FACTORS AFFECTING THE FRACTURE ENERGY
OF A STRUCTURAL ADHESIVE

by

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I. INTRODUCTION

With the move toward lightweight structural materials such as polymers and polymer matrix composites, today's engineers are faced with the problem of designing methods of joining structural components without weakening or damaging the actual members. For example, it is impossible to use conventional penetration techniques without drastically affecting the strength of continuous fiber reinforced polymeric components. For this and similar reasons adhesives have become a desirable alternative. Even in cases where penetration methods are acceptable, adhesives are often used as an additional means of load transfer. Although adhesives seem to be the solution to the problem of joining polymeric materials, many disadvantages have become evident with their use. Assembly-line manufacturing procedures were found to be easily adaptive to adhesive bonding processes, but the industrial environment was also found to contain hard to control contaminants which can drastically reduce bond strength [1]. A desirable feature of adhesive bonding is the reduction or elimination of stress concentrations arising from penetration techniques, but here again, adhesives are found to contain inherent flaws or cracks which result in stress concentrations randomly distributed throughout the adherent. These flaws, which may be due to trapped air, contamination or chemical dissimilarities [2], act to reduce overall joint strength. It is felt that since adhesive strength is heavily influenced by the presence of flaws that fracture mechanics is the
best available tool for evaluation.

Fracture mechanics is the study of the strength of a structural member containing a crack. Although adhesives may not initially contain cracks, when subjected to loads their flaws may develop into cracks. Modern fracture mechanics began with the Griffith criterion for fracture based on equating the strain energy content with the energy to create new surface area at the instant of crack propagation. Thus, for a tensile loaded, edge notched bar [3],

$$\sigma_c = \left(\frac{2E\gamma}{\pi a}\right)^{1/2}$$  \hspace{1cm} (1)

where $\sigma_c$ is the stress at crack initiation, $a$ is the notch depth, $E$ is Young's modulus, and $\gamma$ is the surface fracture energy. Except for exceedingly brittle materials, experimentally determined values for $\gamma$ are orders of magnitude greater than can be accounted for by just the rupture of chemical bonds at the crack tip. Actually, crack initiation involves a number of energy consuming processes within the immediate vicinity of the crack tip including viscoelastic and plastic deformations. Irwin [4] demonstrated that the Griffith equation is formally correct if the surface energy term, redefined by Irwin as the strain energy release rate, $G_c$, is taken to include all the crack tip energy dissipative processes, so that

$$\sigma_c = \left(\frac{G_c E}{\pi a}\right)^{1/2}$$  \hspace{1cm} (2)

where $G_c$ is an index of fracture toughness and in the ideally brittle limit, $G_c = 2\gamma$. 
The fracture energy of isotropic solids is a function of the stress state so that it is necessary to define a strain energy release rate for each of the three principal modes of failure (Fig. 1): opening mode, $G_{IC}$; in-plane shear, $G_{IIIC}$; and torsional shear, $G_{IIC}$.

The quantity most often used to predict failure by crack growth is the stress intensity factor, $K$, a measure of the stress in the vicinity of a crack tip. For an isotropic material the general expression for $K$ is [3,5]

$$K = \alpha P(a)^{1/2}$$  \hspace{1cm} (3)

where $P$ is the applied load, $a$ is the flaw size, and $\alpha$ is a function determined by the stress conditions and the geometry of the structure. The strain energy release rate is related to $K_I$ by

$$G_I = \frac{\pi K_I^2}{1 - \nu^2}/E$$  \hspace{1cm} (4)

where $\nu$ is Poisson's ratio. Equation (4) is valid for the case of Mode I loading and plane strain conditions in an isotropic material. Thus, for a critical value of $G_{IC}$ there is a corresponding value of $K_{IC}$, where $K_{IC}$ is the fracture toughness.

In order to predict the failure stress, $\sigma_C$, the explicit form of Eq. (3) must be determined, $K_C$ must be measured experimentally and the size of the most severe flaw must be known [6,7]. This field of fracture mechanics is devoted to developing stress analyses and the test methodology for fracture toughness determination and flaw detection.
Figure 1  Failure modes
The application of fracture mechanics to adhesive joint design is complicated by the fact that the explicit form of Eq. (3) is generally not known. The problem is that solutions require analyses for the stress distribution at the crack tip and until recently such analyses have not been available for a flaw in an adhesive layer. Very recently, Wang, Mandell, and McGarry [8] developed a stress analysis for a crack in an adhesive layer and found a marked deviation from the classical, linear elastic crack length dependence, i.e., Eq. (3). They note that this analysis indicated the strict use of linear elastic fracture mechanics for joint design is not practical.

The problem can be approached in an alternate, less precise way, if the design analysis is based on the strain energy release rate, $G_C$, rather than the stress intensity factor, $K_C$. The general expression for $G_C$ is given by [6,7,9]

$$G_C = \frac{P^2}{2B} \frac{\partial C}{\partial a}$$

(5)

where $B$ is the material thickness in the vicinity of the crack and $\frac{\partial C}{\partial a}$ is the change in compliance, $C$, of the structure with crack length, $a$. Since $\partial C/\partial a$ is a global property of the specimen, Eq. (5) is independent of the crack tip stress distribution. For simple geometries, analytical solutions exist for Eq. (5).

The explicit form of Eq. (5) for a double cantilever beam is [3,5,9-11]

$$G_{IC} = \frac{4P}{B^2E} \left[ \frac{3a^2}{h^3} + \frac{1}{h} \right]$$

(6)
where $E$ is the elastic modulus of the adherend, $a$ is the crack length, and $h$ is the height of the beam measured normal to the crack tip. However, if the beams are tapered and the bracketed term is constant, then $G_{IC}$ is independent of crack length,

$$G_{IC} = \frac{4P^2}{BC} \text{m}$$

(7)

and only $P_C$ need be measured. This is the case for the tapered double cantilever beam (TDCB) fracture toughness specimen.

In this study the TDCB specimen will be used to calculate the fracture energy of Metlbond 1113-2, a 100% solid modified epoxy film adhesive [12].

The objectives of this investigation are many faceted. Some of the more popular test methods [2,3,5,9-11,13-23] are presented to better acquaint the reader with some of the contemporary methods of testing for fracture strength and fracture toughness. A particular test method is critical in determining desired adhesive material properties. Knowing a test method, one must then understand the limitations of the mathematical model accompanying a specimen. The derivation of Eq. (7) is, therefore, presented [2-4,6,24] with the assumptions and limitations of its use. At this point the adhesive joint should be considered.

The study of adhesive joints can be broken up into three areas: the mechanical and chemical conditioning and the properties of the adherend, the change in properties through the thickness and wettability of the adhesive, and the many factors affecting bond
strength at the interfacial region [1]. Another objective is, therefore, to present the processes of mechanical and chemical adhesion in a detailed discussion including many of the factors affecting bond strength. It has been found that seemingly inconsequential changes in adherend preparation processes and the adherent cure cycle can cause drastic changes in joint strength [1,25]. An investigation of the test preparation factors affecting joint strength for Metlbond 1113-2 was felt to be in order to better define the total test method. Until all factors contributing to a condition of varied strength between specimens for identical test conditions can be eliminated, characteristics like rate and time dependence will be masked by scatter. Once the quality of the joint can be controlled, an investigation of the rate and time dependence of Metlbond 1113-2 should be conducted. Bulk tensile tests [26,27] showed that Metlbond 1113-2 exhibited viscoelastic properties. The intent of this investigation was to determine if the rate dependence showed up over a limited range of rates and if the time dependence could be illustrated with the TDCB specimen.

The final objective was to use a scanning electron microscope (SEM) to perform a fractographic investigation of the fractured surfaces in an attempt to define the mechanisms of failure.
II. SOME STANDARD TESTS FOR EVALUATING ADHESIVE STRENGTH AND MODULUS AND FRACTURE ENERGY

The purpose of this chapter is to acquaint the reader with some of the various adhesive test methods. Basically two types of tests exist, strength and modulus tests and fracture energy tests. The first portion of this chapter is dedicated to briefly describing some of the available tests for determining strength and modulus. The last portion will explain the difference between strength/modulus testing and fracture testing before describing various fracture toughness tests.

Strength and Modulus Tests

Three basic types of strength tests are currently used: tensile tests, shear tests and peel tests. A strength test is one in which a stress-strain response is recorded and a corresponding modulus, ultimate stress and ultimate strain is obtained. Also located in each of the three groups are tests which have been adapted as fracture tests. The mixed-mode fracture test is a type of tensile test, the single lap shear test has evolved into a fracture test, and the peel tests are also fracture tests [2,3,9,13-20]. So it should be understood that one test method may be used for both strength and fracture testing.
Tensile Tests

Tensile tests are among the most common tests for evaluating adhesives. This is despite the fact that experienced engineers, whenever possible, avoid designing adhesive joints so they will be loaded in Mode I [9]. Some of the more common tensile tests are the pi test, bar and rod tests, sandwich tests and the cross-lap test (Fig. 2).

The pi, bar and rod, and sandwich test are all very similar. The pi test specimen is made up of two round rigid adherends bonded together and loaded in tension by means of two U-shaped grips which fit over the annular boss at each end. The bar and rod test, consisting of either a square or round shaft respectively, are simply bonded together and loaded in tension by way of pins through a hole in each end of the specimen. The sandwich test is identical to the pi test except that instead of bonding the rigid adherends together a second adherend is bonded between the two end tab adherends. This second adherend is usually a glass or polymer not easily adaptable to other test methods. Obviously, the material used for the end tabs must develop greater bond tensile strength with the adhesive than that developed between the adhesive and the film. All four of these tests simply require two flat surfaces to be bonded together and loaded in tension.

The last tensile test worthy of noting is the cross-lap test. This specimen was developed to test planar materials such as glass or wood, but has also been adopted for the study of sandwich and honeycomb materials. Rectangular specimens are cut from the material
Figure 2  Tensile tests
to be tested, and the two halves are bonded and loaded as shown in Fig. 2 [9,13,14].

In all of these tensile tests the only desired data is the stress-strain relationship.

Shear Tests

Shear tests are very common because samples are simple to construct and closely duplicate the geometry and service conditions for many structural adhesives. Four types of tests will be discussed here: the single, double, and symmetric lap shear, and the torsional shear stress specimen (Fig. 3).

The stress field of the three lap shear specimens is much more complicated than is indicated by the apparent Mode II tensile loading scheme. All of the tests exhibit much higher stresses at the ends of the bonded overlap than the average stress. The single lap specimen is further complicated by the presence of tensile forces in the adhesive layer due to eccentric loading conditions. Bending forces also exist for the double and symmetric lap shear specimens, but only at high stress levels. Even though the state of stress is complicated, due to the work that has been conducted on establishing clear analyses, the shear strength and shear modulus can be readily calculated from stress-strain data [2,9,13,20].

The last shear test to be mentioned is the torsional shear stress specimen. This test, as is indicated by its name, is used to determine shear strength and modulus by torsional loading. With proper sample construction and alignment, the adhesive is subjected
a. Single lap test

b. Double lap test

c. Symmetric test

d. Torsional test

Figure 3 Shear tests
to a more homogeneous stress distribution in this configuration than
with the lap shear specimens. The shear stress $\tau$ is given
approximately by the expression

$$\tau = \frac{Tr}{J}$$

(8)

where $T$ is the applied torque, $r$ is the radius to a point, and $J$ is
the polar moment of inertia of the adhesive cross section.

**Peel Tests**

Peel tests (Fig. 4) have been used for years to compare relative
strengths of adhesives and effects of surface preparations.
These comparisons are normally made by applying a constant rate
loading to the specimen and recording the applied force vs. time.
An average force (or force per unit width), after the specimen has
reached a maximum load, is reported as the peel strength [9,13,19].

The use of peel strength data in structural integrity analysis
is not straightforward. Using some function of the peel stresses
or strains as a failure criterion is not feasible since both the
stresses and strains predicted by linear elastic analyses become
unbounded as the debond line is approached. Therefore, as first
mentioned, peel tests are best suited for relatively ranking adhesive
strengths and comparing various surface preparation techniques
[9,13,19,21].

**Fracture Energy Tests**

As mentioned earlier, the strength of an adhesive is based on
the maximum load or the maximum load per area or width.
Figure 4  Peel test
Fracture energy is the measure of the energy required to propagate a crack. In strength tests all that is required is the stress-strain relationship. In fracture energy tests all the mechanisms of energy consumption, such as viscoelastic and plastic deformations, must be considered in addition to the load and deflections. Fracture tests give a quantity which relates the energy required to debond or fracture a material.

Many types of fracture energy test have been developed. In this study only the more popular tests will be discussed. The mixed-mode, single lap shear, peel, cone, blister, and cantilever beam fracture energy tests will be presented here.

**Mixed-Mode Fracture Energy Test**

The mixed-mode test specimen is illustrated in Fig. 5. It is well known that the fracture energy for an isotropic material is lowest in a plane normal to the applied load; in other words, a crack will propagate normal to the applied load. In the case of bonded joints a crack cannot always propagate normal to the applied load but must follow the bond line. Therefore, studies must be conducted to find the effects of combined Mode I and Mode II failures. The mixed-mode test was developed to determine the strain energy release rate for both the opening and in-plane shear modes, \( G_{IC} \) and \( G_{IIC} \) respectively [3,5,15-18].

**Single Lap Shear Fracture Energy Test**

As mentioned earlier (Fig. 2) the single lap shear test is one of the most common tests due to its simplicity, and close
Figure 5 Mixed mode test
duplication of actual service conditions. Recently an attempt has been made to make a fracture mechanics analysis of the lap shear joint [20].

Detailed analyses [2,9,13,20] have been conducted to calculate the stresses in the joint and to introduce them into an energy balance to determine the initiation of adhesive fracture. The first step of the process is to evaluate the total strain energy stored in the joint, $U$. Having obtained $U$, it is now possible to apply the Griffith-Irwin energy balance for elastic systems,

$$\frac{\partial U}{\partial a} = \gamma_a$$

(9)

where $\gamma_a$ is the energy required to create a unit area of new fracture surface due to the total extension of the crack over a length $a$.

**Peel Fracture Energy Test**

Theoretically, the peel specimen (Fig. 4) is a very versatile specimen for obtaining adhesive fracture energy, since various combinations of Mode I and Mode II loadings can be applied by varying the peel angle. One of the difficulties in using this specimen has been in providing accurate stress or energy values as required to convert critical load to adhesive fracture energy. A second problem area is in determining the critical load at which debond occurs.

There are particular cases for which energy release rate analysis of peel specimens can be computed analytically. But, in each case many simplifying assumptions must be made. The change in stored energy is then calculated by subtracting the stored energy in
the zero curvature portion prior to debond from the stored energy in the same portion after debond. The work is calculated by the change in displacement of the load and is a function of the angle of applied load.

**Cone Fracture Energy Tests**

One test method which has provided great insight into adhesive fracture processes is the cone test (Fig. 6) [19]. For most adhesive test specimens presently in use, flat surfaces are bonded together. However, in many practical applications, such as bonding fibers in a matrix or crowns to teeth, the mating surfaces are curvilinear. In addition, many of the adhesive applications that involve Mode III loading have axisymmetric geometries. Cone tests can be designed and tested to have various amounts of the three classical loading modes. For example, a cylinder (0° cone) pulled from a matrix or cylindrical hole is mostly a Mode II loading; a Mode I failure is obtained from a tensile loading of a button test (90° cone) with a central flaw; a button test with an initial circumferential debond at the outer bond radius loaded in torsion produces nearly a pure Mode III loading [9,19].

An initial intentional debond simulates a flaw or crack in the bond. Calculating the energy stored at various cone angles can model any possible combination of the three modes of failure fracture energy.
Blister Fracture Energy Test

The blister test (Fig. 7) is an outgrowth and modification of earlier methods proposed by Dannenberg [23] and Maryshev and Salganik [13]. In its simplest form, it consists of a disk or plate which has been bonded to a rigid material, except for a central portion of radius a. When the unbonded region is pressurized, as by the injection of a compressed fluid, the plate lifts off the substrate and forms a blister whose radius stays fixed until a critical pressure, $p_{CR}$, is reached. At this value the radius of the blister increases, signifying adhesive failure along the interface.

The elastic strain energy stored in the disk can be calculated from the input work. Utilizing the energy balance concept, one then equates the energy decrement to the change in adhesive fracture energy. In principle, any thickness or diameter of disk and any debond radius smaller than the disk radius can be used. However, analytical, closed-form engineering solutions for the displacement are currently available only for the near limit cases of a disk using plate theory and the infinite medium, penny-shaped flaw configuration [9,13,19,21-23].

Cantilever Beam Fracture Energy Tests

There are three types of cantilever beam tests, the single cantilever beam, the double cantilever beam, and the tapered double cantilever beam (TDCB) fracture energy tests (Fig. 8). From the standpoint of simplicity both in analysis and from the experimental point of view, there are certain advantages to the TDCB specimen.
Figure 8  Cantilever beam tests

a. Single cantilever beam

b. Double CB

SPACING SHIMS (optional)

P

ADHESIVE

C. TDCB

CRACK LENGTH

7 DEG.
This specimen is contoured in such a way that the energy release rate, $G_{IC}$, is a function of load only, independent of the crack length [2,3,5,9-11,16,18,21]. As discussed in Chapter I, this constant compliance specimen will be used as the fracture energy specimen in this investigation of Metlbond 1113-2.
III. ANALYTICAL METHODOLOGY FOR THE TDCB

The Strain Energy Release Rate

As was previously mentioned in Chapter I, the strain energy release rate is a measure of fracture energy. Two slightly different derivations of the strain energy release rate will be presented for the TDCB. First, however, it will be shown that the work required to extend a crack by a unit area, which is the fracture toughness, is equivalent to the strain energy released by a specimen [2].

Consider a cracked plate of unit thickness (Fig. 9). The plate is then loaded in a fashion described by Fig. 10a, where \( P \) is the applied load and \( L \) is the load deflection. The stored elastic energy, \( W_1 \), related in Fig. 10b, is the area under branch AB of Fig. 10a. The relation between load and deflection for this specimen can be written as

\[
P = ML
\]

or

\[
L = \frac{P}{M}
\]

(10)

where \( M \) is the specimen stiffness. If the response of the specimen is linear elastic over the load range, \( M \) will remain constant. If the specimen response is nonlinear elastic over the load range, \( M \) will change in value. Assuming a linear elastic response, if the load is removed the specimen will return to its original undeformed shape.
Figure 9 Edge cracked plate
Figure 10  Plot of the loading cycle and the work performed in advancing a crack.
Now consider a crack extension as described by branch BC in Fig. 10a. The dimensions of the specimen are controlled so that the load deflection, $L_f$, remains constant. This fixed grip crack extension process will be conducted in such a way the load relaxation represents a release of stored elastic energy equal to $W_2$ (Fig. 10c).

This change affects the parameters of Eq. (10). The load level drops from $P_f$ to $P_e$ while the extension remains constant at $L_f = L_e$. Therefore, the stiffness must decrease from $M$ to $M_e$ due to the reduction in the number of structural elements. This process of elastic crack extension is defined as the progressive rupture of structural elements at the crack tip.

The load is then removed as described by branch CA in Fig. 10a. It should be observed that all the strain is recovered when the load is removed. The area under the branch CA in Fig. 10a is equal to the stored elastic strain energy, $W_3$, illustrated in Fig. 10d.

Through the entire cycle, the unrecovered work, $W_1 - W_3$, is equal to the strain energy released. Thus, the work required for crack extension is equivalent to the strain energy released. The same relation can be developed for a fixed load condition as was demonstrated by Irwin [4].

It should be noted that the stress relaxation in step BC might have been accomplished by processes involving flow, either plastic and/or viscoelastic. This process is much different than the rupture process. If any flow occurs the fundamental basis for linear elastic fracture mechanics is violated. Assuming now that the branch BC of Fig. 10a was accomplished by processes involving flow, where
the remaining load is removed, the relaxation will be less than the original elongation. A permanent set will result with internal stresses. An illustration of this is shown in Fig. 10e, a case for which LEFM would be violated.

It has been stated that for a given stress relaxation load drop in the fixed grip case, or for a given strain relaxation in the fixed load case, the strain energy released by flow processes is much greater than for rupture processes [2]. Thus, plastic deformations obscure desired results. The criterion for the validity of an experimental fracture toughness determination is that no appreciable permanent deformations take place during the test. The much discussed requirement that crack tip radius must meet certain maximum specifications is based on the experience that if the radius exceeds a certain amount (usually experimentally determined), permanent deformation will be excessive [2].

The basis of the derivation for the strain energy release rate, \( G_c \), is the work needed to change the crack area by a unit amount, which may be expressed as the work needed to extend a crack by a unit amount if the crack area is a function only of the crack length.

An expression for \( G_{IC} \) will be reached first by considering a fixed grip condition [2,6], then by considering a moving grip condition [6,7].

The two relations for the deformation and work of deformation as given by Eq. (2) and (3) do not explicitly involve crack dimensions. Differentiating both equations with respect to the crack area, \( A \), will give dimensions suitable for \( G_{IC} \). The starting equations are:
\[ L = \frac{P}{M} \]  
(10)

and

\[ W_s = -\frac{1}{2} PL \]  
(11)

where \( W_s \) is the energy stored due to the work of elastic deformation. After differentiating and dropping the terms involving \( dL/dA \), due to the fixed grip condition, the following equations are obtained.

\[ \frac{dP}{dA} = -PM\frac{\partial \{1\}}{\partial A} \]  
(12)

\[ \frac{dW_s}{dA} = -\frac{1}{2} L \frac{dP}{dA} \]  
(13)

Substituting (10) and (12) into (13) results in,

\[ \frac{dW_s}{dA} = \frac{1}{2} P^2 M \frac{\partial \{1\}}{\partial A} \]  
(14)

The term \( \frac{dW_s}{dA} \) is the change in elastic energy per unit change in crack area, therefore, \( \frac{dW_s}{dA} = G_{IC} \). The change in crack area, \( dA \), is equal to the change in crack length, \( da \), times the plate thickness, \( B \), or \( dA = B da \). Therefore,

\[ G_C = \frac{P^2}{2B} \frac{\partial C}{\partial a} \]  
(15)

where \( C \) is the compliance which is defined as the reciprocal of the stiffness \( M \). Given \( G_{IC} \), the only unknown term in Eq. (15) is the change in compliance per unit change in crack length.

Now consider the condition of the grips being free to move when a load \( P \) is applied. For a plate of unit thickness the condition for crack growth is:
where 

\[ U = \text{stored elastic energy in the plate} \]
\[ F = \text{work performed by external forces} \]
\[ W = \text{energy for crack formation.} \]

The crack extension force or strain energy release rate is

\[ G_c = \frac{d(F - U)}{da} \quad \text{(16)} \]

Now consider a cracked plate of thickness \( B \) and load \( P \), Fig. 9. When the plate is loaded the load-application points deflect by an amount \( \delta \). When the crack increases in size by an amount \( da \) the displacement increases by \( d\delta \). Therefore, the work done by external force is \( Pd\delta \). It follows that:

\[ G_c = \frac{d(F - U)}{da} = \frac{1}{B} \left( Pd\delta/da - dU_{T}/da \right) \quad \text{(17)} \]

where \( B \) is the plate thickness (Note: Eq. (16) is for a plate of unit thickness) and \( U_{T} \) is the total elastic energy in a plate of thickness \( B \). As long as no crack growth occurs, the displacement \( \delta \) is proportional to the load:

\[ \delta = CP \quad \text{(18)} \]

where \( C \) is the compliance. The elastic energy then becomes
U_T = \frac{1}{2} P \delta = \frac{1}{2} P^2 C \tag{19}

Substituting Eqs. (18) and (19) into (17),

\[
G_C = \frac{1}{B} \left[ P \frac{\partial (CP)}{\partial a} - 3(\frac{1}{2} P^2 C) \right] \tag{18}
\]

\[
G_C = \frac{1}{B} \left[ P^2 \frac{\partial C}{\partial a} + CP \frac{\partial P}{\partial a} - \frac{1}{2} P^2 \frac{\partial C}{\partial a} - PC \frac{\partial P}{\partial a} \right]
\]

\[
G_C = \frac{P^2}{2B} \frac{\partial C}{\partial a} \tag{20}
\]

results in an expression for $G_C$ identical to Eq. (15). Now consider the specific geometry of the DCB specimen.

The compliance of a material is equal to the displacement that occurs per unit load,

\[
C = \frac{\delta}{P} \tag{21}
\]

Therefore, the deflection is the quantity that must be determined. For a DCB (Fig. 11) the displacement $\delta$ is [24],

\[
\delta = \frac{8Pa}{Eh^3B} + \frac{8Pa}{EhB} \tag{22}
\]

Therefore, the compliance is,

\[
C = \frac{8a^3}{Eh^3B} + \frac{8a}{EhB} \tag{23}
\]

Thus, the strain energy release rate is,

\[
G_{IC} = \frac{P^2}{2B} \frac{C}{a} = \frac{12P^2a^2}{Eh^3B^2} + \frac{4P^2}{EhB^2}
\]
The modulus of the adherend, thickness, and height: $E$, $B$, and $h$ respectively, are constant for a monolithic DCB of constant thickness $B$. In order to calculate $G_{IC}$ the only data needed are the crack length and load level at incipient fracture. Those data are not easily acquired, however, due to the fact that the crack tip is hard to accurately locate. This problem can be avoided through the proper consideration of the quantity $(3a^2/h^3 + 1/h)$. By setting this quantity equal to a constant, $G_{IC}$ would be independent of the crack length $a$. The geometry associated with making $G_{IC}$ constant for the double cantilever beam gives rise to the TDCB specimen. The height, $h$, of the beam is often machined to give the quantity $(3a^2/h^3 + 1/h)$ a value of 90 in$^{-1}$ (Fig. 12) [11]. The strain energy release rate may now be written as

$$G_{IC} = \frac{4P_C^2}{EB^2} \left( \frac{3a^2}{h^3} + \frac{1}{h} \right)$$

(24)

It should be realized that many $P_C$ data points are obtained from each constant cross head rate test. As the load is increased to $P_C$ the crack will propagate but will arrest when the load is dropped. As the cross head continues its travel the load will again increase to $P_C$. Crack growth will occur until the load relaxes. The process will continue for the length of the specimen.
Refer to 6-32 NC 0.3125 in.

ADHESION LIMITS

ADHESIVE LAYER

CRACK LENGTH

START OF CONTOUR

END OF CONTOUR

\( m = \left[ \frac{3a^2}{2h^3 + h} \right] = 90 \text{ in.}^{-1} \)

Refer to Figure 12 TDCB Specimen
IV. MECHANICAL AND CHEMICAL ADHESION

Bascom and Patrick [1] discuss the topic of mechanical and chemical adhesion in both an inclusive and compact manner. They divide the subject matter into three categories: the surface properties of the adherend, the surface behavior of the adhesive, and the properties of the adhesive/adherend interface. The succeeding discussion is organized accordingly and will be limited to the adhesion of polymer adhesives to metals.

Surface Properties of the Adherend

The surface properties of the metal adherend is the subject which requires the most extensive investigation in the search for the ideal bond. Many things must be considered in selecting and preparing a metal. The kinds and extent of oxide films that form must be known in determining surface characteristics. The mechanical and/or chemical treatments are pertinent to the mechanical properties of the base metal at its surface. The roughness of the metals surface must be considered in understanding how the adhesive will spread. Further, a surface analysis should be conducted to establish such things as the composition, structure, chemical bonding of surface molecules and atoms, and the surface tension of the metal. Each of these items will now be discussed in greater detail.

To properly understand oxide films there are two main properties of the films which should be known, the crystalline structure of the film and its degree of hydration. Abundant information exists on the
growth and chemical formation of metal oxide films. Contained in oxide films are physically and chemically adsorbed water and various contaminants including inorganic salts and organic materials. The inorganic salt contaminants, because they are usually hydroscopic, may lead to the adsorption of many monolayers of water even if the salts are present in trace amounts \((10^{-7} \text{ gm./cm}^2)\). This adsorbed water may interfere with the spreading of liquid adhesives. What is more serious, however, is that water adsorbed by hydroscopic contamination can collect as microdroplets of salt solutions and be strongly alkaline, thus capable of attacking the metal chemically. As for the adsorbed organic materials, which are so hard to control in industrial atmospheres, they may adversely effect the wettability of the adherend. If they exist as more than one molecular layer they may act as a weak boundary.

Mechanical treatments are known to cause various changes in the mechanical properties at the surface of metals. One example of this is machining. Machining a metal causes considerable surface strain. A permanent strain may exist to a considerable depth and may be on the order of 5% to 10% at the surface. This situation is worsened for polished or burnished surfaces. Invariably, any cutting, working or rolling of the metal leaves it in some state of strain. This strained region may be cohesively weak and cause poor bond strength. More importantly, the strain energy at the surface adds to the susceptibility to corrosive attack by moisture and so contributes to moisture induced bond failure.
Chemical treatments are also known to cause major changes in mechanical properties. Usually as-received metals are subjected to a sequence of treatments beginning with washes to remove gross contaminants followed by chemical etches and a water rinse. These treatments have been found to be very important because they remove organic contamination, loose oxides, and some of the strained surface layer. Seemingly inconsequential changes in treatment procedures often result in weak bonds or unusual susceptibility to moisture. One reported example [1] cites that after using acid-chromate etch on aluminum, the final rinse must be made with tap water rather than deionized water. This is because the deionized water leaves a thick weak hydrous aluminum oxide, bayerite, on the surface, whereas, the tap water leaves a thin cohesively strong monohydrate.

In addition to surface cleaning and etching, the metal may receive further treatment to convert the surface to a corrosion resistant nonreactive form. Examples are phosphate steels and anodized aluminums. Bonding to surfaces of these materials has presented problems, some of which were discussed at a 1968 symposium on polymeric coatings. Another method of corrosion protection is by clading an alloy with a more anodic metal. However, bonds to clad surfaces can be more susceptible to moisture than the bonds to unclad metal surfaces.

The roughness of the metal surface is an important parameter in the spreading of liquid adhesives. The scratches in the surface will help in moving the adhesive because of the capillary pressure, due to the radius of curvature of the scratches, "pumping" the
liquid along. Therefore, spreading can occur much faster on a
scratched surface than on a perfectly smooth one. It should be kept
in mind that on surfaces such as milled surfaces the pumping process
may have a preferential spreading direction. In actual practice,
however, adhesive resins are forcibly spread onto adherends at rates
that greatly outrun any capillary spreading phenomena. In the case
of semi-solid film adhesives, as they are heated during the cure
cycle, this capillary action may aid in the thorough spreading of the
adhesive.

In recent years extremely sensitive methods of surface analyses
have been developed which, combined with the more classical methods
of surface examination, make it possible to fully characterize an
adherend surface. Most of these techniques are based on radiation
or particle scattering. In Table 1 the analytical methods are listed
according to the type of information generated. A solid surface
can be fully characterized from its gross roughness down to its
elemental surface composition.

The flow of an adhesive liquid onto the adherend surface is
a wetting-spreading phenomena. There exists a fundamental relation
between the contact angle, $\theta$, and the thermodynamic work of
adhesion, $W_A$,

$$W_A = \gamma(1 - \cos \theta)$$  \hspace{1cm} (26)

where $\gamma$ is the surface tension of the liquid adhesive and $\theta$ is the
contact angle the liquid makes with the solid. Finally, wettability
measurements can give direct information about the molecular
<table>
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<tr>
<th>Method</th>
<th>Description</th>
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<td><strong>Macrostructure</strong></td>
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<td>Surface topography</td>
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<td>Friction measurements</td>
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<td>Ellipsometry</td>
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<td><strong>Molecular Composition and Structure</strong></td>
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<td>Multiple interference reflection spectroscopy</td>
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<td>Raman spectroscopy</td>
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<td>Ellipsometry</td>
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<td>Contact angle measurements</td>
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<td>Surface potential measurements</td>
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<td><strong>Crystal Structure</strong></td>
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<td>X-ray diffraction</td>
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<td>Low energy electron diffraction, LEED</td>
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<td>Reflected high energy electron diffraction, RHEED</td>
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<td><strong>Elemental Composition</strong></td>
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<td>Photoemission spectroscopy</td>
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<td>Appearance potential spectroscopy</td>
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structure of organic and inorganic surfaces. The contact angle is a function of both the adhesive and adherend surface tensions. In order for the contact angle to be zero, the ideal spreading condition, the surface tension of the adherend must be greater than that of the adhesive.

The critical surface tension of a metal or metal oxide surface is reported to be on the order of hundreds of dynes/cm \([1]\). Organic polymers have surface tensions of 50 dynes/cm or less. Consequently, it would be expected that all polymer liquids would exhibit zero contact angles on metals. However, it should be noted that contamination by organic materials or an adsorbed water film can reduce the surface tension of metals to values less than 50 dynes/cm creating a nonspreading condition.

**Surface Behavior of the Adhesive**

The general statement is frequently made that the adhesive must "wet" the adherend. What is meant is that in bringing the adhesive and adherend together no air is trapped at the interface. Ideally three criteria must be met. The resin liquid should exhibit a zero or near zero contact angle, sometime during the bonding process the resin viscosity should be no more than a few centipoise, and the rate and manner at which the adhesive and adherend are brought together should give the resin time to displace the air.

The spreading criterion is usually met for the case of an organic liquid polymer on a dry metal oxide free of organic contaminants. Even if the contact angle is zero, surface tension
gradients may exist at the spreading front (due to thermal or concentrated gradients) which may help or hinder spreading depending on their direction. Here again though, these effects will be overshadowed by the much faster forced flow of the adhesive during fabrication. However, the gradient forces and capillary forces may play a role in the redistribution of the adhesive after the initial application.

The second criterion that the adhesive have a viscosity of only a few centipoise is seldom met in practice. Consequently, if the liquid adhesive is forced rapidly over the adherend, the liquid at the surface cannot keep up with the advancing front so an apparent dynamic contact angle develops. With the typical spreading velocity of 10 cm/sec and a surface tension of 30 dynes/cm a dynamic contact angle of 90° has been observed for most viscosity ranges [1].

In view of this high advancing angle, it is very probable that air is trapped, especially in surface scratches and pores. What happens to this air is unknown, but if it is assumed the air is trapped as a thin air film, capillary forces will tend to gather it up into spherical shapes. This retraction is a liquid/air displacement process and is subject to effects of roughness and surface tension gradients on spreading. The importance of these viscous and capillary effects is most evident in bonding with commercial structural adhesive films, such as Metlbond 113-2.

Structural adhesives are often supplied as semi-solid resins unsupported or supported by organic fibers or glass carrier cloth. Although they are economical and convenient their application
invariably results in trapped air. The sequence of events is illustrated in Fig. 13. When the film is first placed on the metal, regions of thin air film are trapped, Fig. 13a. As the resin softens the air pulls up into bubbles, Fig. 13b, which are displaced into the resin film, Fig. 13c. These events occur if the resin meets the wetting criterion. However, if the wetting criterion is not met then the air remains at the interface, Fig. 13b. Bascom and Patrick cite various methods of removing the unwanted air and thus obtaining higher fracture strength.

Properties of the Adhesive/Adherend Interface

The adhesive/adherend interface is not planar, but rather a region of multiphase -- some adhesive, some adherend or both, with properties differing from the bulk adhesive. This would be so even if the adherend were ideally smooth and chemically homogeneous and if the adhesive polymer were of a single component because the molecular configuration of a polymer at the interface is different than in bulk. The transition from interfacial structure to bulk structure may extend over several thousand angstroms. The fact is, that adherend surfaces are never smooth or homogeneous and adhesives are rarely well defined polymers. These factors have a profound influence on the properties at the interfacial region. For example, if an adhesive fills this roughness of the adherend then it might be considered that the interfacial region is at least as thick as the depth of the scratches.
a. Initial entrapment

b. Partial displacement

c. Complete displacement

Figure 13  Air trapped by film adhesives
Chemical composition of the adhesive near the interface is likely to be different from bulk due to the selective adsorption of one of the constituents. For example, in amine-cured epoxies, amine is preferentially adsorbed by glass and metal substrates. Enrichment of the interface with amine would cause the resin in this region to cure differently than in bulk. In addition, any amine left at the interface could affect the chemistry of stress corrosion. Even if no preferential adsorption takes place the adherend can still affect the solidification of the polymer.

Other problems which occur at the interface are the stresses which occur due to differences in thermal coefficients of expansion, resin shrinkage accompanying cure, resin crystallization and even long range orientation of the adhesive molecules. To some extent relaxation processes in the solid resin may relieve these stresses, but near the interface the adherend will hinder relaxation by mechanical and/or chemical bonding constraints. In addition to resin-thermal effects, interfacial stresses can be induced by surface roughness.

The last topic of discussion is that of primers and adhesion promoters. Their function is to protect the adherend from moisture and other contaminants prior to bonding, increase the adherend wettability, and/or improve the interfacial strength. These adhesion promoters have been shown to improve the moisture resistance of glass/resin and metal/resin bonds, a major step toward solving the problem which has been the most serious deterrent to their widespread use. The primers are usually applied to an adherend as a thin
polymeric film which the resin can penetrate and presumably interact. The fact that the adhesive resin and primer or promoter coating can interdiffuse implies an interfacial layer having properties considerably different than either of the components separately. This is probably the key to the mechanism of adherend surface treating agents.
V. EXPERIMENTAL CONSIDERATIONS

The adhesive investigated in this study was Metlbond 1113-2, a 100% solid unsupported modified nitrile epoxy film, produced by Narmco Materials, Inc. of Costa Mesa, California. All tests were conducted using the tapered double cantilever beam (TDCB) fracture toughness specimen as shown in Fig. 14. The TDCB specimens used in this study are commercially available through the Materials Research Laboratories of Glenwood, Illinois.

Specimen Preparation

As was stated earlier in Chapter IV, the prebond adherend preparation process must be followed exactly to ensure a good bond. The surface preparation procedure for an aluminum substrate is provided by Narmco [12]. This is as follows:

1. Remove all inked markings by solvent wiping with clean rags soaked in methyl ethyl ketone.
2. Rack parts to insure intimate contact with processing solution on all surfaces.
3. Vapor degrease in trichloroethylene by suspending in the vapor zone until vapors no longer condense on the surface. Exceptionally dirty parts may be flushed with clean, hot trichloroethylene liquid and cooled prior to vapor degreasing.
4. Degreased metal is then immersed for 20 ± 2 minutes at 150°F to 160°F in a solution of the following composition:
Fig. 14. TDCB Specimen Being Tested.
Distilled or deionized water  30 parts by weight
Sulfuric acid (sp. gr. 1.84)  10 parts by weight
Sodium dichromate  4 parts by weight

(Potassium dichromate was used in place of sodium dichromate because we were unable to obtain the latter. A correction should be made in using potassium dichromate for the change in molecular weight. More than 4 parts by weight will be needed to get the same amount of \( \text{Cr}_2\text{O}_7 \) in solution.)

5. Rinse thoroughly by either one or a combination of the following methods.

Overflow Rinse: Either one or two tanks may be used for immersion rinsing provided the pH of the final rinse is maintained between 5 and 8.5 and uses deionized water.

Spray Rinse: Spray with water maintained at a pH of 5 to 8.5. All surfaces must be thoroughly flooded with rinse water.

6. Air dry parts by placing in a rack so as to prevent water retention. Thorough draining is required to prevent water stains which might weaken subsequent bonds. Drying may be facilitated by drying in an air circulating oven at not over 150°F after the water film has air dried from the surface, ~15 minutes. Do not use compressed air and/or cloths to dry cleaned surfaces.

After the adherends had thoroughly dried Metlbond 6276 primer was applied. The primer was allowed to come to room temperature before being applied in smooth even coats with a fine brush. It is
important that the primer be continuously agitated during application. To cure Metlbond 6726 allow it to air dry at room temperature for 2 hours. It is not imperative that the joints be prepared immediately as long as the primed surfaces are protected from any form of contamination. It is suggested that primed surfaces be wrapped in non-waxed Kraft paper to store [12].

The Metlbond 1113-2 was received in sheets measuring 12 inches (30.48 cm) square by ~ 0.011 inches (0.02794 cm) thick. The desired bond thickness was ~ 0.030 inches (0.0762 cm); therefore, three layers of adhesive were required. Following the application of the adhesive teflon tape ~ 0.002 inches (0.00508 cm) thick was used as a crack starter. At the instant the crack began to propagate the crack tip would jump from the interface to the center of the adhesive. As shown in Fig. 12 the bond width was 0.5 inches (1.27 cm). Six glass beads ranging in diameter from 0.025 to 0.030 inches (0.0635 to 0.0762 cm) were placed in pairs at three locations along the tapered section of the TDCB specimen to control the bond thickness with steel shims 0.025 inches thick employed at the ends. After the joints were prepared a loading device, Fig. 15, was applied to the specimen that could be placed in the oven during cure. The standard cure temperature of 260°F was used, but the standard cure time was increased 10 minutes to 70 minutes. With this specimen geometry either the pressure or bond thickness can be controlled. Since bond thickness was a test variable we chose to control it. The specimens were then allowed to cool slowly in styrofoam incubators until they reached room temperature, about 8 hours. Due to the small number of TDCB
Fig. 15. Loading Apparatus for Use During Cure.
specimens available, after testing the adherends were machined to remove the fractured adhesive so the specimens could be used again.

**Experimental Procedure**

All tests were conducted on an Instron testing machine using constant cross head rates ranging from 0.005 in./min to 2 in./min (0.0127 cm/min to 5.08 cm/min). The Instron strip chart recorder was used to record the load and cross head deflection. The proportional mode was used to drive the chart at a rate of 50 times the cross head rate. A typical experimental set-up is shown in Fig. 16. The load was introduced through steel grips made specifically for the TDCB specimen.

One creep test was also conducted to determine if the material acts viscoelastically in the bonded state. The Instron testing machine was used with the load cycler set to hold a 500-pound load. The Instron strip chart recorder was again used to record the load and cross head deflection. And again the chart was driven in the proportional mode at 50 times the cross head deflection rate.

All specimens were tested to failure.

**G_{IC} Dependence to the Specimen Preparation Process**

The specimen preparation process was described in detail in the beginning of this chapter. It was not known prior to testing how sensitive the strain energy release rate, $G_{IC}$, would be to the preparation process. Therefore, before presenting data that might be subject to scatter caused by preparing the specimens and not the statistical variations which exist in the adhesive, the specimen
Fig. 16. TDCB Test Set-Up.
preparation dependence of $G_{IC}$ was investigated. Table 2 will be instrumental in illustrating the various effects.

Before continuing, the nomenclature of Table 2 should be well understood. Column one is labeled Specimen No. All of the specimens used in this study had a number stamped on them. Unfortunately we did not have enough specimens to continue experimenting without reusing them. Consider specimens 132-1 and 132-5, both are specimen 132 but the -1 and -5 represents the first and fifth test conducted respectively. Therefore, specimen 132-1 could be referred to as test number 1 and specimen 132-5 as test number 5. Column two is labeled Batch No. Simply, this refers to the specimens that were cured in the oven at the same time. Only two specimens would fit in the oven at one time, consequently, each batch number refers to two specimens. The remaining column headings should be self-explanatory. The bond thickness is the thickness of the adhesive. The cure time refers to the amount of time the adhesive was cured at 260°F. The test rate is the cross head rate. The test duration is the total length of time the test took from initial application of the load to failure. And $G_{IC}$ is obviously the strain energy release rate given by Eq. (25).

Reviewing the adherend preparation procedure, two steps in the process were felt worthy of investigating, the chromate-acid bath and the sensitivity of the cleaned metal surfaces to minor contamination prior to applying the primer.

To this point a close examination of the specimen fracture surfaces revealed all of the specimens failed cohesively through the
<table>
<thead>
<tr>
<th>Spec. No.</th>
<th>Batch No.</th>
<th>Bond Thickness $\times 10^{-3}$ in.</th>
<th>Cure Time $\times 10^2$ Min</th>
<th>Test Rate in $/min$ (cm/min)</th>
<th>Test Duration Min</th>
<th>$G_{IC}$ in-lb/in$^2$ (J/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>132-1$^a$</td>
<td>1</td>
<td>8 (20.3)</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>7.04</td>
<td>12.19 (21.33)</td>
</tr>
<tr>
<td>169-3$^a$</td>
<td>1</td>
<td>8</td>
<td>- 60</td>
<td>0.02 (0.0508)</td>
<td>7.0</td>
<td>7.42 (12.99)</td>
</tr>
<tr>
<td>178-2$^a$</td>
<td>2</td>
<td>8</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>7.68</td>
<td>11.53 (20.13)</td>
</tr>
<tr>
<td>205-4$^a$</td>
<td>2</td>
<td>8</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>7.28</td>
<td>10.63 (18.64)</td>
</tr>
<tr>
<td>132-5$^b$</td>
<td>3</td>
<td>25-30 (63.5-76.2)</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>8.08</td>
<td>32.59 (57.03)</td>
</tr>
<tr>
<td>178-6$^b$</td>
<td>3</td>
<td>25-30</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>3.76</td>
<td>25.04 (43.32)</td>
</tr>
<tr>
<td>169-7$^b$</td>
<td>4</td>
<td>25-30</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>10.20</td>
<td>34.13 (59.73)</td>
</tr>
<tr>
<td>205-8$^b$</td>
<td>4</td>
<td>25-30</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>10.68</td>
<td>33.49 (58.54)</td>
</tr>
<tr>
<td>600-9$^c$</td>
<td>5</td>
<td>25-30</td>
<td>- 90</td>
<td>0.05 (0.127)</td>
<td>11.48</td>
<td>38.64 (67.62)</td>
</tr>
<tr>
<td>602-10$^c$</td>
<td>5</td>
<td>25-30</td>
<td>- 90</td>
<td>0.05 (0.127)</td>
<td>11.04</td>
<td>35.28 (61.74)</td>
</tr>
<tr>
<td>603-11$^b$</td>
<td>6</td>
<td>25-30</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>10.04</td>
<td>30.38 (51.17)</td>
</tr>
<tr>
<td>618-12$^b$</td>
<td>6</td>
<td>25-30</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>9.52</td>
<td>27.73 (48.56)</td>
</tr>
<tr>
<td>623-13$^d$</td>
<td>7</td>
<td>25-30</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>8.32</td>
<td>23.04 (40.32)</td>
</tr>
<tr>
<td>626-14$^d$</td>
<td>7</td>
<td>25-30</td>
<td>- 60</td>
<td>0.05 (0.127)</td>
<td>8.36</td>
<td>23.54 (41.20)</td>
</tr>
<tr>
<td>624-19$^a$</td>
<td>8</td>
<td>25-30</td>
<td>70</td>
<td>0.05 (0.127)</td>
<td>11.32</td>
<td>40.45 (70.79)</td>
</tr>
<tr>
<td>512-20$^a$</td>
<td>9</td>
<td>25-30</td>
<td>70</td>
<td>0.05 (0.127)</td>
<td>11.8</td>
<td>43.56 (75.33)</td>
</tr>
<tr>
<td>613-15$^f$</td>
<td>9</td>
<td>25-30</td>
<td>70</td>
<td>0.05 (0.127)</td>
<td>9.0</td>
<td>24.44 (42.77)</td>
</tr>
<tr>
<td>505-16$^f$</td>
<td>9</td>
<td>25-30</td>
<td>70</td>
<td>0.05 (0.127)</td>
<td>9.88</td>
<td>29.81 (52.17)</td>
</tr>
<tr>
<td>522-17$^f$</td>
<td>10</td>
<td>25-30</td>
<td>70</td>
<td>0.05 (0.127)</td>
<td>8.74</td>
<td>21.68 (37.94)</td>
</tr>
<tr>
<td>629-18$^f$</td>
<td>10</td>
<td>25-30</td>
<td>70</td>
<td>0.05 (0.127)</td>
<td>8.72</td>
<td>21.72 (37.46)</td>
</tr>
</tbody>
</table>

0.008 in. bond thickness - a.
0.025 - 0.030 in. bond thickness - b. - f.
a - recommended preparation procedures followed (RPFP).
b - RPFP.
c - 90 min. cure, otherwise RPFP.
d - short cooling period, otherwise RPFP.
e - 70 min. cure, long cooling period, otherwise RPFP.
f - 70 min. cure, long cooling period, "old" adhesive, otherwise RPFP.
adhesive with tiny spots of adhesive failures along the outer edges of the specimen. Intuitively it was felt that if the adherend was put in the chromate-acid bath at a higher temperature better bonds should result. In contrast, if the cleaned surfaces were contaminated prior to the application of primer, poorer bonds should result. This indeed was the case. Some adherends were chemically treated in the chromate-acid bath at 100°F higher than is recommended and a better bond occurred resulting in no detectable adhesive failures along the specimens' edges. The specimens that were contaminated were done so by touching their surfaces after thoroughly cleaning my hands with methyl ethyl ketone, the main constituent of the primer. Larger than normal adhesive failures were noted at the contaminated locations. However, no appreciable change in $G_{IC}$ could be observed between the two types of tests.

The next specimen preparation procedure to be investigated was the application of the adhesive to the adherend. Two criteria were considered: the age of the adhesive and the thickness of the adhesive layer.

According to Narmco specifications Metlbond 1113-2 has a short life of six months at 40°F or sixty days at 75°F. Specimens 613-15 through 628-18 were prepared using a sheet of adhesive left out of the refrigerator for seven days in a room maintained at 72°F. Specimens 624-19 and 612-20 were prepared using a fresh sheet of adhesive taken from the refrigerator the same day. All other known variables were held constant during the preparation and testing procedures. The result was the specimens prepared with the "old"
adhesive had drastically reduced $G_{IC}$ values. Also the adhesive layer contained many more trapped air bubbles. A comparison of "old" and "new" adhesive (Fig. 17) illustrates the drastic difference. Adhesive stored at room temperature for substantial periods was definitely different than that freshly removed from cold storage.

Bascom et al. [3,5,10,11] reported that the strain energy release rate, $G_{IC}$, is a function of bond thickness for various adhesives tested using the TDCB specimen. A typical plot of Bascom's findings are shown in Fig. 18. A clear bond thickness dependence can be observed with the maximum $G_{IC}$ occurring at about 0.025 in. (0.0635 cm). Two adhesive thicknesses were studied in our investigation, ~0.008 in. (0.02032 cm) and ~0.030 in. (0.0762 cm). The $G_{IC}$ values for the thicker bonds were approximately three times that of the thinner bonds, clearly indicating a strong bond thickness dependence. Again referring to Fig. 18, it can be observed that around the maximum value for $G_{IC}$, $G_{IC}$ is relatively stable for the bond thickness range of 0.015 in to 0.030 in. (0.0381 cm to 0.0762 cm). For this reason a bond thickness of about 0.030 in (0.0762 cm) was felt to be in a range that would be less sensitive to thickness variations which existed between glass beads (all the glass beads were between 0.025 in and 0.030 in. in diameter).

A note should be made about the TDCB specimens received from MRL. In testing the specimens with the 8 mils bond thickness, it was observed that the adhesive thickness varied from about 2 mils to 8 mils. Correspondingly, the results of the test (Fig. 19) reinforced the bond thickness dependence of $G_{IC}$. The bond line was
Fig. 17. Comparison of "Old" to "New" Adhesive.
Figure 18  G\textsubscript{IC} vs bond thickness (for piperidine DGEBA modified with 15\% CTBN at room temp.)
the thinnest in the middle of the specimen where $P_C$ was also at a minimum. The interesting discovery was that the TDCB specimens were not true. The variation in bond thickness for the 8 mils specimens was due to the TDCB specimens having high spots in the middle of the adherend. Any future researchers using these specimens should be aware of this fact. A comparison of the thin bondline specimens with variable thickness and the thick bondline specimens with more uniform adhesive thickness can be observed in Fig. 19 and 20.

The last specimen preparation procedure to be investigated in an attempt to better define the experimental procedure was how the cure time and cool down time would affect $G_{IC}$ values.

Gillham [25] has reported that the strength of an adhesive is strongly dependent on the time and temperature of the cure. A plot of strength vs. time for various temperatures (Fig. 21) indicates the strength remains relatively constant for short and long cure times. At an intermediate cure time, however, the strength of the adhesive is observed to abruptly increase over a relatively short change in cure time. It was believed that the recommended cure times and temperatures for Metlbond 1113-2 are somewhere in this increasing strength transition zone on its cure curve. Two specimens, 600-9 and 602-10, were, therefore, cured for 90 minutes instead of the recommended 60 minutes. The result was an - 21% increase in $G_{IC}$ (not including tests 13 and 14 which were prepared with short cooling periods). All subsequent specimens were cured for 70 minutes in an attempt to reduce $G_{IC}$ variations due to the curing process.
Figure 19  Load vs elongation curve for specimens with variable bond thickness
Figure 20: Load vs elongation curve
Fig. 21. Isotherms: cure of epoxide resin system (TBA).
Since the cure time was found to have a profound effect on $G_{IC}$ it was felt the cool down period may also be a factor. Tests 13 and 14 were conducted after a shorter cool down period and found to have reduced $G_{IC}$ values (~24%). Styrofoam incubators were then fabricated to allow for a longer cool down period in an attempt to cut down on experimental scatter.

A bar graph is shown in Fig. 22 summarizing the findings of this investigation. Each bar is labeled with the conditions under which the listed tests were conducted. The average $G_{IC}$ value was calculated from the test indicated in each bar.

Before closing this chapter a few last comments should be made. As mentioned earlier, a loading device was developed for use during the cure cycle. Even though the exact pressure cannot be controlled when controlling the adhesive thickness, some pressure must be applied and it should be applied uniformly over the length of the specimen. The apparatus illustrated in Fig. 15 was found to do a good job and is very simple to construct. The negative of the adherend shape was traced onto a piece of wood and then cut out. A rubber strip was placed between the adherend and wood pieces. Two clamps were then made for each specimen to be used with four springs in loading each specimen. Good adhesive bonds resulted.

At this point it was felt that uniform adhesive specimens could be prepared for further testing.
Figure 22 Summary of $G_{1c}$ dependence on preparation procedures

NOTE: Standard preparation procedure followed for every specimen except listed procedures.

**ADHESIVE THICKNESS**
- 0.008 in (0.02032 cm)
- 0.030 in (0.0762 cm)

$G_{1c}$ in-lb/in$^2$
VI. REDUCTION OF EXPERIMENTAL DATA

As was previously discussed in Chapter III, all that need be recorded in determining the strain energy release rate, $G_{IC}$, of an adhesive using the TDCB specimen is the load to propagate the crack, $P_C$.

$$G_{IC} = \frac{4P_C^2}{EB^2} M$$

This method is valid provided the material is linear elastic and no plastic deformations take place in either the adhesive or adherend.

A typical load-deflection curve is shown in Fig. 20. An average load value was taken from the peaks of the curve and this value was used to calculate $G_{IC}$.

Rate Dependence of $G_{IC}$

In Table 3 test results from five cross head rates can be observed. In the last column of the table is the batch number. This number is slightly different than the one found in Table 2. Two sheets of adhesive were used in preparing all of the specimens. From each sheet eight specimens could be fabricated. Therefore, from each sheet four batches were made. It should be noted that no two specimens of the same batch were tested at the same rate. This was to eliminate any false rate dependency effects due to one batch of specimens having high or low $G_{IC}$ values.

A plot of the $G_{IC}$ values vs. log (cross head rate), Fig. 23, results in a linearly increasing trend in $G_{IC}$ with increasing cross
### TABLE 3

=G_iC for Various Cross Head Rates

<table>
<thead>
<tr>
<th>Specimen No.</th>
<th>Test Rate in/min (cm/min)</th>
<th>Test Duration min.</th>
<th>$G_{IC}$ in-lb/in² (J/m²)</th>
<th>Average $G_{IC}$ in-lb/in² (J/m²)</th>
<th>Batch No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>613-31</td>
<td>0.005 (0.0127)</td>
<td>109.6</td>
<td>36.00 (63.00)</td>
<td>36.74 (64.28)</td>
<td>1-3</td>
</tr>
<tr>
<td>624-32</td>
<td>0.005 (0.0127)</td>
<td>112</td>
<td>37.45 (65.54)</td>
<td></td>
<td>1-4</td>
</tr>
<tr>
<td>618-21</td>
<td>0.05 (0.127)</td>
<td>8.4</td>
<td>37.90 (66.33)</td>
<td></td>
<td>1-2</td>
</tr>
<tr>
<td>600-22</td>
<td>0.05 (0.127)</td>
<td>12.08</td>
<td>42.77 (74.85)</td>
<td>38.56 (67.48)</td>
<td>1-3</td>
</tr>
<tr>
<td>622-23</td>
<td>0.05 (0.127)</td>
<td>10.72</td>
<td>33.87 (59.27)</td>
<td></td>
<td>2-1</td>
</tr>
<tr>
<td>603-24</td>
<td>0.05 (0.127)</td>
<td>11.6</td>
<td>39.69 (69.46)</td>
<td></td>
<td>2-2</td>
</tr>
<tr>
<td>605-25</td>
<td>0.5 (1.27)</td>
<td>.70</td>
<td>45.48 (79.59)</td>
<td>42.81 (74.92)</td>
<td>1-1</td>
</tr>
<tr>
<td>602-26</td>
<td>0.5 (1.27)</td>
<td>.75</td>
<td>40.14 (70.25)</td>
<td></td>
<td>1-2</td>
</tr>
<tr>
<td>628-27</td>
<td>1.0 (2.54)</td>
<td>.49</td>
<td>47.61 (83.32)</td>
<td>43.88 (76.79)</td>
<td>1-1</td>
</tr>
<tr>
<td>626-28</td>
<td>1.0 (2.54)</td>
<td>.44</td>
<td>40.14 (70.25)</td>
<td></td>
<td>2-1</td>
</tr>
<tr>
<td>623-29</td>
<td>2.0 (5.08)</td>
<td>.16</td>
<td>40.45 (70.79)</td>
<td>41.22 (72.14)</td>
<td>1-4</td>
</tr>
<tr>
<td>612-30</td>
<td>2.0 (5.08)</td>
<td>.29</td>
<td>41.99 (73.48)</td>
<td></td>
<td>2-1</td>
</tr>
<tr>
<td>132-33</td>
<td>Creep Test</td>
<td>690</td>
<td>36.00 (63.00)</td>
<td></td>
<td>2-3</td>
</tr>
</tbody>
</table>
Figure 23  Cross head rate vs. GIC curve

- X: average GIC for each specimen
- O: average GIC for each rate
- Δ: batch 1-1 tests

Cross head rate (in/min)

GIC (in-lb/in²)
head rate with one exception. Batch 1-1 specimen data points shown on Fig. 23 had relatively high values of $G_{IC}$. The reason for this is felt to be because they were the first specimens to be put in the oven to be cured, therefore, the oven door was open only long enough to put those specimens in it. For all subsequent batches the oven door was open longer to remove previously cured specimens before placing more in the oven. This would allow for more heat loss from the oven and a different cure for Batch 1-1 specimens. Therefore, the plot in Fig. 23 is drawn excluding those two data points.

Wang [29] has reported the shape of the TDCB adherend was designed using a simple one-dimensional beam theory to give an approximately linear compliance during the course of crack growth. It has been observed that deformation and fracture are extremely localized within the thin adhesive layer, which the simple beam consideration fails to consider. The variation in $G_{IC}$ with crack length was therefore investigated.

A normalized plot of $G_{IC}$ with crack length is shown in Fig. 24. The normalized $G_{IC}$ was obtained by dividing the value of $G_{IC}$ at each crack location by the overall average $G_{IC}$ for each rate. In this way all specimens, regardless of test rate, could be averaged together. The normalized $G_{IC}$ value is seen to increase slightly with increasing crack length. These results would suggest that the TDCB specimen actually is not a linearly increasing compliance specimen.
Figure 24 Normalized $\frac{G_{IC}}{G_{IC\text{ avg.}}}$ vs crack length
Time Dependence of $G_{IC}$

The one creep test that was conducted was sufficient to conclude that Metlbond 1113-2 is time dependent in the bonded state, but not sufficient to characterize the viscoelastic properties. At the 500-pound (227.27 kg) load the crack propagation rate was calculated to be 0.00725 in/min (0.01842 cm/min). The following equation was used [9],

$$\dot{a} = \dot{U} \frac{EB}{8P_C m}$$

(27)

where $\dot{U}$ is the cross head rate, $E$ is the adherend modulus, $B$ is the specimen thickness, $m$ is the shape factor, and $P_C$ is the applied load in a creep test. The results of the creep test are located in the last row of Table 3.
VII. DISCUSSION AND RESULTS

The TDCB fracture toughness specimen was used here to examine the adhesion and specimen preparation processes and the rate and time dependence of Metlbond 1113-2. The data obtained for the sensitivity of $G_{IC}$ to the specimen preparation process and to rate and time dependence were presented in Chapters V and VI.

Preparation, Rate and Time Dependence

Figure 22 clearly illustrates the necessity of thoroughly understanding the factors affecting bond strength in order to obtain accurate fracture energy results. Slight variations in the cure cycle were found to have drastic effects on $G_{IC}$ values. Figure 23 summarizes the cross head rate dependency of Metlbond 1113-2. A trend of exponentially increasing $G_{IC}$ is observed with increasing cross head rate. Another very strong indication of rate dependency can be found in Table 3. If specimens from the same batch are compared it is observed that the specimen tested at the higher rate had a larger $G_{IC}$ value in every case. This comparison rules out any effects due to cure and provides an accurate comparison.

The time dependency of Metlbond 1113-2 was not investigated in depth. At this time the only desire was to demonstrate the adhesive acted viscoelastically in the bonded state. Renieri [26] performed creep tests on bulk specimens of this adhesive and found that loads near ultimate produced large viscoelastic effects. For this reason a load near ultimate for the TDCB specimen was chosen.
The creep test took 690 minutes to fail at a 500-pound (227.27 kg) load. A very slow crack propagation rate was calculated, 0.00725 in/min (0.01842 cm/min).

The results of investigating the fractured surfaces will now be discussed.

Fractography

Examination of the fractured surfaces revealed some interesting clues as to whether the fracture process for our adhesive was brittle in nature as is assumed by LEFM. Both macroscopic and microscopic investigations were performed with varying results.

Initially a visual macroscopic examination of the fractured surfaces of tests 21-32 indicated that each exhibited similar characteristics. As may be observed in Fig. 25, a light and dark region can be discerned. The light region corresponds to the first portion of each test during stable crack growth. The dark area corresponds to the later portion of each test when each specimen failed catastrophically resulting in fast crack growth.

Figure 26 provides a closer look at the transition zone from slow to fast crack growth for tests 21-30. An interesting observation can be made. In comparing the apparent roughnesses of the light and dark regions the light area was rough while the dark area was relatively smoother. Rough surfaces are generally associated with ductile fracture and smooth surfaces are generally associated with brittle fracture. Thus, it would appear that the slow crack growth of the light region was a result of ductile fracture and fast crack
Fig. 25. Fracture Surface: Cross Head Rates Increasing from .005 in/min to 2 in/min from L. to R. The cracks propagated from top to bottom in this photograph.
Fig. 26. Fracture Surfaces.
1 in/min Cross Head Rate Tests

2 in/min Cross Head Rate Tests

Fig. 26. Cont.
growth of the dark region was a result of brittle fracture.

Microscopic investigations were then conducted on three specimens, 600-9, 602-10 and 626-14. All three specimens were tested at a cross head rate of 0.05 in/min. A scanning electron microscope (SEM) was used for this investigation.

Specimens with extreme high and low values of $G_{IC}$ were used. The SEM photographs for both extremes shed no light on the large variation in $G_{IC}$ values, but they did provide a means for better understanding the mechanisms of fracture. Figures 27 are three SEM photographs of specimen 626-14. Figure 27a was taken in the slow crack region, Fig. 27b was taken at the transition from slow to fast crack region, and Fig. 27c was taken in the fast crack region. The presence of fiber is obvious in Fig. 27a while Fig. 27c contains almost no sign of such fiber. In Fig. 27b an abrupt change from fiber to no fiber can be observed in going from the top to the bottom of the photograph. It now seems that a plane or many planes of fiber exist in the adhesive and that slow crack growth occurs in a plane of fiber.

At a higher magnification another very interesting discovery was made. Figures 28 are SEM photographs of the slow and fast propagation regions. A close examination of both photographs indicates that both regions failed in a brittle manner. Fiber can be easily seen in Fig. 28a while classical brittle fractured surfaces can be seen in both Figures 28a and b. These photographs suggest that the entire length of the specimen failed in a brittle manner with slow crack propagation taking place along a plane of fiber. Note should be made of the large holes in the fractured surfaces;
Fig. 27. Fracture Surfaces at 50X.
a. Slow Crack Region

b. Fast Crack Region

Fig. 28. Fracture Surfaces at 200X.
they are actually air bubbles in the adhesive.

Figure 29 is a photograph taken of the fibers bridging the gap between adjacent fractured surfaces. This phenomenon occurred during each test.

A higher magnification was needed to determine the distribution of elastomeric particles throughout the adhesive. Figure 30 provides a good picture of the uniform dispersion of the elastomer. The nitrile rubber was found to be well distributed throughout all parts of the adhesive investigated.

TDCB Test Specimen Evaluation

Wang [29] has reported that the allowable yield zone in the adhesive for an appropriate use of the fracture mechanics concept is much smaller for typical adhesive joint systems (on the order of $10^{-4}$ inches) than for monolithic materials. Thus, only very brittle adhesives with very small scale yielding, at most, of one-tenth of the adhesive thickness, would qualify for the flaw size limitations in using the TDCB fracture toughness test. For the adhesive joints in which gross yielding is developed over the entire bond line, an energy release rate can still be measured, but its use in the joint failure analysis and design would be severely compromised. Employing this line of thought, two conditions occurred which would imply that the $G_{IC}$ values obtained from the TDCB specimen for Metlbond 1113-2 may not be acceptable as design values.

Preceding the crack tip was a zone of stress whitening or crazing in the adhesive layer. Figure 31 is a series of photographs
Fig. 29. Fiber Presence in the Adhesive.
Fig. 30. Fractured Surfaces at 5,000X.
Fig. 31. Crack Propagation Sequence.
taken of a crack growing. The crazing zone was observed to maintain a constant length of about 0.53 in (1.3462 cm) along the entire length of crack propagation. The author does not feel that this entire zone is a plastic zone but that a plastic zone is located in this crazed zone. Due to the size of the crazed zone it is possible a plastic zone is present which is much larger than is allowable by fracture mechanics standards.

The second condition was that of the plastic deformation of the adherends. Figure 32 illustrates that after testing and mating the two fractured surfaces back together, a difference of 0.050 in. (0.127 cm) could be measured between the two ends. This is not to say plastic deformations of 0.05 in. occurred, but in fact, some flow processes did occur in the adherends.
Fig. 32. Permanent Deformation in a Tested Specimen.
VIII. CONCLUSIONS AND FUTURE CONSIDERATIONS

The objectives of the present investigation were to determine the sensitivity of an adhesive specimen to preparation procedures, the rate and time dependence, and the fracture processes of Metlbond 1113-2 tested with the TDCB specimen. In addition, the applicability of $G_{IC}$ testing with the TDCB specimen for Metlbond 1113-2 was discussed. In summary, the following conclusions can be made.

In preparing the specimens, two factors were found to have significant effects on the $G_{IC}$ of Metlbond 1113-2, the time the adhesive was left out at room temperature and the cure cycle. The most sensitive process in the specimen preparation procedure was that of the cure cycle; therefore, it is felt that an investigation similar to the one conducted by Gillham [25] should be conducted to better understand the cure and cooling down dependence. After the specimen preparation was better defined an investigation of the rate and time dependence illustrated a linear rate dependence and that a time dependence existed for Metlbond 1113-2 in the bonded state at room temperature.

At that point an investigation of the fractured adhesive surfaces were in order to determine the mechanisms of fracture. A visual inspection yielded that the slow crack propagation was the result of ductile fracture and fast crack propagation was a result of brittle fracture. It was then decided to use a scanning electron microscope to study the microscopic mechanisms of fracture.
An interesting conclusion was made; the entire length of the specimen appeared to have failed brittlely with slow crack propagation occurring in a plane of fiber and fast crack propagation occurring in a plane containing no fiber. This was the first time it was known to people at V.P.I. that Metlbond 1113-2 contained fiber. An EDAX examination revealed that the fiber was an organic material. A higher magnification illustrated the uniform distribution of the nitrile rubber elastomer throughout the adhesive. A comparison of Metlbond 1113-2 with other high-performance polymers [28], Table 4, reveals Metlbond 1113-2 exhibited a much higher $G_{IC}$ value than values for other polymers. The reason for this high fracture energy is believed to be because of the good distribution of the nitrile elastomer and the presence of the, until now unknown, fiber in the adhesive.

The final conclusion made was that the mathematical model accompanying the TDCB specimen was not suitable for testing Metlbond 1113-2. The arms of the adherend deformed plastically which violated the theory. One solution to this would be to use a lower value of $m$, the shape factor. This would result in stiffer adherends.

Many questions arose in this investigation that can be answered only by performing more studies. As mentioned earlier, a cure curve investigation should be performed to find the cure dependence of the fracture energy. In conjunction with this, a cost analysis should be performed to determine if the increased strength would be worth the added expense for industry. Further testing should be conducted in order to accurately compare the mechanical
<table>
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<tr>
<th>Polymer</th>
<th>$G_{IC}$ in-lb/in$^2$</th>
<th>GIC KJ/M$^2$</th>
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<tr>
<td>Narmco 5208</td>
<td>0.43</td>
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<tr>
<td>Hexcel F-178</td>
<td>0.69</td>
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<td>Gulf T-600</td>
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<td>Ciba - Geigy NCNS</td>
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<tr>
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<td>11.42</td>
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<td>Union Carbide, RADEL</td>
<td>18.27</td>
<td>(3.2)</td>
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<td>Union Carbide, UDEL</td>
<td>11.42</td>
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</tr>
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<td>ICI, P300</td>
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<tr>
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<td>Amoco 4000</td>
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<tr>
<td>Phillips RYTON PPS</td>
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<tr>
<td>Metlbond 1113-2</td>
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<td>(6.83)</td>
</tr>
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properties of the bonded adhesive to those obtained in bulk testing [26,27]. Also, an investigation of the plastic zone size could be done with further testing in an attempt to model the plastic zone size as was done by Dugdale. Finally, other types of tests should be made using various specimens to provide a comparison of $G_{IC}$ values for Metlbond 1113-2.

The above items would provide for a coherent picture of the response of a material due to complex interactive effects.
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FACTORS AFFECTING THE FRACTURE ENERGY
OF A STRUCTURAL ADHESIVE

by
Daniel George O'Connor

(ABSTRACT)

A fracture investigation was conducted on a modified epoxy adhesive (Methylbond 1113-2). Initially various adhesive fracture strength and energy tests and the mechanisms of mechanical and chemical adhesion were discussed. A critical study was then made of the sensitivity of the strain energy release rate to specimen preparation. The rate and time dependence of the adhesive were then investigated using the TDCB specimen. The fractured surfaces were also studied using scanning electron microscopy to determine the mechanisms of failure.