DOC NO.
NARF-63-18T
FZK-9-194

USAF

NUCLEAR AEROSPACE RESEARCH FACILITY

31 MARCH 1964

STUDY OF THE EFFECTS OF NUCLEAR RADIATION ON THE MECHANICAL PROPERTIES OF ACETAL RESINS DELRIN AND CELCON

E. G. FRITZ

CONTRACT
AF 33(657)-7201

SECTION II ITEM 20
OF FZM-2665B

ISSUED BY THE
ENGINEERING
DEPARTMENT

GENERAL DYNAMICS | FORT WORTH

ABSTRACT

Two commercial acetal resins (Delrin and Celcon) were exposed to reactor radiation at room temperature in air to five levels of absorbed dose: 3.07×10^8, 6.8×10^8, 1.53×10^9, 3.83×10^9, and 1.18×10^{10} ergs/gm(C). The tensile strength of both resins was found to decrease rapidly with increasing dose: 50% of the original value is reached at about 0.3 gigaergs/gm(C) for Delrin and at about 0.75 gigaergs/gm(C) for Celcon. At about 1 gigaerg/gm(C), both materials had virtually lost their mechanical usefulness. The Shore-D hardness of the two resins was found to decrease exponentially with dose.

On the basis of weight-loss measurements, the G-values for formaldehyde formation were conservatively estimated to be 15.4 and 8.9 for Delrin and Celcon, respectively. Depolymerization appears to be the predominant mode of degradation.

REPORT SUMMARY

Tensile specimens of two acetal resins (Delrin and Celcon) were irradiated in the Ground Test Reactor Radiation Effects Testing System at room temperature in air to five levels of absorbed dose: 3.07×10^8, 6.8×10^8, 1.53×10^9, 3.83×10^9, and 1.18×10^{10} ergs/gm(C). In the unirradiated state, both resins show a stress-strain curve typical of a hard, strong plastic. Upon irradiation, the shape of the curves of both Delrin and Celcon changed to that typical of a hard, brittle plastic having a high modulus and low elongation at break. The ultimate-tensile-strength values of the two resins showed a good conformance with the Gumbel survivorship function. The dependence of the most probable ultimate tensile strength, $\tilde{\sigma}(D)$, on dose D was found to follow the empirical relationship

$$\tilde{\sigma}(D) = \tilde{\sigma}(0)/(1 + AD^n),$$

where $\tilde{\sigma}(0)$ = most probable ultimate tensile strength at D = 0 and

A, n = material parameters.

In the case of Celcon, the probability of survival as a function of strain is described by a straight-line relationship whose slope decreases progressively with dose.

The shore-D hardness of both resins decreased approximately exponentially with dose according to the relationship

$$H_D = H_0 \, e^{-0.043 \, D},$$

where H_D = Shore-D hardness after an absorbed dose D gigaergs/gm(C) , and

H_0 = original Shore-D hardness.

On the basis of weight-loss measurements, the G-value for formaldehyde evolution was estimated to be 15.4 and 8.9 for Delrin and Celcon, respectively. In this estimate, the residual dissolved gas and the possible weight increment due to oxygen sorption are neglected.

It is concluded that depolymerization is the predominant mode of radiation-induced degradation in these two resins.

TABLE OF CONTENTS

TABLE OF CONTENTS (Cont'd)

LIST OF FIGURES

LIST OF TABLES

I. INTRODUCTION

Acetal resins are recently developed polyoxymethylenes whose unbranched chains are composed of formaldehyde mer units:

$$\left[\begin{array}{c} H \\ | \\ -C- \\ | \\ H \end{array} \right] - O - \Bigg]_n ,$$

where $n > 1000$.

The linearity of the chains results in a high degree of crystallinity ($\sim 75\%$ for Delrin). As a consequence, this thermoplastic is characterized by a high melting point ($\sim 347^{\circ}F$), high strength, high resistance to creep and fatigue, good solvent resistance, and a good retention of these properties at elevated temperatures. In addition, it possesses very desirable electrical properties.

The behavior of this material in a radiation environment has, to this investigator's knowledge, not been studied previously.

Two investigations on a chemically related compound, poly(ethylene oxide), are summarily discussed in Reference 1. According to the first investigation by Pearson, this polymer (mer structure: $-CH_2CH_2O-$) shows increased solution viscosity upon exposure to moderate doses of radiation. This increase was observed to be higher for samples irradiated in air than for samples irradiated *in vacuo*. Longer exposure to air was

found to result in oxidative degradation.

In the second study, by Okamura, a gel-point dose of 5×10^9 ergs/gm was determined for poly(ethylene oxide) specimens (number-average molecular weight $\overline{M}_n = 9 \times 10^3$) irradiated in vacuo. On the basis of this investigation, a G-value of 0.53 for crosslink formation was calculated.

In the main chain of poly(ethylene oxide), C-C groups alternate with C-O groups, while the acetal main chain contains only C-O groups. For this reason, the foregoing studies are of interest and relevant to the present study for comparative purposes. Unfortunately, no data were found on radiolytic gas liberation and radiated-induced changes in the mechanical behavior of this polymer. Therefore, no quantitative comparisons with the results of the present investigation are possible.

Two commercially available acetal resins, marketed under the trade names of Delrin (a product of E. I. du Pont de Nemours & Co.) and Celcon (a product of Celanese Corp. of America) were selected for the present study.

From the technical literature obtained from the manufacturers, it appeared that the two resins do not appreciably differ from each other in their molecular characteristics. However, no details were furnished on the respective polymerization processes and the average degree of polymerization attained. Furthermore, the degree of crystallinity for Celcon was not known.

II. EXPERIMENTAL METHOD

2.1 Preparation of Specimens

The samples of both resins were router-milled from white opaque sheet stock in the form of dumbbell specimens as specified in ASTM Procedure D 638-61T (Ref. 2). The thickness of the Delrin and Celcon samples was 0.269 ± 0.0054 in. and 0.0788 ± 0.001 in., respectively. The specific gravity of both types of materials was 1.4 gm/cm^3.

Of each of the two resins, 90 such samples were prepared. Thus, 15 samples were available for each of the six experimental regimens, including the control condition.

2.2 Pre-irradiation Experimental Procedure

Prior to the irradiation of the samples, the following measurements were carried out:

1. Thickness and width were measured for each sample at three different locations of the gage section by means of a dial gage of 0.0005-in. accuracy.

2. Shore-D hardness of each sample was measured at either end of the dumbbell specimen.

3. Each sample was weighed in air with a balance of 0.0001 gm accuracy.

4. Specific gravity measurements were performed on ten randomly selected samples.

The samples were then individually wrapped in aluminum foil. The wrapped samples were placed, side by side, on perforated aluminum trays and attached to the trays by means of thin steel wire. Each tray accomodated five samples.

The loaded trays were, in turn, affixed to rectangular, 22- by 26-in., perforated aluminum panels. On each of five such panels, three trays of Delrin samples and three trays of Celcon samples were arranged, with equidistant spacing, in a circular configuration around the center of the panel. The approximate distance from the center line of t e trays to the panel center was about 8 in. On each panel, three dosimetry packets were mounted adjacent to the sample trays.

Fifteen samples of each of the two materials were kept as control specimens in the laboratory at a temperature of $78^{o} \pm 5^{o}F$.

2.3 Radiation Source

The Ground Test Reactor (GTR) served as the mixed-field radiation source. The GTR is a 3-Mw, water-cooled, water-moderated, thermal reactor utilizing MTR-type fuel elements. The irradiation cell is a portion of the reactor pool from which water is excluded by means of a dam. The water-filled portion of the pool contains the reactor. A rectangular recess approximately 30-in. wide and 3-ft deep down the center of the dam forms a closet into which the reactor is moved for operation. The reactor containment thus protrudes into the irradiation cell allowing access to three faces of the reactor for irradiation of specimens. The irradiation of materials and assemblies is implemented by means of a shuttle system which transports the test items into and out of the three irradiation positions adjacent to the reactor.

The NARF radiation-effects test facilities are described in detail in Reference 3.

2.4 Irradiation of Test Specimens

The radiation exposure was monitored by gamma and neutron detectors placed adjacent to the specimens. The detectors consisted of:

Nitrous-oxide: Gamma dosimeter

Tetrachloroethylene: Gamma Dosimeter

Sulfur foils: Fast neutrons, $E > 2.9$ Mev

Aluminum foils: Fast neutrons, $E > 8.1$ Mev

Copper foils: Thermal neutrons, $E < 0.48$ ev

The details of nitrous-oxide gamma dosimetry are described in Reference 4. Standard foil-counting procedures were used for neutron measurements, with data reduction by IBM computer. Techniques employed in neutron-flux measurements are described in detail in Reference 5.

The results of the dosimetric measurements are given in Table I.

The surface temperature of the samples during irradiation was monitored by thermocouples. Although the ambient temperature could be adjusted within a wide range by means of a refrigerated air current, the temperature recorded at the surface of the samples could not be kept constant in all cases because of gamma-ray heating effects. The temperature history of the samples during irradiation is shown in Table II.

2.5 Testing of Samples

After removal from the radiation field, the samples were stored in the laboratory at $75^{\circ} \pm 5^{\circ}$F for a period of 7 days. Thereafter, the samples were tested on an Instron testing machine.

TABLE I

DOSIMETRIC DATA FOR THE DELRIN AND CELCON IRRADIATION

Dosimetric Parameter	Dose Level				
	1	2	3	4	5
Integrated Power, Mw-hr	2.75	2.75	2.75	24	24
Avg Gamma Dose Rate, ergs/gm(C)-hr	1.12×10^{8}	2.47×10^{8}	5.56×10^{8}	4.79×10^{8}	1.48×10^{9}
Gamma Dose, ergs/gm(C)	$3.07 \pm 0.16 \times 10^{8}$	$6.8 \pm 0.53 \times 10^{8}$	$1.53 \pm 0.12 \times 10^{9}$	$3.83 \pm 0.18 \times 10^{9}$	$1.18 \pm 0.06 \times 10^{10}$
Avg Neutron Flux, n/cm^2-sec-w					
Sulfur	4.26×10^{3}	1.05×10^{4}	2.30×10^{4}	6.63×10^{3}	2.15×10^{4}
Aluminum	-	-	-	2.38×10^{2}	7.87×10^{2}
Copper	-	-	-	1.78×10^{3}	2.67×10^{3}
Integrated Flux, n/cm^2					
Sulfur	$4.22 \pm 0.21 \times 10^{13}$	$1.04 \pm 0.02 \times 10^{14}$	$2.28 \pm 0.24 \times 10^{14}$	$5.73 \pm 0.22 \times 10^{14}$	$1.86 \pm 0.19 \times 10^{15}$
Aluminum	-	-	-	$2.06 \pm 0.09 \times 10^{13}$	$6.80 \pm 0.85 \times 10^{13}$
Copper	-	-	-	$1.54 \pm 0.25 \times 10^{14}$	$2.31 \pm 0.74 \times 10^{14}$

TABLE II

TEMPERATURE HISTORY OF SAMPLES

DURING IRRADIATION

Samples Irradiated to Dose Level	Surface Temperature at Start of Irradiation	Thermal Equilibrium Temperature During Irradiation	Time from Start of Irradiation to Attainment of Thermal Equilibrium	Time at Thermal Equilibrium
1	57°F	66°F	48 min	117 min
2	59°F	86°F	108 min	57 min
3	60°F	102°F	108 min	57 min
4	62°F	52°F	84 min	396 min
5	80°F	140°F	120 min	360 min

The samples were uniaxially strained at a constant crosshead displacement rate of 0.2 in./min until rupture occurred.

In the calculation of the tensile strain, it was assumed that the crosshead displacement rate, dx/dt, was related to the strain rate, dε/dt, by the expression

$$d\epsilon/dt = (1/L_{eff})\ (dx/dt)\ , \qquad (1)$$

where L_{eff} = effective gage length (in the present case L_{eff} = 2.25 in.). Accordingly, the average strain rate used in the present case was 0.0889 in./in. per min.

Comparative tests with unirradiated samples in which the directly measured strain rate was in agreement with the value of the strain rate as determined from jaw displacement and effective gage length according to Equation 1.

The hardness of all samples was determined by means of a Shore-D hardness gage. The measurements were carried out on the end pieces of the tensile specimens.

III. EXPERIMENTAL RESULTS

The experimental results of the stress-strain measurements are represented in Table III.

The secant moduli σ_2/ϵ_2 are listed in Table IV.

The average Shore-D hardness values are tabulated in Table V.

The changes in sample weight are shown in Table VI.

TABLE III

STRESS STRAIN BEHAVIOR OF IRRADIATED ACETAL RESINS

Gamma Dose [ergs/gm(C)]	Stress σ_1 at Strain ϵ_1 (lb/in.^{2})	Probable Error of σ_1	Strain ϵ_1 (in./in.)	Probable Error ϵ_1	Ultimate Tensile Strength σ_2 (lb/in.^{2})	Probable Error of σ_2	Ultimate Tensile Strain ϵ_2 (in./in.)	Probable Error ϵ_2
(a) Delrin								
Controls	6574	437	0.0684	0.0052	10144	91	0.2357	0.0174
3.07×10^8	----	---	----	----	5143	546	0.0535	0.0048
6.8×10^8	299	64	0.0154	0.003	977	429	0.0292	0.0003
1.53×10^9	----	---	----	----	93	19	0.0014	0.0001
3.83×10^9	----	---	----	----	90	23	0.0015	0.0005
1.18×10^{10}	----	---	----	----	21	8	----	----
(b) Celcon								
Controls	4617	657	0.048	0.008	7934	126	0.4370	0.066
3.07×10^8	4450	679	0.0448	0.005	7807	169	0.1108	0.0119
6.8×10^8	----	---	----	----	4133	440	0.0268	0.0034
1.53×10^9	----	---	----	----	1496	431	0.0071	0.0027
3.83×10^9	----	---	----	----	352	2	0.0017	0.0001
1.18×10^{10}	----	---	----	----	---	---	----	----

TABLE IV

SECANT MODULI OF IRRADIATED ACETAL RESINS

Gamma Dose [ergs/gm(C)]	Secant Modulus (lb/in.^{2})	
	Delrin	Celcon
0 (Controls)	43,040	18,160
3.07×10^8	96,130	70,460
6.8×10^8	33,460	154,220
1.53×10^9	66,430	210,704
3.83×10^9	60,000	207,060
1.18×10^{10}	---	---

TABLE V

SHORE-D HARDNESS OF IRRADIATED

ACETAL RESINS

Gamma Dose [ergs/gm(C)]	Delrin Shore-D Hardness		Celcon Shore-D Hardness	
	Average	Standard Deviation	Average	Standard Deviation
0 (controls)	83.8	0.8	80.5	0.8
3.07×10^8	83.1	0.5	80.9	0.7
6.8×10^8	82.1	0.9	81.1	0.7
1.53×10^9	78.9	1.3	80.2	0.9
3.83×10^9	71.1	2.1	72.6*	2.4
1.18×10^{10}	50.3	4.6	45 **	---

* Many of these samples broke upon measurement of the hardness. In these cases, the highest value shown on the gage was recorded.

** Most of these samples crumbled into small, chalky pieces.

TABLE VI

WEIGHT CHANGES OF IRRADIATED ACETAL RESINS

Gamma Dose [ergs/gm(C)]	Delrin			Celcon		
	$\overline{\Delta W}$ (mg)	S(ΔW)	% Change	$\overline{\Delta W}$(mg)	S(ΔW)	% Change
0	0	0	0	0	0	0
3.07×10^8	+240.6	31.2	+0.69	-5.1	4.4	-0.05
6.8×10^8	+222.3	6.3	+0.64	-15.7	10.5	-0.16
1.53×10^9	+150.8	16.1	+0.43	-19.4	2.0	-0.19
3.83×10^9	-330.8	41.2	-0.95	-76.8	25.0	-0.77
1.18×10^{10}	-2903.5	164.6	-8.35	-413.6	41.2	-4.16

$\overline{\Delta W}$ = mean change in weight.

S(ΔW) = sample standard deviation from the mean.

% change is with respect to average preirradiation sample weight (for Delrin: 100% = 34.7565 fm: for Celcon: 100% = 9.9317 gm)

IV. DISCUSSION OF RESULTS

4.1 Stress-Strain Characteristics

Upon irradiation, the shape of the stress-strain curves of Delrin and Celcon changes from that typical of a hard, strong plastic (high modulus, high yield point, and moderate ultimate elongation) to that characteristic of a hard, brittle plastic (high modulus, no well-defined yield point, and low elongation at break).

In the case of Delrin, the stress-strain curve of the unirradiated samples (see Fig. 1) reveals a continuous increase of stress up to rupture. The yield point, though high, was invariably lower than the ultimate tensile stress. The stress-strain curves of the irradiated Delrin samples (see Fig. 1) show an apparently complete disappearance of the yield point and a substantial decrease in the ultimate elongation. However, there is initially [at 3.07×10^8 ergs/gm(C)] an increase by a factor of 2.23 in the secant modulus (see Table IV) followed by a drop at 6.8×10^8 ergs/gm(C) and then an increase at 1.53×10^9 ergs/gm(C).

In the case of Celcon, the stress-strain curve of the unirradiated samples (see Fig. 2) manifests a yield point that is invariable higher than the value of the ultimate tensile strength. Furthermore, its ultimate strain is nearly twice that observed for unirradiated Delrin. This behavior appears to indicate

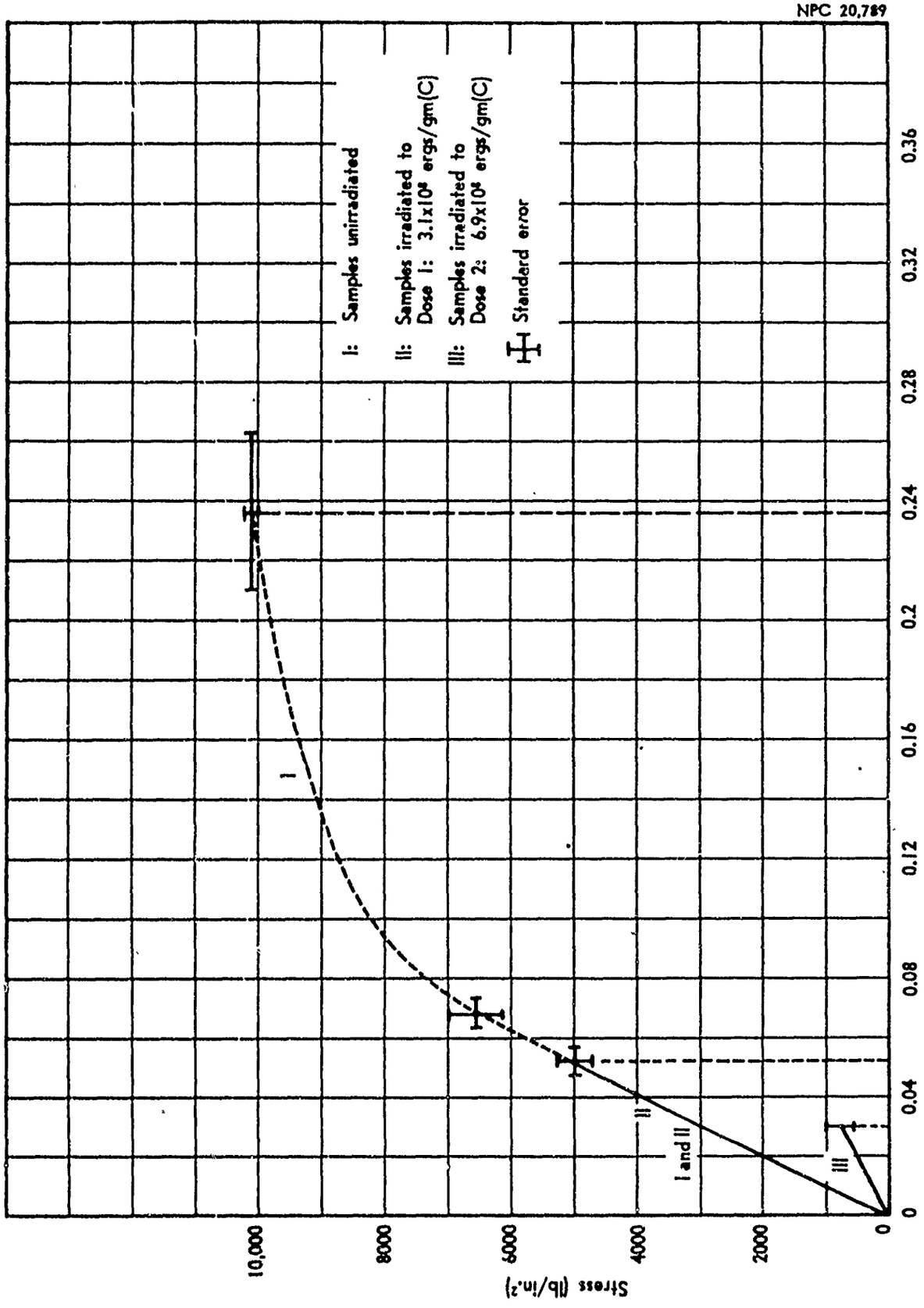

Figure 1 Stress-Strain Curve of Unirradiated and Irradiated Delrin Acetal

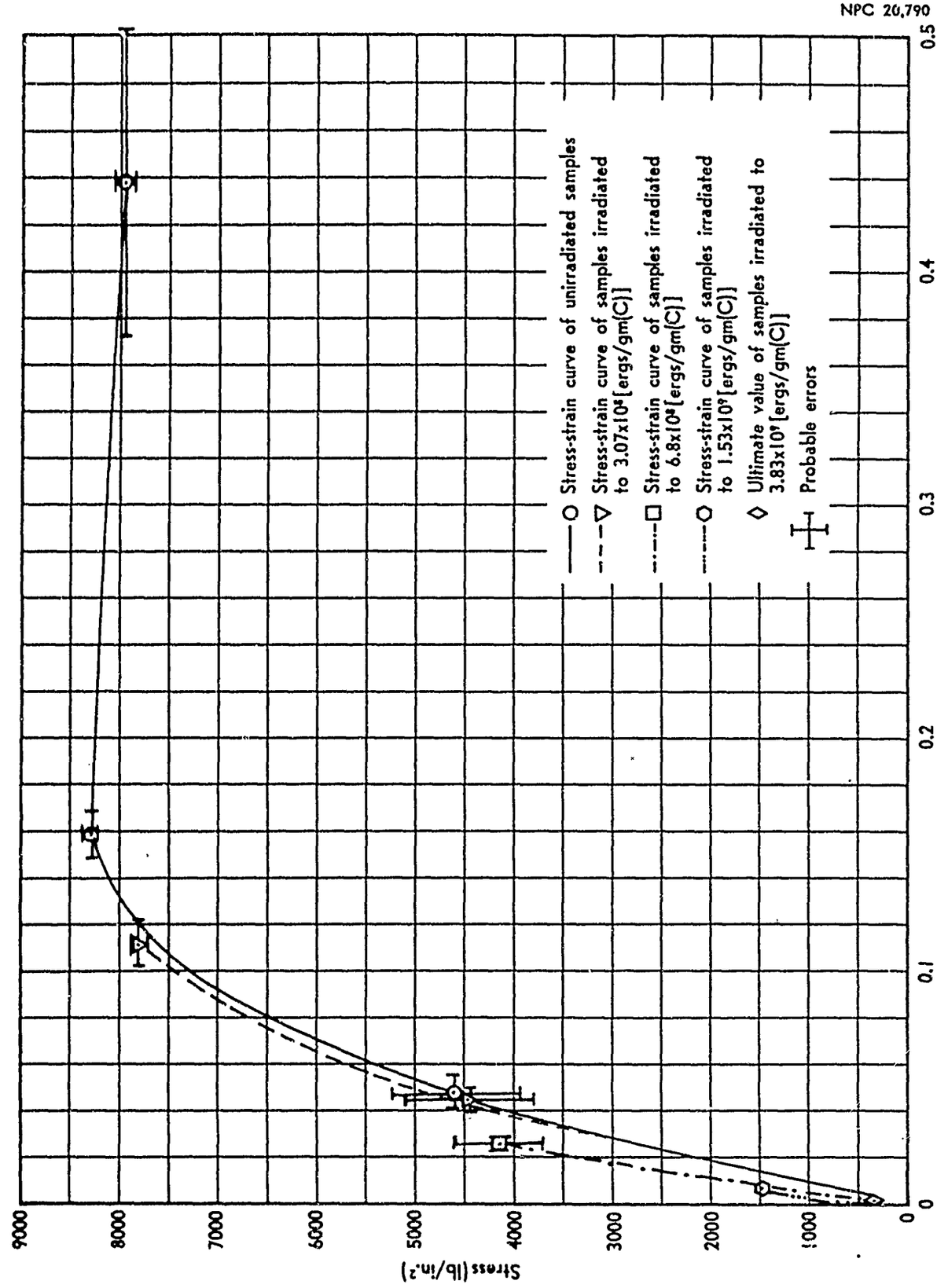

Figure 2 Stress-Strain Curve of Celcon Acetal

that the initial degree of crystallinity of Celcon is considerable lower than that of Delrin.

The secant modulus of Celcon (see Table IV) increases steadily with dose up to 1.53×10^9 ergs/gm(C) . Only a small drop in this parameter is encountered at 3.83×10^9 ergs/gm(C).

This difference in secant modulus behavior cannot definitely be explicated at this time. However, the following tentative qualitive interpretation of this behavior appears reasonable on the basis of the evidence on hand:

A number of molecular events are induced by radiation in acetal resins. Some of these are gas liberation, destruction of crystallites, crosslinking, and chain scission.

Destruction of crystallites, chain scission, and gas bubble formation are antagonistic to crosslinking in their effect on modulus. In the more highly crystalline Delrin, the probability of crosslinking is expected to be higher than in Celcon because of the better chain alignment. But this effect, which tends to increase the modulus, is counteracted by the concomitant destruction of crystallites, which tends to decrease the modulus. In Celcon which, on the basis of the secant modulus, has a much lower initial degree of crystallinity, the effect on the modulus remains predominant up to Dose 3 $\left[1.53 \times 10^9 \text{ ergs/gm(C)}\right]$. Any negative contribution from crystallite destruction is thus concealed.

At Dose 4, the effect of depolymerization becomes predominant in both polymers.

The appreciably lower moduli for Delrin at Dose 2, 3, and 4 may be attributed to the greater probability of gas bubble

formation in the thicker Delrin specimens.

An extremal probability analysis (Ref. 6) of the ultimate tensile strength values yielded the statistical parameters shown in Table VII.

The survivorship functions of the ultimate-tensile-strength values for Delrin and Celcon are represented in Figures 3 and 4, respectively. In both cases, the distribution parameter α^{-1} initially increases with dose and then decreases again at higher doses. This behavior is most likely due to the circumstance that the strength-reducing defects tend to be more heterogenous at first but that, eventually, the defect distribution becomes so narrow that the tensile strength approaches an equiprobable value. In general, there is a very excellent adherence to the straight-line behavior predicted by the Gumbel function.

The most probable values of ultimate tensile strength were found to follow the empirical function found to apply to polycarbonate (Ref. 7):

$$\tilde{\sigma}_2(D) = \tilde{\sigma}_2(0)/(1 + \beta D^n) \ , \qquad (2)$$

where $\tilde{\sigma}_2(D)$ = most probable ultimate tensile strength after absorption of Dose D $\left[\text{gigaergs/gm(C)}\right]$,

$\tilde{\sigma}_2(D)$ = most probable ultimate tensile strength of the unirradiated material, and

β, n = material parameters (for Delrin: $\beta = 24.6$ and $n = 2.5$; for Celcon: $\beta = 1.39$ and $n = 2.9$).

In Figure 5, the course of Equation 2 together with the calculated values of $\tilde{\sigma}_2(D)$ is represented for Delrin and Celcon, respectively.

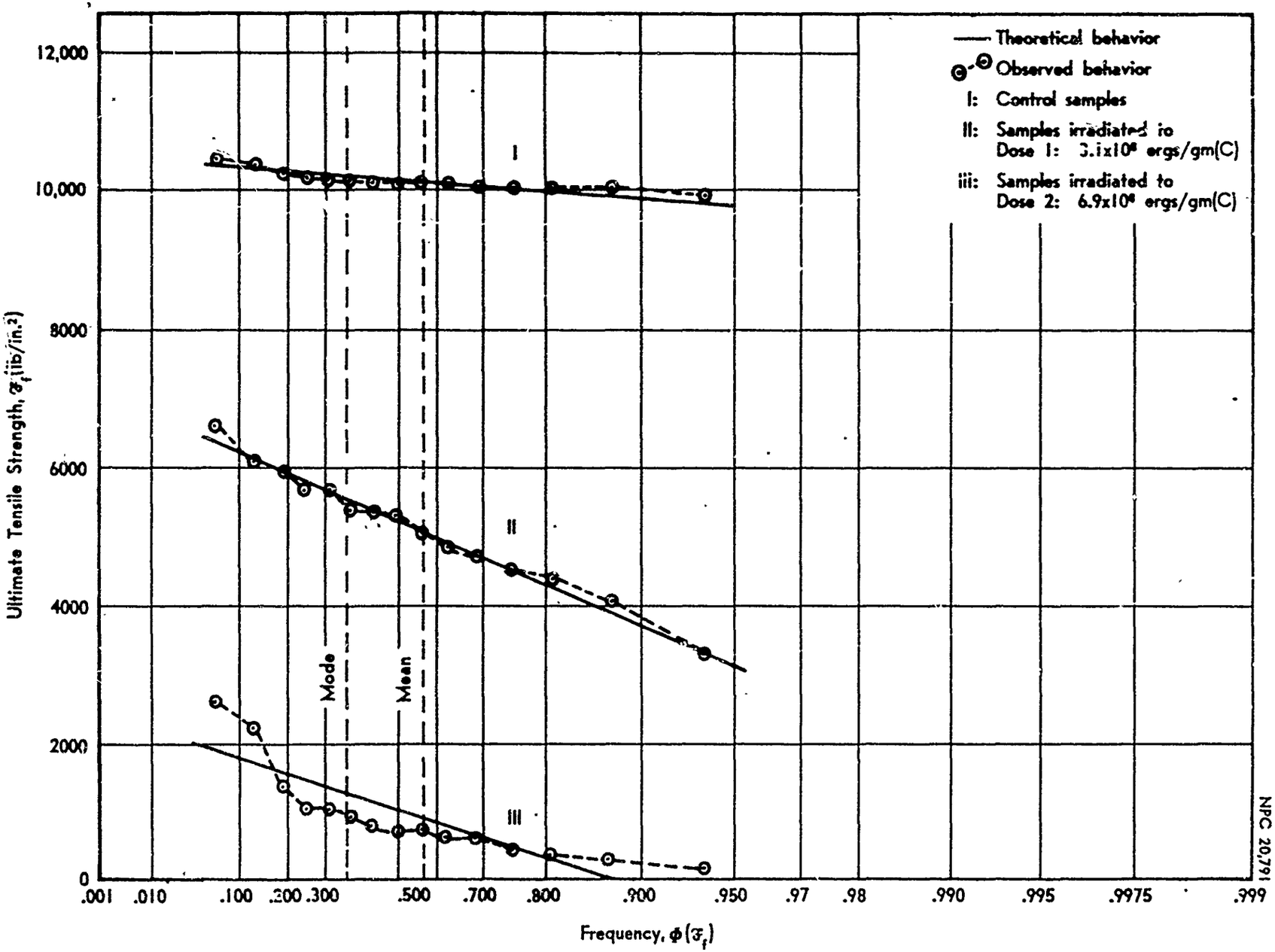

Figure 3 Survivorship Function of Irradiated Delrin Acetal

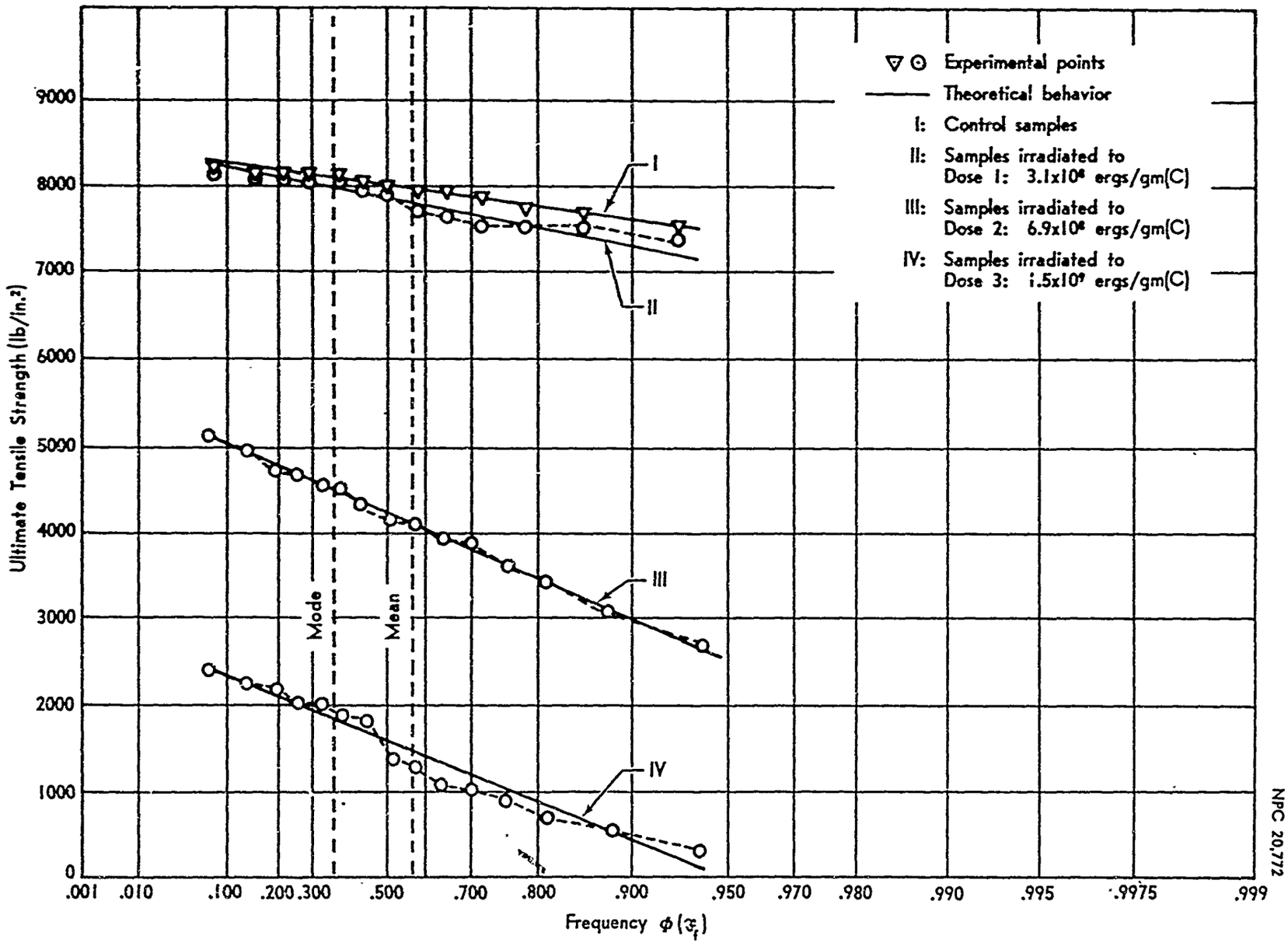

Figure 4 Survivorship Function of Irradiated Celcon Acetal Resin

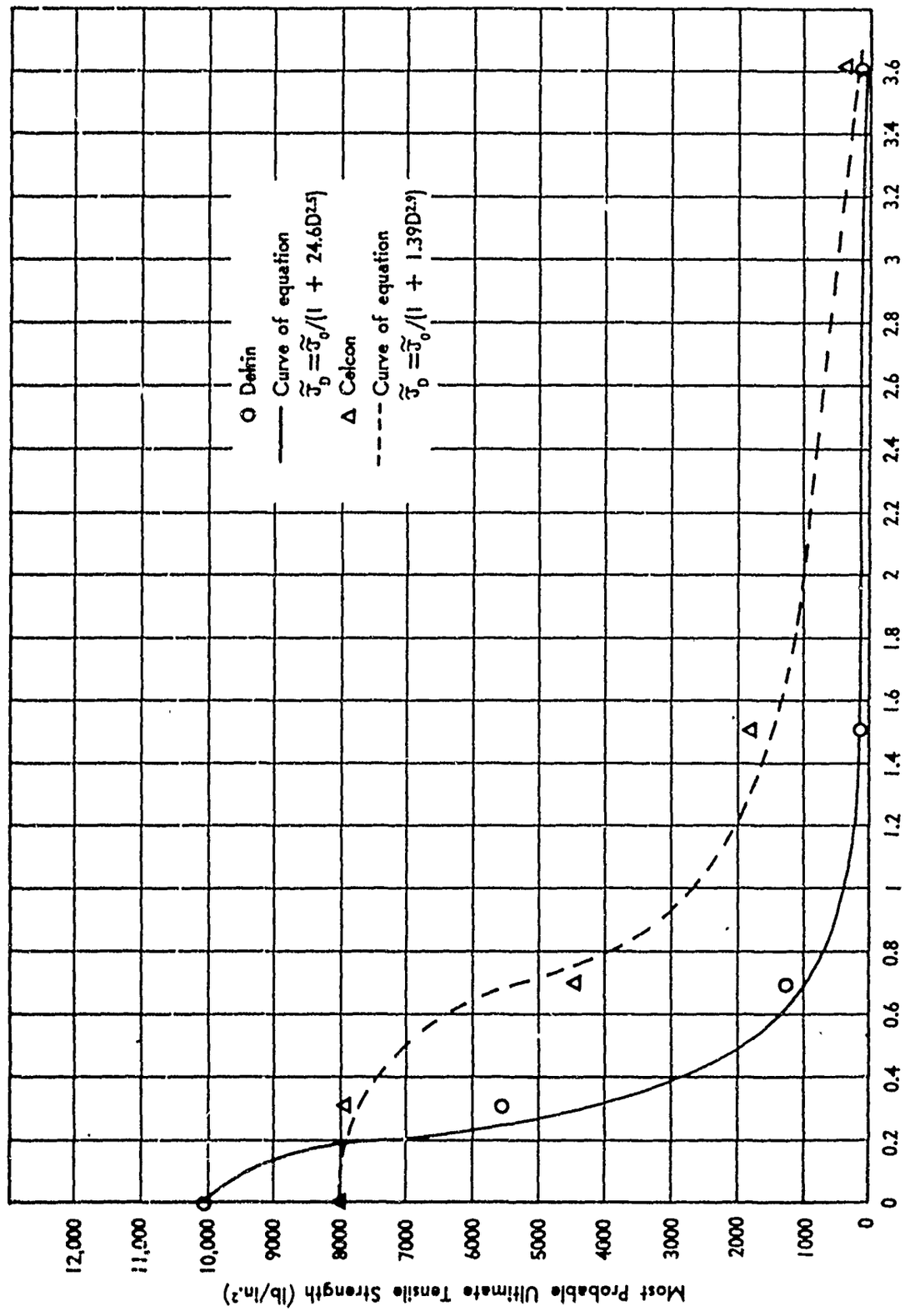

Figure 5 Most Probable Ultimate Tensile Strength of Delrin Acetal and Celcon Acetal as a Function of Absorbed Gamma Dose

TABLE VII

STATISTICAL PARAMETERS OF THE ULTIMATE TENSILE STRENGTH OF ACETAL RESINS

Treatment	$\tilde{\sigma}_2$ (lb/in.^{2})	$\bar{\sigma}_2$ (lb/in.^{2})	S	(1/α)	n
(a) Delrin Samples					
Controls	10211	10144	134	132	15
Dose 1	5550	5143	810	794	15
Dose 2	1297	977	637	624	15
Dose 3	107	93	28	29	7
Dose 4	115	90	35	53	6
Dose 5	33	21	12	29	3
(b) Delcon Samples					
Controls	8026	7934	186	217	13
Dose 1	7931	7807	251	292	15
Dose 2	4462	4133	653	640	15
Dose 3	1818	1496	640	627	15
Dose 4	367	352	2	37	2

$\tilde{\sigma}_2$ = most probable value of the ultimate tensile Strength σ_2,

$\bar{\sigma}_2$ = mean value of σ_2,

S = samples standard deviation from the mean,

(1/α) = calculated slope of the curve of ultimate strength versus frequency $\Phi(\sigma_2)$, and

In addition, it was found for Celcon that the probability of survival when plotted on normal probability paper as a function of ultimate strain resulted in straight-line relationships whose slope decreases progressively as a function of absorbed dose (see Fig. 6). Within the dose range examined, the logarithm of the mean ultimate strain of Celcon showed a linear decrease with the logarithm of the absorbed dose (see Fig. 7).

All Delrin and Celcon samples, both in the unirradiated and irradiated state, exhibited brittle fracture.

4.2 Shore-D Hardness

The Shore-D hardness of both resins decreased approximately exponentially with dose. In Figure 8 the observed hardness values are plotted as a function of dose together with the curve of the equation

$$H_D = H_0 \, e^{-0.043D} \qquad (3)$$

where H_D = Shore-D hardness after exposure of the samples to dose D [gigaergs/gm(C)], and

H_0 = original Shore-D hardness.

It can be seen that this equation gives an adequate fit to both sets (Delrin and Celcon) of data.

4.3 Correlation of Weight Changes with Molecular Behavior

In Figure 9, the observed changes in weight (see Table VI) are plotted as a function of dose. Accordingly, the Delrin samples initially show a gain in weight upon irradiation then, at around 10^9 ergs/gm(C), progressively lose weight. The Celcon samples, on the other hand, do not manifest this initial weight gain. Rather, they exhibit a continuous loss in weight with increasing dose.

These data appear to indicate that there is a competitive

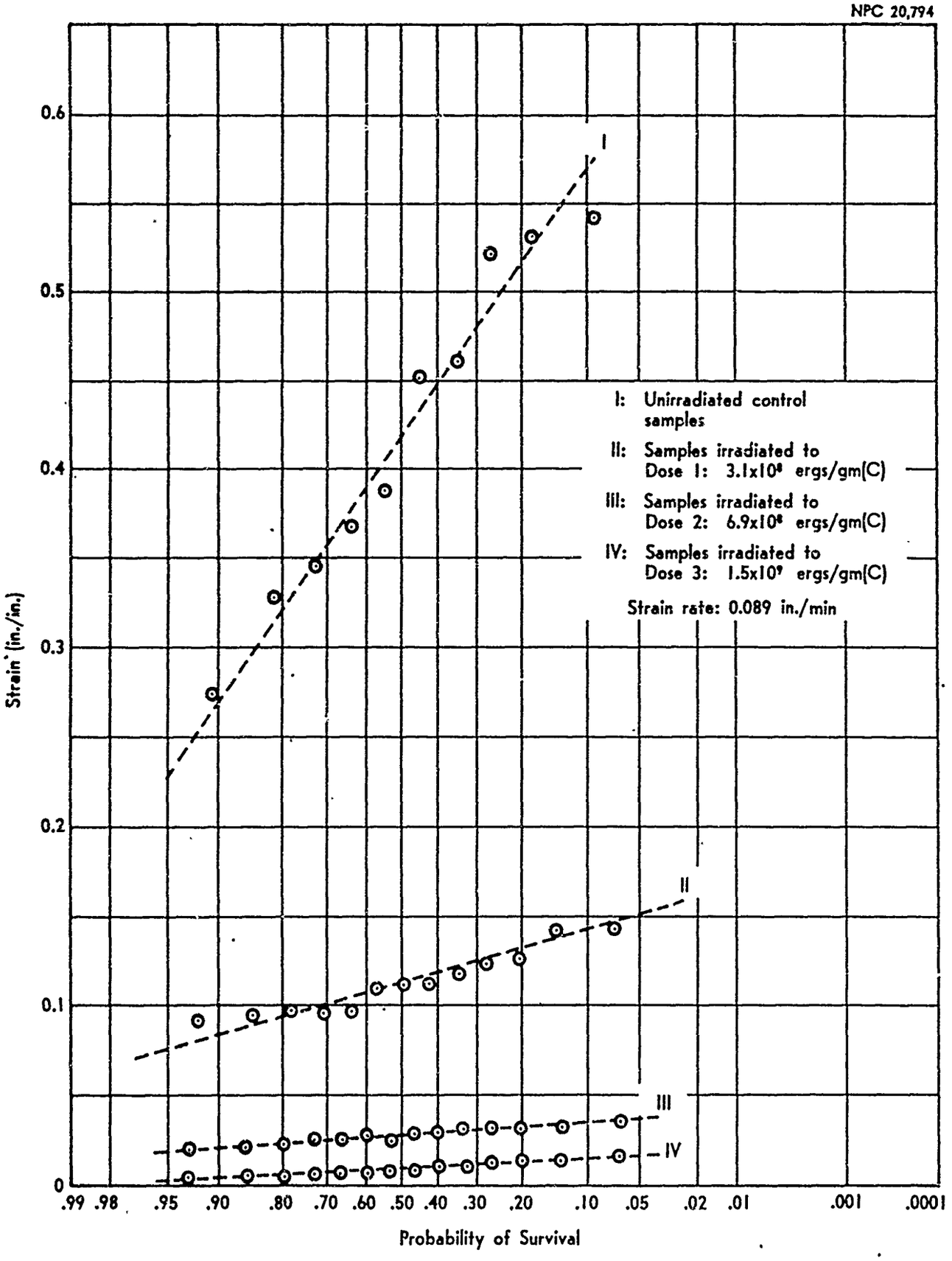

Figure 6 Probability of Survial of Celcon Acetal as a Function of Strain and Radiation Dose

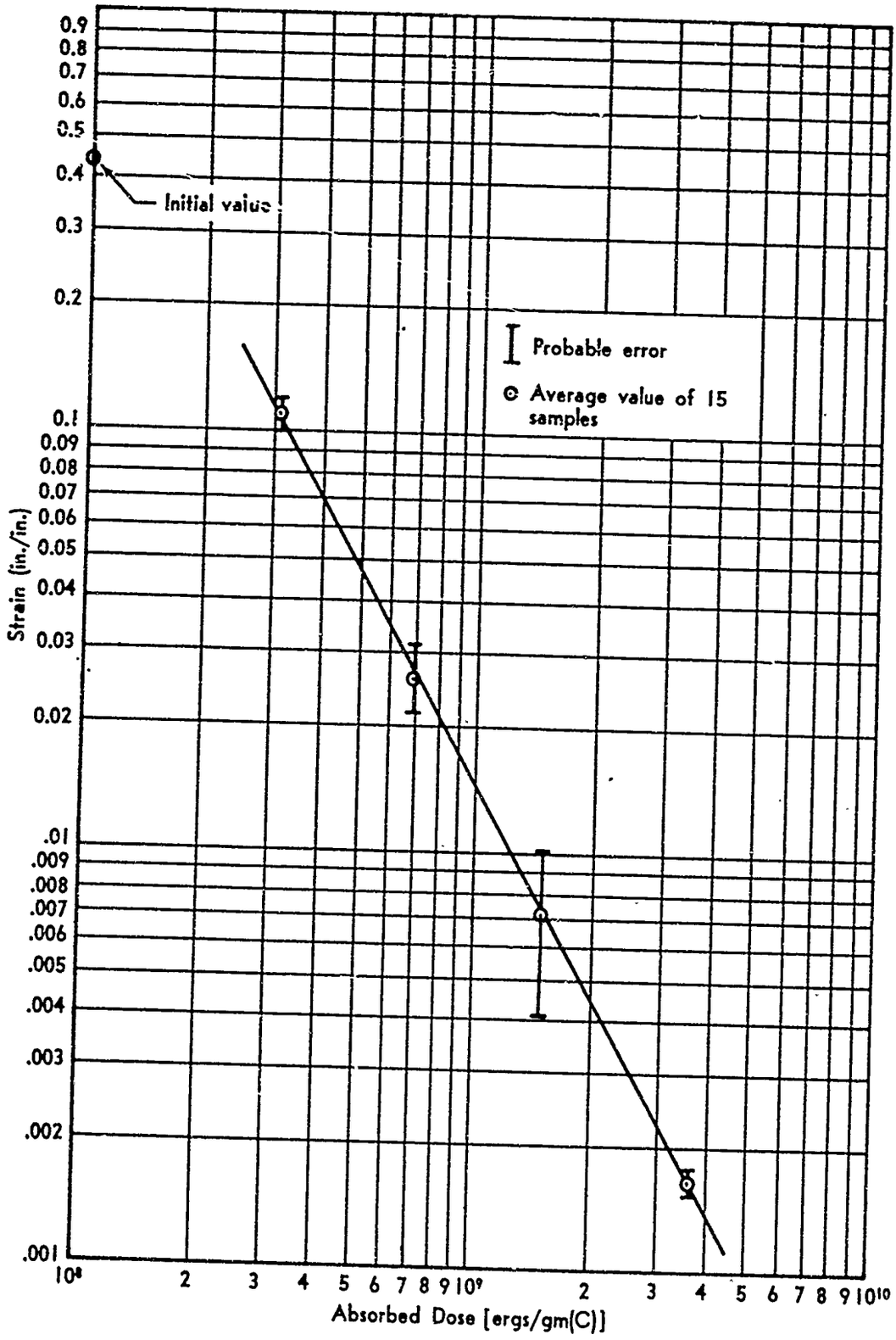

Figure 7 Ultimate Strain of Celcon Acetal as a Function of Absorbed Gamma Dose

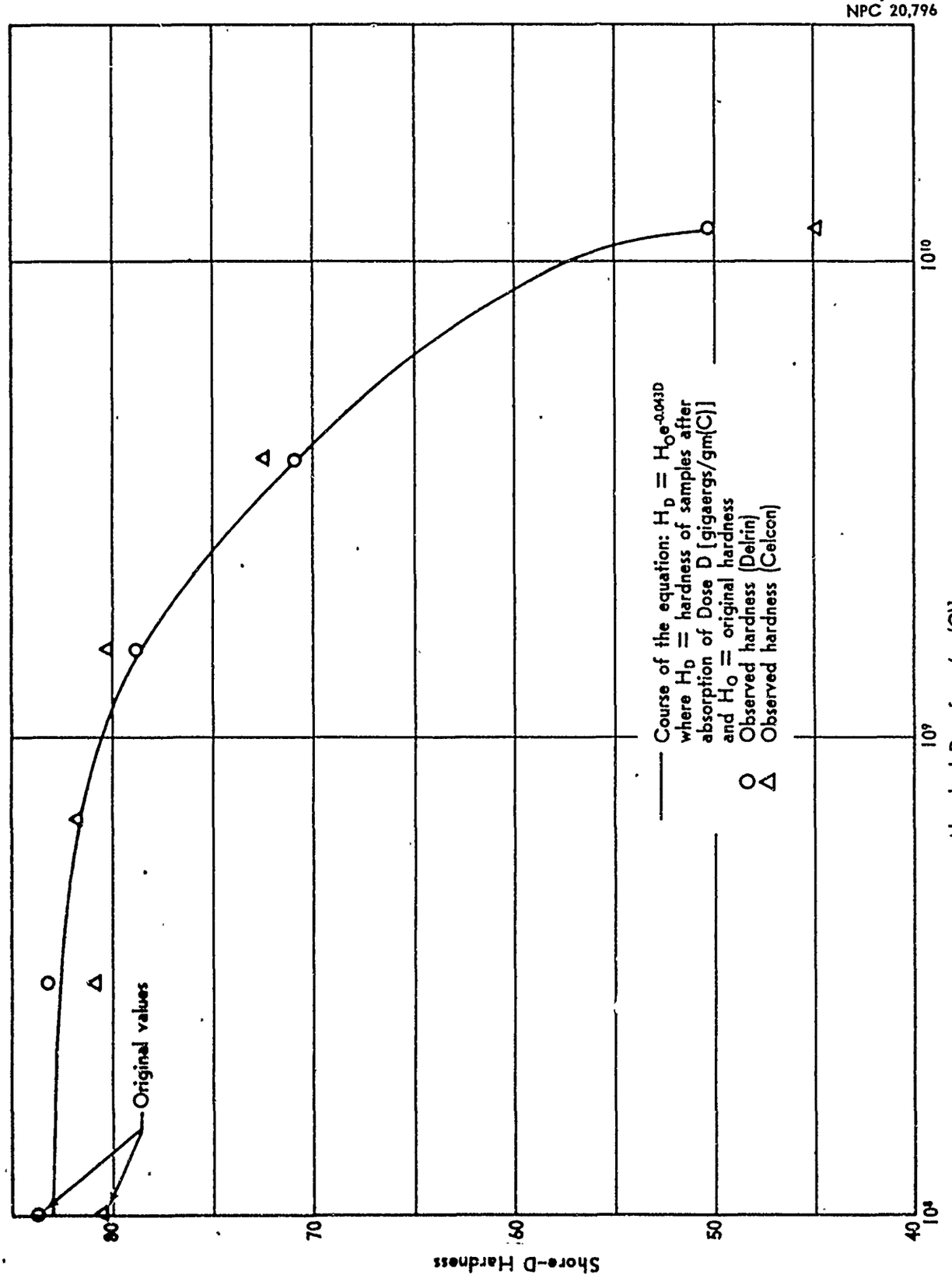

Figure 8 Shore-D Hardness of Delrin and Celcon Acetal as a Function of Absorbed Gamma Dose

NPC 20,797

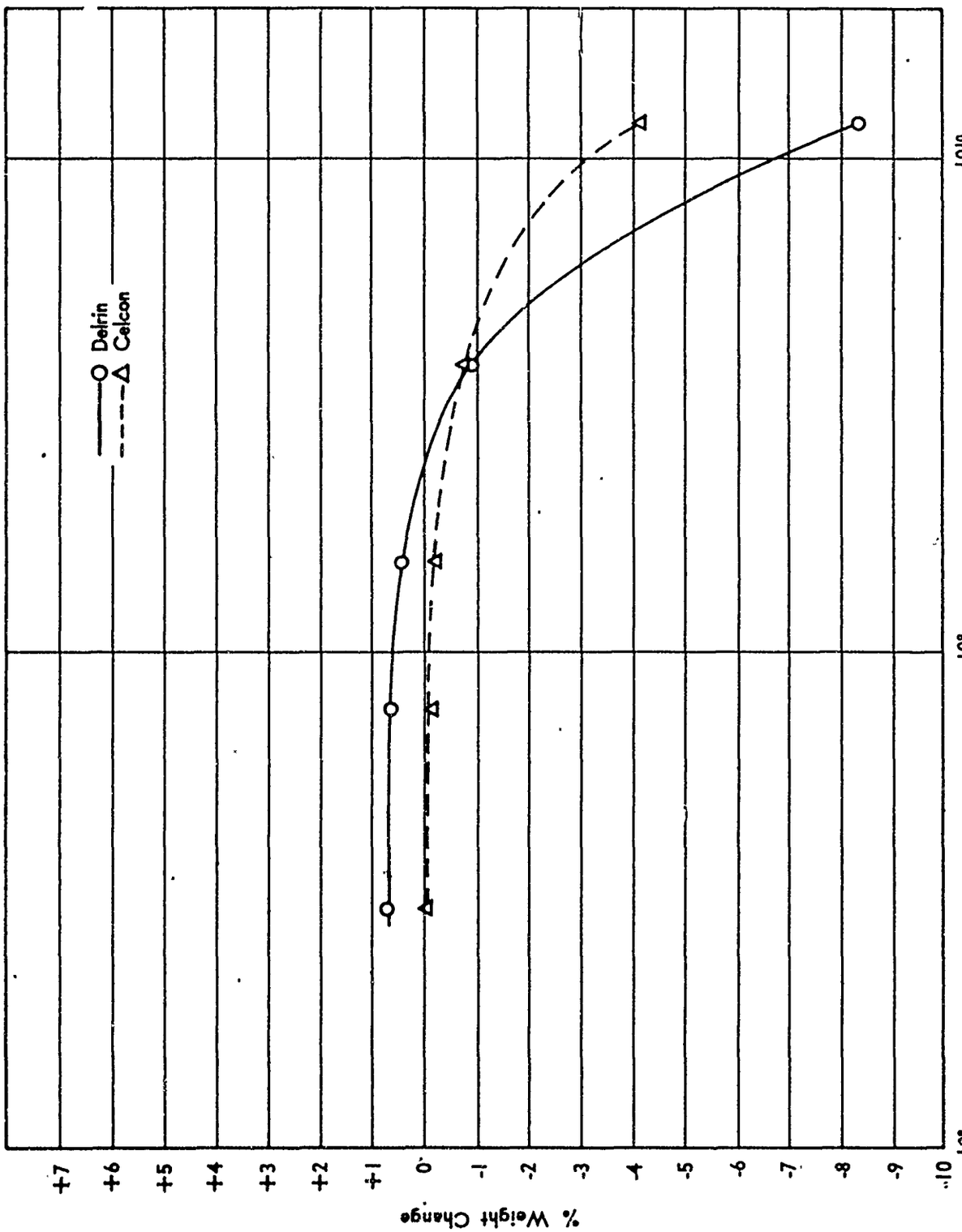

Figure 9 Weight Loss of Delrin and Celcon as a Function of Absorbed Gamma Dose

process taking place between oxygen diffusion into the sample and diffusion of radiation-produced gases out of the samples.

Although this investigation did not include a specific analysis of the gases evolved upon irradiation, the presence in the irradiated samples of formaldehyde was evident from its typical pungent odor. This gas is also known to evolve upon pyrolysis of acetal resins. If we assume that HCHO is the principal gas evolved, then the total weight change W is given by the difference between the weight increment due to oxygen sorption and the weight decrement due to diffusion of HCHO out of the sample.

On the basis of a diffusion constant of 2×10^{-6} cm^2/sec for HCHO in acetal at 25°C, the induction period for attainment of steady-state conditions during irradiation was calculated to be 5.4 hours for the Delrin samples and about 30 min for the Celcon samples, so that at the termination of the 8-hr irradiation it may be assumed that a uniform concentration, c_o, of HCHO existed in the samples. The concentration, c, of HCHO at the midpoint of the samples at time t after cessation of the irradiation can be shown (Ref. 8) to be approximately given by the equation

$$c(\mathrm{HCHO}) = \frac{4}{\pi} c_o \sum_{m=o}^{\infty} \frac{-(-1)^{m+1}}{(2m+1)} \exp\left[\frac{-D(2m+1)^2\pi^2 t}{d^2}\right], \quad (4)$$

where D = diffusion constant

t = time after cessation of irradiation, and

d = sample thickness

An evaluation of Equation 4 (taking again $D = 2 \times 10^{-6}$ cm^2/sec) reveals that the residual concentration of HCHO in both types of samples is expected to be vanishingly small after 7 days, i.e., at the time the samples were weighed.

Equation 4 does, however, not take into account the solubility of the formaldehyde monomer in its polymer matrix. Probably, a considerable quantity of this gas is thus retained in the polymer at room temperature. For example, if the solubility were as high as the sample volume (which it is for some monomers in their polymer matrix), the Delrin and Celcon samples could at 25°C solvate up to 33 mg and 9.6 mg HCHO, respectively.

Furthermore, some of the evolved gas collects in pores within the samples. This became visually evident in the samples irradiated to 1.53×10^9 ergs/gm(C). At this dose, small (up to about 0.15-in. diam) whitish circular maculae appeared on the surfaces of both the Delrin and Celcon samples. These maculae formed the base of conical fracture zones whose subsurface apexes were gas pockets. In addition, a net-like system of tightly closed filamentary fissures appeared on the surface of the Delrin samples.

The density of the fracture maculae on the surface of the samples increased with dose. At 3.83×10^9 ergs/gm(C), both the Delrin and Celcon samples showed a mean density of about 20 maculae/$in.^2$ which imparted a marble-like appearance to the samples.

At 1.18×10^{10} ergs/gm(C), the network of fissures in the Delrin samples had completely opened up, so that the sample disintegrated readily in handling. The Celcon samples irradiated

to that dose did not show this type of fissures, but the density of the maculae was increased to about 70/in.^{2}.

These fracture phenomena suggest that considerable internal gas pressures develop in the material. In the thicker Delrin samples, this build-up in pressure is greater because the diffusion loss from the gas pockets is smaller. It is probably for this reason that the Delrin samples develop the reported network of filamentary fissures. As these fissures open up, the gas trapped in the interior gas pockets can escape. This mechanical disruption is, therefore, likely to be the cause of the observed fact that the Delrin samples show greater relative weight loss than the Celcon samples (see Fig. 9).

On the basis of the weight loss measurements, the G-value for HCHO evolution can be estimated if the residual dissolved gas and the weight increment due to oxygen is neglected. Accordingly,

$$G(HCHO) = \frac{1.602\ \Delta W\ N}{10^{10}\ M \cdot D \cdot W} \left[\frac{\text{molecules HCHO}}{100\ \text{ev}}\right], \qquad (5)$$

where ΔW = weight decrement (gm) after dose $D \left[\frac{\text{ergs}}{\text{gm(C)}}\right]$,

W = sample weight (gm),

M = molecular weight (gm/mole) of HCHO, and

N = Avogadro's number.

At $D = 3.83 \times 10^9$ ergs/gm(C), the mean apparent G(HCHO)-values thus calculated are 7.99 and 6.49 for Delrin and Celcon, respectively. The discrepancy between these two sets of values is, at least partially attributable to the aforementioned release

of trapped gas due to sample disintegration at the highest dose. Thus, since the Delrin samples suffer a considerable higher degree of mechanical deterioration, the apparent increase of G-value from Dose 3 to Dose 4 is higher (an increase by a factor of 2.85) for the Delrin samples than for the Celcon samples (an increase by a factor of 1.7).

The average of the two sets of G-values is 15.4 for Delrin and 8.9 for Celcon. These values must be considered minimum estimates.. Besides, a more rigorous determination of the G(HCHO)-value in acetals may reveal that this G-value varies with dose because the rate of gas formation may be concentration-dependent. At any rate, the relatively high G-values determined in the present study strongly indicate that the radiolytically initiated HCHO gas formation is propagated by a chain reaction that may be dependent on the presence of oxygen.

4.4 Physical Appearance of the Samples

In the unirradiated state, both the Delrin and the Celcon samples were opaque and had a white ivory-like, glossy appearance. This discoloration became faintly but noticeably more pronounced with increasing dose up to and including Dose 3 [1.53×10^9 ergs/gm(C)]. In the samples irradiated to Dose 4 [3.83×10^9 ergs/gm(C)], the discoloration had reverted to approximately the same tint as observed in the samples irradiated to Dose 1. The surface gloss seemed to be unaffected up to Dose 4. After absorption of Dose 5 [1.18×10^{10} ergs/gm(C)], all samples had drastically assumed a chalky-white, mat appearance.

As described in detail above, circular fracture maculae emanating from subsurface gas pockets appeared in the samples

irradiated to Dose 3. The density of these maculae on the surface of both the Delrin and Celcon samples increased severalfold at Dose 4 and, in the case of the Celcon samples, increased still more at Dose 5. In the Delrin samples irradiated to the latter dose, the maculae were absent. Instead, the densely intermeshed and (up to Dose 4) tightly closed filamentary cracks that first appeared at Dose 3 and increased in density at Dose 4 had opened up widely. These samples readily crumbled into small fragments upon handling.

V. CONCLUSIONS

5.1 Shape of the Stress-Strain Curve

In the unirradiated state, both Delrin and Celcon show a stress-strain curve typical of a hard, strong plastic having a high modulus, a high yield point, and moderate ultimate elongation. The Delrin samples showed a continuous increase in stress with increasing strain, up to rupture, while the Celcon samples manifested a yield point that was invariably higher than their ultimate tensile strength.

Upon irradiation, the shape of the stress-strain curves of both Delrin and Celcon changed to that typical of a hard, brittle plastic having a high modulus, no well-defined yield point, and low elongation at break.

5.2 Secant Modulus

Delrin showed a seemingly erratic behavior in its secant modulus. It increased at 3.07×10^8 ergs/gm(C), decreased at 6.8×10^8 ergs/gm(C), increased again at 1.53×10^9 ergs/gm(C) and decreased again at 3.83×10^9 ergs/gm(C). An interpretation of this behavior is offered in terms of competing molecular processes.

Celcon showed a continuous increase in secant modulus up to and including 1.53×10^9 ergs/gm(C). Upon further irradiation, the modulus manifests a decrease.

5.3 Ultimate Tensile Stress and Strain

The ultimate-tensile-strength values of both Delrin and

Celcon show a good conformance with the Gumbel survivorship function. The dependence of the most probably ultimate tensile strength on Dose D was found to be describable by the relationships following.

$$\text{Delrin: } \tilde{\sigma}(D) = \tilde{\sigma}(0)/(1 + 24.6\ D^{2.5})$$

$$\text{Celcon: } \tilde{\sigma}(D) = \tilde{\sigma}(0)/(1 + 1.39\ D^{2.9}).$$

The probability of survival as a function of strain for Celcon followed a straight-line relationship whose slope decreased progressively with dose. The logarithm of the mean ultimate strain of Celcon showed a linear decrease with the logarithm of absorbed dose.

5.4 Shore-D Hardness

The Shore-D hardness of both Delrin and Celcon decreased exponentially with absorbed dose.

5.5 Gas Liberation

On the basis of the weight loss measurements, the G (formaldehyde)-values for Delrin and Celcon were conservatively estimated to be 15.4 and 8.9.

5.6 General Remarks

The observed initial increases in modulus suggest that acetal resins may initially crosslink to some extent. At around 3×10^9 ergs/gm(C), depolymerization appears to become predominant, resulting in virtually complete loss of mechanical strength at 10^{10} ergs/gm.

REFERENCES

1. Bolt, R. O., and Carroll, J. G., editors, Radiation Effects on Organic Materials. New York: Academic Press (1962), pp. 215-216.

2. ASTM Standards 1961, Part 9. Philadelphia: American Society for Testing Materials (1962), pp. 448-459.

3. NARF Facilities Handbook. GD/FW Report FZK-185 (March 1964).

4. Fiory, D. A., and McIntosh, W. R., Nitrous-Oxide Dosimetry System. Convair-Fort Worth Report FZK-9-152 (NARF-60-34T, January 1961). U

5. Dungan, W. E., and Lewis, J. H., Nuclear Measurement Techniques for Radiation-Effects Environmental Testing. GD/FW Report FZK-9-175 (NARF-62-4T, March 1962). U

6. Gumbel, E. J., Statistics of Extremes. New York: Columbia University Press (1958).

7. Fritz, E. G., The Effects of Nuclear Radiation on the Mechanical, Optical, and Electrical Properties of Merlon Polycarbonate. GD/FW Report FZK-9-195 (March 1964).

8. Barrer, R. M., Diffusion in and through Solids. Cambridge (1951).