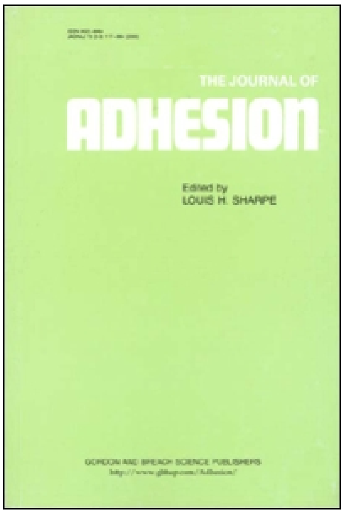

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Adhesive Fracture Energies of Some High Performance Polymers

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Adhesive Fracture Energies of Some High Performance Polymers

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A fracture mechanics approach was applied to determine the adhesive fracture energy of various high performance polymers. These polymers, including both thermosetting and thermoplastic materials, generally offer higher temperature capability than conventional epoxies. Double tapered cantilever beam specimens were used for fracture tests at both room temperatures and 225°C. The adhesive fracture energies of a tetrafunctional epoxy and a phthalocyanine resin were also determined at low temperatures. Adhesive fracture behavior of polymers at high temperatures was found to depend on polymer glass transition temperature, whereas at low temperatures it was related to secondary relaxation processes in the glassy state.

INTRODUCTION

Increasing application of fiber-reinforced organic composites as structural components in aerospace and marine systems has placed great demands on adhesive-bonding technology. This is because structural adhesive bonding is a very versatile and highly desirable method for joining composite structural elements either to themselves or to metals. In order to design adhesive bonded structures with reliability, one needs to recognize that structural adhesives are relatively brittle and stiff materials. Their failure mode is characterized by flaw growth and progressive crack propagation. The flaws that may be anticipated include internal cracks, surface cuts and microvoids inherently present as a result of the processing methods employed. Since continuum fracture mechanics is concerned with the strength of real solids with the presence of flaws and with flaw propagation under stress, the application of fracture mechanics to adhesive joint failure is considered. The energy criteria for

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fracture, based on the works of Griffith[1] and Irwin,[2] will be adopted. It supposes that fracture occurs when sufficient energy is released from the stress field to generate new fracture surfaces at the instant of crack propagation. This strain energy release rate provides a measure of the energy required to extend a crack over a unit area, and is termed the fracture energy. In this paper, the fracture energy of an adhesive layer in an opening mode will be determined for various high temperature adhesives since this property has been widely recognized as the appropriate criterion for adhesive failure.[3]

EXPERIMENTAL

Adhesive Fracture Mechanics

Based on linear fracture mechanics, the displacement l in the direction of a load P is

$$l = CP \tag{1}$$

where C is the compliance of the specimen. Under a fixed-load condition, any change in l may be related to a change in the crack length, a, by

$$\delta l = P\frac{\mathrm{d}C}{\mathrm{d}a}\delta a \tag{2}$$

The strain energy is $\varepsilon = 1/2P\delta l$, which defines the strain energy release rate, or fracture energy, G:

$$\varepsilon = 1/2P\delta l = Gb \cdot \delta a \tag{3}$$

where b is the specimen thickness. From Eqs. (2) and (3), one finds

$$G = \frac{P^2}{2b}\frac{\mathrm{d}C}{\mathrm{d}a} \tag{4}$$

Once $\mathrm{d}C/\mathrm{d}a$ is determined for a specific specimen geometry, a proper expression for G may be obtained to directly relate it to the load P and specimen dimensional parameters.

A tapered double-cantilever beam specimen as devised by Mostovoy and Ripling[4] was used for adhesive fracture evaluations. Figure 1 gives the schematic of this specimen. Neglecting the compliance of the adhesive, for this geometry the explicit form of Eq. (4) for an opening-mode fracture (Mode 1) at the onset of crack propagation is

$$G_{Ic} = \frac{4P_c^2}{b^2E}\left[\frac{3a^2}{h^3} + \frac{1}{h}\right] \tag{5}$$

where h is the beam height corresponding to the crack length a. The advantage

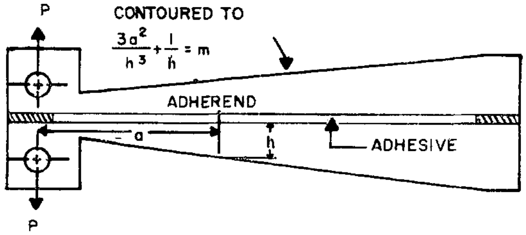


FIGURE 1 Double-tapered cantilever beams for adhesive fracture test.

of the double tapered cantilever beam is that the specimen may be tapered in such a way that the quantity in the bracket of Eq. (5) becomes a constant. The fracture energy therefore is independent of the crack length, and can be easily calculated once the failure load P_c is known. The Young's modulus E in this case is that for aluminum.

MATERIALS

The temperature range of conventional epoxy-based adhesive formulations is very limited. Recently, polymers offering high temperature capabilities in the range of 180° to 260°C are becoming available. These "high performance" polymers include both thermosetting and thermoplastic systems. In the following are given brief descriptions of materials that have been evaluated:

a) *Hexcel 976*: This resin is a condensation-type polyimide supplied as a 70% paste in N-methyl-pyrrolidone (NMP). It is claimed that this adhesive has high strength retention at 260°C for continuous service. The curing process is quite complicated (see Table I).

b) *HR 602*: The commercially available polyimide called Thermid-600 (formerly HR 600 developed by Hughes Aircraft Research, marketed by Gulf Oil Chemicals) has been chemically modified by Hughes into this new thermosetting resin HR 602. This new polymer was reported as having good flow-characteristic and superior lap shear strength.[5] Samples were provided by the Hughes Research Group in both powder and adhesive prepreg forms. Previous study[6] showed that the acetylene-terminated polyimide (Thermid 600), although low in fracture energy as typical of all thermosetting polymers, seemed to exhibit very good thermal stability. After heating at 350°C for 240 hours, the G_{Ic} value for this material practically did not change.

c) *FM 73*: This is the so-called PABST adhesive of the Air Force, an epoxy-based material manufactured by American Cyanamid Co. It was supplied as a yellow adhesive film to be used in conjunction with a primer, BR-127. Since this material is well-known, it was also tested for comparison purposes.

d) *FM 300K:* Also manufactured by American Cyanamid Co., this adhesive was claimed to have 150°C capability and was being considered for application in F-18 aircraft. The material was supplied as a dark green adhesive prepreg with a polyester woven reinforcement.

e) *FM-34B-18:* This is a polyimide adhesive system from the American

TABLE I

Adhesive cure schedule

Polymer	Supplier	Temperature (°C)	Time (min)
HX 976	Hexcel	135	60 (degas)
		185	75
		204	60
		232	60
		260	60
		288	60
		316	60
HR 602	Hughes	177	5 (primer)
		316	240
FM 300K	Cyanamid	121	30 (primer)
		177	60
FM 73	Cyanamid	121	60 (primer)
		121	60
FM-34B-18	Cyanamid	285	90
C-6 PC	NRL	220	48 hrs
C-10 PC	NRL	220	48 hrs
C-22 PC	NRL	200	24 hrs
C-36 PC	NRL	220	72 hrs
Plastilock 655	Goodrich	177	85
Plastilock 650	Goodrich	260	45
LARC-13/AATR	NASA	70	30
		125	60
		175	30
		300	30
SR-5208	NARMCO	93	20 hrs
		121	180
		149	120
		177	120
		204	240
Upjohn 2080	Upjohn	340	20
Torlon 4000	Amoco	188	30
NRO56X	DuPont	82	10 (degas)
		316	120
P-1700	Union Carbide	260	10 (degas)
		260	5
P-1700 (melt)	Union Carbide	371	5

All adhesives cured at *ca.* 0.35 MPa pressure.

Cyanamid Company, claimed to retain high lap-shear strength for long exposure to temperatures up to 360°C. NASA-Langley is studying this material for possible applications in the CASTS (Composites for Advanced Space Transport System) Program.[7]

f) *Plastilock 650 and 655:* Two nitrile-rubber phenolic resins from B. F. Goodrich Company were provided in the form of thin sheets of pure resin with no reinforcements. Both adhesives were supposed to offer 260°C capability.

g) *SR 5208:* This epoxy resin is essentially tetraglycidyl methylenedianiline (TGMDA) cured with diaminodiphenyl sulfone (DDS) along with some minor constitutents. The material was obtained from the Narmco Materials Inc. in powder form.

h) *LARC-13/AATR:* This adhesive is a high temperature resin developed by NASA-Langley. Basically it is a polyimide modified with 15% in-chain butadiene-acrylonitrile elastomer. The samples were supplied by NASA in both 50% solution in dimethylformamide (DMF) and in adhesive film form. A rather complex B-staging cycle is required.

i) *Phthalocyanines:* Four phthalocyanine resins[8] containing 6, 10, 22 and 36 carbon units in the aliphatic chains linking the stable phthalocyanine nuclei were tested as adhesives. They were designated as the C-6, C-10, C-22 and C-36 phthalocyanines. The resins were applied upon melting to coat the adherend surfaces, and specimens were cured in an oven according to the specified cure cycles for each resin.

j) *Torlon 4000 T:* This is a poly (amide–imide) thermoplastic compound developed by the Amoco Chemicals Corporation. It has a glass transition temperature $T_g = 274°\text{C}$ as determined by torsion pendulum analysis. Resin fracture toughness was exceedingly high, a G_{Ic} value of 3.9 kJ/m^2 being reported.[9]

k) *Upjohn 2080:* This thermoplastic polyimide material was supplied by the Upjohn Company as a 55% solution in DMF. Characterization of the bulk polymer shows it to have a $T_g = 326°\text{C}$ and a fracture energy $G_{Ic} = 0.92$ kJ/m^2.[9]

l) *NR 056 X:* This is a DuPont polyimide adhesive derived from NR-150 solutions to give a linear amorphous polymer structure free of crystallinity and uncrosslinked. The material was supplied as a concentrated solution in DMF.

m) *Udel P1700:* This thermo-plastic polysulfone was manufactured by Union Carbide Corp., and was supplied as molding pellets and as extruded sheets of various thicknesses. For the pellets, DMF was used as a solvent to prepare a polysulfone solution ($\sim 10\%$) for coating the adherends. A hot melt method was employed in order to use the extruded sheet. A thin strip of Udel material was cut to size and clamped between aluminium beams. The specimen was then placed in an oven to melt the thermoplastic strip for bond formation.

TABLE II

Time-temperature cycles for the preparation of thermoplastic adhesive films

Polymer	(°C)/(min)	(°C)/(min)	(°C)/(min)	(°C)/(min)	(°C)/(min)
20% Upjohn 2080 in DMF + 22% Al	82/60	100/20	120/20	140/20	
10% P1700 in DMF + 20% Al	80/120	110/45	120/30	130/35	140/45
35% T4000 in NMP + 21% Al	90/20 180/30	105/20 200/35	115/20	140/30	160/30
35% NRO56X in DMF + 35% Al	85/40	100/20	120/20		

The cure cycles required for the adhesives are listed in Table I. Manufacturers' recommended processing procedures were generally followed. In some cases, the cure cycle was adjusted to available laboratory equipment capabilities until satisfactory adhesive bonding was achieved. This usually included a visual inspection of the bond before fracture test and a microscopic examination of the fractured adhesive surface after the test to ensure that the presence of blisters or voids was minimized, and that failure was of a cohesive type instead of an interfacial fracture. For the thermoplastic polymers, when applied as a solution coating, the solvent was not completely released within the 0.025 cm thick bond-line. Numerous trapped gas bubbles caused the adhesive layer to become partially unfilled. This phenomenon consistently occurred even when the coated beam surfaces were degassed before being clamped together. In order to alleviate this gas entrapment problem, adhesive tapes were prepared for each thermoplastic polymer. A low concentration solution (10–35% solid content) was first prepared by using either DMF or NMP as the solvent. Atomized #400 aluminum powder (Reynolds, 90% particles $< 13\mu$, and 50% $< 7\mu$) was added to the solution, which was warmed to *ca.* 85°C. The mixture was brushed onto a piece of #112 glass cloth with A1100 (siloxane) finish. Finally, the cloth was placed in an oven and subjected to various time-temperature cycles shown in Table II to remove some of the solvent. The end product was a dry adhesive film about 0.018–0.025 cm thick. The presence of the glass cloth provided a path for the release of volatiles during the fabrication of the adhesive bond and minimized the formation of small gas bubbles within the bond-line.

FRACTURE TEST

The adhesive was first applied to the adherends, which were 5086 aluminum alloy, cleaned by acid-chromate etching. After the adhesive was properly

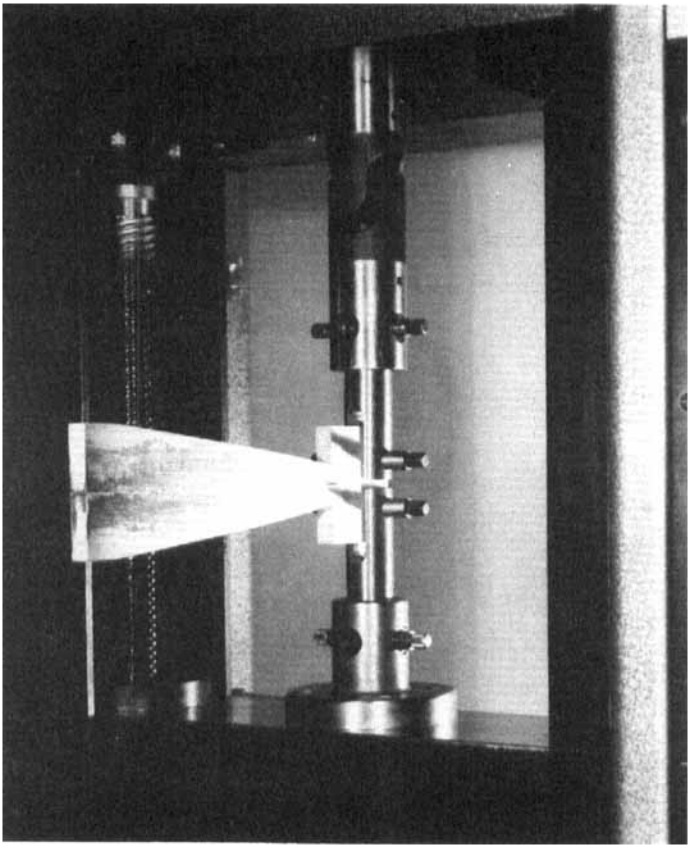


FIGURE 2 Specimen mounted in an INSTRON machine, ready for fracture test.

applied, the two aluminum half beams were clamped together with 0.025 cm Teflon spacers, which established the bond-line thickness. The complete beam assembly was then placed in an air-circulating oven for cure. Specimens were tested in an INSTRON, as shown in Figure 2, with the cross-head moving at 0.125 cm/min until fracture in order to determine P_c. The adhesive fracture energy was calculated by using Eq. (5).

Adhesive fracture tests were performed both at room temperature and at 225°C. For the high temperature tests, the specimen was mounted in the INSTRON with an environmental chamber, and heated from room temperature to 225°C at a rate of 3°C/min. The temperature was held at 225°C for five minutes to ensure thermal equilibrium before the specimen was fractured.

RESULTS AND DISCUSSION

The adhesive fracture test results obtained at room temperature are given in Table III. Materials are listed from top to bottom in the order of increasing adhesive fracture energy. It can be seen that both the Plastilock adhesives and the PABST FM-73 epoxy adhesive exhibited very high fracture energy ($G_{Ic-RT} > 1$ kJ/m^2). For the acetylene-terminated polyimide (HR 602) a G_{Ic} value of 815 J/m^2 was measured, but the other thermosetting materials tested showed G_{Ic} values less than 400 J/m^2. For the FM 300K adhesive system, the fracture performance is so poor that one would wonder about its application in F-18 aircraft for bonding graphite composites to titanium. Figures 3 and 4 show the post-fracture surfaces of the FM-73 and the HR 602 adhesive systems, respectively. In both cases, it is clear that cohesive-bond fracture has taken place. The adhesive layer generally looked uniform and free of any void or blister.

The thermoplastic polyimides (Upjohn 2080, DuPont NR-056X) and Amoco Torlon 4000 amide-imide polymer showed a toughness similar to that of the thermosetting LARC-13 adhesive. A polysulfone resin (Union Carbide Udel P1700), among all thermoplastics, gave the highest fracture energy, *ca.* 1.7 kJ/m^2. Bascom, Bitner and Cottington[9] have determined the fracture energy of various high performance polymers in neat-resin form by using

TABLE III

Room temperature adhesive fracture energy (Opening Mode Fracture)

Thermosets	Thermoplastics	G_{Ic-RT}(J/m^2)
C-6 phthalocyanine		56
C-36 phthalocyanine		63
NARMCO SR 5208		82
Hexcel HX 976		94
C-10 phthalocyanine		124
Cyanamide FM-300K (film)		191
	Udel P1700 (melt)	306
	Upjohn 2080 (film)	310
C-22 phthalocyanine		373
Cyanamide FM-34B-18 (film)		385
LARC-13/AATR (film)		387
	Torlon 4000T (film)	480
	DuPont NRO56X (film)	620
Hughes HR602 (film)		815
Plastilock 650 (film)		1037
Plastilock 655 (film)		1513
	Udel P1700 (film)	1670
Cyanamid FM-73 (film)		2107

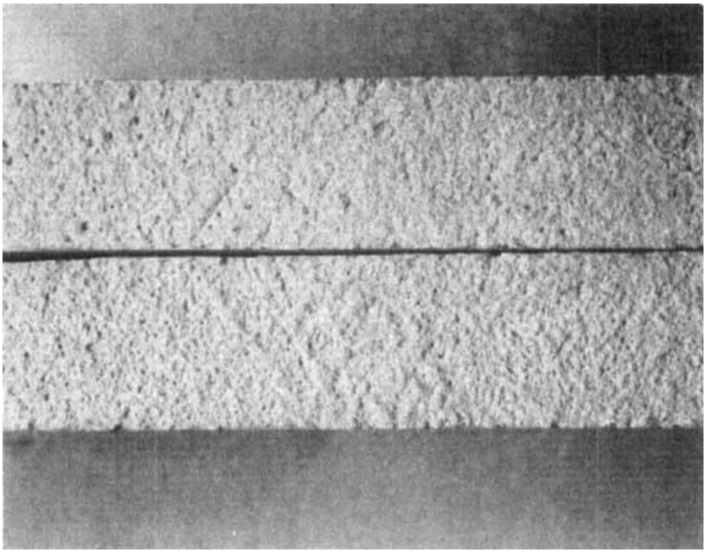


FIGURE 3 Fracture surface of FM-73 adhesive.

compact-tension fracture specimens. The general observation was that the thermoplastic polymers exhibited much higher fracture energies than the thermosets. However, the adhesive fracture energies measured here are considerably lower than those reported for bulk thermoplastic polymers. One

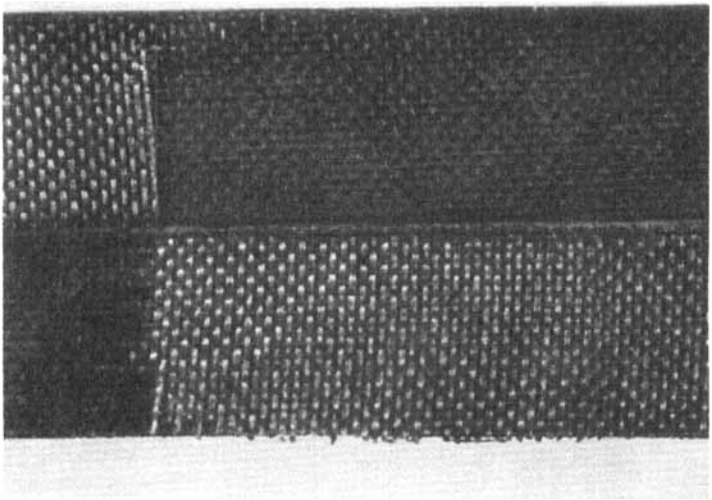
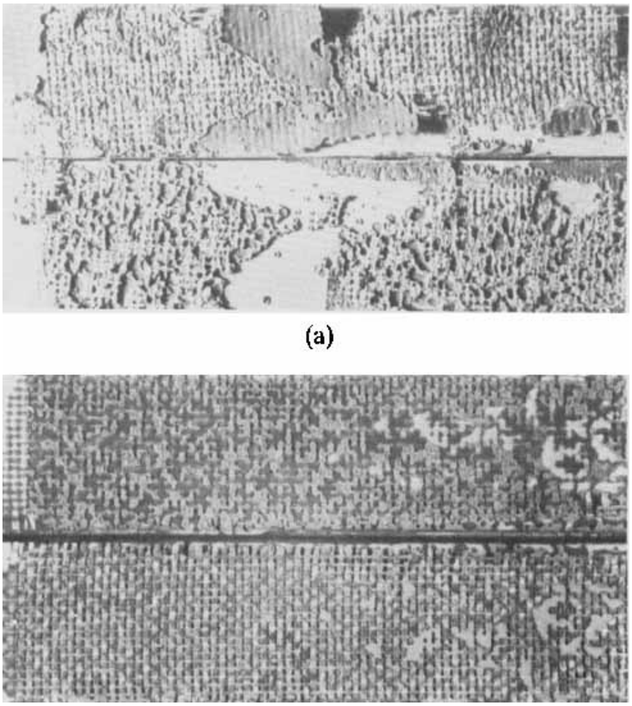


FIGURE 4 Fracture surface of HR-602 adhesive.

reason may be related to the bond fabrication technique used for these adhesives. The optimum processing conditions for these thermoplastic adhesives have not been established. Manufacturer-recommended conditions for the extrusion or molding process require 200–300 psi pressure applied over very narrow temperature "windows" as high as ~700°F (385°C). These temperature and pressure requirements are essential for achieving sufficient melt flow, which has been difficult to obtain when preparing an adhesive bond in the laboratory.

One reason that the Udel resin showed a higher fracture energy than other thermoplastics may be related to its low glass transition temperature (174°C) and hence better processability. Furthermore, since polymer solutions were used to prime the specimen beams and for impregnating glass fabric to prepare an adhesive film, some volatiles released during bonding still produced voids within the adhesive layer. Figure 5, showing the post-fracture surfaces of polysulfone specimens, illustrates these difficulties well. The specimen of Figure 5a was briefly heated at 260°C without a degassing cycle nor sufficient


(a)

(b)

FIGURE 5 Fracture surface of Udel-P1700 adhesive.

pressure. This resulted in an adhesive bond having very poor fracture performance. Interfacial failure was evident and the bond line had numerous voids, even when a reinforcement cloth was used. When a higher pressure was applied to the specimen, which was also degassed before final "cure" at 260°C, the bond line, as seen in Figure 5b, was improved in terms of uniformity and void-content. Consequently, the measured adhesive fracture energy was also increased.

In addition to the processing problem, the presence of a thin bond-line may severely limit the extent of plastic deformation at the crack tip.[3] This could also contribute to causing the poor adhesive fracture performance of thermoplastic polymers. The results from tests performed at 225°C are shown in Table IV, in which both the adhesive fracture energy G_{Ic-225} and the retention ratio of fracture energy G_{Ic-225}/G_{Ic-RT}, are listed. The glass-to-rubber transition temperature, T_g, for each resin system is also tabulated. This temperature was determined for each polymer by using a torsional pendulum apparatus,[6] except for the LARC-13 material. In that case, the T_g data were obtained by NASA using the torsional braid method.[10] For thermosetting materials, since T_g depends on the degree of cure, the listed values indicate only the approximate limiting use temperature of the resin. For materials such as epoxies and phenolics (which have T_g lower than the test temperature), it is clear that their toughness was lost rapidly at temperatures higher than T_g. In those cases, the test results show that the retention ratios range from 0.01 to 0.32. On the other hand, the high temperature polyimide resins remained effective, retaining ~90% or more of their room temperature toughness values when tested at 225°C. The Udel polysulfone material has a glass transition

TABLE IV

Adhesive fracture energy at 225°C
(Opening Mode Fracture)

	Thermoplastics	G_{Ic-225}(J/m^2)	G_{Ic-RT}(J/m^2)	$\frac{G_{Ic-225}}{G_{Ic-RT}} \times 100\%$	T_g(°C)
Cyanamid FM-300K		23	191	12	
Cyanamid FM-73		27	2107	1	
C-10 phthalocyanine		59	124	48	360
Plastilock 655		131	1513	9	
	Torlon 4000T	185	480	39	275
Plastilock 650		322	1037	32	
Cyanamid FM34B-18		342	385	89	
LARC-13/AATR		399	387	100	~280
	DuPont NRO56X	515	620	83	365
Hughes HR 602		749	815	92	330
	Udel P1700	862	1670	52	174

temperature of only 174°C, which is less than the test temperature. Its adhesive fracture energy was therefore reduced to *ca.* 862 J/m^2 at 225°C, approximately half of its room temperature value, but remained to rank the highest among all resins tested at 225°C.

The temperature dependence of adhesive fracture was further examined by using the SR-5208 epoxy and the C-10 phthalocyanine resin. The results, given in Figure 6, show a large increase in the fracture energy of phthalocyanine with decreasing temperature. This behavior is rather surprising for thermosetting resins which usually exhibit little change in adhesive fracture energy with temperature except near the glass transition temperature,[11] such as shown by the SR-5208 data. This behavior of the C-10 resin is believed to be associated with the dynamic mechanical response of this material. Torsion pendulum analysis[12] revealed that two low-temperature relaxation processes exist for the C-10 phthalocyanine polymer at −60°C and −130°C. For many thermoplastic polymers, it has been observed that the fracture energy reaches a maximum near a temperature corresponding to a secondary β-transition in the dynamic loss tangent curve.[13] A similar situation may explain the temperature dependence of adhesive fracture energy found in the C-10 polymer.

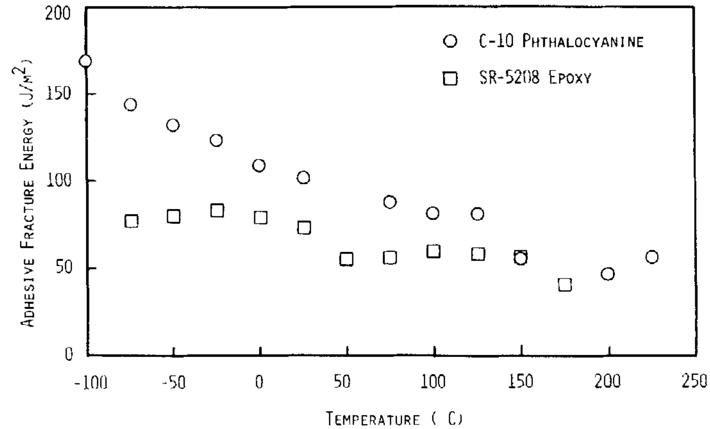


FIGURE 6 Temperature dependence of the adhesive fracture energies of C-10 and SR5208 resins.

Currently available high performance adhesives have been evaluated for their adhesive fracture energies both at the room temperature and at 225°C. Low temperature adhesive toughness for a tetrafunctional epoxy and a phthalocyanine resin was also determined. The results indicate that high resin toughness of thermoplastic polymers does not necessarily translate into high adhesive toughness, mainly due to processing difficulties and adhesive bond thickness effects. It also indicates that adhesive fracture energy is greatly reduced at temperatures above the glass transition temperature of the polymer. On the other hand, the adhesive fracture behavior of high performance polymers at low temperatures seems to be related to the appearance of secondary relaxation peaks observed in a dynamic mechanical analysis.

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