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INTERLAMINAR FRACTURE TOUGHNESS OF THERMOPLASTIC COMPOSITES

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INTRODUCTION

Thermoplastics are currently being considered for use as matrix resins in high performance composites. Besides the potential advantages of unlimited shelf life and rapid, inexpensive processing, a major reason for the interest in these materials is their much greater fracture toughness relative to typical 350°F-cure epoxy resins. Improvements in resin toughness are desirable as one approach to improving delamination resistance and damage tolerance in composite structures.

Extensive testing using the double cantilever beam (DCB) test has shown a reasonable correlation between resin toughness, as measured by compact tension tests on neat resin castings, and composite interlaminar fracture toughness [1]. However, two complications arise in the DCB testing for interlaminar fracture toughness: $G_{IC}$ values as measured by the DCB test may be affected by fiber bridging and the adhesion between carbon fibers and the thermoplastic matrix may be poor.

The present work examines the interlaminar failure process in four experimental composite materials using both the double cantilever beam (DCB) and the edge delamination tension (EDT) tests. The EDT test was chosen to give an alternate measure of interlaminar fracture toughness that would not be influenced by fiber bridging, and would quantify the influence of residual thermal stresses on delamination onset. One set of experiments was conducted on composites with a model thermoplastic resin matrix to illustrate the effect of varying fiber surface properties on delamination toughness. The other set of experiments was conducted on composites with novel high-temperature thermoplastic polyimides. The latter tests illustrate the significant effect of thermal stresses on delamination onset strain in composite laminates made at high consolidation temperatures.
Materials and Processing

The fibers, AS4 (Hercules, Inc.) and XAS (Hysol Grafil)* were supplied unsized, but with the manufacturer's proprietary surface treatment. Previous work had shown that these two fibers behave very differently toward polycarbonate in single-fiber adhesion tests [2]. Polycarbonate resin (Lexan 101 from General Electric Co.) was selected as a model tough thermoplastic, largely because its behavior in neat resin form is well-characterized. Prepreg was made by drum-winding where the resin was applied as a 17% w/w solution in a 50:50 mixture of chloroform: methylene chloride. Before laminating, prepreg was dried for one hour at 400°F in a forced-air oven. Thermogravimetric analysis of the prepreg after drying showed less than 1% weight loss in heating to 570°F.

Laminating was performed in a matched metal mold in a heated press at 200 psi. A 15-minute hold at 500°F was followed by a 2-hour hold at 473°F. Multidirectional laminates showed small areas of visible fiber waviness in the surface plies after consolidation, whereas unidirectional panels had relatively straight fibers (Figure 1). This fiber waviness has been commonly observed to occur in other thermoplastic composites [3,4]. However, ultrasonic C-scan evaluations indicated good consolidation in all panels, with the exception of the cross-plied XAS laminates where some attenuation was noted. As will be shown later, dye-penetrant-enhanced radiography of the EDT specimens of this XAS/polycarbonate material revealed

*Use of trade names or manufacturers does not constitute an official endorsement, either expressed or implied, by the National Aeronautics and Space Administration.
extensive ply cracking in every ply direction. These cracks were present even in an untested specimen.

The polyimide blends consisted of 1:1 mixtures of commercial LARC-TPI powder with a polyamic acid (either LARC-TPI or polyimidesulfone). They were prepregged onto AS-4 fiber using a slurry process [5]. Each blend also contained 2.5 weight percent of the diamic acid formed by the reaction of p-diaminobenzene and phthalic anhydride. This additive had been shown to improve the flow of thermoplastic polyimides [6]. For simplicity, the two blends will be referred to simply as TPI blend and polyimidesulfone blend. The prepreg was dried and imidized for one hour at 500°F then 3" x 6" laminates were press-molded in a 3 to 4-1/2 hour cycle with a maximum temperature of 660°F and 1000 psi pressure. Laminates prepared at lower pressures had a high void content, as judged by C-scan. Repressing these panels at 660°F and 1000 psi gave acceptable laminates.

Test Procedures and Calculations

Specimens for the polycarbonate double cantilever beam test were cut from 24-ply unidirectional laminates containing a 0.005"-thick x 1.5" wide Kapton film at the midplane as a crack starter. Pin-loading was introduced through 1/2" aluminum blocks bonded to the beam ends. Results were analyzed using the compliance calibration method [7]. Crosshead speed was 0.05"/min, and specimen compliance was determined from the opening load vs. time record. Crack propagation was steady. In the case of the polycarbonate matrix laminates, extensive fiber bridging caused the apparent $G_{IC}$ to increase rapidly as the crack advanced from the Kapton insert, typically reaching a steady-state value after a crack extension of only 0.5". The steady-state values were typically 30-100% larger than the initial values.
Initial values only are reported, since they are regarded as more characteristic of the toughness which would be obtained in the absence of fiber bridging. For all of the tests, three to five specimens were tested, and the results were averaged. Procedures for the polyimide matrix DCB tests were identical, except the specimens were only twelve plies thick. The data reduction took into account geometric nonlinearity by the method of Devitt et al [8].

Edge delamination tests were performed on (+45/−45/0/90)_s specimens that were 0.5" or 1" wide with a 3" section between the grips. No differences in delamination strain were seen between the two different widths. A layup containing 0° plies was chosen to minimize non-linearity in the stress-strain curve before onset of delamination, and sixteen plies were used to insure that the delamination strain was below the failure strain of the 0° fibers [4,9,10]. Delamination was detected visually on the free edges, which had been coated with water-based typewriter correction fluid. Total critical strain-energy release rates are calculated via the formula

\[ G_c = \frac{\varepsilon_c^2}{2} \left( E_{\text{lam}} - E^* \right) \]  

where \( \varepsilon_c \) is the delamination strain, \( t \) is the laminate thickness, \( E_{\text{lam}} \) is the original laminate modulus, and \( E^* \) is the modulus of a completely delaminated specimen, which may be calculated using the rule of mixtures equation

\[ E^* = \frac{1}{t} \sum E_i t_i \]  

where \( E_i \) and \( t_i \) are the modulus and thickness, respectively, of the sublaminates formed by the delamination [3,9,11]. The sublamine moduli
may be calculated from ply properties, or from the measured stiffness of symmetric sublaminates [3]. For the materials used in the present study, these customary procedures had to be modified slightly. For each material, ply properties were obtained as before from tensile measurements on \((0_8), (90_{12}),\) and \((\pm 45)_{2s}\) laminates [11]. The results are shown in Table I.

These properties were used with classical laminated plate theory to predict the modulus of the quasi-isotropic layup employed in the EDT test. When this prediction was compared with the measured values \(E_{1am}\), however, it was found that the actual specimen moduli fell below the predictions by 5 to 30 percent. Since it was known that the specimens contained wavy fibers, the discrepancy between the measured moduli and the laminate theory prediction was attributed to fiber waviness in the quasi-isotropic laminates. Such waviness was also noted in Ref [4] for AS-4/PEEK. The rather large variability in \(E_{1am}\) among specimens cut from the same plate was assumed to be due to variations in the degree of fiber waviness across the plate - primarily in the \(0^\circ\) plies, since they dominate the tensile modulus. It follows, then, that a proper value of \(E^*\) for each specimen should take account of this variability. Therefore, the following procedure was adopted. Various values of \(E_{11}\) were used in the laminate theory until the measured value of \(E_{1am}\) was obtained. This "adjusted" ply modulus, \(E_{11}\), was then used to calculate the corresponding sublamine modulus \(E^*\) for that specimen. Typically, the adjustment amounted to about 15% of \(E_{11}\). This procedure gave the most accurate values of \((E_{1am} - E^*)\) for each test specimen, and yields the most realistic values of \(G_c\) from Eq. (1).

The effects of thermal stresses introduced during cool-down from the processing temperature were evaluated using a finite-element (FEM)
calculation [12]. Total $G$ could have been calculated using plate theory analysis [13], but FEM was used for convenience since it was available. The mesh used is shown in Figure 2 in Reference [12]. The rectangular mesh had 367 nodes with 102 eight-noded parabolic elements. This element size at the delamination tip has been shown to yield accurate strain energy release rate components [14].

The stress-free temperature for each material was determined by fabricating a $(0_2/90_6)$ laminate, which bowed upon cool-down. A strip of this laminate was heated in an oven at approximately $4.4^\circ$C/min and the height of the arc was monitored with a DCDT (Figure 2a). The temperature at which the strip flattened completely was taken as the stress-free temperature (Figure 2b). As expected, this temperature closely matched the glass transition temperature of the matrix resin.

Thermal expansion coefficients of the laminae were assumed to be zero in the fiber direction. Transverse expansion coefficients were measured near room temperature using an interferometric technique, or calculated from the resin and fiber properties using the concentric cylinder model of Hashin [15]. In the two cases where both were available, the measured and calculated values showed fairly good agreement, indicating the technique was reasonably accurate. Results are shown in Table II.

RESULTS AND DISCUSSION

Initial $G_{IC}$ values for the AS-4/polycarbonate and XAS/polycarbonate obtained from the first increment of crack growth beyond the insert in the DCB test, were 7.4 and 5.1 in-lb/in$^2$, respectively. Scanning electron
micrographs (SEM) of the fracture surfaces show, in both cases, extensive matrix deformation (Figure 3). There does seem to be a qualitative difference in fiber/matrix adhesion in the two cases, however. On the AS-4/polycarbonate (PC) fracture surface (Figure 3a), many fibers are judged by SEM examination to be completely bare, stripped of resin, and threads of drawn polymer litter the surface. In the XAS composite, by contrast, most fibers seem to retain shreds of polymer (Figure 3b). These observations are consistent with the degrees of adhesion measured for the two systems using embedded-fiber fragmentation tests [2]. Table III reproduces some results from Reference [2]. The critical fragment length \( l_c \), which provides a quantitative measure of fiber/matrix adhesion, seems to be quite large for AS-4/PC, indicating very poor adhesion. As a point of reference, the critical length for AS-4 in an epoxy resin is about 0.4 mm. The much smaller critical length for XAS/PC is indicative of better adhesion, although one would need to know the tensile strengths of the two fibers at submillimeter gauge lengths to calculate the relative strengths of the interfacial bonds. A second, independent line of evidence, however, tends to confirm the difference in adhesion to the two fibers. This is the birefringence pattern which arises around the broken fiber ends. It is quite distinctive, and shows characteristic features of poor adhesion with AS-4 and good adhesion with XAS. Based on the data above, therefore, poor fiber/matrix bonding, such as that between AS-4 and polycarbonate, appears to yield higher composite interlaminar fracture toughness as measured by the DCB test. This is a surprising result, and should be regarded with caution. In Reference [16], fiber/matrix debonding in DCB tests was said to contribute to increased \( G_{IC} \) by increasing fracture surface area, by
promoting fiber bridging, and by relieving stress triaxiality, thereby allowing more resin deformation. These effects, and especially fiber bridging, are normally observed after the delamination has grown some distance from the insert [17]. However, in the present study, increased toughness was found for initiation values. A possible explanation would be that in this case fiber bridging began to develop immediately at the insert. This conclusion must be regarded as tentative, though, because the hypothesized bridging was not detected directly.

In the edge delamination tests, delamination occurred, as expected, at the 0/90 interfaces with the failure plane wandering back and forth through the central 90° plies [3,9,11]. Dye-penetrant x-ray photos (Figure 4a) show that in the AS-4/PC composites, the 90° cracks do not extend much beyond the delaminated region indicating that they form after the delamination [11]. In contrast dye penetrant-enhanced radiographs of the XAS/PC showed extensive matrix or interfacial cracks throughout the laminate width in all plies. As mentioned earlier, this cracking was present before any mechanical load was applied. Micrographs of the 0/90 delamination fracture surfaces of both the AS-4/PC and XAS/PC EDT specimens are dominated by what appear to be bare fibers and resin tracks left by fibers which peeled out cleanly (Figure 5). The resin in the XAS/PC composite appears to have fractured brittlely (Figure 5b). This apparent matrix brittleness was completely unexpected, and two possible explanations for it have been considered. If polymer crystallinity was being nucleated by the fiber surface [18], the apparent brittle behavior might have been understandable, but no evidence of matrix crystallinity was found by differential scanning calorimetry or by wide-angle x-ray scattering. Another possibility - that
trace impurities on the fiber surface could catalyze resin degradation - was also ruled out, since resin dissolved from the XAS composite had not decreased in inherent viscosity. Thus the reason for the brittle appearance of the resin in Figure 5b is still not clear. The EDT results are compared with those from the DCB test in Figure 6, in which the superscripts \( M \) and \( T \) stand for mechanical and thermal stress contributions to \( G_C \). Both tests indicate that the AS-4 composite possesses the higher interlaminar toughness. Note, however, that the total \( G_C \) as measured by the EDT is lower than the DCB result for \( G_{IC} \). This trend has been observed in other materials [3], but with polycarbonate the difference is striking. Including thermal stresses in the EDT calculations raises the EDT results, but only by less than 20% because the \( \Delta T \) between the consolidation temperature and room temperature is not very large. The large differences between the DCB and the EDT values in this case are tentatively attributed to the effects of fiber bridging in the DCB test, although this has not of course been shown conclusively. The processing [1] and other factors which lead to bridging in unidirectional specimens are not yet fully understood.

**AS-4/Polyimide Blends**

Double cantilever beam specimens of these materials showed much less obvious fiber bridging than the polycarbonate, although an increase in \( G_{IC} \) with crack length was again noted. Because there was no resin squeeze-out during fabrication of these panels, the fibers probably could not nest effectively, and the fracture surfaces were quite flat.

In the edge delamination tests, these two materials behaved similarly, and their fracture surfaces again show regions of bare fibers and resin troughs where fibers have peeled out (Figure 7). The SEM of the PISO\(_2\)/LaRC-
TPI surface in Figure 7b indicates some fine-scale heterogeneity, which may result from incomplete blending of the LaRC powder with the PISO2 binder. Whether better mechanical mixing is needed, or whether these two polymers are thermodynamically incompatible is not known.

With the higher softening temperatures of these polyimides relative to conventional epoxy matrices, the issue of thermal stresses assumes much greater importance, as will be clear from an examination of the EDT results in Figure 8. The strain-energy release including thermal stresses \( G^{M+T} \) is almost twice as large as that due to the mechanical strain only, \( G^M \). As mentioned earlier, one reason for using the EDT test is to illustrate this role of residual stresses in delamination. The EDT test is performed with a realistic laminate which inherently contains residual thermal stresses \([4,10,13]\). In the case of these thermoplastic polyimides, the contribution of residual stresses to delamination is significant, amounting to 28 and 32 percent of \( G_c^{M+T} \) for the TPI and polyimidesulfone blends, respectively.

Figure 8 also shows the relative magnitudes of \( G_{IC} \) determined from the DCB test and total \( G_c^{M+T} \) calculated from the EDT test. For the polyimide materials, unlike the polycarbonate, one sees that total \( G_c \) is comparable in magnitude to \( G_{IC} \). The layup chosen for the EDT test in this work produces almost a pure mode I delamination, so this would be expected. Furthermore, Johnson and Malgalgiri \([19]\) have shown that for other tough resin composite systems, including the thermoplastic PEEK APC2, \( G_{IC} = G_{IIc} = G_c \) at delamination onset.
SUMMARY AND CONCLUSIONS

The edge delamination test and DCB test gave similar toughness rankings for the fiber/resin combinations studied here. Fiber bridging seems to greatly affect the DCB results for the tough thermoplastic, even at onset from the insert, although this effect is not fully understood.

A procedure based on adjusting the modulus of $0^\circ$ plies in a laminate is a reasonable way to account for the effects of fiber waviness on composite laminate stiffness in thermoplastic materials. This procedure was needed to accurately measure $G_C$ from the EDT test.

Thermal residual stresses must be considered when analyzing results of EDT tests on higher-temperature matrix materials. In one graphite/polyimide system, the thermal contribution amounted to 32% of the total $G_C$.

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# TABLE I

## PLY PROPERTIES

<table>
<thead>
<tr>
<th>MATERIAL</th>
<th>$E_{11}$</th>
<th>$E_{22}$</th>
<th>$G_{12}$</th>
<th>$v_{12}$</th>
<th>Fiber Volume [%]</th>
<th>Average Ply Thickness $h$, x10$^3$ in</th>
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<tr>
<td>AS4/Polycarbonate</td>
<td>17.7</td>
<td>1.10</td>
<td>0.71</td>
<td>0.37</td>
<td>55.8</td>
<td>6.08</td>
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<td>XAS/Polycarbonate</td>
<td>19.0</td>
<td>1.37</td>
<td>0.44</td>
<td>0.37</td>
<td>55.1</td>
<td>5.63</td>
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<tr>
<td>AS4/LARC-TPI + LARC-TPI Powder</td>
<td>20.8</td>
<td>1.64</td>
<td>0.91</td>
<td>0.34</td>
<td>56.5</td>
<td>5.21</td>
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<tr>
<td>AS4/Polyimidesulfone + LARC-TPI Powder</td>
<td>18.4</td>
<td>1.29</td>
<td>0.78</td>
<td>0.34</td>
<td>52.0</td>
<td>6.55</td>
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**TABLE II**

**THERMAL EXPANSION PROPERTIES**

<table>
<thead>
<tr>
<th>LAMINATE</th>
<th>MEASURED STRESS-FREE TEMPERATURE, °C</th>
<th>RESIN</th>
<th>CALCULATED COMPOSITE $a_2$</th>
<th>MEASURED COMPOSITE $a_2$</th>
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<tr>
<td>AS4/Polycarbonate</td>
<td>130</td>
<td>67.5</td>
<td>41.2</td>
<td>36.7</td>
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<tr>
<td>XAS/Polycarbonate</td>
<td>--</td>
<td>67.5</td>
<td>51.5</td>
<td>--</td>
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<tr>
<td>AS4/TPI blend</td>
<td>229</td>
<td>45</td>
<td>29.3</td>
<td>--</td>
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<tr>
<td>AS4/Polyimidesulfone blend</td>
<td>243</td>
<td>45*</td>
<td>31.9</td>
<td>27.9</td>
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*Assumed*
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<tr>
<th>FIBER/MATRIX</th>
<th>CRITICAL FRAGMENT LENGTH*, mm</th>
<th>BIREFRINGENCE PATTERN</th>
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<tr>
<td>AS-4/PC</td>
<td>0.74</td>
<td>Poor Adhesion</td>
</tr>
<tr>
<td>XAS/PC</td>
<td>0.36</td>
<td>Good Adhesion</td>
</tr>
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</table>

*The critical fragment length is inversely proportional to the fiber/matrix interfacial shear strength if fiber breaking strength is constant.
Figure 1b) (0°/90°) AS-4/7894 blend showing relatively straight fibers in surface plies.
Figure 2a) Apparatus for determination of stress-free temperature (schematic).
DETERMINATION OF STRESS-FREE TEMPERATURE

Figure 2b) Arc height of (0_290_6)_T laminate as a function of temperature.
DOUBLE CANTILEVER BEAM FRACTURE SURFACE

AS-4 UNSIZED / LEXAN POLYCARBONATE

Figure 3a) Scanning electron micrographs (SEMs) of polycarbonate DCB fracture surfaces.
DOUBLE CANTILEVER BEAM FRACTURE SURFACE

XAS UNSIZED / LEXAN POLYCARBONATE

Figure 3b) SEM of XAS/polycarbonate AS-4/DCB fracture surface.
DYE-PENETRANT-ENHANCED RADIOGRAPHS OF DELAMINATED SPECIMENS POLYCARBONATE / AS-4

Figure 4. Dye-penetrant enhanced x-ray photographs of EDT specimens after testing. a) AS-4/PC
DYE-PENETRANT-ENHANCED RADIOGRAPHS
OF DELAMINATED SPECIMENS
POLYCARBONATE / XAS

Figure 4. Dye-penetrant enhanced x-ray photographs of EDT specimens after testing. b) XAS/PC
0/90 DELAMINATION SURFACE

POLYCARBONATE / AS-4

[+45 2/ -45 2/ 0 2/ 90 2] s LAMINATE

Figure 5. SEM photomicrographs of 0/90 delamination surfaces in EDT specimens.
   a) AS-4/PC
0/90 DELAMINATION SURFACE

POLYCARBONATE / XAS

[+45₂ / -45₂ / 0₂ / 90₂]ₜ LAMINATE

Figure 5. SEM photomicrographs of 0/90 delamination surfaces in EDT specimens.
   b) XAS/PC
Figure 6. Comparison of $G_{IC}$ (from DCB test) with total $G_c^{M+T}$ (from edge delamination test) for polycarbonate laminates.
0/90 DELAMINATION SURFACE

1:1 LARC TPI : LARC TPI / AS-4

\([+45_2/-45_2/0_2/90_2]_s \) LAMINATE

Figure 7a) SEM micrographs of fracture surface of AS-4/TPI blend EDT specimens.
0/90 DELAMINATION SURFACE

1:1 PISO₂:LARC TPI / AS-4

[+45₂/-45₂/₀₂/9₀₂]ₛ LAMINATE

Figure 7b) SEM micrographs of fracture surface of AS-4/polyimidesulfone blend.
Figure 8. $G_{lc}$ (from DCB) and $G_{c}^{M+T}$ (from EDT) for polyimide blends.
Interlaminar fracture toughness values for the thermoplastic polyimide composites (LARC-TPI and polyimidesulfone) were 3-4 in-lb/in². Scanning electron micrographs of the EDT fracture surfaces suggest poor fiber/matrix bonding. Residual thermal stresses account for up to 32% of the strain energy release in composites made from these high-temperature resins.