

Chapter 7

Wedge and Double Cantilever Beam Tests on a High Temperature Melt Processable Polyimide Adhesive, TPER-BPDA-PA

7.1 Introduction

This work focuses on with the wedge and double cantilever beam tests on a novel high temperature polyimide that is based on 1, 3-bis (4-aminophenoxy) benzene (TPER or 1,3 (4) APB) and 3, 3', 4, 4'-biphenyltetracarboxylic dianhydride (BPDA). The chain ends are endcapped with phthalic anhydride (PA). This semicrystalline polyimide henceforth referred to as TPER-BPDA has already been discussed in earlier chapters and demonstrates a high T_g of ca. 210°C and a peak DSC melting point of 395°C. In chapter 5 and in chapter 6 the crystallization kinetics, thermal stability, crystalline morphology, melting behavior and rheology of this polyimide has been discussed. Additionally, the excellent adhesive properties of this polyimide have been demonstrated using the lap-shear test geometry.

Several promising features of this polyimide when used as a high temperature adhesive and relevant with respect to the present work are:

- The polyimide demonstrates exceptional thermal stability with little change in its crystallization behavior after 30 minutes in the melt at 430°C.
- Very fast crystallization kinetics from the melt is demonstrated and no additional annealing steps are required to introduce crystallinity (even when the polyimide has been quenched from the melt).
- A simple and solvent free '*Grit Blasting*' as the surface treatment is sufficient in providing a strong and durable interface as determined by cohesive failures at room temperature, after aging and testing at higher temperatures of 177°C and 232°C, and after exposure in various solvents (as revealed by the presence of polymer on both

faces of the fractured coupons. SEM was utilized to examine the lap-shear fracture surfaces after various tests).

- High lap-shear strengths ranging from 6600-8400 psi were obtained at room temperature after various aging times at aging temperatures of 177°C, 232°C and ambient. The strengths remained still high at ca. 4400 psi when tested at 177°C and ca. 2500-3500 psi when tested at 232°C. These values also demonstrate the excellent adhesive strengths at high temperatures and good durability of the adhesive after elongated exposures at high aging temperatures.
- The adhesive bonding procedure is simple as it is solvent free, involves no adhesive tape preparation using the scrim cloth and relatively short cycle times.

In light of these results, it was decided to further evaluate this polyimide as an adhesive by using the wedge and double cantilever beam (DCB) test geometry's.

7.2 Wedge test (experimental methodology):

The Boeing wedge test is a commonly utilized method to test the durability of fractured and stressed adhesive joints when exposed to different environments¹. This fracture test is an ASTM standard (ASTM D 3762) and utilizes a mode I specimen configuration (see Figure 7.1). The test consists of creating an initial crack by inserting a wedge, and then following the propagation of the crack with time. The driving force for the propagation of crack comes primarily from the stiffness of the beams separated by the wedge and this driving force decreases as the crack propagates. It is important to note that in this test the cracked specimen also experiences simultaneous environmental attack at the crack site (when the specimens are placed in that environment). Upon introduction of the wedge, the crack propagates to length 'a'. This results in creation of two new surfaces (each of area A), and release of elastic energy stored in the beams. If this released elastic energy by the beams is given by U_E and the energy to create the two new surfaces is given by U_S , then:

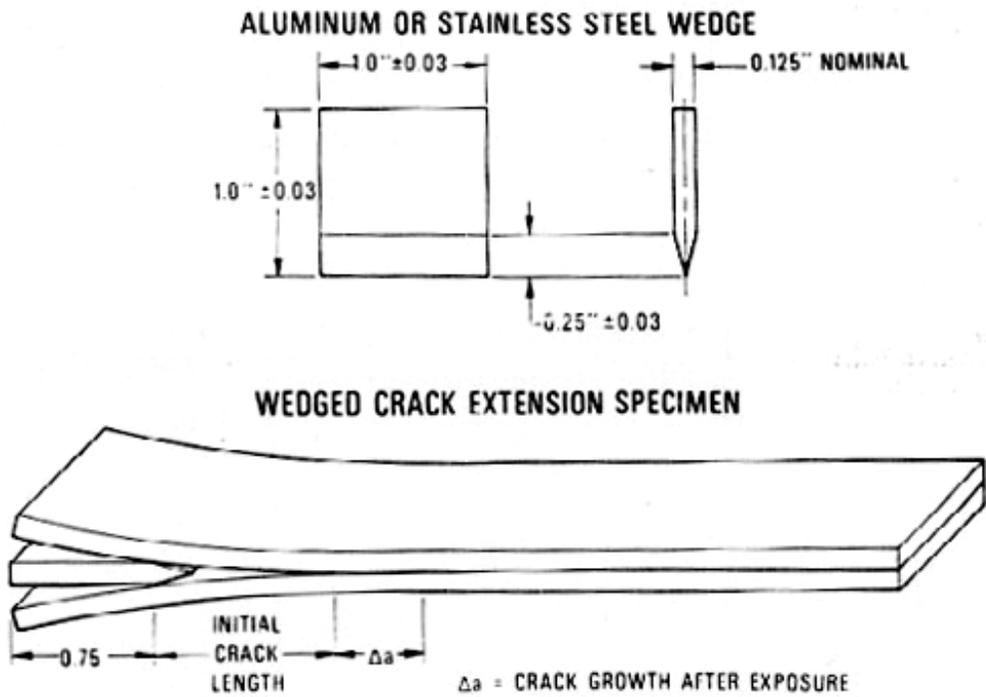


Figure 7.1 Specimen configuration for the wedge test.

$$\text{Release rate of elastic energy is given by, } G = \partial U_E / \partial A \quad \{7.1\}$$

$$\text{Energy needed to create a unit surface}^2 \text{ is, } W_s = \partial U_s / \partial A \quad \{7.2\}$$

The crack propagation stops when $G=W_s$ (this is also known as Griffith's criterion)¹. Till 'G' is higher than W_s , the crack continues to propagate. The value of G, also known as the strain energy release rate (the 'rate' refers to 'release of energy per unit *area*' and not 'release of energy per unit *time*') is calculated to be,

$$G = \frac{3Et^3h^2}{16a^4} \quad \{7.3\}$$

where, E = young's modulus of the beam

t = thickness of the beam

h = wedge thickness

a = crack length

An important assumption in this test is that adherends should not deform plastically. This is usually not a problem when using thick and stiff adherends like the ones utilized in the present study. The decreasing effective cleavage load results in the crack stopping at some equilibrium value, the value itself dependent upon the system conditions. Any contributions due to the viscoelastic properties of the adhesive are not taken into account in the above calculations³. One of the disadvantages of the wedge test is that it is often necessary to remove the specimens from the test environment to make crack length measurements. Also, the cracks may not be easy to view or may propagate unevenly across the specimen width.

The wedge test may test the adhesive strength or cohesive strength depending upon whether the crack propagates on the adhesive interface or purely in the polymer itself (cohesive failure). This test is widely utilized when comparing different surface treatments, especially when the mode of failure is interfacial.

7.3 Double cantilever beam (DCB) test (experimental methodology):

This popular test (ASTM 3433) is used to obtain the mode I fracture energy of the adhesive bonds, which is a measure of the fracture toughness of the adhesive in the presence of flaws. Similar to a wedge test, a crack is initiated first by inserting a wedge. The specimen is then loaded by pulling apart the two beams at a certain rate, this increasing load resulting in increased deflection of two beams. At a certain critical load, the crack begins to propagate resulting in a slight drop in the load (due to the increased compliance). At this point, the beams are stopped from moving apart, thus keeping the deflection constant. The drop in load (due to increasing crack length) and the crack length are carefully followed. Following the equilibration of the crack, the specimen is consecutively unloaded and then loaded. Ideally, the compliance of the fixture should remain the same during these two cycles if there is no further propagation of the crack. This overall procedure is repeated several times leading to total cleavage of the specimen. The data finally collected at various times consists of load, deflection, crack length and the compliance. This data can then be analyzed using several different approaches, two of which are discussed next.

ASTM method:

The ASTM method calculates the fracture toughness, G_{1c} (from load to start of crack), in joules per square meter as:

$$G_{1c} = \frac{(4L^2(\max))(3a^2 + h^2)}{EB^2h^3} \quad \{7.4\}$$

and the fracture toughness, G_{1a} (from arrest load), as follows:

$$G_{1a} = \frac{(4L^2(\min))(3a^2 + h^2)}{EB^2h^3} \quad \{7.5\}$$

where:

L(max) = load to start crack, N

L(min) = load at which crack stops growing, N

E = tensile modulus of adherend, MPa

B = specimen width, mm

a = crack length, mm (distance from crack tip to pin hole centers)

h = thickness of the adherend, normal to plane of bonding, mm

These equations have been established on the basis of elastic stress analysis, and hold for a sharp-crack condition under severe tensile constraint. It is assumed that the crack-tip plastic region is small compared with the size of the crack^{4,5} (an assumption that may not strictly hold for tough adhesive systems). Thus systems of similar toughness should only be compared when using these equations. Also, the analysis can be used to understand the effect of various environments on a particular type of bonded system.

Compliance Method

In the case of compliant adhesives, the adhesive properties become important, as there may be crack tip deflections and rotations. To account for these adhesive properties, bond thickness and other system dependent factors, the compliance method is used which calculates the fracture energy as⁶:

$$G = \frac{9\Delta^2(EI_{eff})}{4B(a+x)^4} \quad \{7.6\}$$

where:

B = specimen width

C = compliance (C = Δ/P)

a = crack length

x = apparent crack length offset

EI_{eff} = effective flexural rigidity

Δ = specimen's opening displacement at point of load application

The parameters EI_{eff} and 'x' are determined as:

$EI_{\text{eff}} = 2/(3m^3)$ and $x = b/m$

The factors 'b' and 'm' are calculated as the slope and y-intercept of $C^{1/3}$ vs. 'a' curve, the two factors being often related linearly.

7.4 Experimental:

Surface Preparation of Ti-6Al-4V

Surface preparation of titanium alloys often plays a dominant and critical role in obtaining good adhesion strengths and in deciding the long-term durability of the adhesive joints. Based on the earlier work⁷, grit blasting was chosen as the surface treatment for this study. The titanium coupons were first carefully selected so that their thickness' matched closely and that the thickness was constant across the area of the coupons. A special carbide drill was used to carefully drill the holes in titanium specimens used for the DCB tests. Titanium coupons were grit blasted (using alumina particles) just prior to bonding. The coupons were washed with water, dried and then wiped with acetone. The wedges (for the wedge test) were made out of standard stainless steel.

Preparation of Polyimide Strips for the Adhesive Bonding

One of the problems with the present polyimide was its unavailability in films of sufficient size (the problem is related to film casting process during the imidization). In

order to circumvent this problem and obtain a large number of strips of size 7" X 1" needed for the adhesive joints, strips were made from the powder. For this purpose, the available film was first ground to fine powder. A mold of size 7" X 1" was constructed for making films of the exact size needed for bonding. The powder (four grams) was evenly spread between two Kapton sheets, placed in the mold, and consolidated in a hot press. A force of 20,000 pounds and a temperature of 700°F for 12 minutes were used. The initial thickness of the polyimide films obtained was ca. 0.9 mm.

Bonding Conditions for the Wedge tests

The conditions optimized earlier for the lap-shear study were again utilized. These are:

Bonding Pressure = 100 psi	Bonding Temperature = 430°C
Bonding time = 20 min	Cooling rate = 21°C/min

Bonding Conditions for the DCB tests

While the bonding pressure and temperature were kept the same as above, bonding time and cooling rate were varied for this study to understand the effect on the fracture energy. The bonding times tried were 2 min, 20 min and 30 min respectively. For the cooling cycle, in addition to cooling at 21°C/min, some specimens were quenched directly to room temperature while some specimens were held at 365°C for 2.5 hours and then cooled to room temperature. While all the above experiments utilized a $M_n = 15,000$ daltons polymer, some specimens were evaluated for a $M_n = 30,000$ daltons polyimide (while keeping the bonded conditions same) to understand the effect of molecular weight on the fracture energy. A higher molecular weight polymer is expected to demonstrate increased toughness though it often requires higher bonding pressures to make a good bond. In this regard, it was to be seen whether a low bonding pressure of 100 psi was sufficient in adequately bonding the higher molecular weight ($M_n = 30,000$ daltons) polyimide. Additionally, some specimens were made using both the molecular weight versions (with the surface consisting of 15K polymer and the bulk core of 30K

polyimide) to see if improvements in fracture energies could be obtained. In this case, the lower molecular weight polyimide was kept closer to the metal surface whereas the higher molecular weight polyimide constituted the bulk of the polymer adhesive. The reasoning behind such a design was that the lower molecular weight version would facilitate adequate spreading to ensure a good adhesive interface while the bulk of the adhesive would show increased toughness as it was constituted of the higher molecular weight polyimide. However, it remained to be seen whether the low bonding pressure of 100 psi was sufficient in adequately mixing the two different molecular weight versions of the polyimide.

7.5 Results and discussion

One of the most desirable characteristics often required of the adhesive is the resistance to attack from a variety of solvents. To this end, the presence of crystallinity in the polymer (like in the polyimide under discussion) is especially useful as it generally leads to improved solvent resistance. From this viewpoint, in a previous study⁷, TPER-BPDA lap-shear adhesive specimens were exposed to a variety of solvents typically used in aerospace applications. The results achieved in that study were very promising, as there did not seem to be any effect by any of the solvents even after a period of nine days. For specimens exposed to boiling water for as long as 72 hours, the lap-shear strengths were still high at above 4300 psi. These results also compared favorably with other similar studies reported in the literature⁸⁻¹³.

7.5.1 Wedge Tests

While such an initial lap-shear study provided some qualitative idea about the degree of solvent resistance, it was realized that a 'lap-shear' specimen geometry is not best suited for testing the solvent resistance of adhesive bonds. This is because any environmental

attack may be limited to the edges of the bond and not over the total specimen. The effect due to different solvents then depends upon the diffusion of the solvent into the central regions of the bond and towards the adhesive interface. Also, any degradation due to the solvent attack is non-uniform across the bonded area. Such conditions are thus not ideally suited for testing the effect of environment on the adhesive.

A wedge test provides a better and a more severe way of testing the effect of various solvents on the bond performance. In this test, the solvent attacks closer to bondline and directly at the site of the initiated crack. It is thus not surprising that wedge tests often lead to interfacial fracture surfaces. This feature has also made the 'wedge test' a method of choice when testing the efficacy of various surface pretreatments.

For the present study the same solvents as the ones used in the previous lap-shear testing were utilized. This also included the 72-hour water boil test, which is usually one of the most severe conditions utilized in such measurements. Due to the experimental nature of the present polyimide, a large amount of this polymer was unavailable. As the amount of polymer required per sample is relatively large for such tests, the testing was restricted in that only two samples were utilized for each solvent exposure. Although, this sometimes resulted in significant differences between the results for the two samples, it is believed that it still provided sufficient understanding of the adhesive performance on exposure to different solvents.

For the wedge tests, the bonding conditions utilized were the ones optimized in an earlier lap-shear study⁷. As the mode of fracture and testing method is different for the wedge test, these conditions may not represent the best possible conditions for a wedge test geometry. For this preliminary study, the objective was to gain a better understanding of the fracture behavior in different solvents. It was also important to see if the 'grit blasting' surface treatment, found sufficient in an earlier lap-shear study, was still effective in providing cohesive failures and not clean interfacial failures instead. The bond thickness was kept similar for all the bonds and averaged at ca. 0.20 ± 0.05 mm with only minor variations (always less than 0.05 mm) along the bonded area for any particular bond.

The results for the wedge tests are shown in Figure 7.2(a) and 7.2(b), with the results for the two samples plotted separately (in no particular fashion). It is clear that for

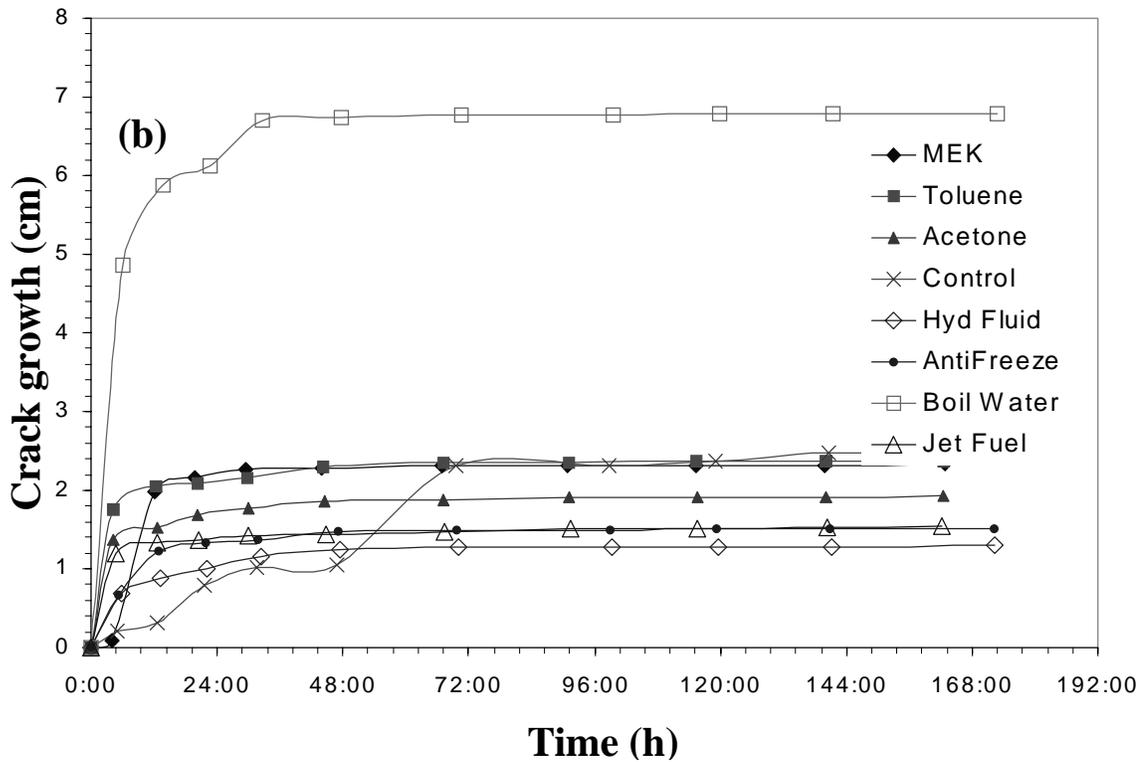
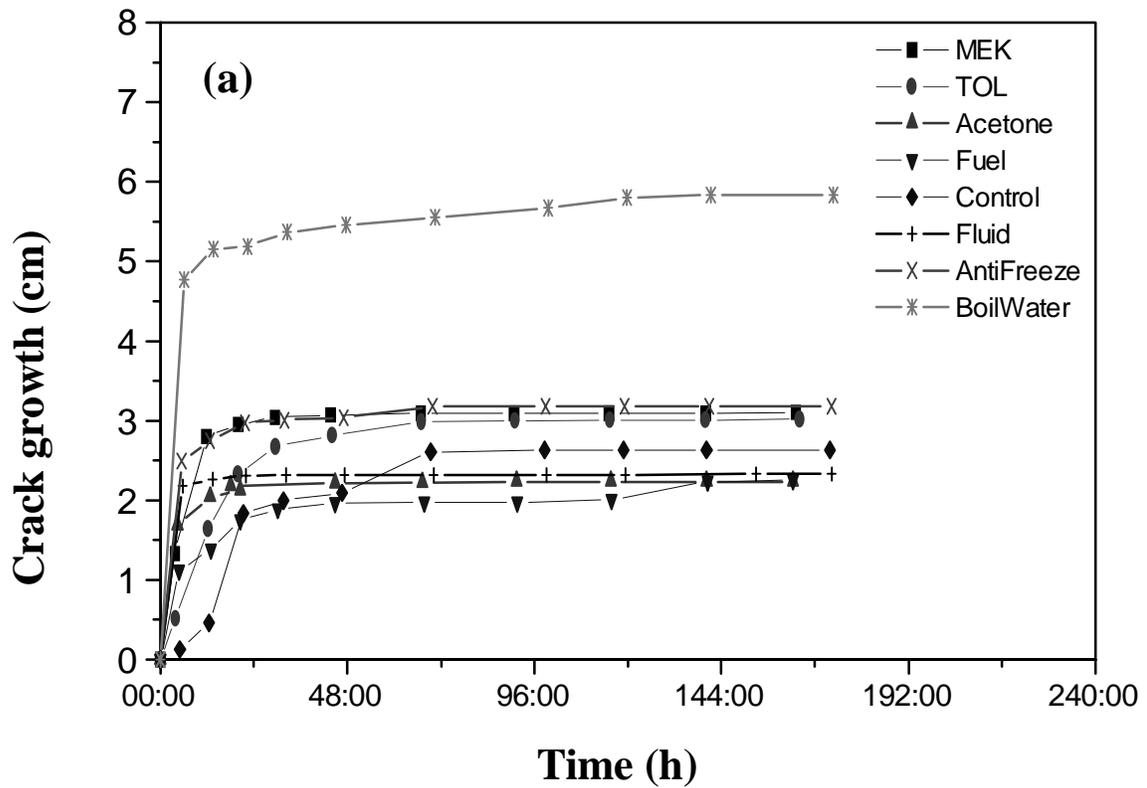


Figure 7.2 Crack growth vs. time in various solvents. (a) and (b) represent the data for each of the two samples.

most of the samples, a significant percentage of the total crack growth takes place in the first 24 hours of the experiment, where the driving force for the crack is at a maximum. The crack growth then tends to stabilize towards a particular value. The total crack growth value, however, depends upon the solvent being used. From the results it is clear that boiling water results in maximum crack growth (ca. 5-7 cm) whereas the rest of the solvents lead to only a modest crack growth of ca. 1.05 to ca. 3.00 cm. It is, however, observed that due to the nature of the test, subtle differences exist in the results obtained for the two samples for any particular solvent. Thus it can only be argued that 'boiling water' stands out as clearly the most severe environment whereas the rest of the solvents are similar in the effect they cause on the adhesive. Furthermore, it is noted that there are no clear differences in the crack propagation between the control specimen (placed in a dessicator) and that for samples placed in various environments. This suggests that the various solvents (except the boiling water) are no more effective in propagating the crack than the control environment itself. This then clearly indicates the relative stability of the adhesive bonds on exposure to various solvents.

The arrest strain energy release rate for various solvents is calculated by using the stabilized value of the crack growth in the equation presented earlier. This results in strain energy release rates of ca. 100-200 J/m² for bonds in boiling water and 900-1000 J/m² in other solvents. Figure 7.3 shows the photomicrographs of samples that were dipped in acetone and boiling water and were later completely fractured after the completion of the test. The fracture surfaces clearly reveal polymer on both sides of the specimen thus indicating a cohesive failure. In fact, an interfacial failure was not observed for any of the wedge samples. This clearly demonstrates the effectiveness of the grit blasting surface treatment and the utilized bonding conditions in providing a suitably strong interface. These results thus reinforce the previously derived conclusions from the lap-shear study about the efficacy of the simple 'grit-blasting' surface treatment.

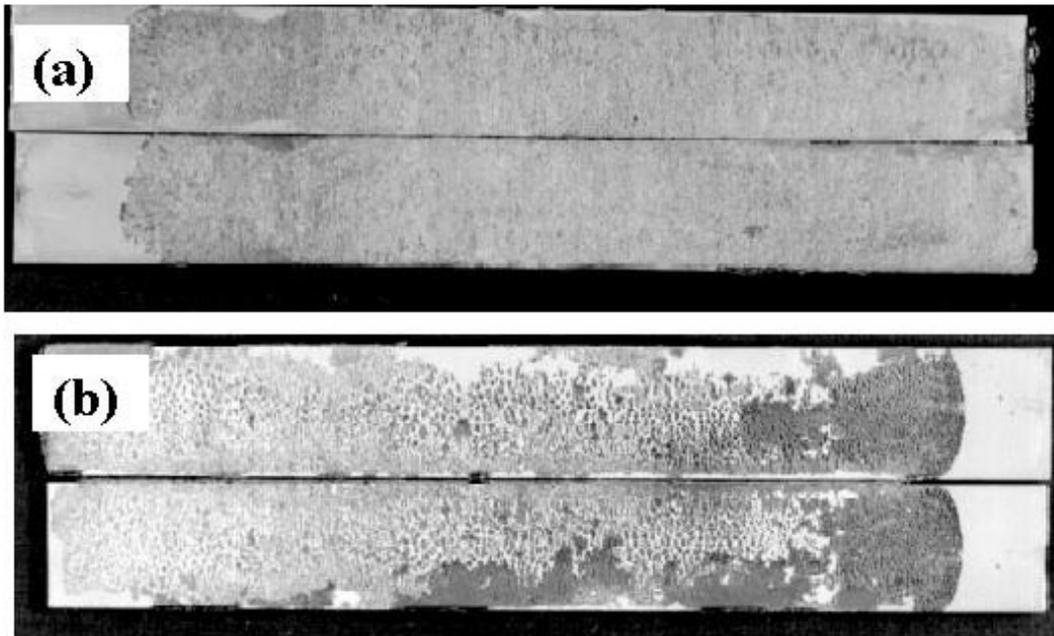


Figure 7.3 Fractured wedge test samples in environment (a) acetone (b) boiling water.

7.5.2 Double cantilever beam tests

The bond thickness for the various specimens was similar to the wedge test specimens and averaged at 0.20 ± 0.05 mm. The first set of specimens consisted of samples that used the bonding conditions utilized earlier in the lap-shear and the wedge test study. The load vs. displacement curves for one of the samples is shown in Figure 7.4(a). Figure 7.4(b) also shows the corresponding plot for the cube root of compliance vs. crack length that was utilized to calculate the fracture toughness using the compliance method. Good results were obtained for both of these samples and are plotted in Figure 7.5. The maximum strain energy release rate G_{\max} was found to be ca. 1600-2000 J/m² for the two samples. The arrest strain energy release rate was found to be ca. 1200-1600 J/m². While the calculated values for the strain energy release rates were similar, it was found that the standard deviation and the differences between the two samples were much less when the compliance method was utilized. The mode of the failure for both these samples was purely cohesive as is clearly visible in the photomicrograph of one of the samples (Figure 7.6). For closer examination of the fracture surface, small sections of the fractured specimen from both sides were cut and observed using the scanning electron microscope. Figure 7.7(a), which is a lower magnification micrograph, shows the fracture surface representative of the total area on both sides of the specimen. The fracture surface shows considerable roughness with the polymer being pulled apart in long striations running parallel to the width of the specimen. A higher magnification micrograph in Figure 7.7(b) better illustrates the considerable ductility exhibited by the polymer. These observations suggest considerable toughness exhibited by the adhesive and go along with the results achieved.

Additionally some samples were bonded for only 2 min (instead of 20 min for the standard conditions) in order to see whether such a short bonding time could be sufficient in attaining good fracture strengths. The results shown in Figure 7.8, reveal a considerable drop in fracture toughness with G_{\max} decreasing to 1000 J/m² and ca. 500 J/m² for the two samples. The arrest strain energy release rate also shows a considerable decrease and falls to ca. 800 J/m² and 375 J/m² for the two samples. The

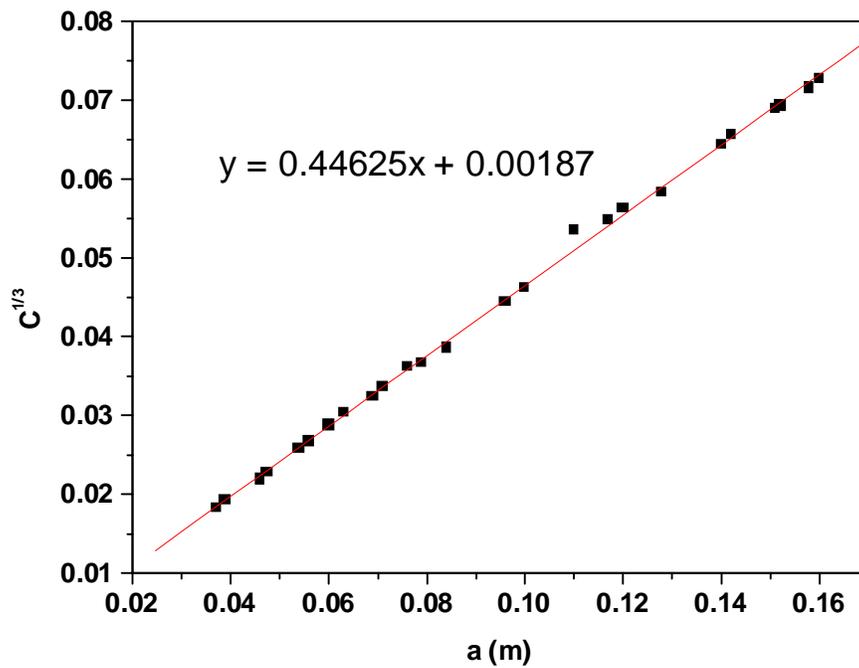
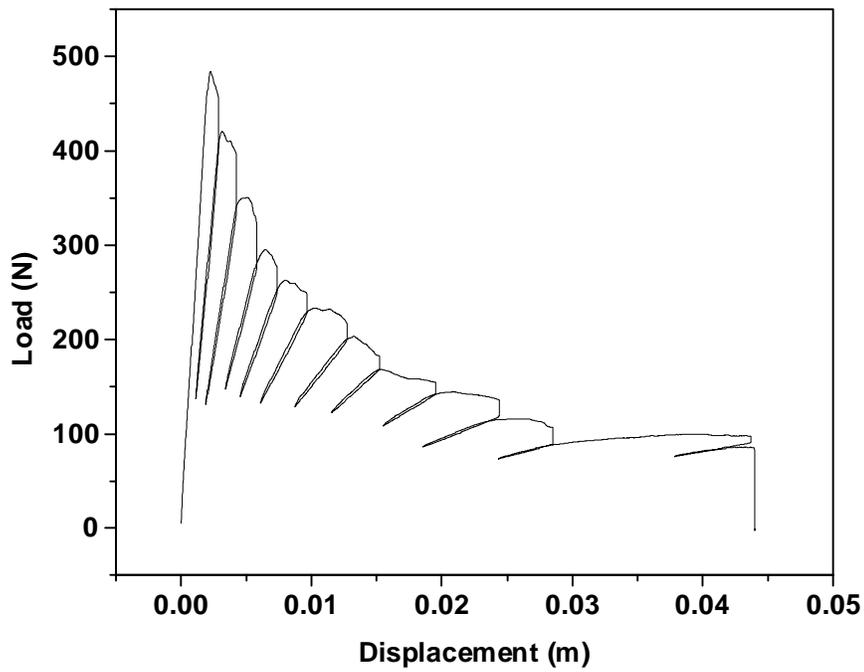


Figure 7.4 (a) Collected data for the DCB sample for the standard bonding condition (b) Calculation using the compliance method.

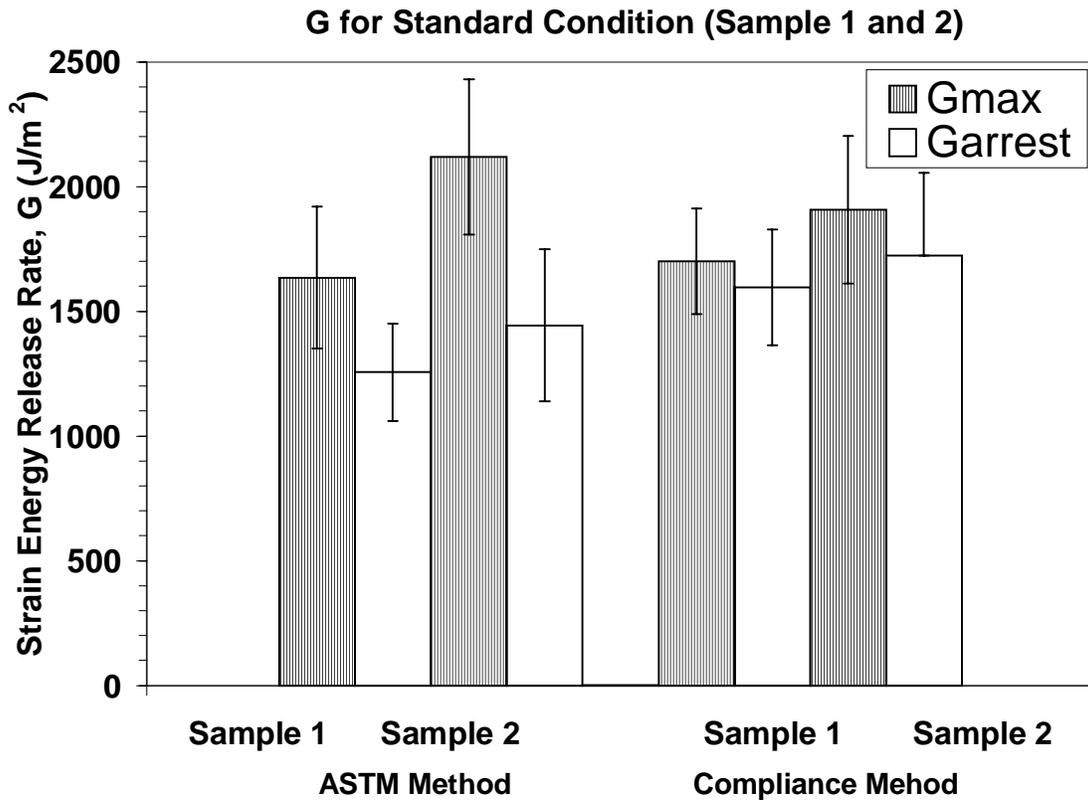


Figure 7.5 Maximum and Arrest strain energy release rates for samples bonded under the standard bonding conditions. Both ASTM and Compliance method are used to calculate the results.

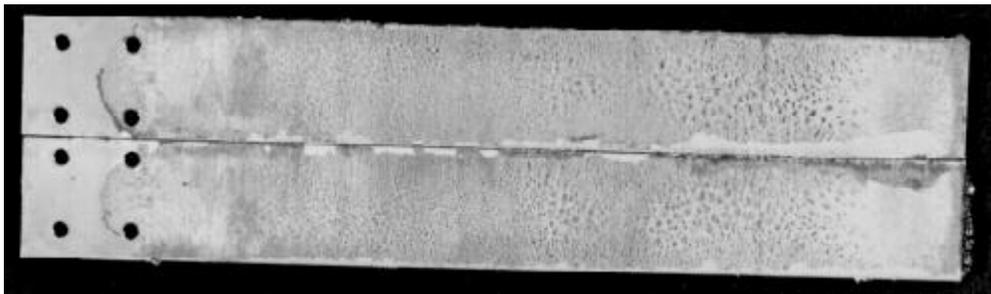


Figure 7.6 Photomicrograph of the fractured DCB specimen that was bonded under the standard bonding conditions.

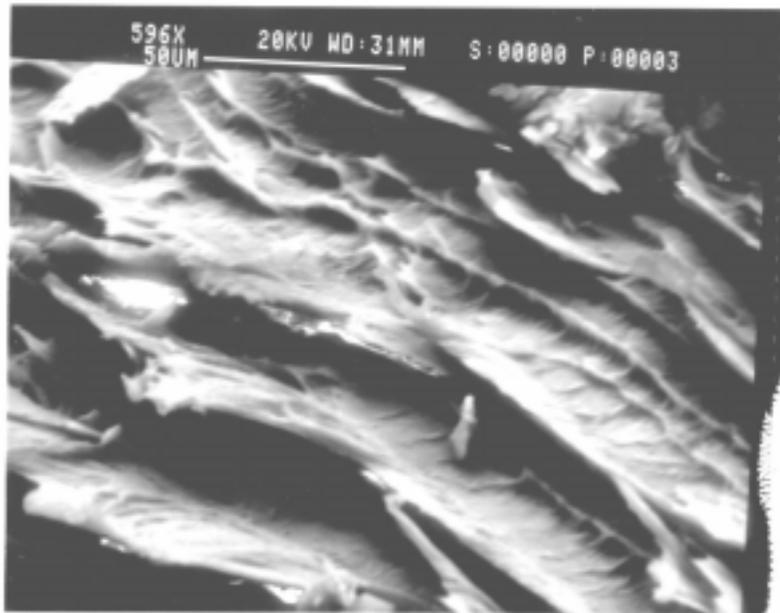
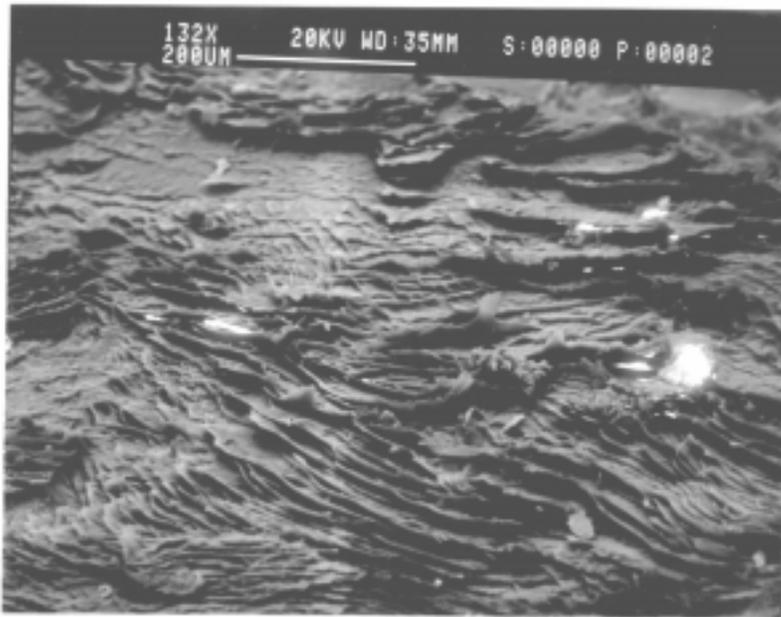


Figure 7.7 Scanning electron micrographs of the fractured DCB specimen that was bonded under the standard bonding conditions. (a) Lower magnification (b) Higher magnification

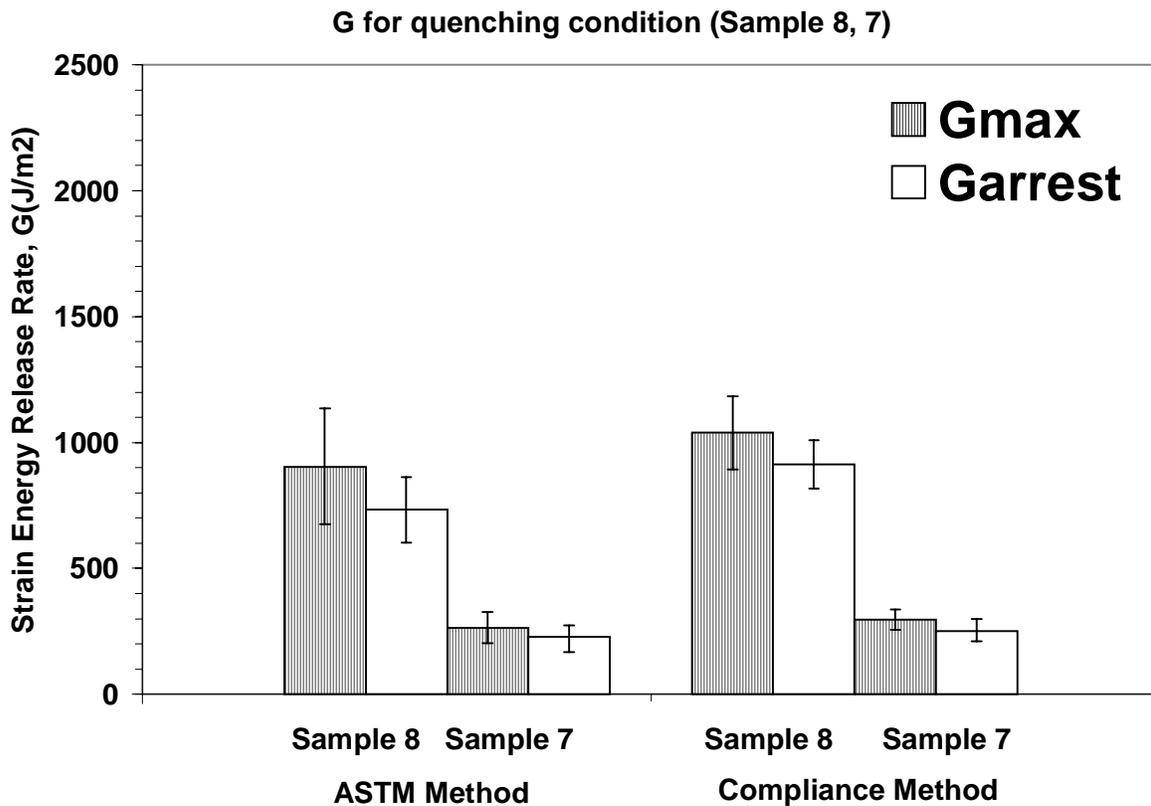
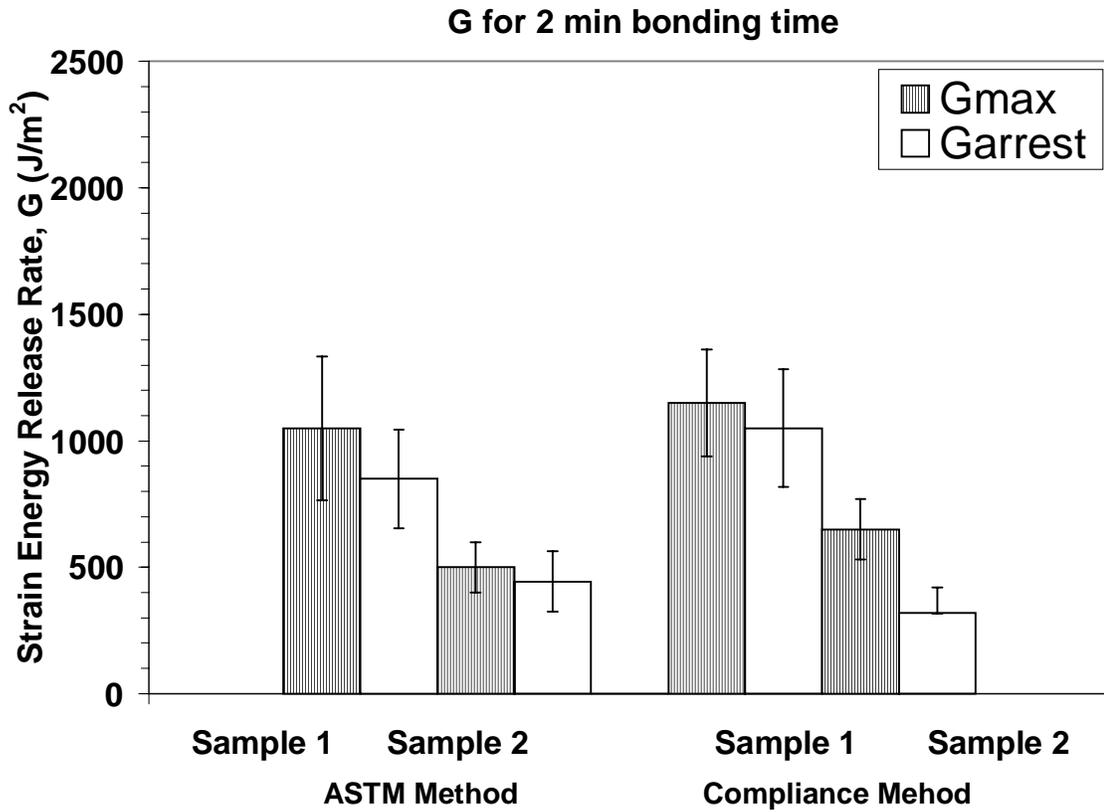


Figure 7.8 Results for the samples (a) that were only bonded for 2 min and (b) that were quenched to room temperature from the standard bonding conditions.

photomicrographs for the better sample is shown in Figure 7.9 and seems to exhibit considerable interfacial failure (visual observation only). This indicates the poor wetting of the surface achieved in such a short bonding time.

Another variation tried in the bonding conditions was quenching the bonded samples to room temperature instead of cooling at ca. 20°C/min. Though the photomicrographs suggest cohesive failure (not shown here), the obtained fracture energy values are much lower at ca. 900 and 200 J/m². This indicates relatively poorer consolidation of the sample at such fast cooling rates. Some samples were also held at 365°C for 2 hours from the melt before being cooled to room temperature. Based on earlier studies, these conditions should promote large sized spherulites instead of the fine grainy morphology promoted by the standard bonding conditions. These samples were thus expected to show lower toughness that is associated with such a coarse spherulitic morphology. *Interestingly, both samples that were bonded at these conditions exhibited 'catastrophic failures' along the complete length of the specimen when the wedges were inserted!* This brittle fracture was purely cohesive (Figure 7.10) and is thereby representative of the poor adhesive mechanical properties that result due to such conditions.

7.6 Conclusions

It is clear that TPER-BPDA-PA adhesive exhibits excellent solvent resistance even when the fracture surface is exposed to variety of solvents in a wedge-opening mode. While none of the common solvents seems to have any major effect on the fracture toughness of the adhesive, 'boiling water' results in significant drop in 'arrest strain energy release rate'. Most of the crack growth for any environment occurs in the first 24 hours after which the crack growth seems to slow down significantly. Also it is clear that 'grit-blasting', as surface treatment is effective in providing a strong interface, as indicated by mostly cohesive failure for most of the samples.

The double cantilever beam tests yield the best results for the bonding conditions utilized for the wedge test study and the previous lap-shear study, thus re-emphasizing the effectiveness of these bonding conditions in making a strong, tough and durable adhesive bond. The photomicrographs reveal a clear cohesive fracture surface whereas the SEM investigations indicate considerable ductility in the fractured polymer and a rough fracture surface, which go along with the high strain energy release rates for the specimens. Reducing the bonding time or quenching the bonds quickly to room temperature results in a lowering of the fracture toughness. The prior conditions also promote interfacial failures possibly due to incomplete wetting of the substrate. Interestingly, promoting a coarse spherulitic morphology by changing the bonding condition results in very brittle bonds that fail catastrophically along the complete length of the specimen on insertion of the wedge.

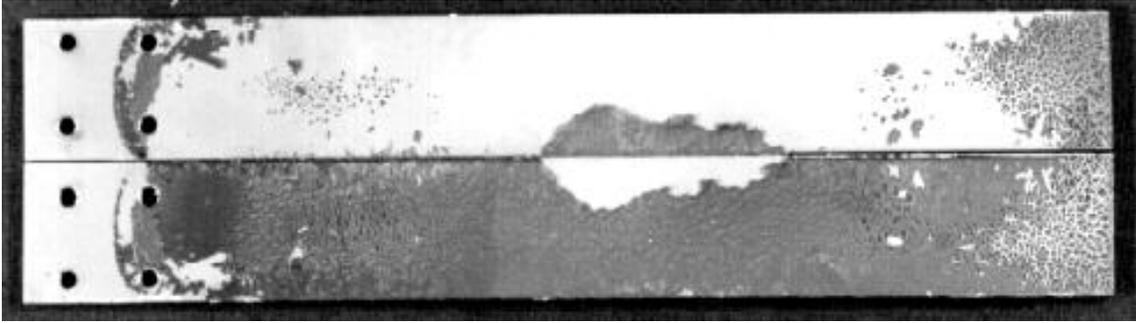


Figure 7.9 Photomicrograph of the fractured DCB specimen that was bonded for only two minutes.

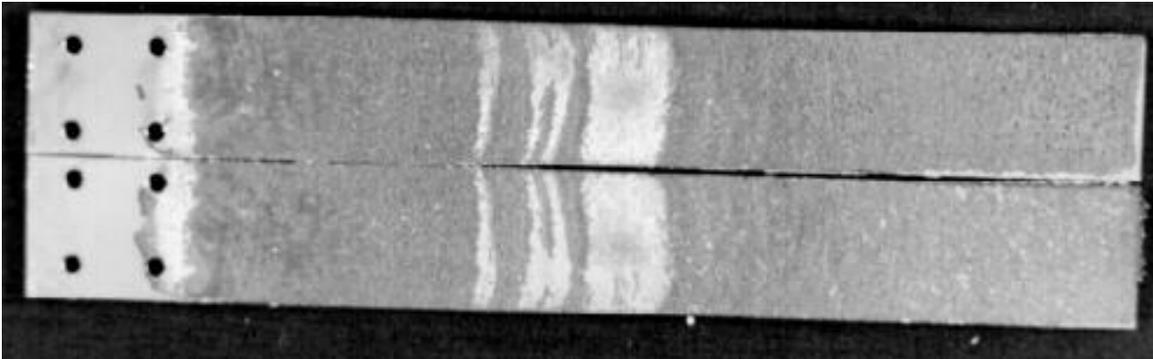


Figure 7.10 Photomicrograph of the fractured DCB specimen that was held at 365°C for 2 hours before cooling to room temperature.

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