

Seraph
8/11

19126

The Chemistry and Fracture Testing of Durable Low-Temperature-Curing Adhesives

by

C. Arah, J. Vogin, D. McNamara, M. Mecklenburg
 J. Ahearn, A. Desai, T. Fritz, and H. Hand Conservation Analytical Laboratory
 Martin Marietta Laboratories The Smithsonian Institution
 1450 South Rolling Road Washington, DC 20560
 Baltimore, MD 21227

Presented @ Sorpol Conference *Resin* *on Science of Adhesion*
Poster presentation *U.S. 1987*
will not be published *New Hampton, New Hampshire*

July 17-21

ABSTRACT

The need for lightweight materials for a variety of needs has led to the fabrication of bonded composite-metal prototype structures. For bridge applications or high-humidity environments, the bonding system must overcome two fundamental problems affecting bond strength and durability: 1) the thermal expansion mismatch between metals or metal alloys produced at the conventional bonding temperatures of 250° - 350° F, which leads to delaminations at use temperatures (-50° to +160°F); and 2) the strength loss upon exposure to high-moisture environments.

To respond to these critical needs, we have been working to develop adhesives that are practically insensitive to moisture effects and can achieve high bond strengths upon curing at or around use temperature. In this effort, supported by the U.S. Army Troop Support Command's Belvoir RD&E Center, we are formulating adhesives with strength-improving and moisture-resistant additives and then screening/selecting the most promising compositions. To date, we have achieved durable bulk compositions curing at temperatures below 70°C (158°F), by advancing epoxy compositions to epoxy-equivalent-weights of approximately 300 with stiff, hydrophobic chain extenders containing azo and fluoro groups.

While studying the effects of chemical modifications on adhesive embrittlement, we concluded that the elastic energy release rate, G , alone does not adequately characterize the fracture resistance of the adhesives. However, a useful measure of total fracture resistance was derived when an unload compliance test was applied to 1/2-CT-plan ($B=0.25$ in.) bulk-adhesive specimens. This measure of total fracture resistance was shown to better characterize adhesive resistance to crack propagation than the elastic energy release rate, and can thus be used to evaluate improvements in adhesive formulation.

Further, we show that for very brittle adhesives in which the energy-partitioning analysis is not possible (i.e., those specimens in which crack initiation results in rapid unstable crack growth that splits the test specimen), a relationship can be established between stored potential energy and released elastic energy, as expected from Rice's original J -integral theory.

APPROACH

DESIRED PROPERTY*

RESIN MODIFICATION

- | | |
|-------------------------------|---|
| 1. ROOM TEMPERATURE CURING | REACTIVE RT CURING AGENTS;
LOW VISCOSITY RESINS;
ALTERNATIVE REACTIONS |
| 2. TOUGHNESS | INCREASE M_c (EEW 250-300);
REACTIVE ELASTOMERS |
| 3. ENVIRONMENTAL DURABILITY | HYDROPHOBIC CHAIN EXTENDERS;
NON-RING-OPENING REACTIONS;
HYDRATION INHIBITORS |
| 4. MODULUS AND SHEAR STRENGTH | STIFF ADVANCEMENT AGENTS;
MODIFIERS, FORTIFIERS AND COUPLING AGENTS |

*SOME GOALS ARE CONTRADICTORY

FORMULATION PROCEDURE

Chain Advancement



Advancement agents: cyanates, diols, diacids

Catalyst: phosphines, cobalt naphthenate, amines

Curing Reaction



Diluent: functional reagents, modifiers, coupling agents,
rubber tougheners

Curative: amines, cobalt naphthenate/MEK peroxide

Scheme 2: Epoxy advancement reaction

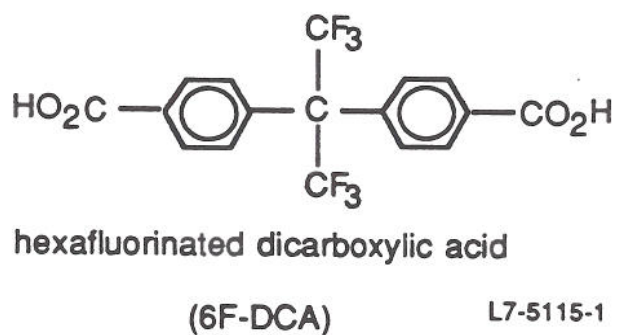
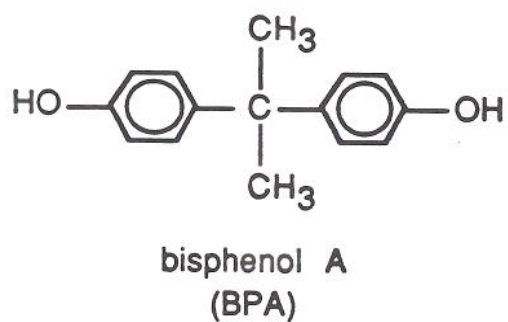
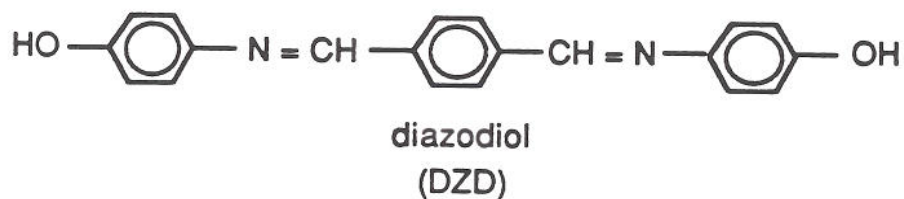
Esterification



Etherification



Advancement Agents



L7-5115-1

Formulation Data

Formulation	Additive (pph)	Rubber ^a (pph)	Calculated E.E.W. (approx.)	Curative ^b (pph)	T _{soft} ^c (°C)
BPA-250	5.7	12	250	9.76	56
BPA-300	6.8	12	300	8.27	56
DZD-250	7.6	10	250	9.85	55
6F-DCA	8.1	10	250	9.96	58

a) Hycar CTBN 1300X13.

b) pph triethylenetetramine (TETA) of advanced resin.

c) Peak height of DSC endotherm.

CHARACTERIZATION

(1) THERMAL BEHAVIOR AND TRANSITIONS

(2) CHEMICAL STRUCTURE

(3) MECHANICAL BEHAVIOR

(4) FRACTURE TESTING

MECHANICAL TEST DATA FOR ADHESIVES

Specimen	Dry (Ambient Conditions) ^a			Conditioned (80% RH, 120° F) ^b		
	UTS (psi)	Modulus (ksi)	Elongation (%)	UTS (psi)	Modulus (ksi)	Elongation (%)
M1 ^c	7651	395	3.1	5853	238	2.9
M3 ^c	6663	343	3.2	2648	180	5.7
V1 ^c	2166	112	10.6	1846	87	12.6
D1 ^c	11556	685	2.8	8082	512	2.2
H1 ^c	10938	1080	4.0	7708	740	2.2
H2 ^c	6752	416	4.3	6061	320	3.3
BPA 250 ^d	10653	519	5.4	9188	515	3.0
BPA 300 ^d	10868	570	3.2	8810	565	2.7
DZD 250 ^d	12150	599	3.5	8879	495	3.1
6F DCA ^d	12560	655	6.3	9262	500	3.2

a) Average of 5 tests.

b) Average of 3 tests.

c) Commercial composition.

d) In-house formulation.

COMPARATIVE DATA FOR THE ADHESIVES FROM LLD RECORDS

Specimen	Crosshead displacement rate (in/min)	G^c (in-lb/in ²)	I^c (in-lb/in ²)	J^c (in-lb/in ²)	P_{max} (lb)
M1 ^a	0.02	8.0	9	10.0	27
M2A ^a	0.01	5.5	9	6.6	26
M3 ^a	0.01	6.0	15	9.0	27
V1 ^a	0.01	7.0	60	16.2	16
H1 ^a	0.01	7.0	25	15.0	31
H2 ^a	0.01	4.5	9	6.0	45
D1 ^b	0.005	9.0	0	9.0	35

a) Stable fracture (crack arrest was possible).

b) Unstable fracture.

c) At 0.03-in. crack extension.

The work, W , done by the external load, P , can be related to the internal energy, U , by

$$dW = dU_s + dU_e + dU_p$$

where

W = work done by external load

U_s = stored elastic strain (potential) energy

U_e = elastic energy released during crack extension

U_p = plastic energy dissipated during crack extension.

Area $OAA'O'$ = ΔU_p

Area $O'A'B$ = ΔU_e

Area OAC = U_s prior to new crack extension (U_{si})

Area $O'BD$ = U_s after crack extension (U_{si+1})

$$J_{ENSEP} = G + I = \frac{1}{B_n} \frac{dU_e}{da} + \frac{1}{B_n} \frac{dU_p}{da}$$

where,

J_{ENSEP} = the total rate of energy release to the specimen

G = the elastic energy release rate

I = the plastic energy dissipation rate

B_n = the net specimen width between side grooves

COMPARISON OF GENSEP WITH G_q FROM ASTM E399

During the test program, G_q was calculated as

$$G_q = \frac{K_q^2}{E} (1 - \nu^2)$$

where

$$K_q = \frac{P}{B_n W^{1/2}} f(a/w)$$

The value of P is taken at the top of each unload-load increment, $\nu = 0.03$ and E is taken to be the modulus of elasticity used to determine crack extension from the unload compliance equation. The resulting plots of G_q and GENSEP versus crack extension are nearly identical and suggest that the E399 can be successfully used for non-metallics. Furthermore, the comparison indicates that the adhesive tested is in plane-strain fracture mode and thereby quite brittle.

J-integral

$$J = \int_{\Gamma} (W dy - T \frac{\partial u}{\partial x} ds)$$

where

Γ is a curve surrounding the notch tip (crack)

W is the strain energy defined by

$$W(x,y) = W(\epsilon) = \int_0^{\epsilon} \sigma_{ij} d\epsilon_{ij}$$

T is the traction vector defined according to the outward normal along Γ

x,y are cartesian coordinates

$\epsilon = [\epsilon_{ij}]$ is the infinitesimal strain tensor

u is the displacement vector

J can take the form, $J = \eta \frac{U}{Bb}$, where U is the area under the LLD record. For both linear and non-linear elastic materials, U is the stored potential energy or strain energy in the body. We, therefore, define U as U_s . For a true elastic-plastic body, the area under the LLD plot prior to crack initiation is a combination of U_s and U_p . But, U_p is a non-recoverable energy, not a potential energy, and, therefore, does not meet the exact requirements of Rice's J-integral. However, if we assume non-linear elastic-plastic equivalence, U_p then represents a "plastic" component of the total potential energy. Hence, $J_p = \eta \frac{U_p}{Bb}$ which is currently used. Clearly, J_p is not the absolute plastic energy dissipation rate, I , nor is it a truly valid J-integral component.

Interestingly, the expression, $J_e = \eta \frac{U_s}{Bb}$, which is not currently used, appears to be valid.

Energy separation analysis (ENSEP) is not possible with a brittle material with rapid, unstable crack growth because Δa , ΔU_p , or ΔU_e cannot be determined. All that is known is U_s . However, if J_e is in fact G , then

$$G = \eta \frac{U_s}{Bb} = \frac{K_q^2}{E} (1 - \nu^2) \quad (\eta = 2.3)$$

Using D1, a brittle adhesive, G was calculated from G_q , plotted against crack extension, and compared to G derived from a plot of J_e against load-line displacement. In both cases, $G = 9.0$ in-lb/in² at crack initiation, suggesting that,

$$G = \eta \frac{U_s}{Bb} = \frac{1}{B_n} \frac{dU_e}{da}$$

This equivalence establishes a relationship between stored potential energy and the elastic energy release rate, as is expected from Rice's original J-integral.

The cumulative values of U_p , U_e , and a (crack extension) are the simple summations:

$$\frac{U_p}{B_n} = \frac{1}{B_n} \sum_{i=1}^n \Delta U_{p_i}; \quad \frac{U_e}{B_n} = \frac{1}{B_n} \sum_{i=1}^n \Delta U_{e_i}$$

$$a = \sum_{i=1}^n \Delta a$$

The slope of the lines for U_e/B_n and U_p/B_n versus crack extension at any point provides the elastic and plastic energy rates, G and I , respectively,

where

$$G = \frac{1}{B_n} \frac{dU_e}{da}$$

and

$$I = \frac{1}{B_n} \frac{dU_p}{da}$$

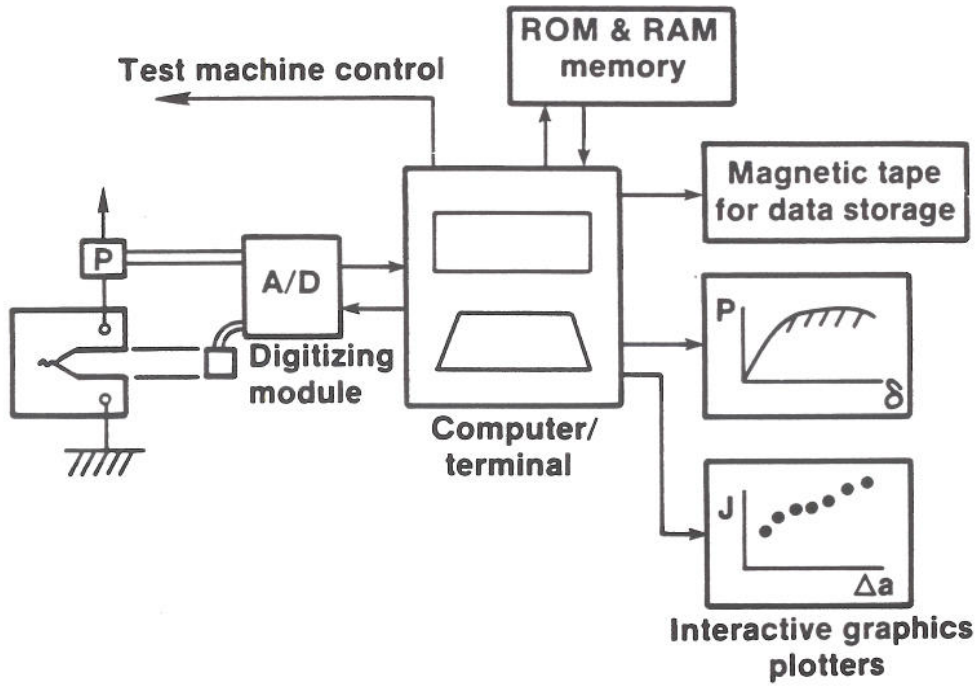


Figure 19. Schematic of the interactive computer test apparatus.

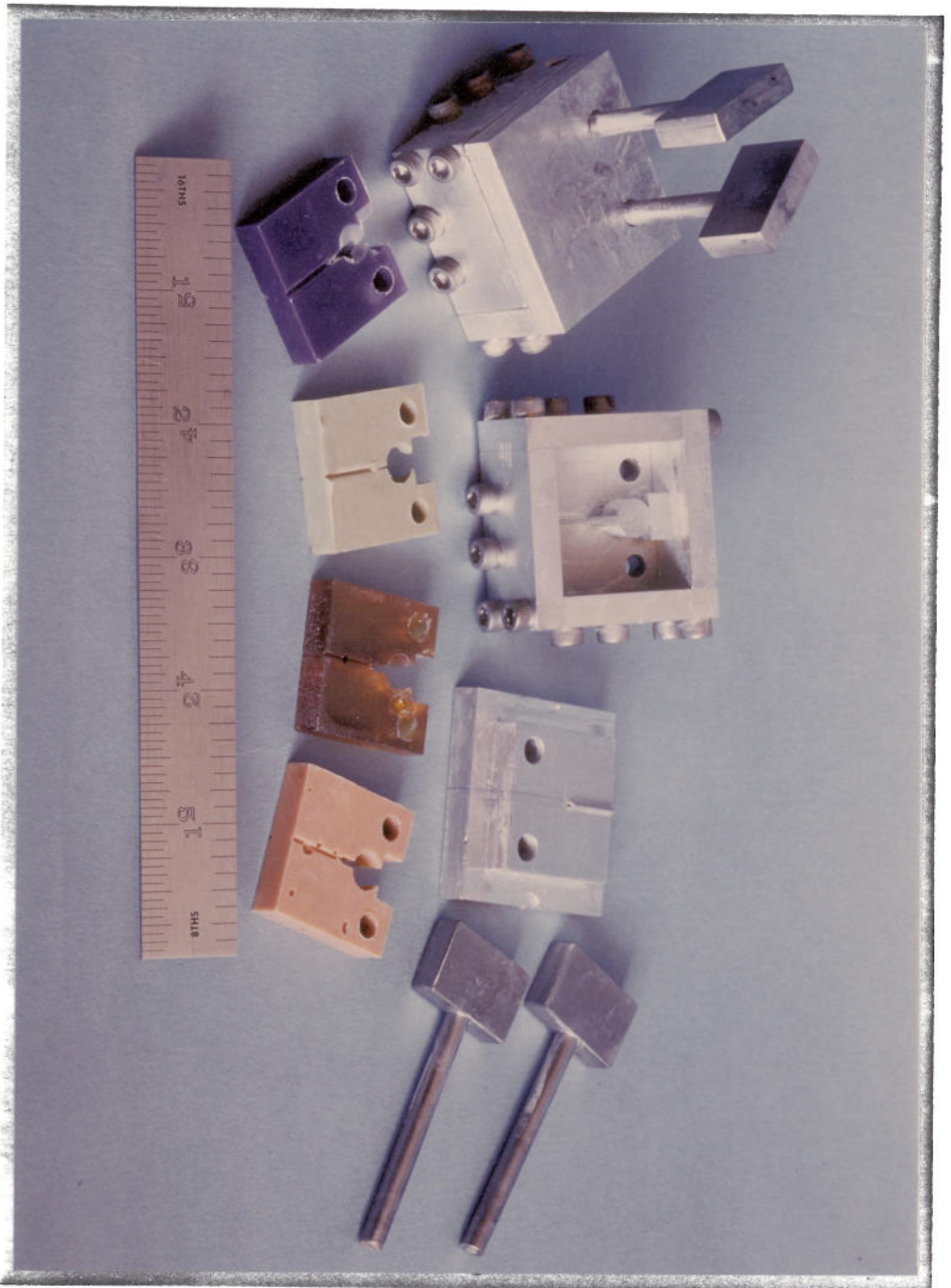
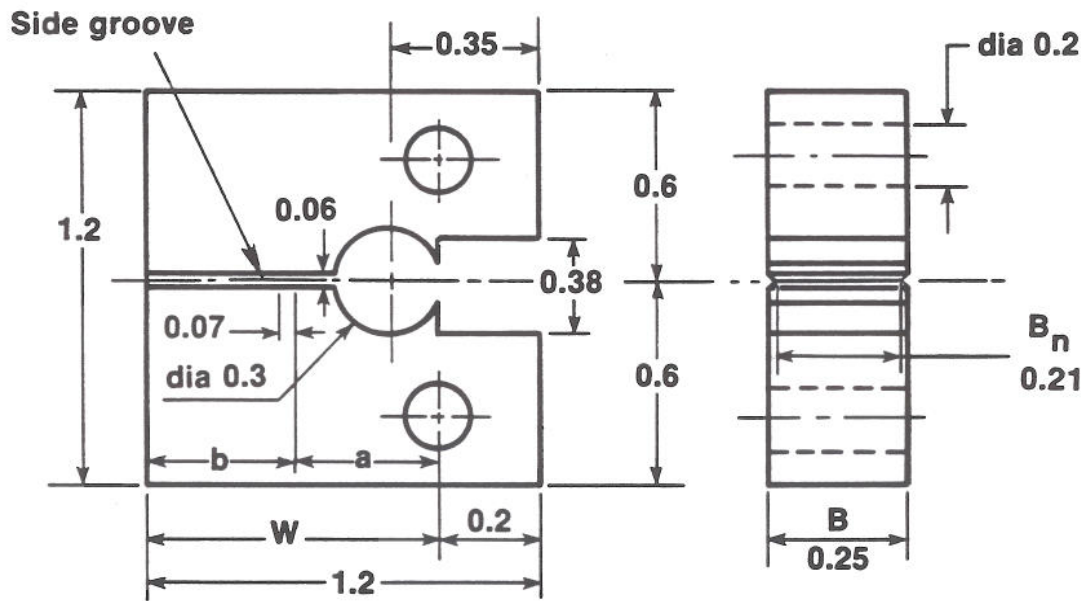


Figure 3. Mold, mold arrangement, and molded compact tension specimens.



(dimensions in inches) $a_0 \approx 0.509$

Figure 3. Dimensional diagram of 1/2-CT-plan specimen.

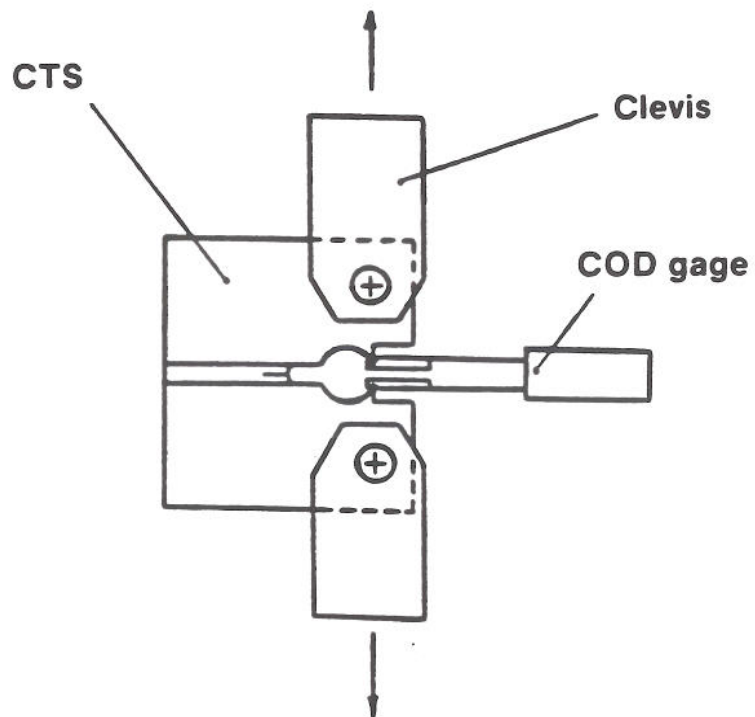


Figure 5. Schematic diagram of the fracture toughness test showing the load arrangement

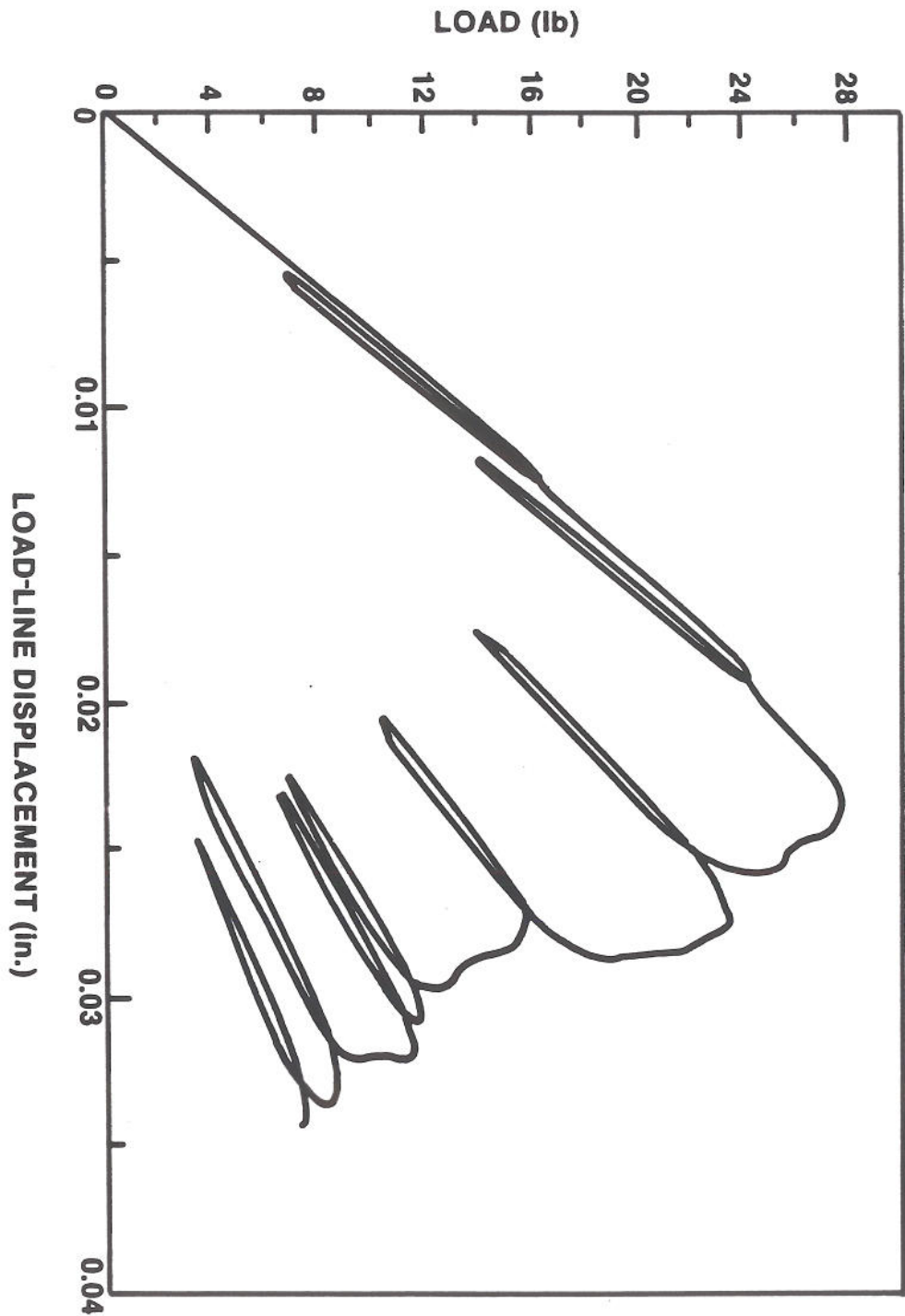


Figure 17. Load versus load-line displacement record for specimen M1.

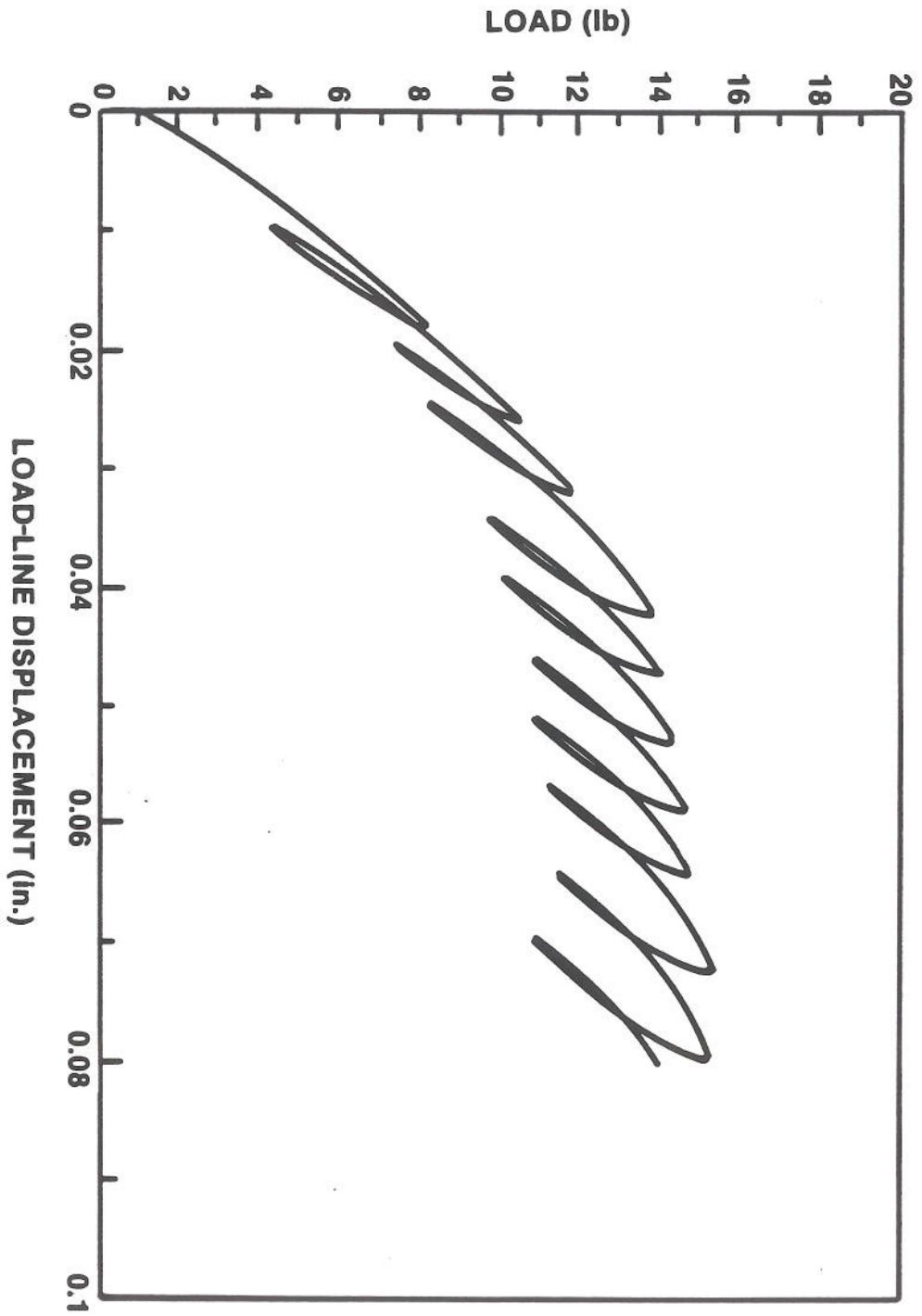


Figure 13. Load versus Load-Line displacement record for specimen VI.

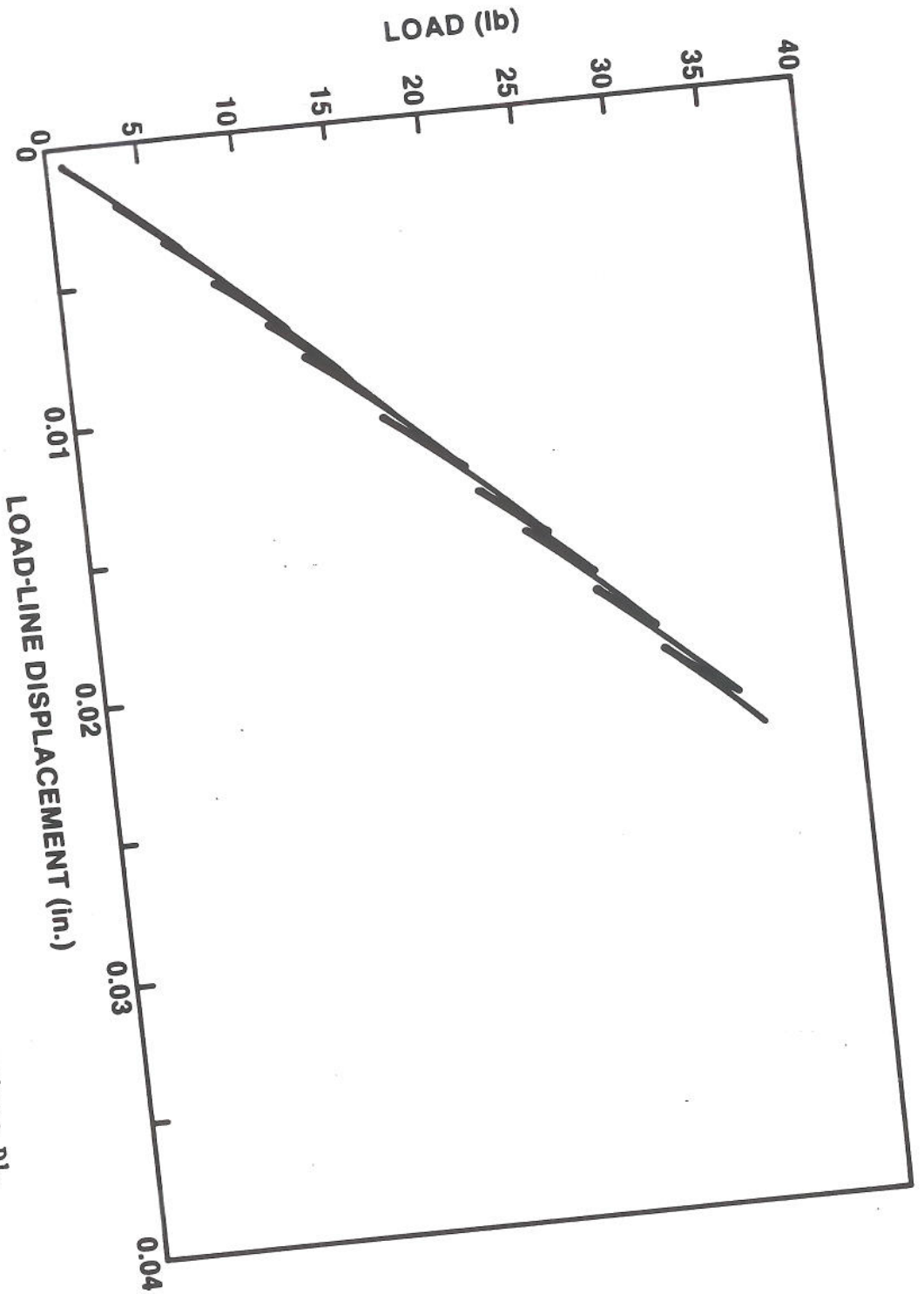
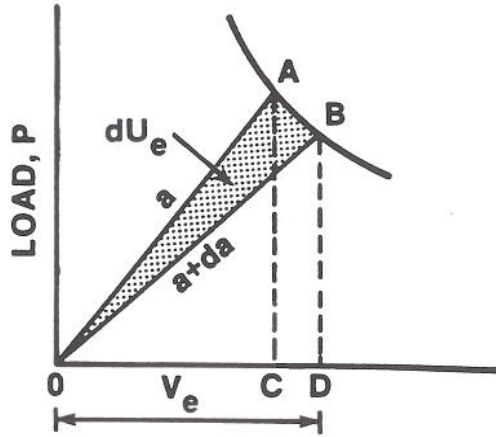
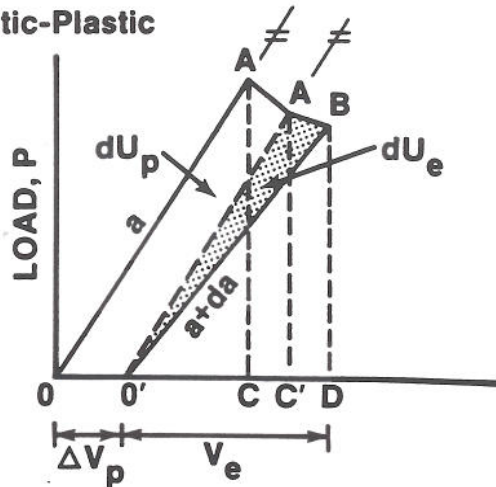


Figure 14. Load versus load-line displacement record for specimen D1.

(a) Elastic



(b) Elastic-Plastic



(c) Unloading Compliance

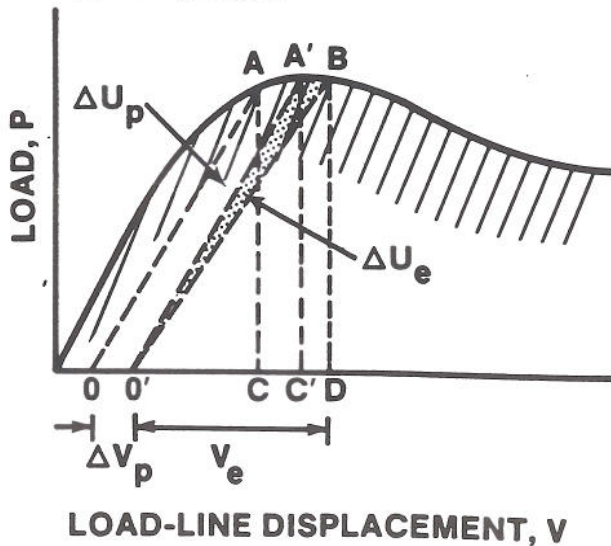


Figure 6. Energy components defined for typical load versus load-line displacement records.

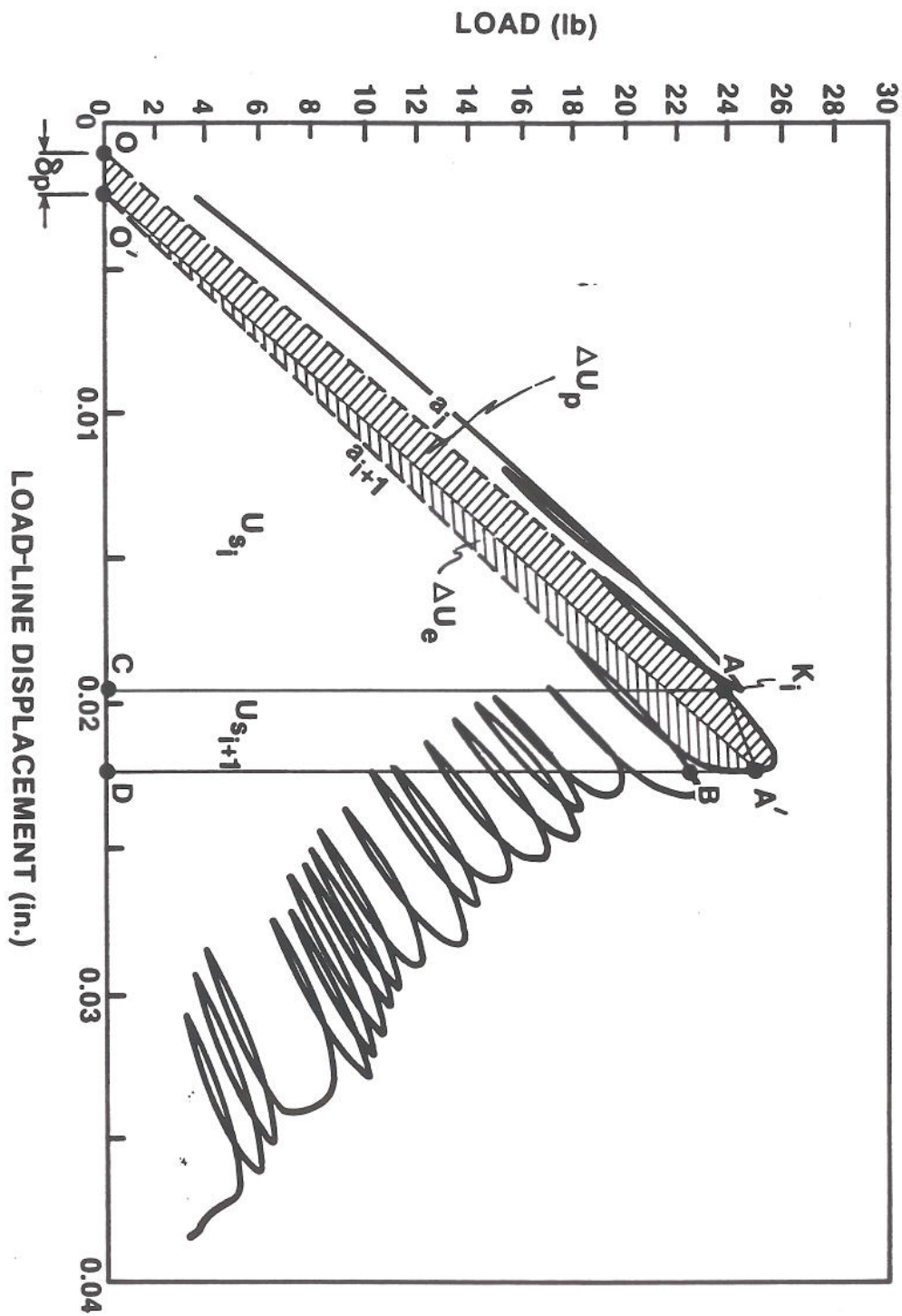


Figure 5. Partitioned load versus load-line displacement record for specimen M2A.

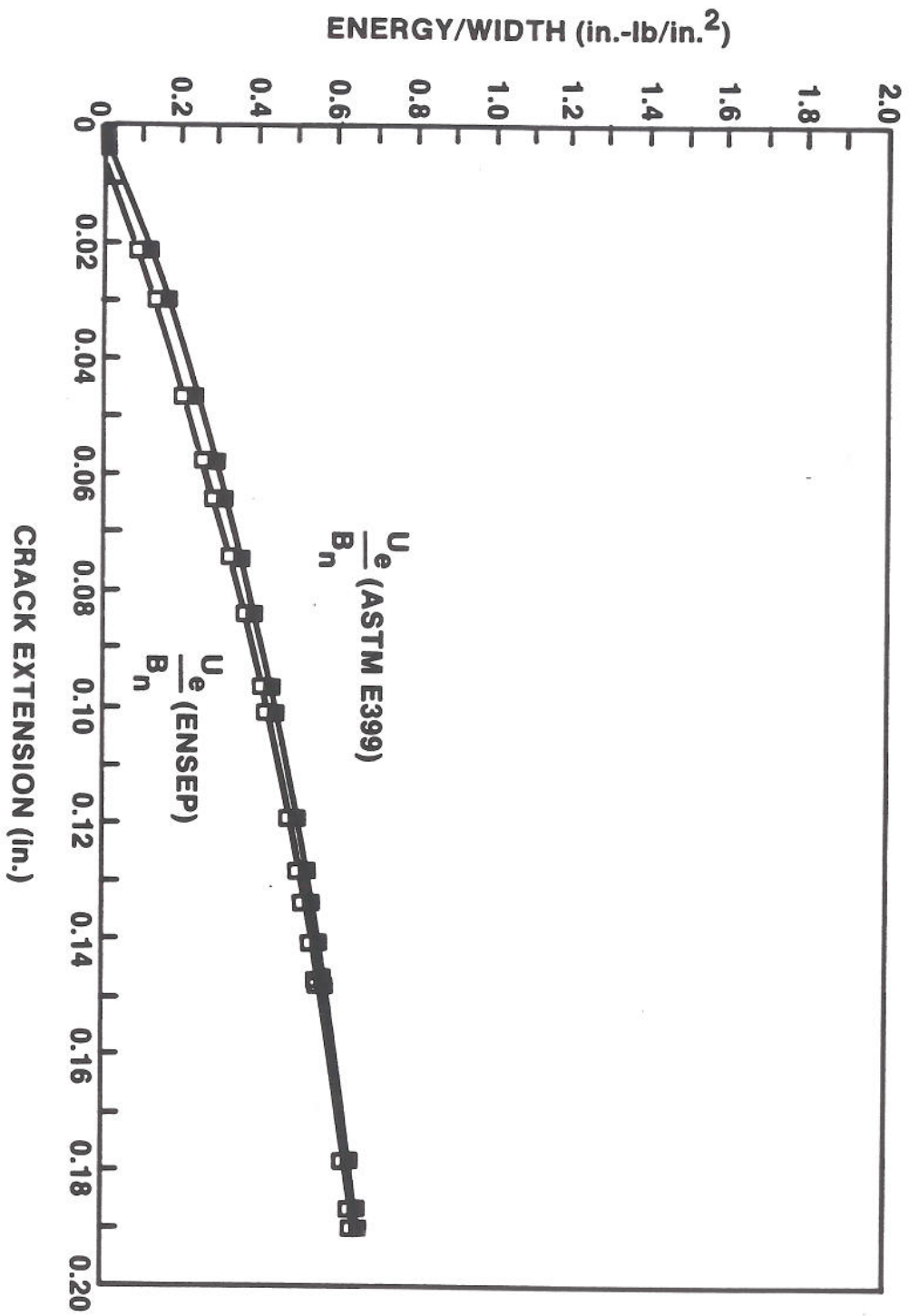


Figure 16. Elastic energy released during crack growth as calculated from ASTM E399 and energy separation versus crack extension for specimen MZA.

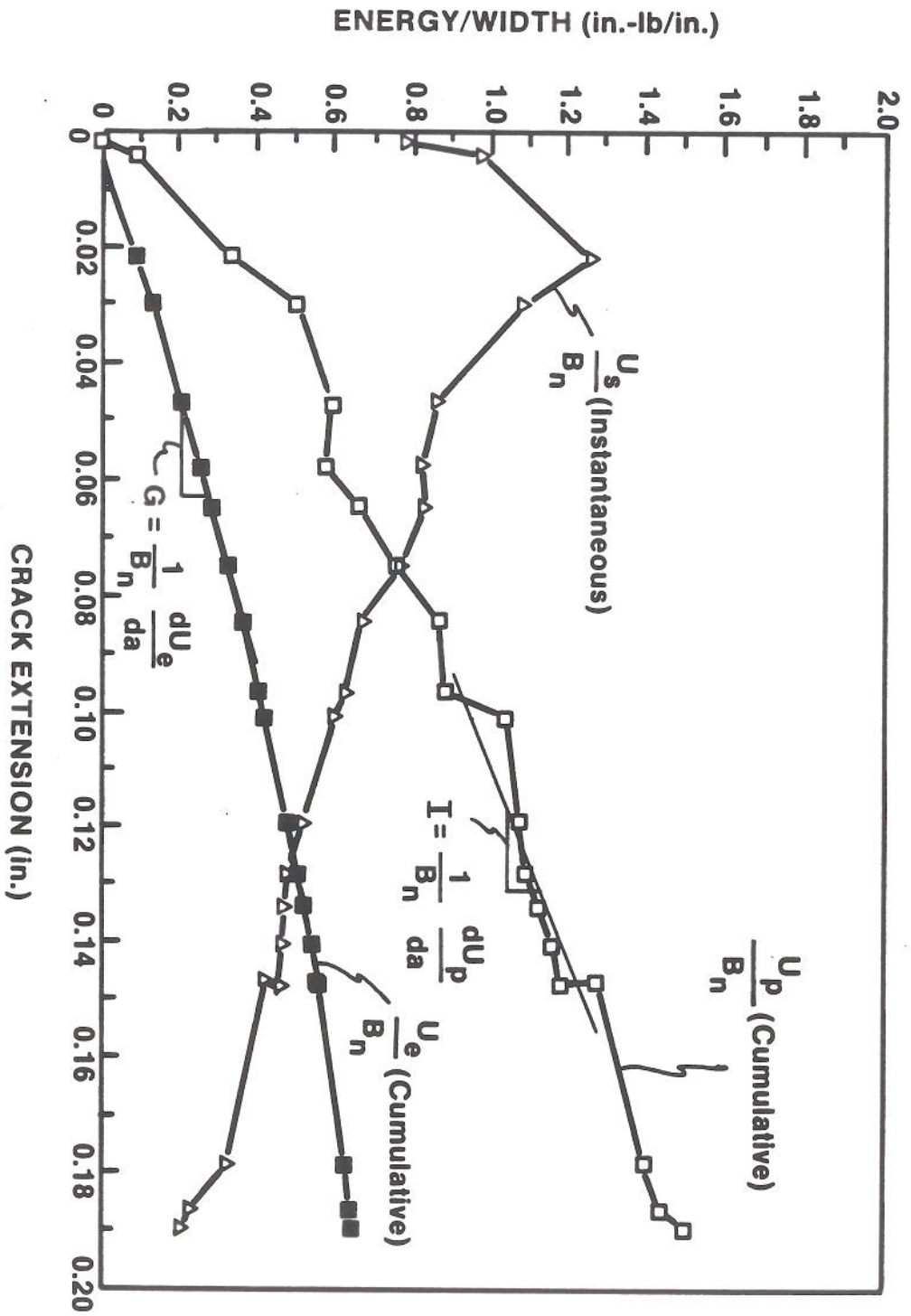


Figure 6. Cumulative energy released (elastic) and dissipated (plastic) and the instantaneous energy stored versus crack extension for specimen M2A.

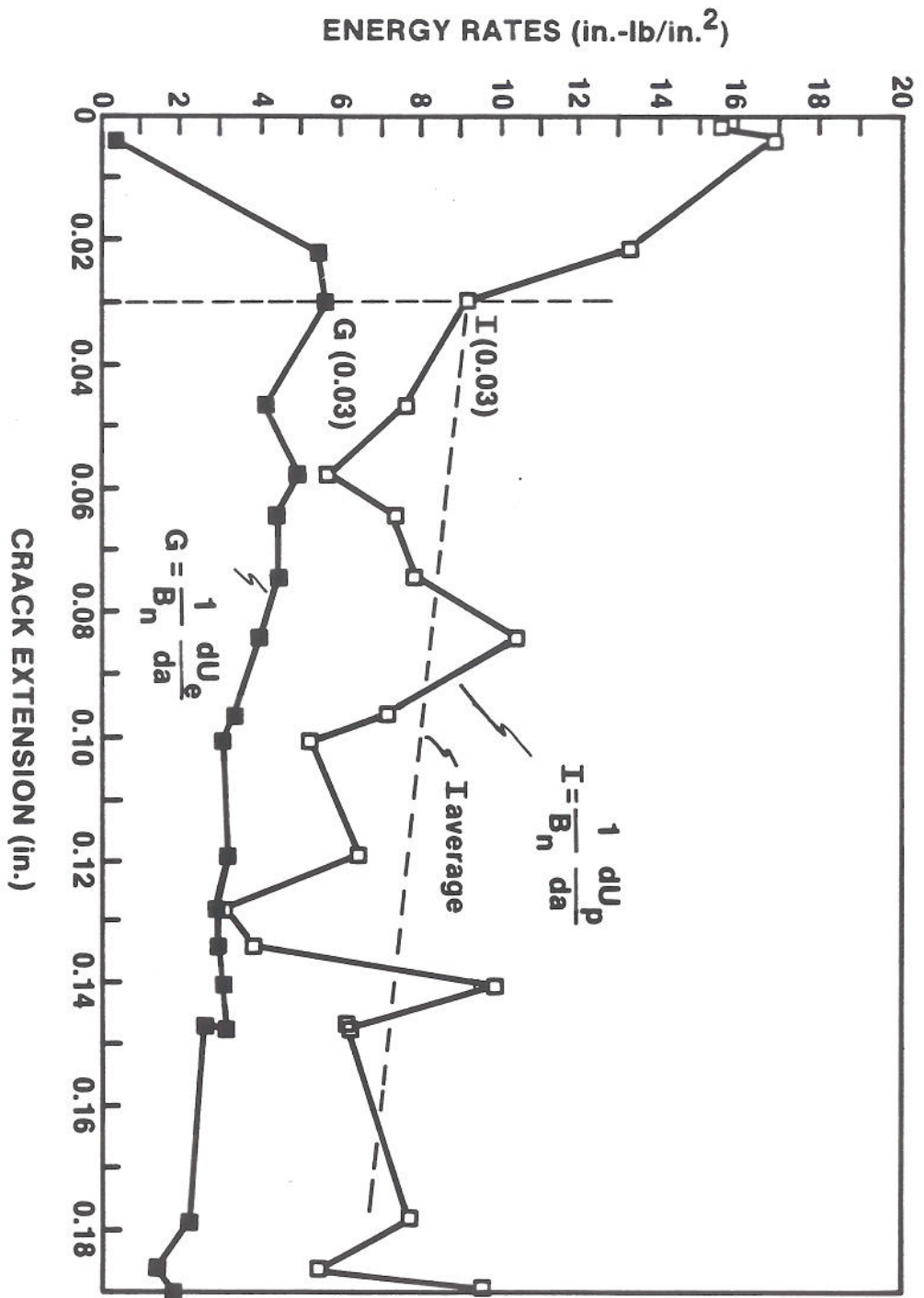


Figure 7. Elastic energy release rate and absolute plastic energy dissipation rate versus crack extension for specimen M2A.

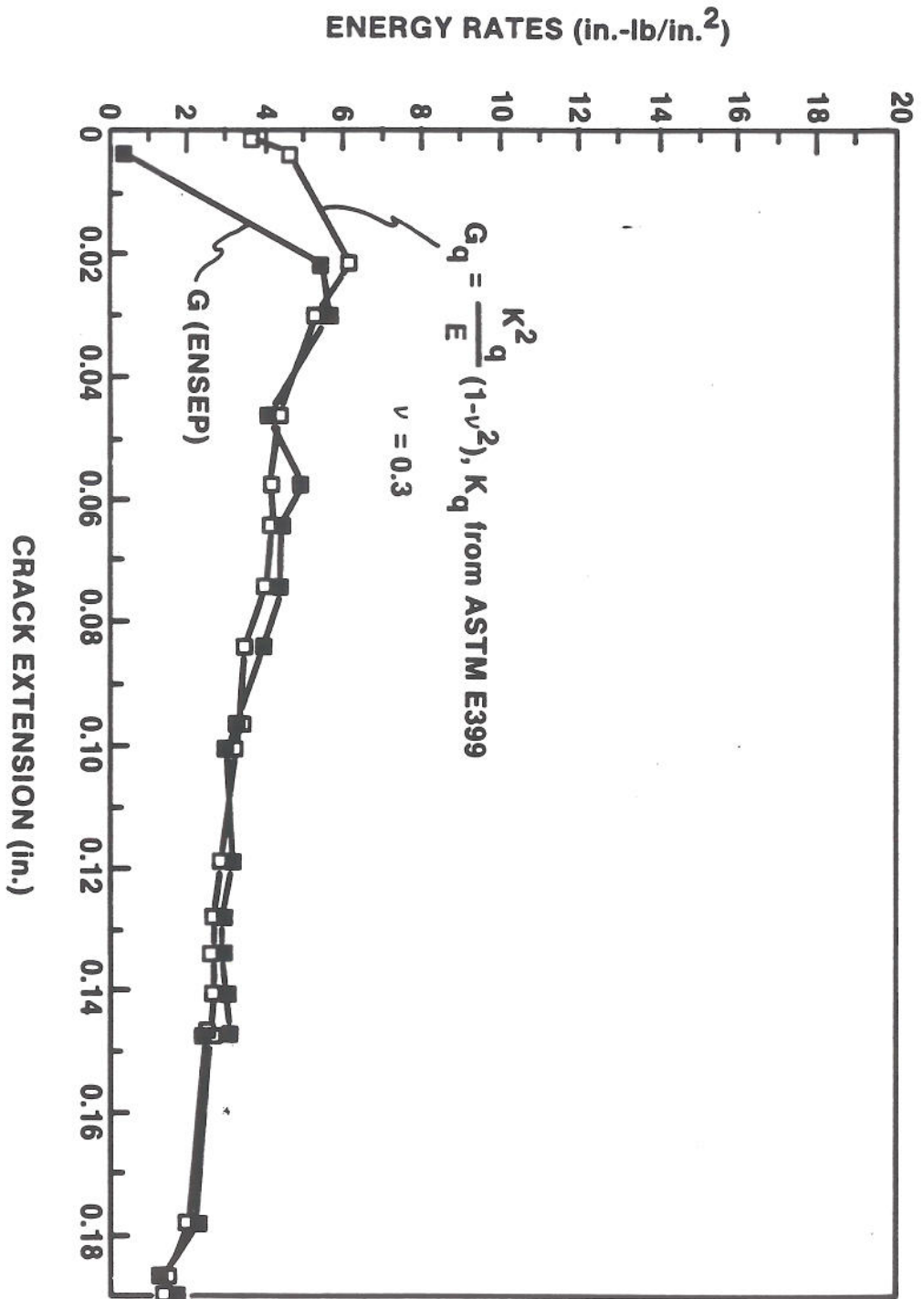


Figure 10: Elastic energy release rates as calculated from ASTM and energy separation versus crack extension for specimen M2A.

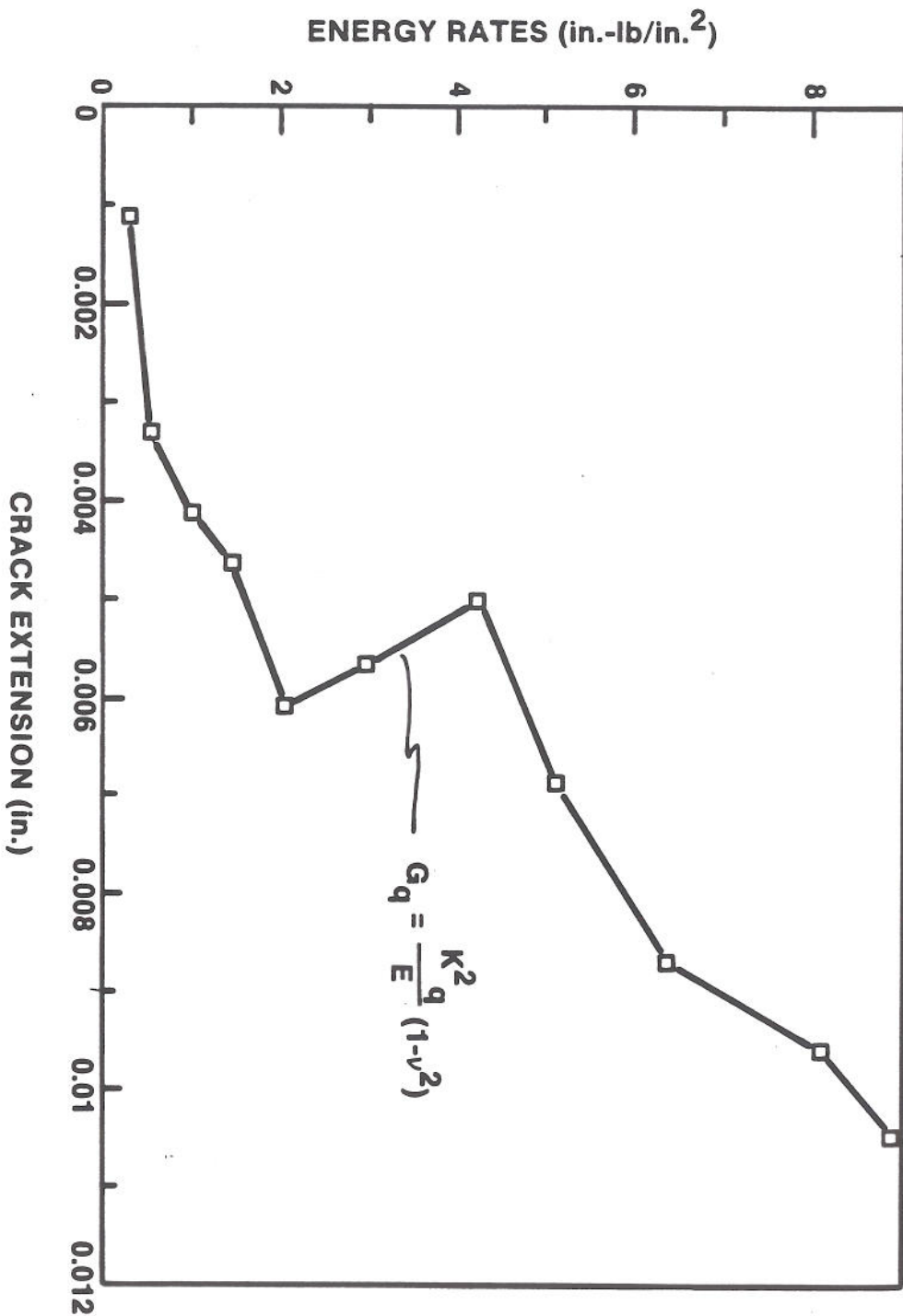


Figure 11. Elastic energy release rate as calculated from ASTM E399 for specimen D1.

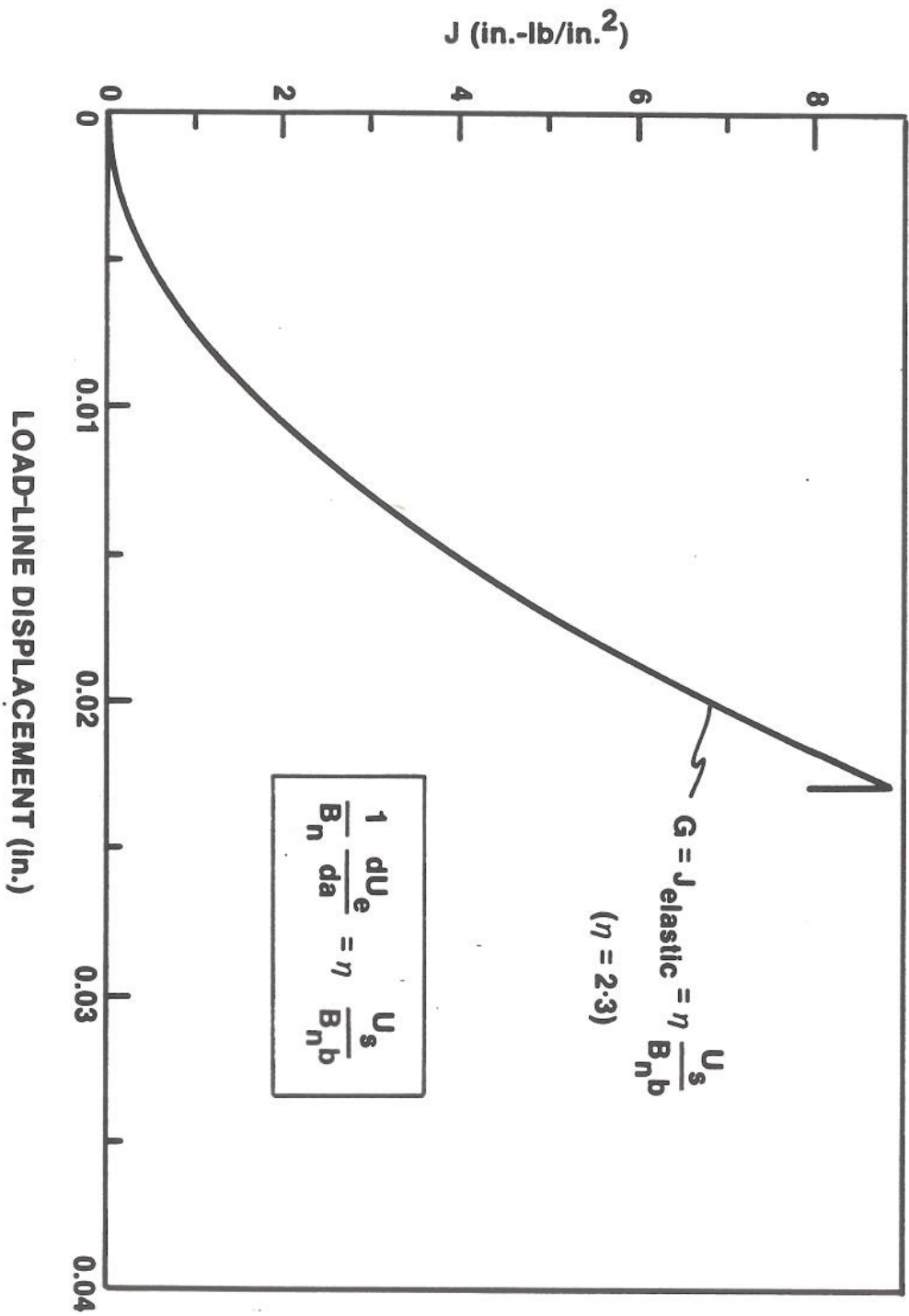


Figure 12. J versus load-line displacement for specimen D1.

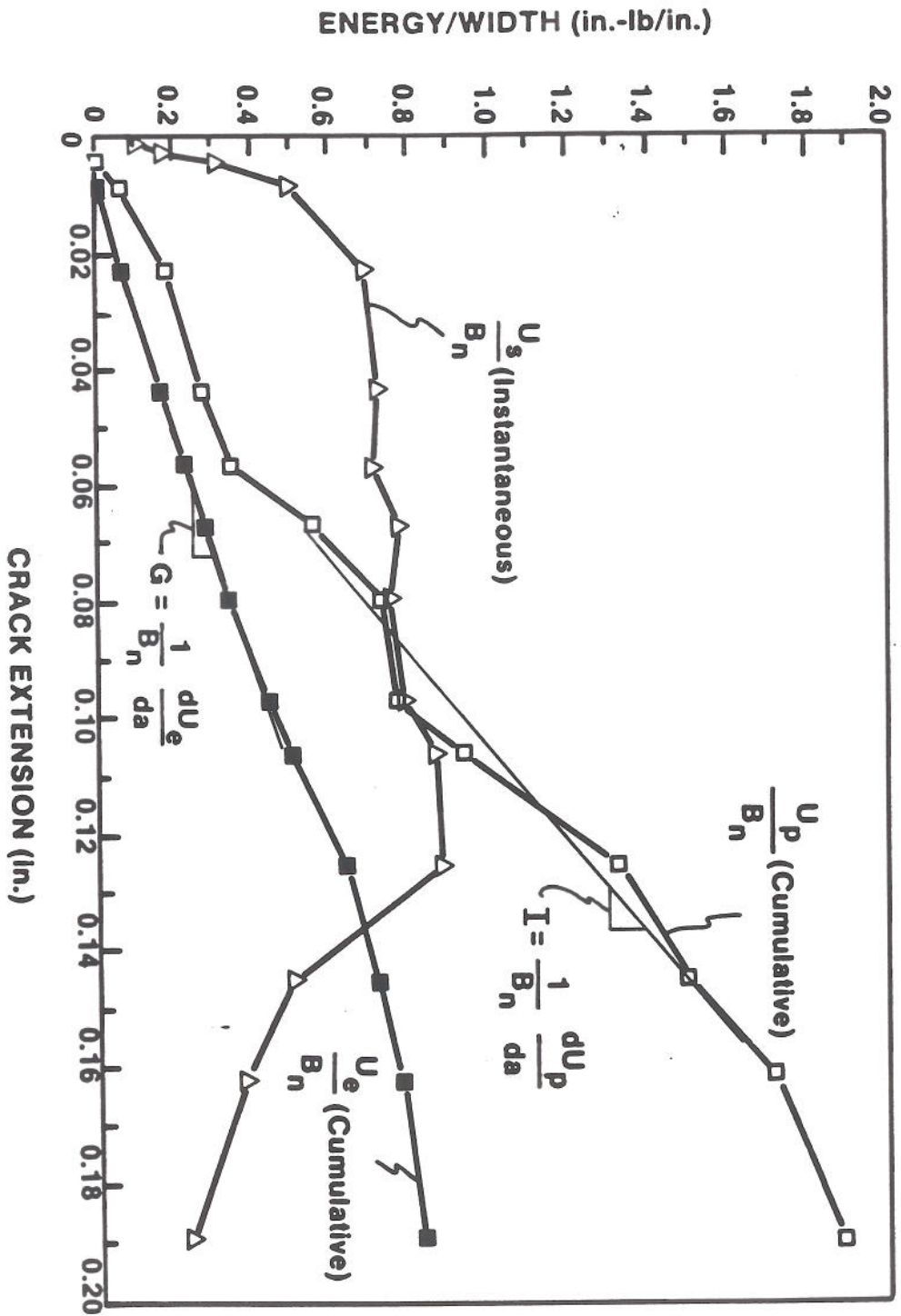


Figure 15. Cumulative energy released (elastic) and dissipated (plastic) and the instantaneous energy stored versus crack extension for specimen H2.

CONCLUSION

Durable bulk-adhesive compositions, containing stiff and hydrophobic (azo and fluoro) chain extenders, have been developed in the search for adhesives that are moisture-resistant and can achieve high bond strengths upon curing at or around the use temperature. While investigating the effects of chemical modifications on the embrittlement that accompanies increased durability in these adhesives, we concluded that the elastic energy release rate, G , alone does not adequately characterize their fracture resistance. By correctly partitioning the area under the unload compliance test record for a 1/2-CT-plan bulk-adhesive specimen, we were able to evaluate the elastic and plastic energy components in terms of current elastic-plastic parameters, and provide a useful measure of total fracture resistance for the specimen. Further, we show that for very brittle adhesives in which the energy-partitioning analysis is not possible (i.e., those specimens in which crack initiation results in rapid unstable crack growth that splits the test specimen), a relationship can be established between stored potential energy and released elastic energy, as expected from Rice's original J -integral theory.