminate. The darkness in the micrograph is created as a result of no reflecting surface where the delamination is present.

Figure 2.1c(ii) is a 100X magnification micrograph of a cross sectional sample taken from the middle boss plies of duct A. Note that the dark region in this micrograph ends before it reaches the borders of the picture. This area represents a void or resin starvation which verifies the C-Scan data.

Duct B greatly exemplifies the case of mass void growth around the boss areas of the duct component structure. The upper right corner of the C-Scan in fig. 2.1d indicates severe discontinuities at the edges of the hatchet pad. The severity of the discontinuities is clearly marked by the violet color in

DUCT A FIGURE 2.1C

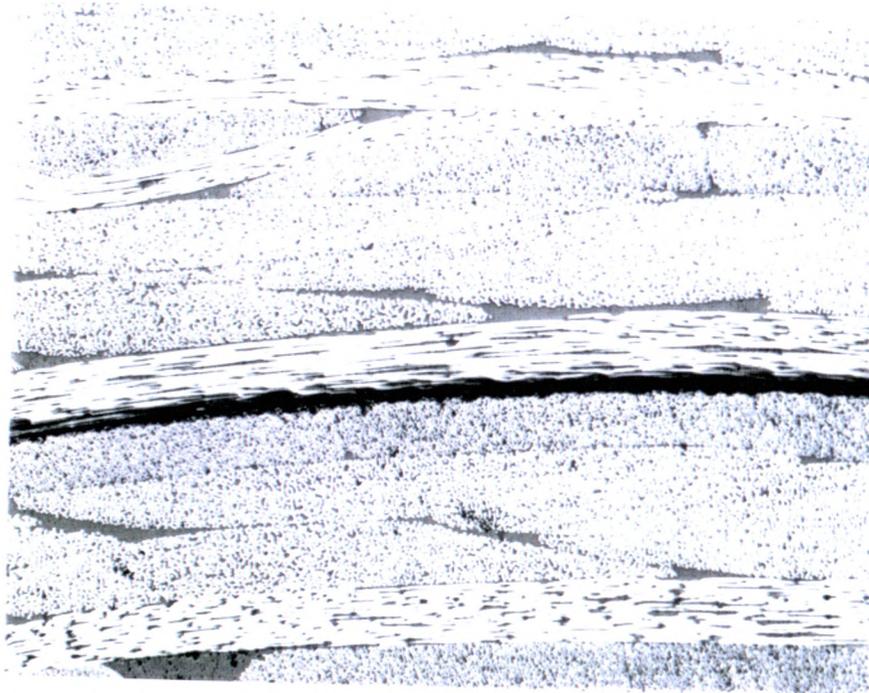


Fig. 2.1c(i) 50X

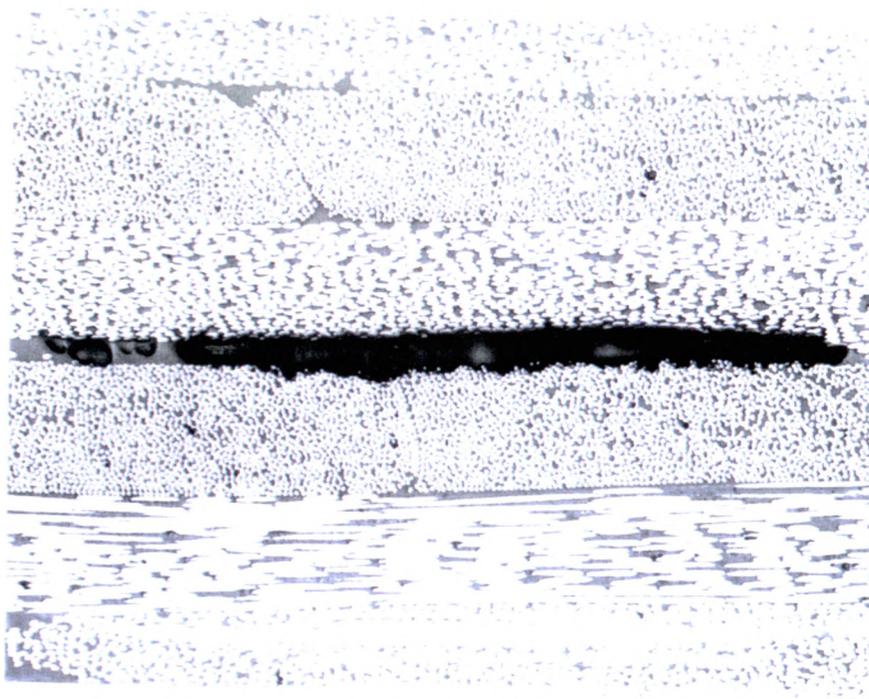
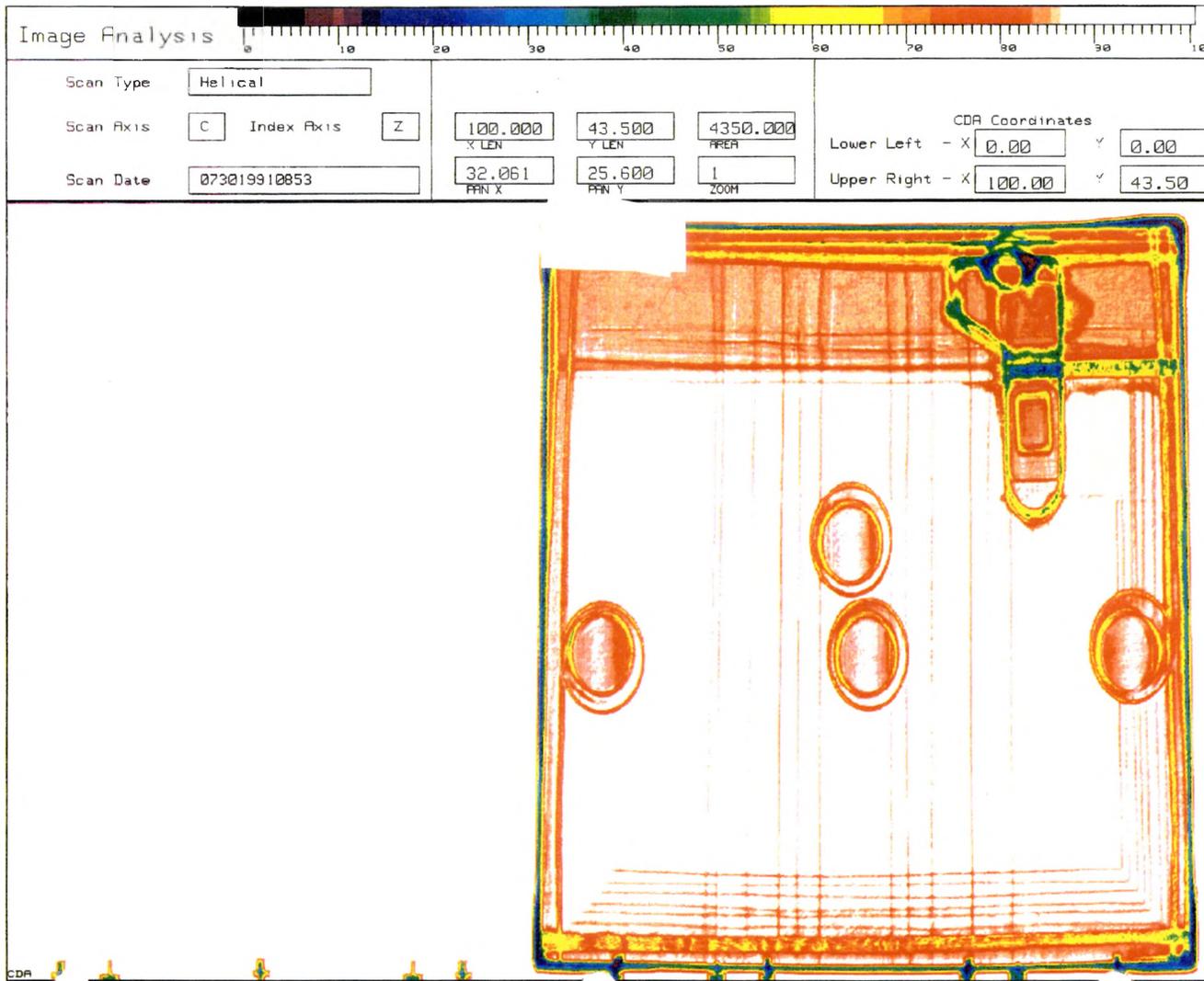


Fig. 2.1c(ii) 100X

Figure 2.1 d DUCT B



the defect region of fig. 2.1d.

The same microscopic analysis was performed on duct B as that on duct A. Samples for the microscopic study were taken from cross sections in the hatchet pad region of duct B. The samples were prepared in a similar manner to those in the microscopic study of duct A. Results from this analysis are displayed in fig. 2.1e and differ somewhat from those in the same analysis of duct A. Figure 2.1e(i) is a micrograph of a sample cut along the axial direction of the hatchet pad. This micrograph was taken at 50X magnification and reveals many voids in the specimen. Note that a large number of voids cover this micrograph and the sizes of these voids are large in comparison to the void region of fig. 2.1c(ii). These observations tend to support that the prepreg laminate in this region of the mold may not have been completely purged of trapped air or volatile contents. The sample for figure 2.1e(ii) was cut perpendicular to the axial direction of the hatchet pad. This micrograph was taken at a magnification of 50X and shows a similar picture to that of fig. 2.1e(i). However, the voids in this micrograph are not as wide as those in fig. 2.1e(i) because of the direction from which the view was taken.

The final duct analyzed (Duct C) did not fail inspection immediately following the curing process. The failure occurred during a pressure test stage of the component processing scheme. This test was implemented to ensure that service pressure exerted on the interior walls of the engine duct would not exceed specified limits.

DUCT B FIGURE 2.1 E

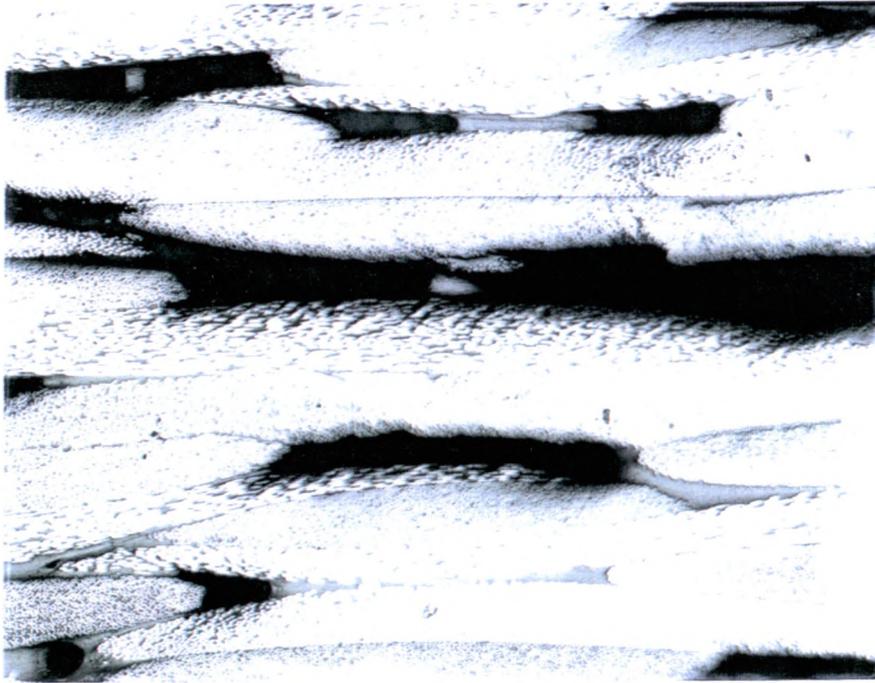


Fig. 2.1e(i) 50X

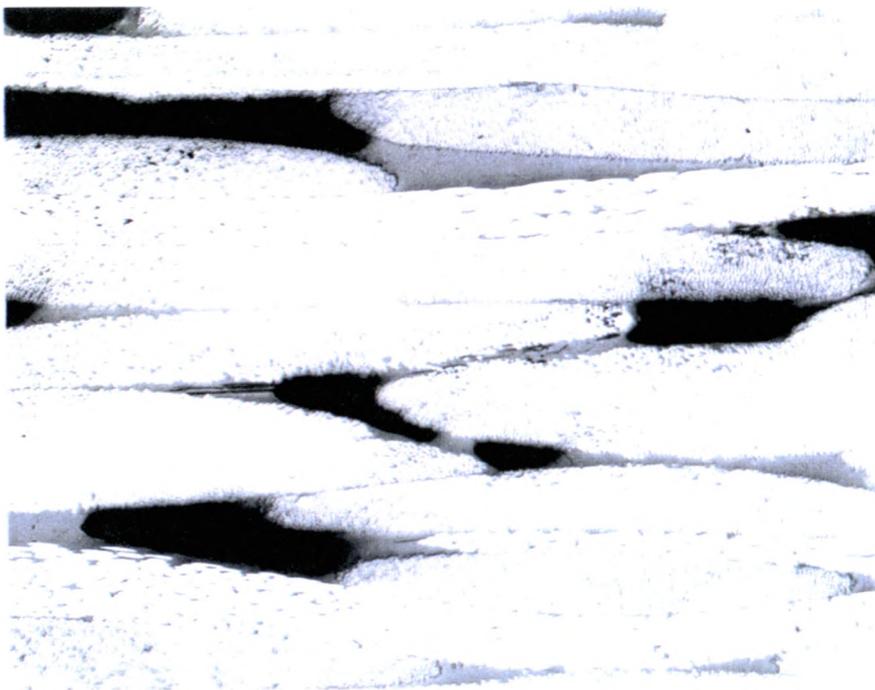


Fig. 2.1e(ii) 50X

The C-Scan prior to the pressure test is pictured in fig. 2.1f. It differs from the C-Scans of fig. 2.1b and fig. 2.1d in that both halves of the duct are displayed. Note the green line that runs along the far right side of fig. 2.1f. These lines are present around the edges of all three duct C-Scans because of how the sound beam is reflected and refracted along these edges. The line in question runs along the axial length of the duct half, and is fairly uniform until it reaches the top and bottom corners. Figure 2.1g displays a magnified image of fig. 2.1f in the lower right hand corner of the right half. Note once again the fair uniformity of the green line until it reaches the bottom corner.

Figure 2.1h is a C-Scan of the duct halves following the pressure test. The Scan appears virtually identical unless it is closely inspected. At the bottom right corner, the uniformity of the green line changes and therefore implies a defect in the component. A magnified image of this area in fig. 2.1h is shown in fig. 2.1i on the following page. Comparing the specified lines of figures 2.1f and 2.1h, one can observe a highly notable difference. The blue color of the line in fig. 2.1h implies a larger degree of attenuation of the ultrasonic signal. The increased signal loss indicated that a delamination was created during the pressure test.

The development of the above mentioned defect in duct C may have occurred as a result of a foreign substance introduced into the laminate. This could have resulted by virtue of not removing all of the polyethylene backing film on a PMR-15 prepreg sheet while the duct was being molded. If this were

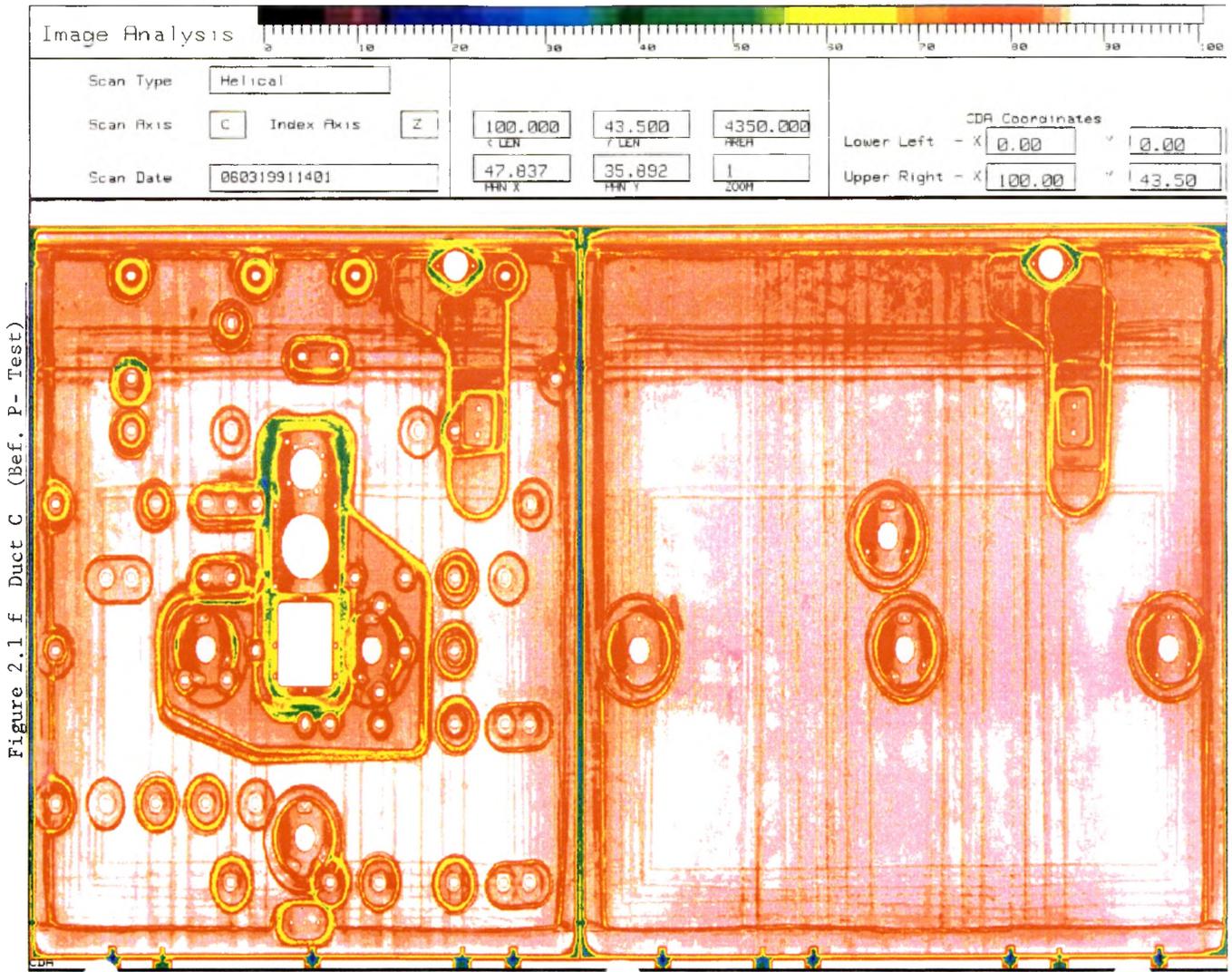


Figure 2.1.f Duct C (Bef. P-Test)

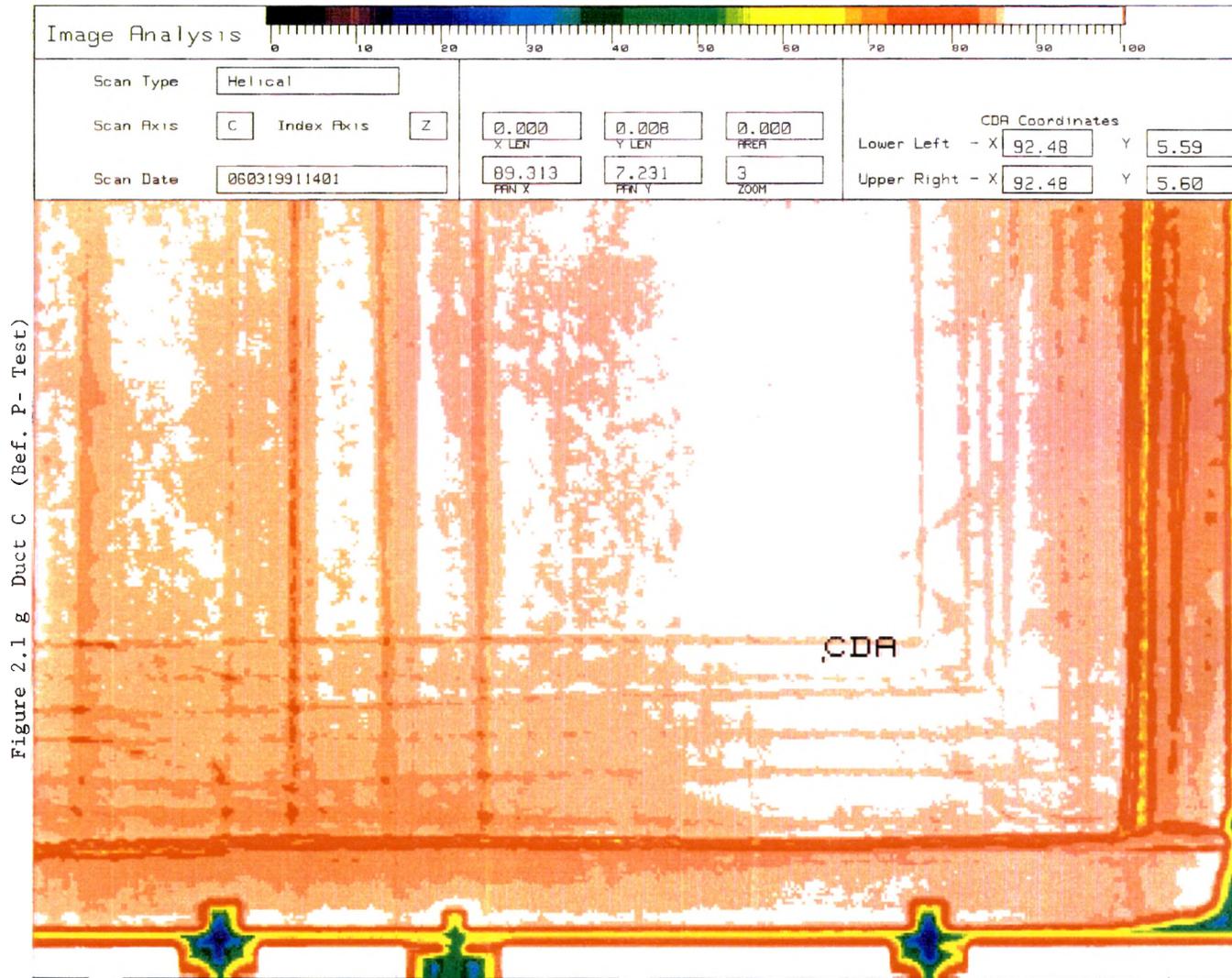


Figure 2.1 g Duct C (Bef. P- Test)

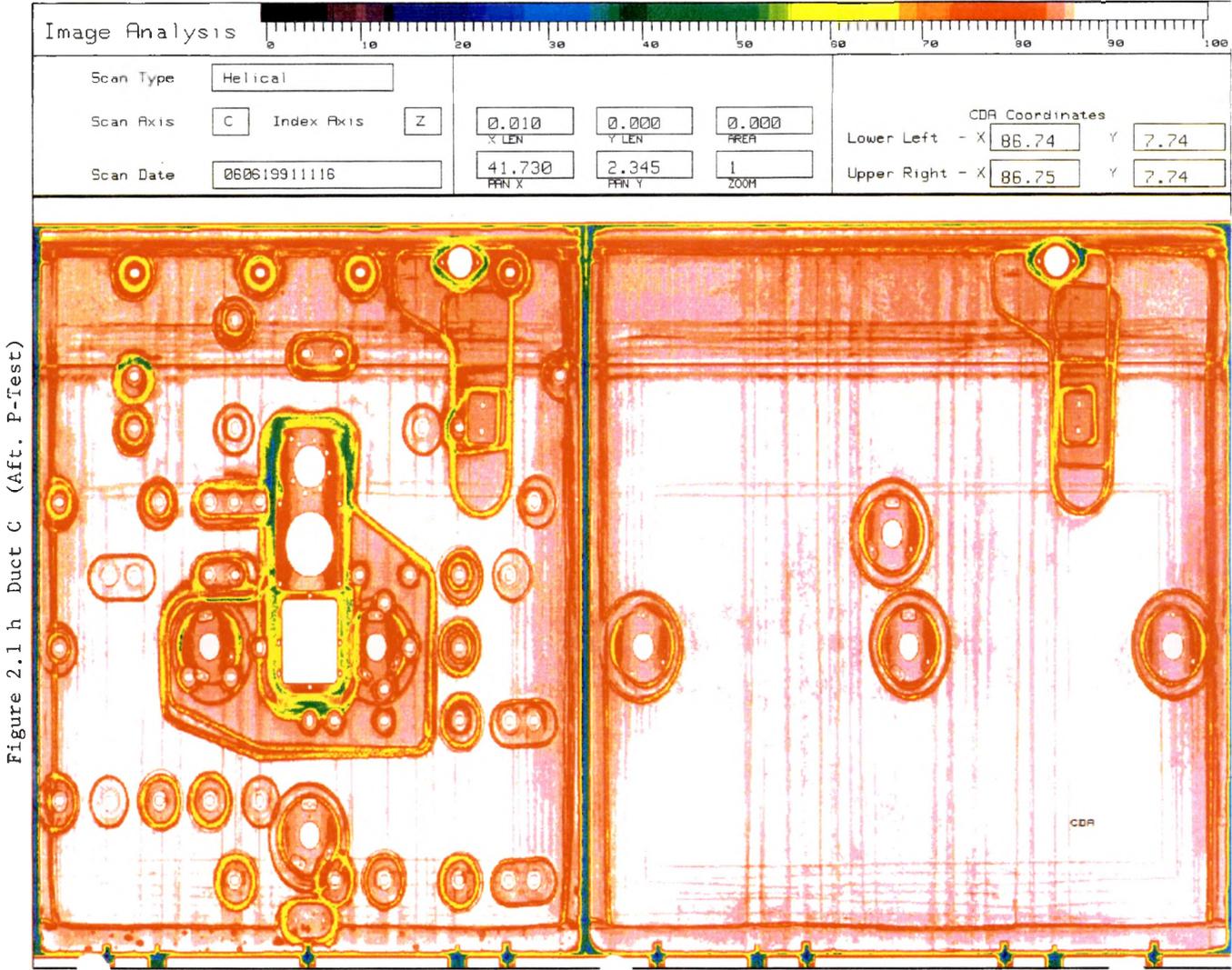


Figure 2.1 h Duct C (Aft. P-Test)

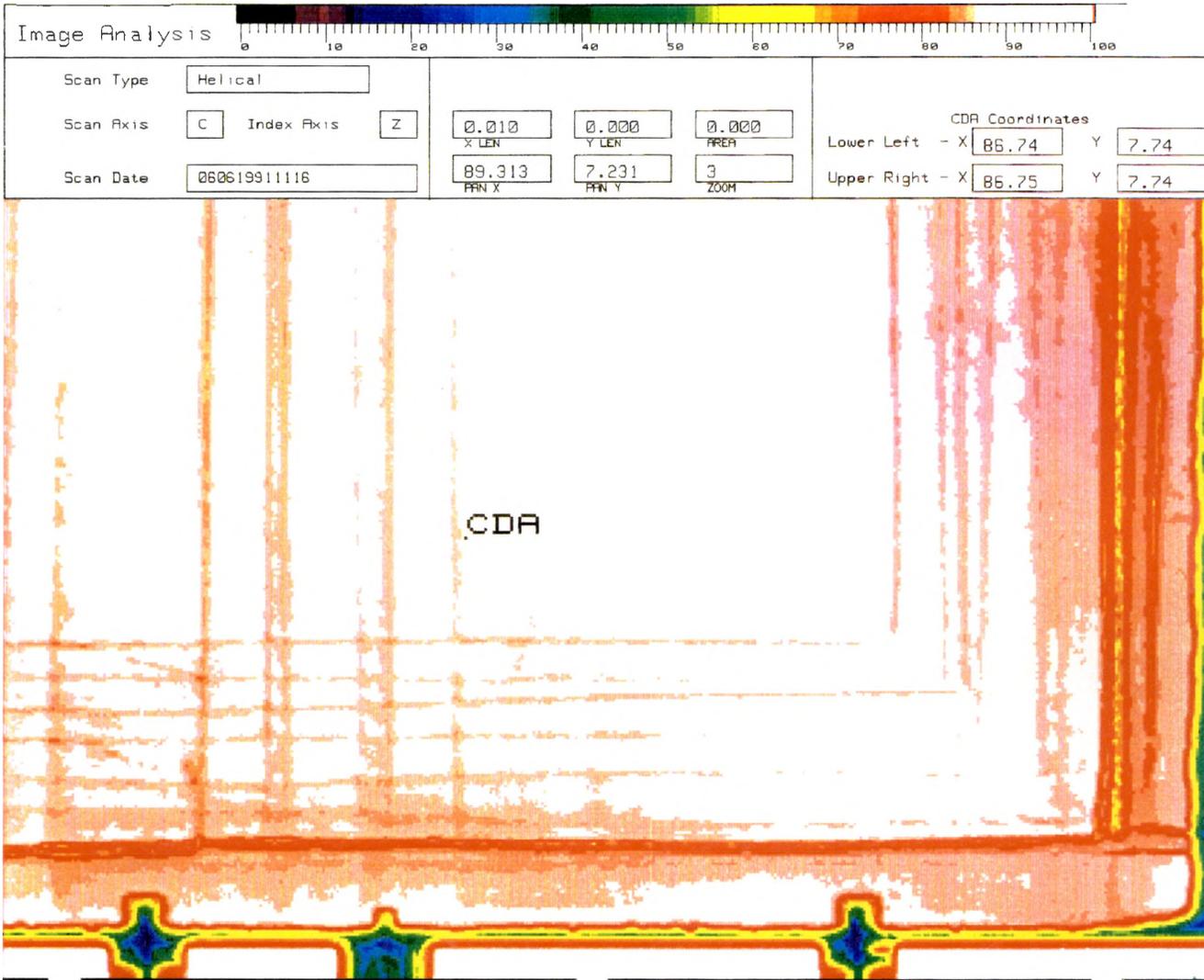


Figure 2.1 i Duct C (Aft, P-Test)

the case, it would answer two pertinent questions. The first question is why did the C-Scan before the pressure test not indicate the presence of the foreign material? This is easily explained since the melting point of polyethylene is between 230 - 270 °F.[6] If the polyethylene was baked into the duct, the maximum temperature of the cure would be more than sufficient to completely melt the piece of polyethylene film. Upon melting, the film would diffuse into the laminate and chemically combine with the PMR-15 resin at this point. When the duct was C-Scan inspected, the foreign material would not have been detectable because of its mixture into the PMR-15 resin. This is conceivable by virtue of the fact that the C-Scan signal is attenuated by a material boundaries of differing density. The melted polyethylene and PMR-15 would become a material of uniform density. This would render the C-Scan inspection unable to detect the presence of the foreign material.

The second question is why did the duct fracture during the pressure test? Since the polyethylene is a foreign material to the PMR-15 matrix, it caused poor covalent bonding to be achieved between the interlaminar interfaces. As a result of this, the fracture was created by the force imposed during the pressure test on the interior walls of the duct.

The above discussion provides clear justification for the failure of duct C. One can also gather from the above discussion that the introduction of foreign materials into a PMR-15/Carbon laminate may be detrimental to it.

PMR-15/Carbon Cure Processing Experimental Study

Purpose and Theory

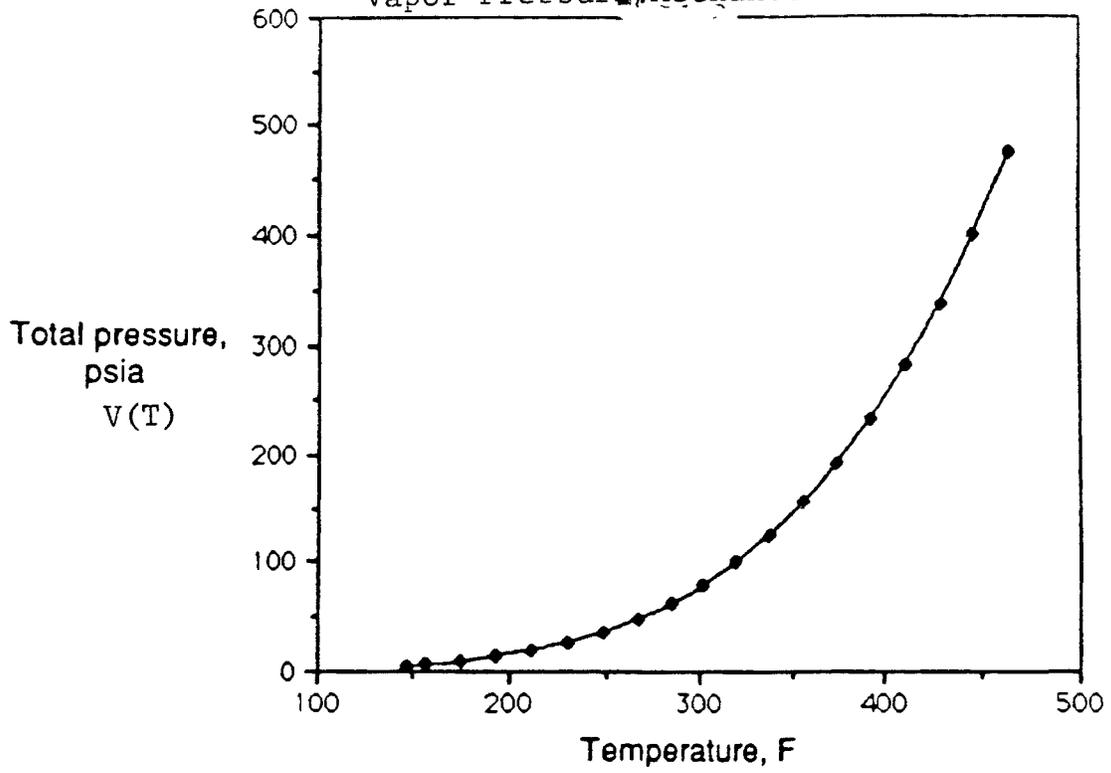
This experiment is designed to study both interlaminar and intralaminar defects in PMR-15/Carbon composite materials. This will be accomplished by curing and postcuring two separate PMR-15/Carbon composite panels. Each panel will be prepared such that voids or delaminations may be induced into one or both of them.

The hypotheses of this experiment is best stated as follows; the entrapment of volatile contents within a PMR-15/Carbon laminate may induce voids or generate a means by which delaminations will result from postcuring the laminate. It is easy to conceptualize the creation of voids from the entrapment of volatile contents. This may happen when a volume of methanol and water vapor is trapped between the layers of the prepreg. Methanol and water vapor are mentioned because they are the primary condensation volatile products of the PMR-15 curing reaction. If these volatile products were trapped, the bubbles would experience growth as a result of the rising vapor pressure within the bubbles due to increasing temperature during autoclave curing.

Delaminations that could result from the entrapment of volatile contents

are an entirely different phenomenon. If a volume of methanol and water vapor were to be trapped between the plies of a laminate during autoclave curing, it could remain entrapped after removing the laminate from the autoclave. In a normal processing procedure, the laminate would be placed into the postcuring oven following the autoclave cure. As the temperature of the postcuring oven rose, the vapor pressure of the confined volatile products would also rise. A vapor pressure curve of methanol water vapor is illustrated in fig. 2.2a.[7] This curve demonstrates that if a sufficient volume of methanol and water vapor were trapped, then the temperatures reached in the postcure would be adequate to allow the generation of very large forces on the interior of the laminate. The centers of force resulting from the high vapor pressure within the volume of trapped volatile contents might even be large enough to exceed the fracture strength of the laminate, resulting in a delamination.

Figure 2.2 A
Vapor Pressure/Methanol-Water PMR-15



Introduction

In order to induce defects into one of the laminates, three different materials were cut into strips of equal area and placed at the same depth in the panel. The three materials are brass, teflon, and graphite. The dimensions of each insert are listed in Table 1 as follows;

Table 1

Material	Thickness	Dimensions	Mass	Melting Point
1.) Brass	1 ml.	1 x 0.25 in.	0.0240 g	~ 1750 ° F
2.) Graphite	5.5 ml.	1 x 0.25 in.	0.0379 g	6422 ° F
3.) Teflon	3 ml.	1 x 0.25 in.	0.0178 g	620 ° F

The other laminate was prepared such that it would not be able to properly expel its volatile contents. It was prepared in this fashion to test the experimental theory pertaining to delaminations created in the postcure.

For the sake of organization, the laminate with the foreign materials baked into it will be referred to as laminate A and the other, laminate B. Both laminates A and B are twenty prepreg plies thick and were cured using the same molding tool.

Procedure

1.) Polishing of molding tool surface.

A.) Solvent must be applied to clean surface of molding tool.

B.) Mold release application (Teflon solution to prevent laminates from adhering to the surface of molding tool.).

2.) Heat polished mold for approximately 30 minutes in oven at 150° F.

3.) Lay - up procedure.

LAMINATE A

A.) Place foreign materials 10 plies deep into prepreg laminate.

B.) Layer of release-ease over surface of laminate.

C.) Perforated resin barrier on top of release-ease.

D.) Four sheets of small pore breather cloth (Fiberglass).

LAMINATE B

A.) Non-perforated resin barrier.

1.) Small crease in resin barrier to prevent vacuum bag from rupturing.

LAMINATES A AND B

AA.) Adhesive tape was placed around the edges of the mold to ensure a good vacuum bag seal was present.

BB.) Large pore, fiberglass breather cloth was placed around both laminates.

CC.) 69in. x 54in. Kapton vacuum bag was placed over mold in order to draw volatile contents from laminate A.

Experimental Data Before Autoclave Cure

Table 2

Laminate	Panel A	Panel B
Average Thickness	2 ml	2 ml
Mass	629.6 gr	645.2 gr
Width	6.13 in	6.30 in
Length	12.3 in	12.3 in
Area	0.517 sq ft	0.538 sq ft

Experimental Data Following Autoclave Cure

Prior to Postcure

Table 3

Laminate	Panel A	Panel B
Avg. Thickness	0.27 in	0.27 in
Mass	502.18 gr	529.46 gr
Width	6.13 in	6.30 in
Length	12.35 in	12.30 in
Area	0.517 sq ft	0.538 sq ft

- COMMENTS -

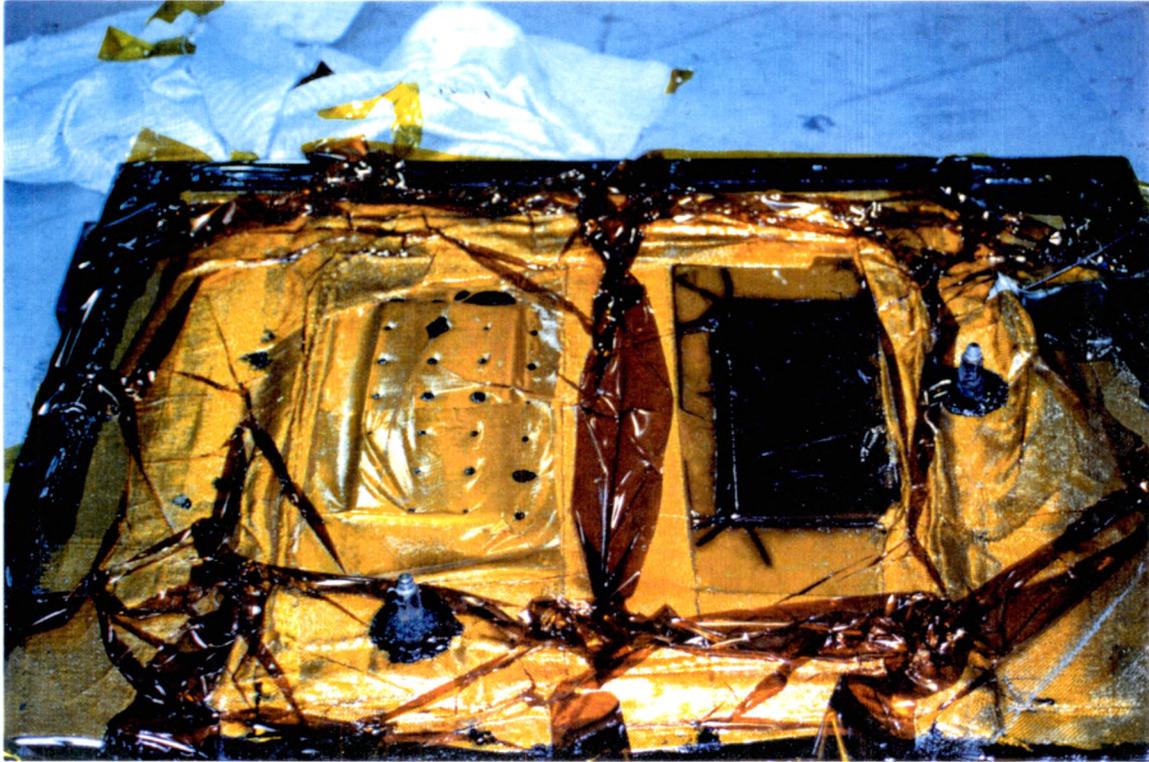
- (A.)
- 1.) Rough surface, with wrinkles spanning length of panel.
 - 2.) Much notable bleeding of resin through breather.
cloth over perforations in resin barrier (Bag).
 - 3.) Resin concentrated around edges of vacuum ports (Bag).
 - 4.) Lost 20.2% of weight due to expelled volatile contents.

- (B.) 1.) Smooth surface, with wrinkles running across panel surface.
- 2.) Much resin bleeding around edges of panel (Bag).
- 3.) Lost 17.9% of weight due to expelled volatile contents.

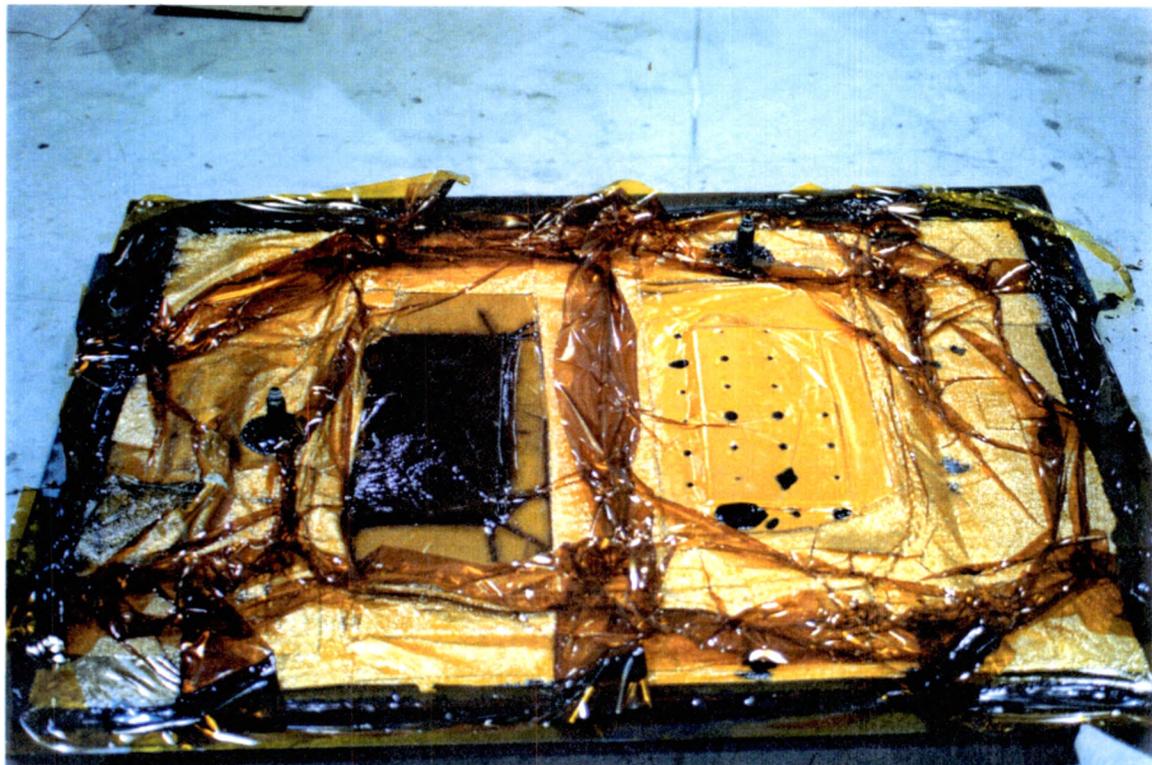
- Condition of mold and bag -

Bleeding apparent around edges of breather cloth and bag.

Figure 2.2 a

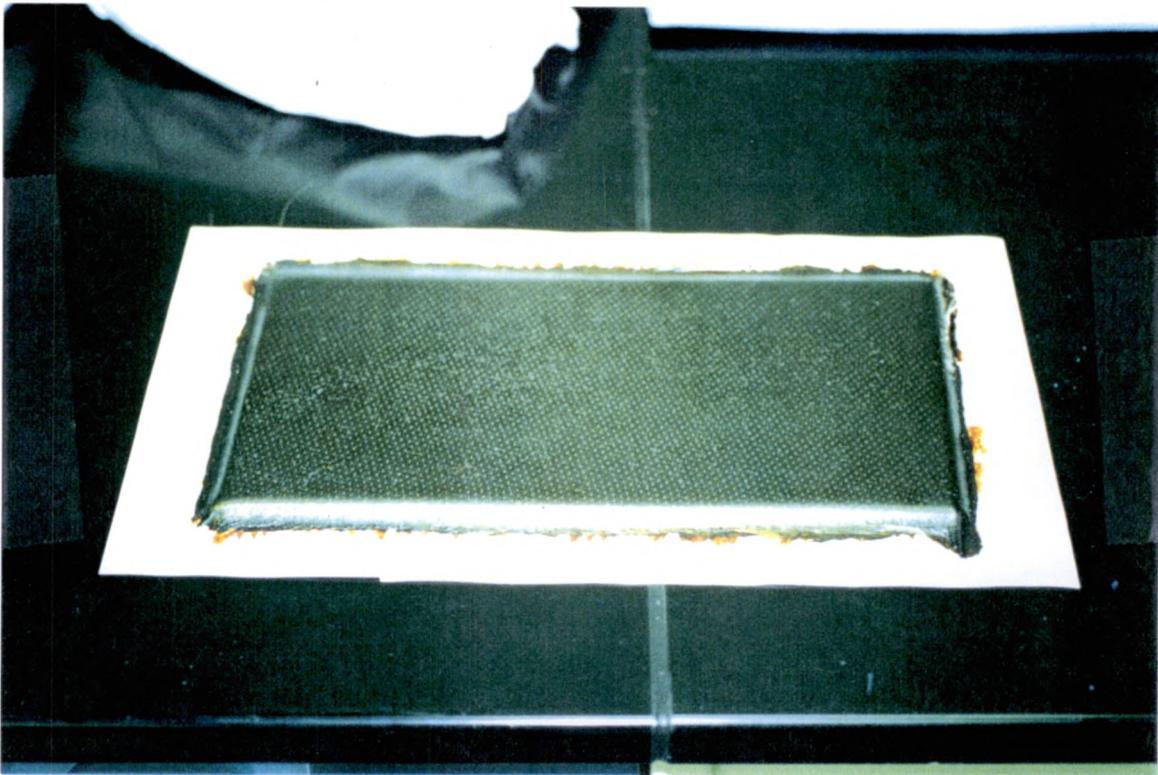


VACUUM BAG/MOLD PANEL A & B



VACUUM BAG/MOLD PANEL B & A

Figure 2.2 b (Bef. Post Cure)



PANEL A



PANEL B

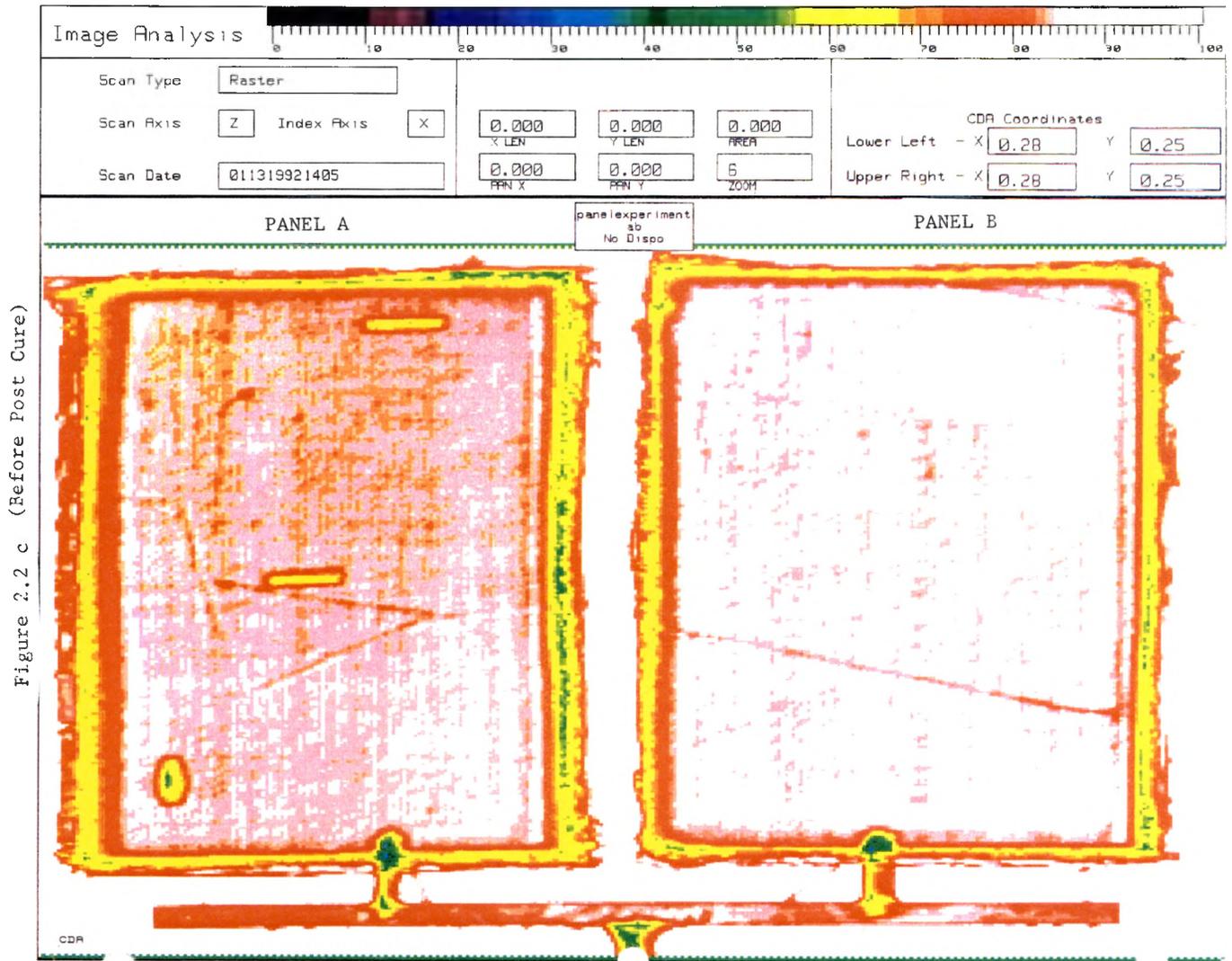
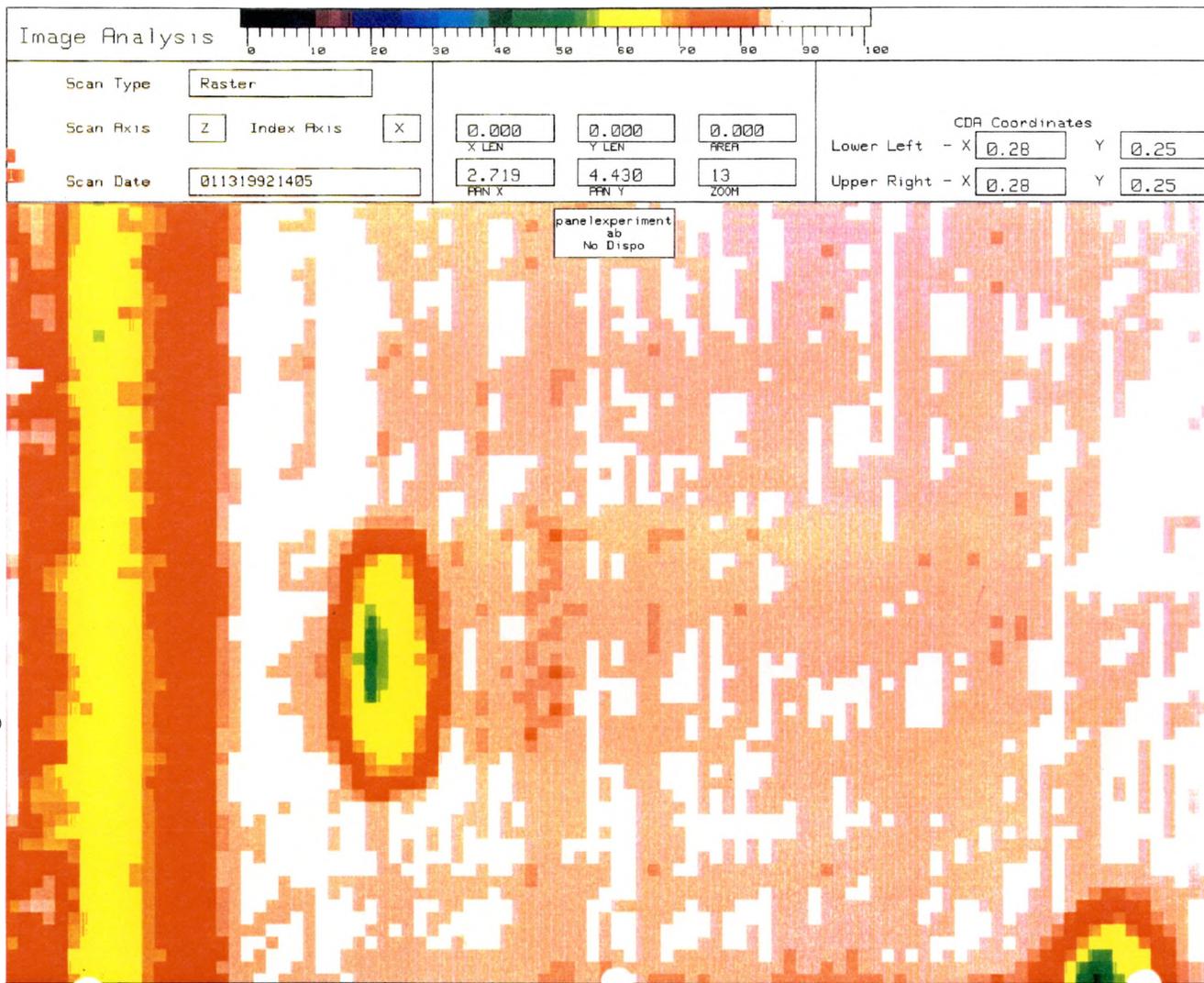


Figure 2.2 c (Before Post Cure)

Figure 2.2 d Teflon Insert



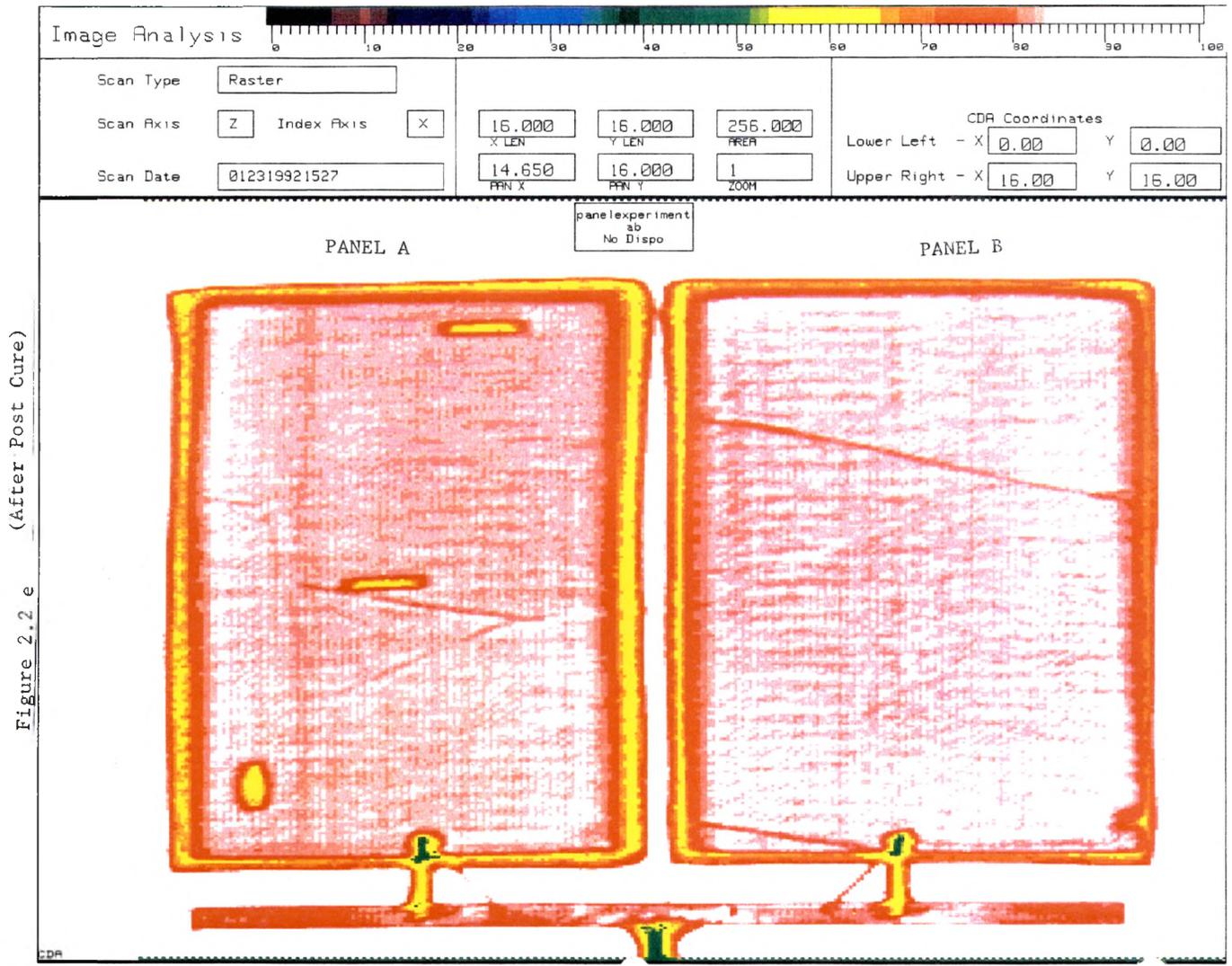
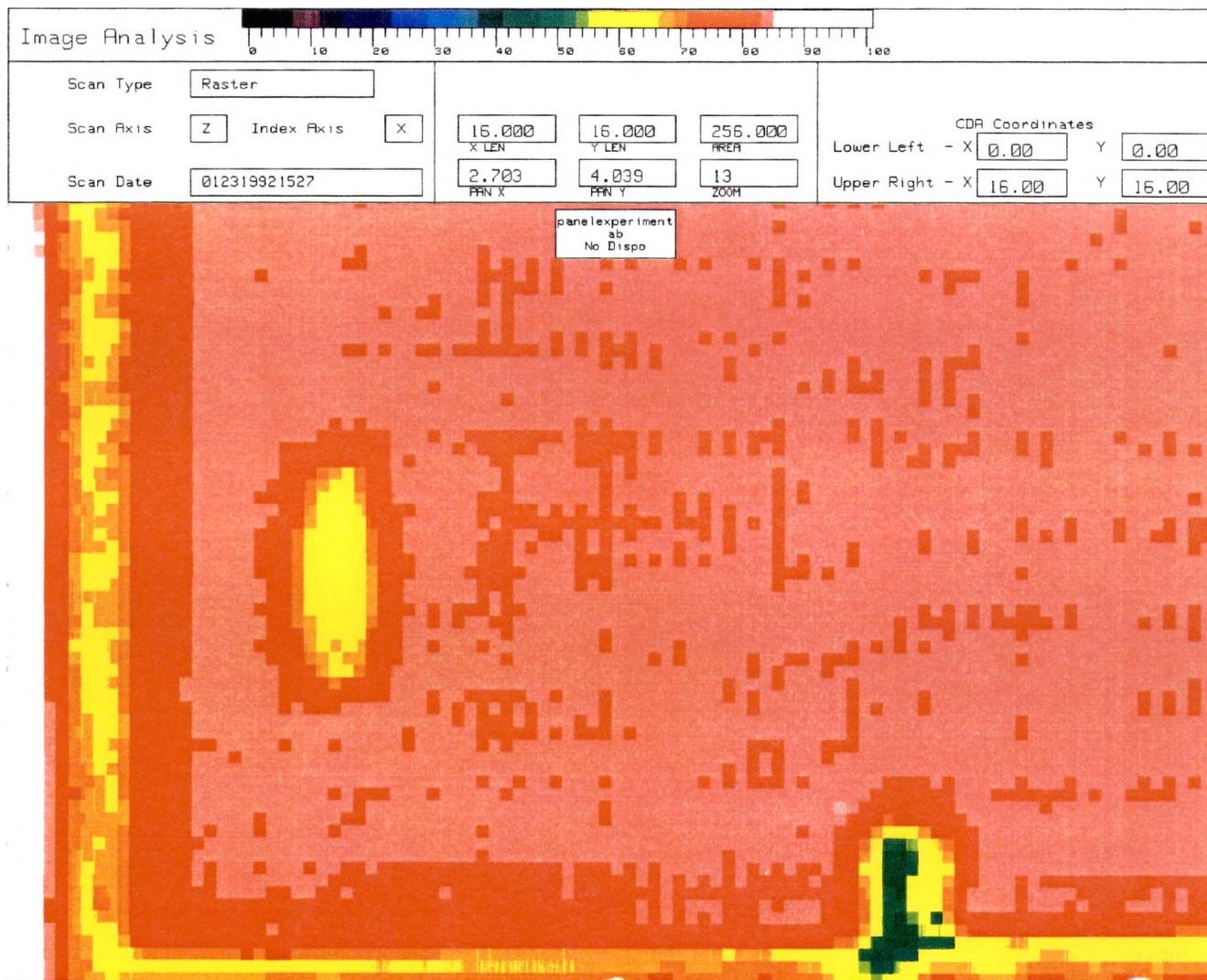


Figure 2.2 e (After Post Cure)

Figure 2.2 f Teflon Insert



Results and Discussion

After being subjected to the Autoclave curing process, panel A and B were examined by both visual and ultrasonic means. The visual inspection was made by observing the contents of figure 2.2a and figure 2.2b. An ultrasonic inspection was made using the C-Scan method before and after postcuring the panels. These scans are represented by figures 2.2c - 2.2f. Note also, that each panel was removed from the vacuum bag mold in fig. 2.2b.

Figure 2.2a is a photograph of the panels taken while they were still enclosed in the vacuum bag on the mold surface. The vacuum bag is represented by the gold colored plastic sheet covering the mold surface. The results of the visual analysis indicated that panel A (Left side of fig. 2.2a(i)/Right side of fig 2.2a(ii)) did lose some of its resin when a full vacuum was applied to the bag over the mold. This is illustrated in fig. 2.2a by the black dots on the surface of the breather cloth.

Panel B (Right side of fig. 2.2a(i)/Left side of fig. 2.2a(ii)) however, which was not properly ventilated, revealed that the resin sought to escape from under the non-perforated resin barrier. This is illustrated by the presence of the black edges of panel B and the "Crow feet" lines at the corners in fig. 2.2a. Panel B also retained 2.3% more of its original prepreg weight because of poor exhaustion of its volatile contents and the inability of the resin to

escape through the breather cloth. Upon visual inspection of the panel surfaces outside of the bag, it was noted that panel A (Figure 2.2a(i)) had a rough surface contour and panel B (Figure 2.2(ii)) had a smoother surface. Each panel had notable creases across their width. The creases could have been caused by virtue of the fact that panel A was under a compaction force of over 15,000 lbs. and panel B, a force of over 15,000 lbs. during a pressure application in the autoclave.

The results of the ultrasonic C-Scan inspection reveal some interesting details and can be used to explain the results of table 3. The scans were made using 5 MHZ ultrasonic transducers with spherical acoustic lenses. The purpose of a spherical acoustic lens is to focus the sound beam to a fine point of high intensity in order to increase the sensitivity of the scanning instrument.

The C - Scan image in fig. 2.2c shows the panels following the autoclave cure, prior to the post cure. This figure indicates that laminate A was fully consolidated except for the areas in which the material inserts were placed. The brass insert is at the top right of the C-Scan, the graphite insert is in the middle and the teflon insert is at the bottom left of fig. 2.2c. From fig. 2.2c, it can also be noted that the teflon insert appeared to have expanded during the autoclave cure which can be accounted for by the fact that teflon will cold flow under pressure. A closeup C-Scan of the teflon insert is pictured in fig. 2.2d from which it appears that the center of the insert is more dense as a result of the green color. The center of the insert could have become more dense as

a result of the compression forces generated within the laminate. The compression forces acting on the sides of the insert could have caused the center of the teflon insert to become more dense. This is conceivable by virtue that teflon is a thermoplastic polymer and its molecular structure can be easily reoriented.

Laminate B appeared fully consolidated as well with the exception of the edges where the majority of the volatile contents generally escape in a PMR-15/Carbon panel type laminate. Also note the red line across the panel width, which represents the previously mentioned crease.

After post - curing, the panels were inspected by the same means once again. Visual observation revealed nothing more unusual about the exterior of the laminates. The second ultrasonic C-Scan picture in fig. 2.2e appeared identical to the first other than a slight difference in the teflon insert region (Panel A) which could be attributed to the thermal properties of a thermoplastic polymer. To elaborate, the illustration in fig 1.1a demonstrates that the mechanical properties of thermoplastic polymers change as a result of a temperature increase. Consider the subjection of Panel A to the heat of the postcure oven. The long heating soaks of the postcure could conceivably reorient the molecular structure of the teflon insert. The change of molecular structure might allow the insert to obtain a more uniform density instead of having a greater central density (Recall the central green region of fig. 2.2d.). It is clear that the teflon insert must have endured a physical change by

inspecting figures 2.2d and 2.2f. The uniform density of the insert would then reduce the attenuation of the ultrasonic sound beam.

In conclusion, the results of this experiment were not consistent with the original expectations. A possible reason for this is explained by Kantz in reference one. In this explanation, the volatile content of a twenty ply PMR - 15/Carbon prepreg laminate is 19.1% of its weight by volume.[1] "Two to twelve percent of its weight is excess methanol, to provide drape and tack." [1] Panel A lost 20.2% of its original prepreg weight and panel B lost 17.9% of its original prepreg weight. Panel A's weight loss can be accounted for by considering the resin bleeding through the breather cloth over the laminate. Recall also that panel A was properly ventilated to ensure the maximum expulsion of the volatile contents.

Panel B was not properly ventilated, therefore neither the volatile contents or any large quantities of resin could escape from its prepreg laminate form. By this reasoning, one can conclude that Panel B retained a higher resin content than did Panel A.

After conducting this experiment, it was found in a similar study that the results of this experiment were further justified. In the similar study (Reference 7), PMR-15/Carbon panels having ply thickness from 24 to 54 were investigated. The dimensions of the panels were 12 inches by 18 inches. Each panel was prepared with a non-perforated resin barrier (Similar to Panel B) such that it could not properly exhaust its volatile contents. The results of

the experiment proved identical to the results obtained in this study. The conclusions of the experiment maintain that laminates with the above dimensions do not need to be ventilated to achieve the full consolidation quality.[7] These findings are concurrent with the results of this study by reasoning that the areas of Panel A and Panel B are approximately three times the area of the panels investigated in the related experiment.

PMR-15/Carbon Fracture Mechanism Experimental Study

The purpose of this study was to understand the primary fracture mechanism in PMR - 15/Carbon composite laminates. The results were used to determine whether the resin and or the fibers are responsible for failure of the above mentioned material when the material is subjected to some type of loading.

In a fracture mechanism study of advanced composite materials, fracture surfaces of the material in question are generally obtained to observe with a microscopic instrument. Both optical and scanning electron microscopes (SEMs) can be used in this type of study.

In this experiment, four specimens were observed to determine the primary fracture mechanism of PMR-15/Carbon. Three specimens were obtained by sectioning Panel A of the experimental study in section 2.2 of the text. The fracture surfaces of these specimens were observed with an SEM instrument.

Panel A was cut into three pieces with one of the foreign material inserts in each section. The sections containing the teflon and the graphite inserts were cracked open by inserting a wedge between the plies and exerting a force on the wedge to fracture the laminate. The plies were peeled apart on each section and revealed that the teflon insert had been compressed and the

graphite had bonded to the interlaminar surfaces. Since teflon tends to exhibit poor adhesive qualities, the insert was easily removed from the surface. The surfaces were then cut across their mid section to be examined.

The section containing the brass insert, was cracked by application of a shear stress along the section. After cracking the section, the laminate was peeled apart and the surfaces exposed an unchanged brass insert which was easily removed.

The fourth specimen was extracted from the delaminated region of Duct C, discussed in section 2.1 of the text. Its fracture surface was made by the same procedure used to make the teflon and graphite surfaces.

Procedure

In this experiment, an SEM was chosen to be used for its ability to produce high quality three dimensional images and to attain a correlation to a similar study. In addition, it is impossible to sharply focus an optical microscope on an ACM fracture surface.

Since the PMR-15/Carbon composite material's major components are thermoset plastic and amorphous carbon/graphite fibers, this material should exhibit a low conductivity. This required that each sample be coated with a substance possessing a high conductivity to avoid a space charge build up. A thin film of aluminum was deposited with a standard laboratory evaporator.

Other considerations of the investigation were the weight of samples before and after the thin film deposition, magnification necessary to achieve a valid correlation, and other SEM parameters.

The ultimate goal of the study will be to obtain photomicrographs of suitable resolution for purposes of determining the fracture mechanism in the PMR-15/Carbon composite material.

FRACTOGRAPHY DATA

Specimen # 1

Origin of Specimen: Teflon Insert From Panel A

Mass of sample before coating: 1.6959 g

Mass of sample after coating: 1.6952 g

Magnification: 29 X

Other SEM parameters: Contrast of Backscattered and Secondary Electrons

Comments:

- 1.) Fracture Mechanism: Failure in both resin and fibers

FRACTOGRAPHY DATA

Specimen # 2

Origin of Specimen: Brass Insert From Panel A

Mass of sample before coating: 1.6246 g

Mass of sample after coating: 1.6237 g

Magnification: 20 X

Other SEM parameters: Contrast of Backscattered and Secondary Electrons

Comments:

- 1.) Fracture Mechanism: Failure in both resin and fibers

FRACTOGRAPHY DATA

Specimen # 3

Origin of Specimen: Graphite Insert From Panel A

Mass of sample before coating: 1.7429 g

Mass of sample after coating: 1.7419 g

Magnification: 30 X

Other SEM parameters: Contrast of Backscattered and Secondary Electrons

Comments:

- 1.) Fracture Mechanism: Failure in both resin and fibers

FRACTOGRAPHY DATA

Specimen # 4

Origin of Specimen: Duct C (Figures 2.1f-g)

Mass of sample before coating: 0.2747 g

Mass of sample after coating: 0.2739 g

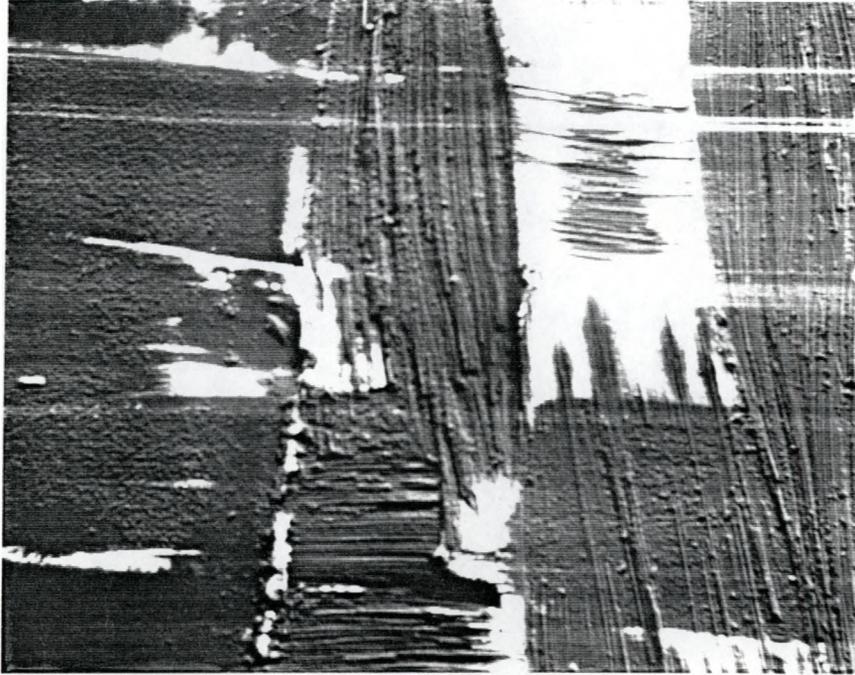
Magnification: 25 X

Other SEM parameters: Contrast of Backscattered and Secondary Electrons

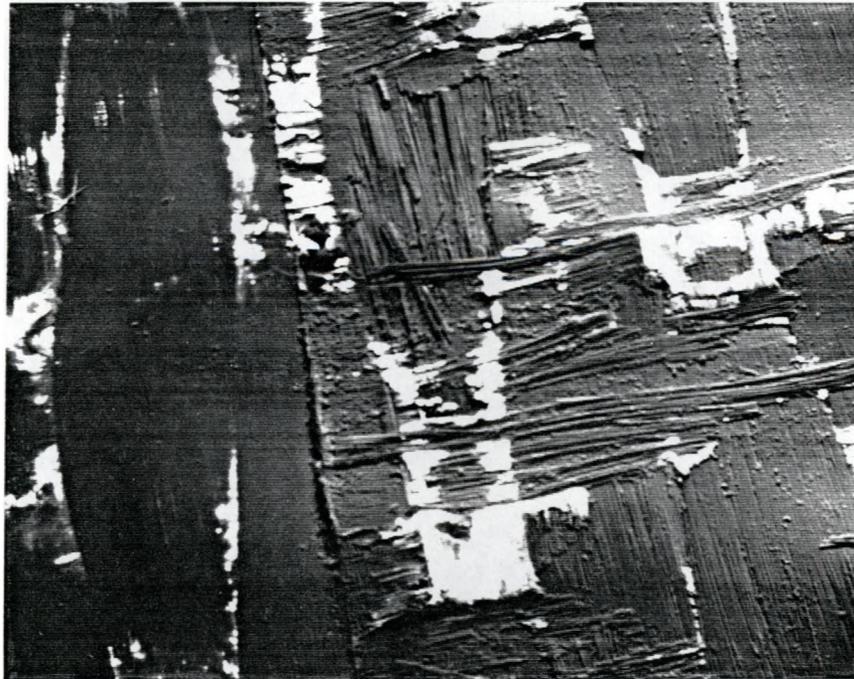
Comments:

1.) Fracture Mechanism: Failure by resin alone

Figure 2.3 a

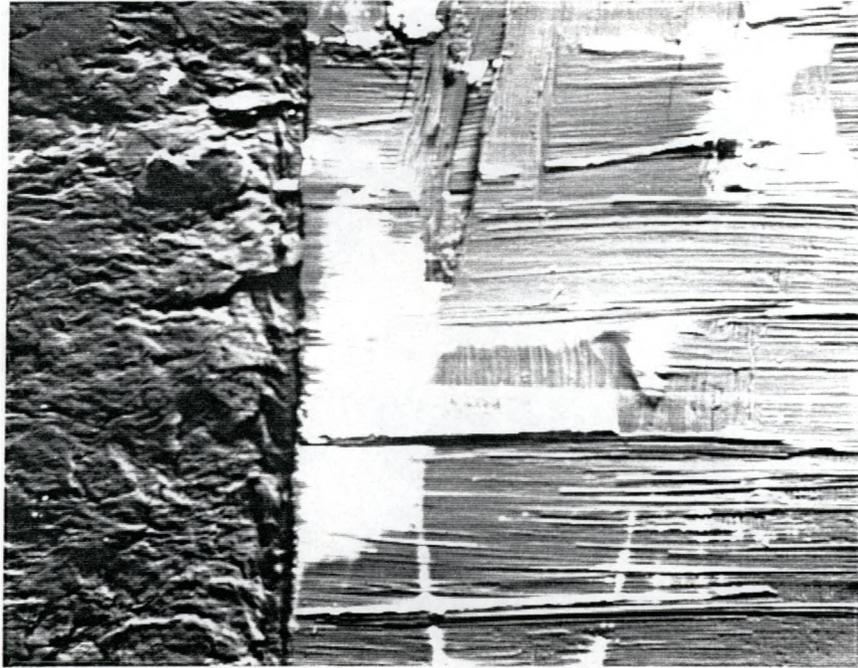


Teflon Insert/Panel A 2.3a(i)



Brass Insert/Panel A 2.3a(ii)

Figure 2.3 b



Graphite Insert/Panel A 2.3b(i)



Delamination Duct-C 2.3b(ii)

Results and Discussion

The electron micrographs made in this study revealed two modes by which a PMR-15/Carbon composite material laminate may fail. The micrographs were made from fracture surfaces of the inserted defects in test panel A of the panel Experiment (Section 2.1) and the fracture surface of the delaminated area of a PMR-15/Carbon engine duct (Duct C). It was discovered after the failure of the duct, that a piece of polyethylene may have been baked into the laminate. If this were the case, the polyethylene would have diffused into the laminate during an early stage of the cure cycle and contaminated the resin component of the composite material laminate.

If the fracture surfaces of specimen one, two and three are examined closely in figures 2.3a and 2.3b(i), a line down the middle of each can be noted. This line represents a division between the surface of one of the inserted materials in test panel A and the surface of an interlaminar region next to the defect. The surface of fig. 2.3a(i) reveals a rough surface contour over the area where the teflon insert was positioned and to the right of that is the interlaminar region where it appears that the resin and fibers both contributed to the failure of the laminate. The brass insert surface in fig. 2.3a(ii) does not resemble the teflon insert surface, it appears that this surface is smoother. A reason for this difference could be attributed to the cold flow properties of the teflon insert under the extreme compaction force within the autoclave during

the application of maximum pressure. To the right of the insert surface the interlaminar region appears to have fractured in a similar manner to that of fig. 2.3a(i).

In fig. 2.3b(i) the graphite insert surface shows a well defined three dimensional image which may be a result of the graphite's conductive properties. The division line between the insert surface and the interlaminar surface is clearly defined in this micrograph. The interlaminar surface greatly resembles the interlaminar surfaces picture in fig. 2.3a implying a similar mode of failure. The interlaminar surfaces of figures 2.3a and 2.3b(i) show a strong correlation to a fracture surface obtained in a similar study by Kwarteng, Dumbleton, and Stark (Reference 8). This study maintains that the fracture surface resembling that of the above mentioned figures was created by a combination failure of the resin and the fibers in a fiber reinforced composite material.

Another detail common to figures 2.3a and 2.3b(i) is the white areas covering approximately 30% of the interlaminar surface regions of each micrograph. One possible explanation for this is that these areas could be the result of an uneven distribution of the aluminum thin film covering the surface of the specimens. If this were the case, these areas would become charged by the electron beam and reveal no surface details. One other explanation could be that the electron beam was reflected from the surface at a critical angle in which there was total reflection of the beam energy into the SEM

detector.

Figure 2.1d is an electron micrograph of the fracture surface of a delaminated region from the above mentioned engine duct. The majority of the fracture surface appears to be well ordered, implying that the mode of failure is not a combined failure of both the fibers and the resin. A majority of the fibers are not distorted which suggests that the failure mode was attributed to the resin alone. In consideration of the above deductions, one can assume that poor interfacial bonding was achieved between the plies of the laminate because of the contaminated resin in the area of the delamination.

In conclusion, PMR-15/Carbon composite material laminates can be subject to at least two modes of failure. If the resin component of the material is uncontaminated, then the material will fail by means of both the fibers and the resin. This is explained by an equal loading of the matrix and the fibers when the laminate is under a sufficient stress to break the interfacial bond between plies (Figures 2.3a and 2.3b).

The second mode of failure can be attributed to an inconsistency in the chemical make up of the resin which prevents a high number of covalent bonds to form between the ply interfaces (Figure 2.3b(ii)).

CHAPTER 3

CONCLUSIONS

The processing behavior of PMR-15/Carbon is dependent on several parameters. These include the quality of the prepreg material, the precision in the design of the complete curing cycle, and the plumbing used to draw volatile products from the molded laminates. One can also conclude that the introduction of foreign materials to a laminate can have adverse effects on the mechanical properties of the laminate.

Several specific conclusions can be drawn from the experimental analysis in chapter two. These are (1) a laminate that is properly ventilated during autoclave curing will expel approximately 20% of its prepreg weight, (2) a laminate that is not properly ventilated during autoclave curing will lose approximately 18% of its prepreg weight, and (3) a PMR-15/Carbon laminate with an area of 216 square inches or less does not need a perforated resin barrier to become a fully consolidated laminate.

Conclusions from the fracture surface experiment in section 2.3 can be stated as follows; (1) The fracture mechanism of a pure PMR-15/Carbon laminate is a combination of the resin and the fibers and (2) a PMR-15/Carbon laminate with possible resin contamination will fracture by the resin alone.

The experimental chapter of this study (Chapter 2) also provided evidence that the entrapment of methanol and water vapor within a laminate may cause voids or delaminations to appear in the finished product. On this note, an entirely new study could be focused on this theory alone. Figure 3.1a is an illustration of an interlaminar void model for PMR-15/Carbon. Within the void of trapped methanol and water vapor, the arrows represent center of force vectors produced from the vapor pressure of the volatile contents at a given temperature. The purpose of this model is to suggest a method for a finite element analysis study. If the researcher knew the precise value for the vapor pressure of the volatile contents as a function of temperature, he could perhaps determine the minimum volume of methanol and water vapor needed to exceed the fracture strength of the laminate at some given temperature.

A full scale study of the complete curing cycle is also recommended to further optimize the quality of the PMR-15/Carbon components. The greater the precision in applying heat, vacuum and pressure in the autoclave, the better the quality of the components. Another aspect of a cure study would be to examine the effect of cooling rates on the material. It is conceivable that microcracking can be a result of rapid cooling rates imposed at the end of the autoclave and postcure portions of the processing scheme. Tooling materials must also be considered carefully to ensure low expansion differentials between the mold and the PMR-15/Carbon components.

In conclusion, processing-related defects can be the result of many

factors. If careful consideration is given to these factors, the number of components generated with defects can be minimized.

DELAMINATION MECHANISM MODEL
PMR-15/CARBON

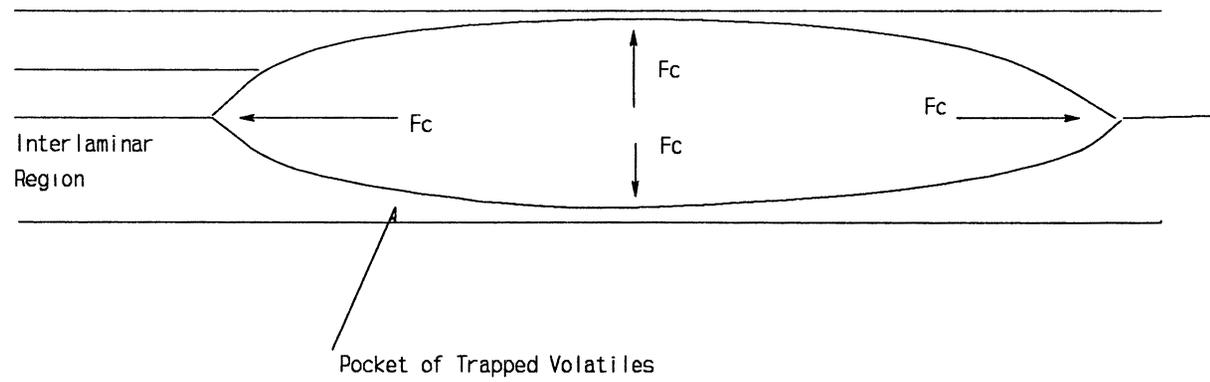


FIGURE 3 1 a

APPENDIX

Thermomechanical Analysis

Thermomechanical Analysis is an industry standard method for determining the glass transition temperature of a thermoset composite material. The procedure of this method is very simple and expends little time to carry out.

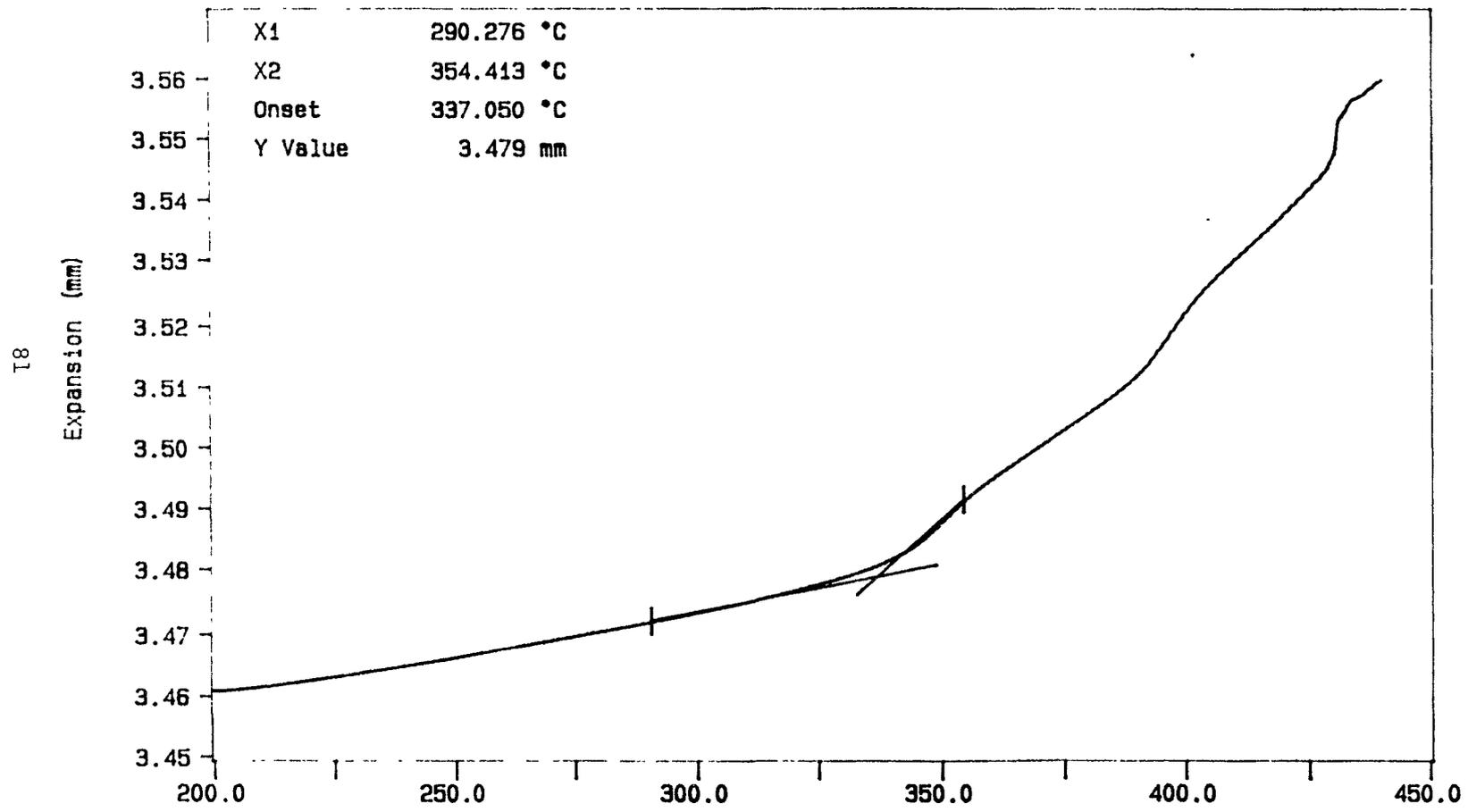
One simply takes several specimens of composite material in question and prepares them as follows. Each specimen is cut into a small square approximately 1 cm sq. in area by 0.25 cm in depth. The specimen is then mounted under a probe and the probe is lowered to contact the specimen. A force is programmed into the thermomechanical analyzer (5 mN) and a temperature span over which the specimen is allowed to heat. An oven door is then closed and the heating program begins. As the thermoset composite specimen begins to absorb heat, it expands first slowly and then more rapidly. This behavior is exemplified by PMR-15/Carbon in fig. A1 - A3.

The plots in figures A1 - A3 represent the expansion of the specimen on the ordinate vs. the temperature of the oven on the abscissa. In the region of lower temperature, the curve's slope is almost uniform and continues to exhibit this behavior until about 300 °C. At this temperature the slope of the curve

begins to rapidly increase and indicates that the material is beginning to break down. In other words, the material has reached its glass transition temperature.

In order to obtain the Tg of the material, one must draw tangent lines to the curve where it begins to increase rapidly on both sides. From the point at which the lines intersect, the computer will extrapolate the value of the material's Tg. An average value of the Tg for PMR-15/Carbon by these data is found to be 336.7 °C.

Curve 1: TMA in Expansion
File info: tc7p3bo195Fri Dec 14 10:51:58 1990
Sample Height: 0.000 mm

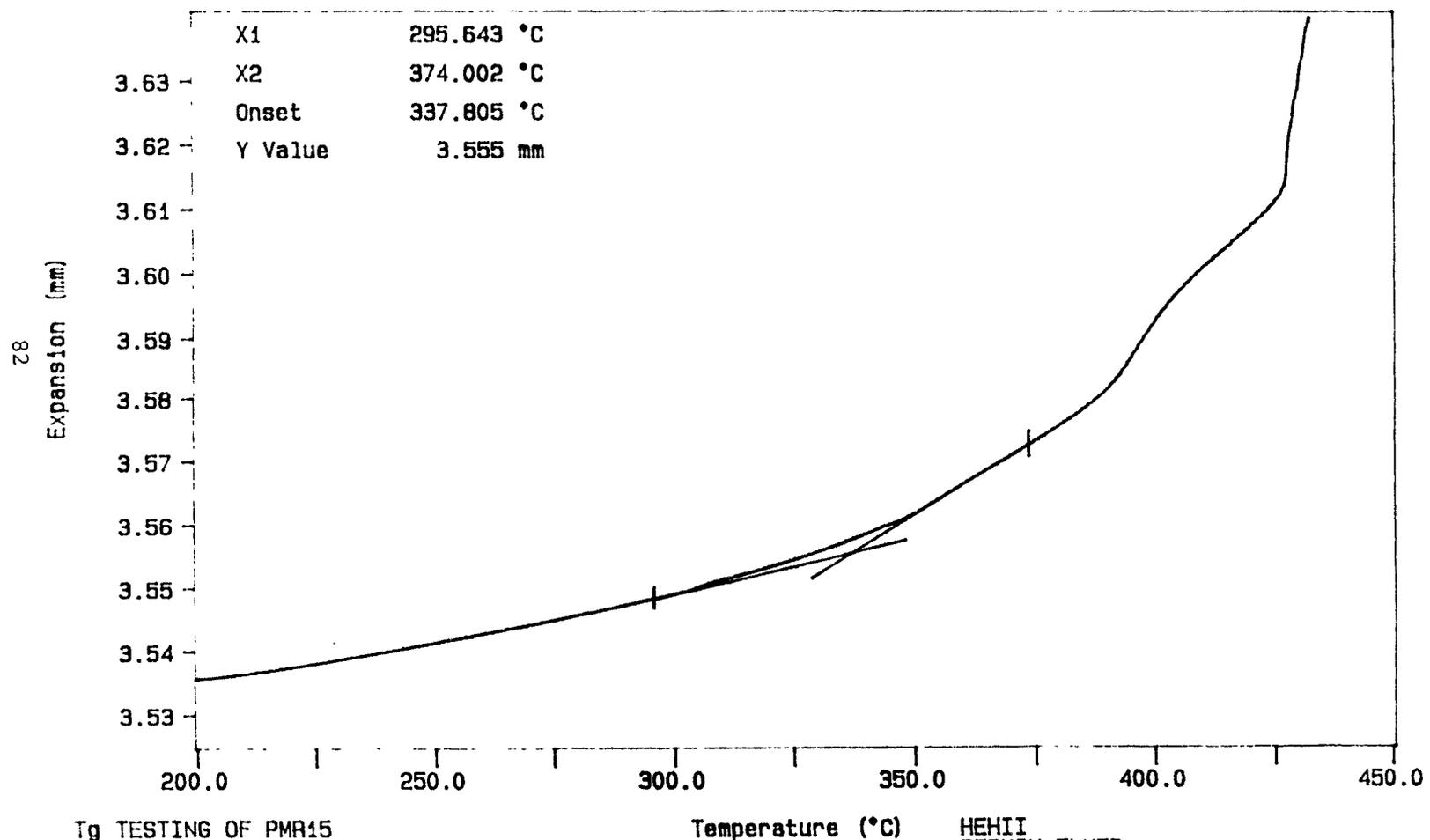


Tg TESTING OF PMR15
TEMP1: 200.0 C TIME1: 0.0 min RATE1: 20.0 C/min
TEMP2: 450.0 C

Temperature (°C)
HEHII
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Dec 14 11:17:41 1990

Figure A1

Curve 1: TMA in Expansion
File info: tc7uni195 Fri Dec 14 14:00:28 1990
Sample Height: 0.000 mm



Tg TESTING OF PMR15
TEMP1: 200.0 C TIME1: 0.0 min RATE1: 20.0 C/min
TEMP2: 450.0 C

HEHII
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Dec 14 14:03:32 1990

Figure A2

Curve 1: TMA in Expansion
File info: tc7p2bo195Fri Dec 14 14:24:46 1990
Sample Height: 0.000 mm

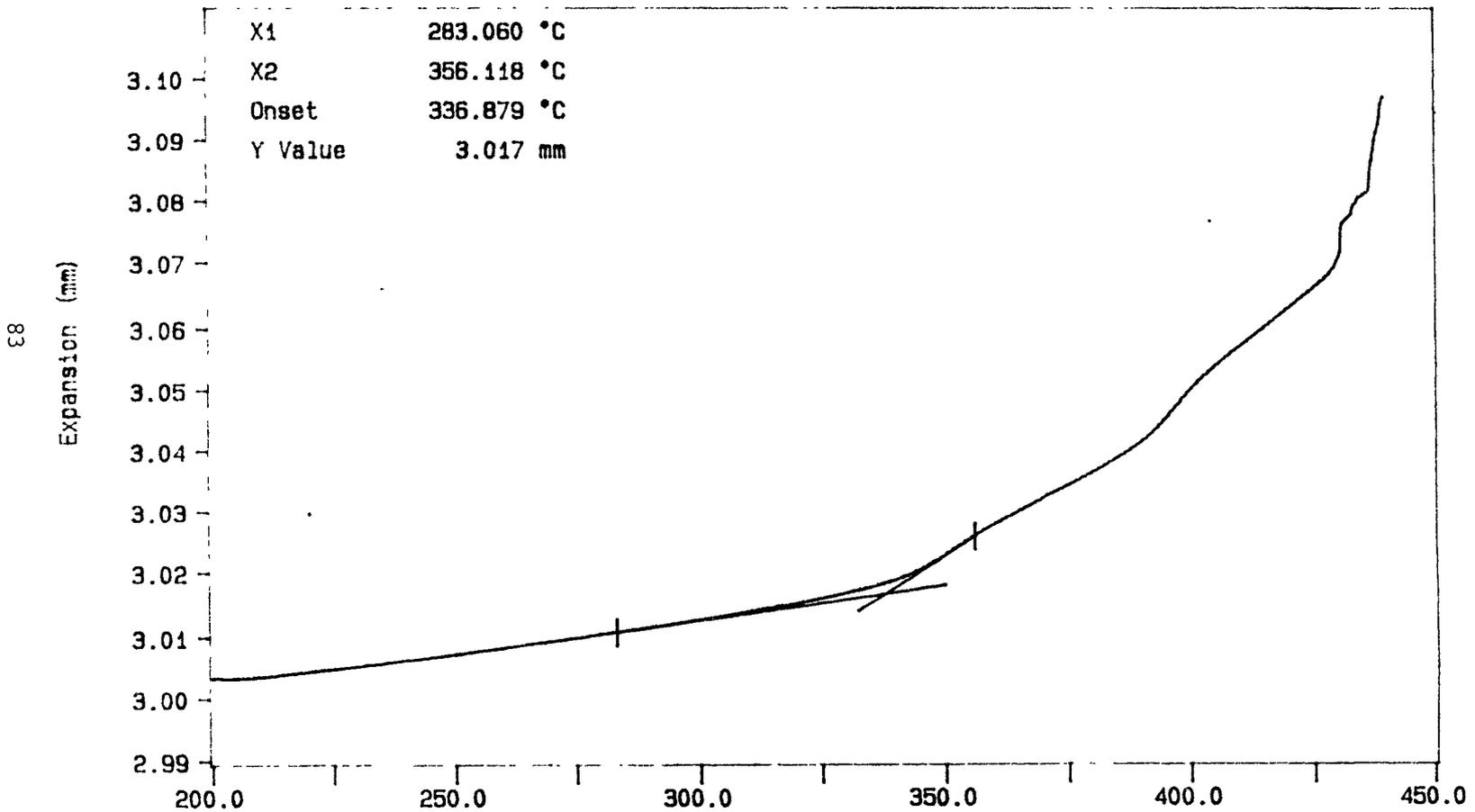


Figure A3

Tg TESTING OF PMR15
TEMP1: 200.0 C TIME1: 0.0 min RATE1: 20.0 C/min
TEMP2: 400.0 C

Temperature (°C)

HEII
PERKIN-ELMER
7 Series Thermal Analysis System
Fri Dec 14 14:28:58 1990

Reference List

- [1] M.J. Casate and E.M. Gilchrist, Black Magic, The Terminology of Advanced Composite Materials (Lear Fan Limited, 9/82)
- [2] P.K. Mallick, Fiber Reinforced Composites, Materials, Manufacturing and Design (Marcel Dekker, Inc., New York 1988)
- [3] M. Kantz, "Processing of PMR-15 Prepregs for High Temperature Composites," Ferro Corp. Composites Division, Los Angeles, CA 90016
- [4] N. Hadden, Basic Liquid Chromatography (Varian Aerograph, 1972)
- [5] R.D. Pratt and A.J. Wilson, "Fabrication Process of A High Temperature Polymer Matrix Engine Duct," NASA Conference Publication 2385, NLRC 3/16 - 3/18
- [6] W.F. Smith, Principles of Materials Science and Engineering (McGraw Hill Inc., 1986)
- [7] P. Honka, "Processing Parameters for Carbon/PMR-15 Composite Flat Panels," SAMPE Quarterly 23, 10/91
- [8] K. Kwarteng, J. Dumbleton and C. Stark, "Interlaminar Fracture Mechanisms In Graphite Thermoplastic Composites," SAMPE Quarterly 23 10/91