EFFECT OF REACTOR IRRADIATION ON TENSILE PROPERTIES AND HARDNESS OF EPOXY MATERIAL

by

Richard William Mattes

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Major Subject: Nuclear Engineering

Iowa State University
of Science and Technology
Ames, Iowa

1961

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I. INTRODUCTION

Since the discovery of radioactivity by Becquerel in 1896, and the ensuing avalanche of information concerning the nature of the various types of radiation, much work has been done to determine the effect that this form of energy has on matter. This work has been rapidly accelerated since the discovery of the fission process and the controlled chain reaction. However, in spite of all this effort, the understanding of radiation effects is still in the early stages.

The increasing importance of plastic materials in engineering has caused them to come under investigation with respect to the effects of radiation.

One of the relatively new and more versatile of the plastics is the epoxy. Among its important characteristics are included a high degree of adhesiveness, low shrinkage, ease of handling, and the inertness of the cured system. The ability to vary the properties of an epoxy by the proper selection of curing agents and modifiers enables its use in surface coating, casting, potting, encapsulation, sealing, and bonding. Relatively strong metal-to-metal bonds have been formed employing epoxy adhesives (1).

Commercial production of epoxy resin began in 1946. Some thirty million pounds were produced in 1957 and this figure increases each year. New applications of this material are continuously being made. It is not unreasonable to expect that it may soon be used as an electrical insulator and a sealer in radiation detection devices located in high energy radiation environments.

In view of the effects of radiation on some polymers, which are discussed in the following section, it is conceivable that a significant improvement may be made in the properties of epoxies by subjecting them to radiation during or after ordinary manufacturing assembly processes.

II. REVIEW OF LITERATURE

Interest in the effects of ionizing radiation on polymers began in the late 1930's. It was found that electron bombardment caused changes in their melting properties. Extensive investigation, however, was not possible due to the limitations of source strength at that time (2). Improvements in charged particle accelerators soon enabled investigators to continue their work.

In 1943, Burr and Garrison (3), while conducting beta- and gamma-irradiation studies by means of a Van de Graaff generator, reported changes in tensile strength and hardness of a number of plastics, although no attempts were made to explain the results. They did conclude, though, that the useful thermal range of a material could be taken as being indicative of its relative stability under high intensity radiation. This is also reported by Aitken and Ralph (4) in work with some epoxide systems.

The radiation quality and dose rate were determined to have an effect on the changes produced in the physical properties of plastics (3). Work during the early 1950's by Sisman and Bopp (5), (6), (7), employing reactor irradiation and individual types of radiation, seemed conclusively to reverse this opinion, and the concept of total energy absorption is presently the accepted theory (2), (8), (9).

Allen (10), in 1949, gave a broad treatment to the effects of radiation on materials in general. He pointed out the fact that organic materials belonged to the class of compounds in which the atoms are held together by covalent bonds. The ionization potential of a molecule of

such compounds is greater than the energy necessary to break the bonds within the molecule. Consequently, once such a molecule has been ionized by some form of radiation, and subsequently neutralized, it has sufficient energy to fracture at least one of the internal molecular bonds. Such a fracture may cause the molecule to break up into fragments. At the time of Allen's writing, it was well known that diffusion of the fractured molecule took place in gases and liquids. However, the small amount of information known at that time concerning the effect of radiation on solids left unanswered the question as to whether the restriction placed on motion therein would cause the molecule to remain in its position with the subsequent possibility of the reformation of the original molecule.

The discovery of the existence of crosslinking, the formation of C--C bonds between molecules of irradiated polyethylene reported by Charlesby (11) in 1952 aided in clearing this stumbling block. In experimentation with reactor irradiation on polyethylene, he noticed an increase in strength. In the course of further experiments with the polyethylene in vacuum, hydrogen gas was found to exist in the specimen container after irradiation. This fact, combined with the loss of weight experienced by the specimen, led to the explanation of the increased strength. Since polyethylene is composed of only carbon and hydrogen, it was concluded that hydrogen atoms had been severed from the polymer chain in spite of the fact that the C--H bond is stronger than the C--C bond. Within months after this was reported, other investigators (12), (13), using various forms of radiation, confirmed Charlesby's findings. It was also reported by Lawton et al. (13) that certain polymers underwent

degradation (breaking of the main polymer chain) upon exposure to radiation. Thus, two previously known and employed processes, theretofore brought about by chemical means, were found to be the primary effects of radiation on polymers.

In 1954, Sisman and Bopp (14) further stated that the two processes occurred simultaneously, and that the apparent end effect was a matter of one of the two predominating. They also theorized that the rate of crosslinking may be controlled by the diffusion of the hydrogen from the polymer since this would tend to govern the rate of the molecular segments closing on one another.

In order to utilize efficiently the beneficial effects of radiation and protect against the undesirable ones, it is necessary to have knowledge of the mechanisms through which crosslinking and degradation are brought about. Many theories have been proposed since these processes were discovered. A number of the more promising of these are reviewed by Charlesby (2) and Bovey (15) along with the more important objections to them.

The most serious problem existing in the field of radiation effects applies to the study of all materials and is not restricted to polymers alone. Basically, the problem is lack of information. Many materials have been investigated. However, reports of the results have not been sufficiently accurate and detailed. This fact has been realized and steps have been and are being taken to remedy the situation.

III. PURPOSE OF INVESTIGATION

The purpose of this investigation was to determine the effect of reactor irradiation on certain mechanical properties of an epoxy material. Specifically, the properties selected for study were tensile strength, percentage elongation, modulus of elasticity, and Rockwell hardness. Half of the specimens were tested for these properties as soon as they could be safely handled after irradiation to determine the immediate effect. The remaining specimens were tested seven days later to observe the influence of aging on the irradiated material.

IV. EXPERIMENTAL PROCEDURE

A. Preparation of Specimens

Forty-five specimens were prepared using Dow Epoxy Resin 334, which contains a diluent of butyl glycidyl ether, with a hardener of diethylene triamine (DETA) in the ratio of ten parts DETA per hundred parts of resin by weight. No filler material was included.

The liquid resin was weighed out in four batches of one kilogram each (to the nearest gram) in clean, disposable metal containers. The disposable containers were used since the epoxy-hardener system, once hardened, must be removed from the surface to which it adheres by such means as burning, sandblasting, or treatment with hot glacial acetic acid. After the resin was ready, the DETA was weighed out to the nearest tenth of a gram according to the above mentioned ratio into a beaker. Due to the toxicity of this substance, caution was taken to wear rubber gloves, a protective mask which covered the entire face, and otherwise to protect exposed skin areas. Ventilation was provided by opening laboratory windows. Only necessary personnel were allowed in the laboratory. The DETA was poured into the resin and initially mixed for one minute with a stirring rod. Immediately thereafter, the process was continued with a variable speed electrical mixer using a rotation of sixty rpm for a total mixing time of twenty minutes. The position of the impeller was varied to obtain thorough mixing. This preparation was then cast in a prepared mold. All nondisposable items of equipment which came into contact with the mixture were thoroughly cleaned with methyl chloride as soon as possible.

The molds, fabricated of three-eighths inch plywood sheet, consisted of a base to which one inch strips were nailed. All parts of this assembly were sanded to insure smooth, flat surfaces. Each mold was capable of forming five specimen blanks (3/8 by 1-3/16 by 9-13/16 in.). Originally, one large mold with a capacity of forty-five blanks was used. However, in casting, this configuration yielded an excessive amount of heat during hardening, which caused spoilage of a large number of the blanks due to air bubbles. It was believed that the heat being given off by the blanks surrounding any given one prevented proper heat dissipation. This was apparently true since the blanks in the center of the mold were the most affected. Because of the extremely adhesive nature of the epoxy material, a releasing agent in the form of a film of silicone grease was applied to the surfaces of the mold. All exterior joints of mating strips and of base and strips were coated with paraffin to prevent possible leakage from the mold.

The resin-hardener mixture has a gel time of approximately thirty minutes in the volume of the mixing container. Therefore, a timer was begun at the initial mixing of each batch to insure equal mix time and casting prior to gel time. Each batch, which formed approximately fifteen blanks, was entirely poured within five minutes of the termination of mixing.

Two precautions were observed in casting the specimen blanks. First, the mold itself was leveled in order to produce a blank of uniform thickness. Secondly, care was taken to insure against overfilling, which could result in fracture of the cured blank upon removal from the mold.

The reduced volume of the material required approximately one hour to harden to the touch. Once hardened, the specimens were allowed to cure for eighty-four hours before removal from the molds. A visual inspection of these blanks revealed no nonuniformities or air entrapment.

Upon removal from the mold, the razor-like edges of the blanks were removed with a fine sandpaper and milled to the proper size and shape as specified in ASTM Standard D638-58T (16). The configuration of the specimen is indicated in Fig. 1.

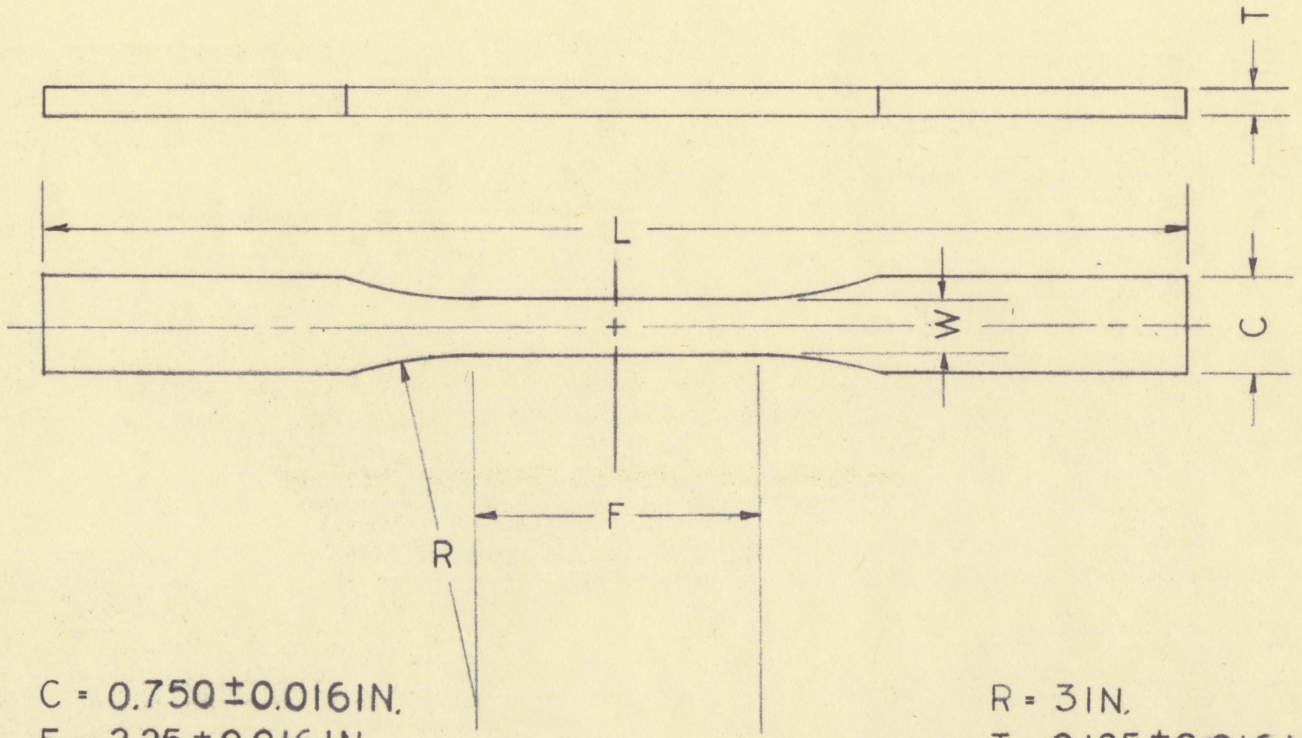
B. Irradiation

The specimens were irradiated in batches of ten at four different levels of integrated thermal neutron flux, 10^{11}, 10^{12}, 10^{13}, and 10^{14} nvt. The Iowa State University Training Reactor was used for this purpose. Physically, the specimens were located in the experimental well situated between the two core tanks.

In order to insure location of the specimens in the area of maximum flux and to facilitate insertion, containment, and removal of the specimens, a container was constructed of three-eighths inch plywood, employing only glue in its fabrication (Fig. 2). Incorporated into the removable top of this device were two wooden posts on which were mounted gold foils, one bare and one cadmium covered, for the purpose of more accurately determining the flux to which the specimens were exposed. The foils were located within the container at a position corresponding to the center of the length of the specimens.

Irradiation of each batch of specimens was performed in the following manner. After machining, each specimen was numbered, and, using

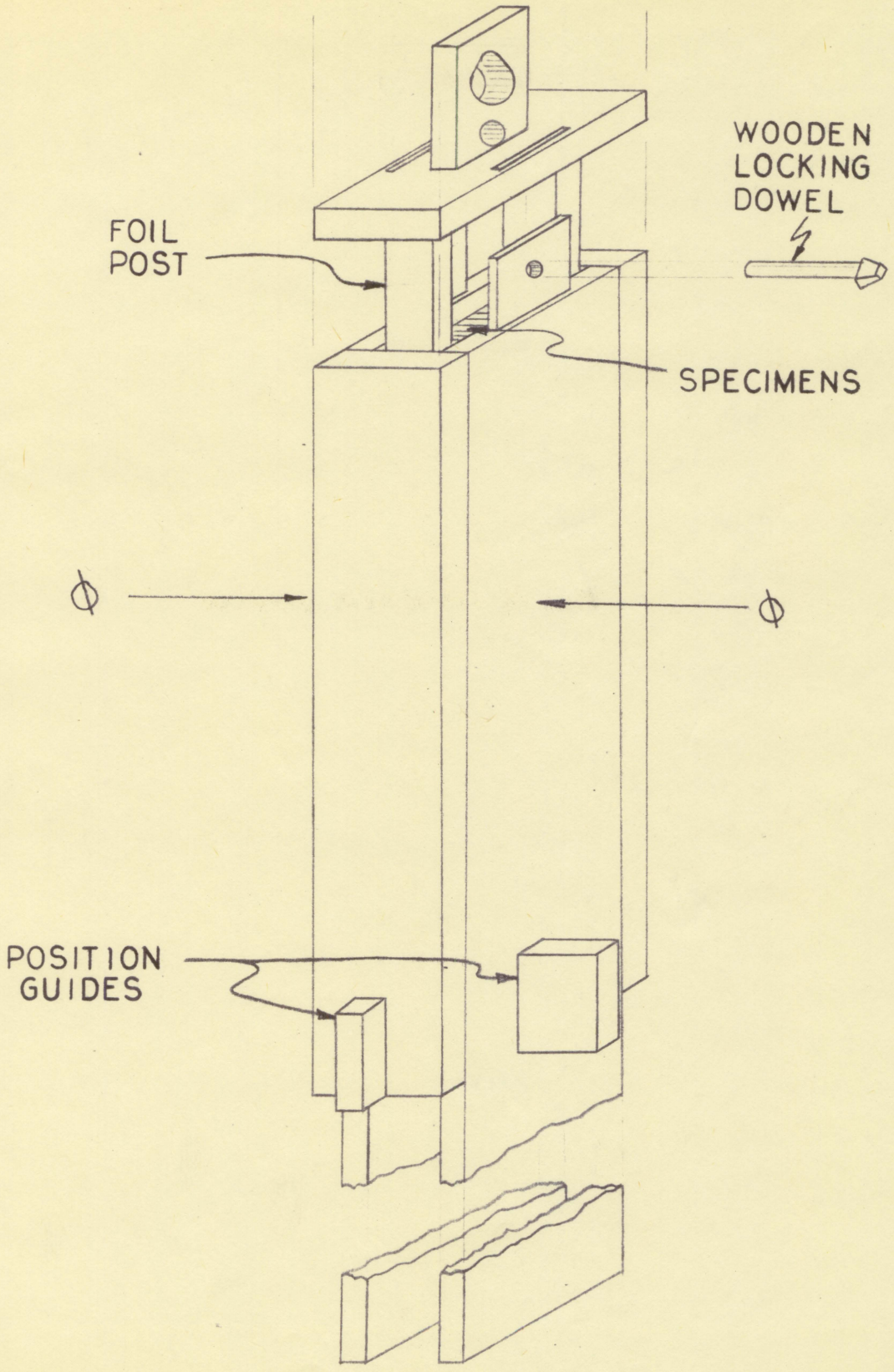
Fig. 1. Standard tensile test specimen



C = 0.750 ± 0.016 IN.
F = 2.25 ± 0.016 IN.
L = 8.5 IN.

R = 3 IN.
T = 0.125 ± 0.016 IN.
W = 0.500 ± 0.010 IN.

Fig. 2. Irradiation container


WOODEN
LOCKING
DOWEL
FOIL
POST
SPECIMENS
ϕ
ϕ
POSITION
GUIDES

a table of random numbers, four groups of ten and one group of five specimens, to be used for control purposes, were selected. Each group of ten was bound together, face to face, by means of a one-eighth each strip of tape at either extremity. The relative position of each specimen within its respective group was recorded. For each irradiation, a group of ten specimens was placed in the irradiation container; the foils were mounted; and the top of the container was secured by means of a wooden locking dowel. Insertion and removal of the container from the experimental well was accomplished by means of a long-handled metal hook.

The reactor was then brought to the appropriate power level and held there for the length of time estimated necessary to provide the desired integrated flux value. At the termination of this time, the reactor was scrammed. Due to the high level of activity present in the experimental well after shut down, the container and specimens were left in the reactor overnight, a period of approximately seventeen hours. Upon removal from the reactor the specimens were ready for testing, and the foils were placed in storage for varying periods up to a week.

C. Determination of Flux

The activities of the gold foils were determined over periods varying up to one week from the time of exposure. The use of absorbers was necessary in all cases. Two-minute counts were taken on each foil and the time noted. A proportional gas flow counter was used to determine the activity of the foils.

The method of flux determination was a comparison with a standard

uranium foil. The expression* employed to obtain thermal neutron flux directly from the activity of the gold foil is:

$$\phi_{th} = \left[\frac{\frac{A}{W} \times \frac{CR - 1}{CR}}{K} \right] \left[\frac{S_{cr}}{S'_{cr}} \right]$$

where:

ϕ_{th} = neutrons per cm^2 per second,

$A = \dfrac{A_t}{(1 - e^{-\lambda T})(e^{-\lambda t})}$,

W = weight of bare gold foil (gm),

CR = ratio of activity of bare gold foil to activity of cadmium covered foil,

K = 2.1284; a constant for the Iowa State University training reactor to convert expression to units of flux,

S_{cr} = counting rate of standard uranium foil at time of calibration (cpm),

S'_{cr} = counting rate of standard uranium foil at time of gold foil comparison (cpm),

A_t = activity of bare gold foil at time t (cpm),

λ = decay constant for gold,

T = time of foil exposure in reactor (hr), and

t = time from reactor scram to time of foil counting (hr).

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*Danofsky, Richard, Department of Nuclear Engineering, Iowa State University of Science and Technology, Ames, Iowa. Absolute thermal flux determination in the Iowa State University training reactor. Private communication. 1961.

Once the thermal neutron flux was determined, the integrated flux was calculated by

$$\text{Integrated flux} = \phi_{th} \times T,$$

the units of which are thermal neutrons per square centimeter, when T is expressed in units of seconds.

D. Testing of Specimens

1. Hardness

The indentation hardness test of the specimens was performed in accordance with Method A of ASTM Standard D785-51 (16) by means of a Rockwell hardness tester. The Rockwell M scale was used, employing the red scale of the tester, a ten-kilogram minor load, a one-hundred kilogram major load, and a one-quarter inch ball penetrator. Since the specimens were one-eighth of an inch in thickness, scrap pieces of the material were tested to verify that the hardness values were not affected by the supporting surface and that no imprint showed on the under surface of the specimen after testing. This determination was made with both a single specimen and with a pair of specimens, one on top of the other. In order to insure against the specimen overhang affecting the hardness values, the portion of the specimen projecting beyond the anvil was supported.

The dash pot on the tester used was adjusted so that the operating handle completed its travel in five seconds with no specimen on the machine, which was set up to apply a major load of one hundred kilograms.

With the specimen located to allow the penetrator to be applied

approximately to the specimen's centerline, the minor load was applied and the zero setting made within ten seconds. Immediately thereafter, the major load was applied and a stop watch started. Fifteen seconds after the operating handle was tripped, the major load was removed and fifteen seconds later, the reading, to the maximum nearest full-scale division, was taken. In all cases the needle passed through zero on the red scale twice in applying the major load and once on removal thereof. Therefore, all readings were taken without correction.

2. Tensile properties

The tensile properties of the epoxy material were tested by means of a 20,000 pound capacity, universal, lever-type load follower, screw-type cross-head movement, hand operated test machine. It was operated using a poise which enabled operation in the 0-2000 pound range, thus permitting load determination down to a half-pound. The testing procedure was carried out insofar as possible according to ASTM Standard D638-58T (16). Since a certain amount of skill is required to accurately follow the applied load, the speed of testing (rate of cross-head movement) was set at 0.035 inches per minute (twelve rpm on cross-head operating handle).

The extensometer employed was of the mechanical lever type. It consisted of two yokes with a gage length of two inches. The specimen was clamped in the extensometer by means of small pieces of epoxy material acting as load spreaders between the test specimen and the clamping screws. In order to reduce stress concentration at the point of attachment, flat bottomed clamping screws were used. The relative movement of

the yokes was measured with a dial indicator having a least count of 0.001 inch. The multiplication ratio of the extensometer was determined by measurement of the appropriate dimensions to be 2.012.

The test specimen with extensometer attached was placed in the grips of the testing machine and aligned visually since self-aligning grips were not available. Once clamped in place, a small load was applied to tighten the specimen in the jaws. This load did not exceed four pounds.

A crew of three was used in performing the tests. One person equipped with a stop watch operated the cross-head and called for readings. A second individual operated the load following mechanism, while the third crew member observed the extensometer dial and recorded all loads, dial readings, and the time of 0.02 strain and failure. Readings were taken every ten seconds from the beginning of the test. The drop of beam method was used to determine the maximum load.

3. Schedule of testing

The five control specimens and five of the first irradiated batch were tested the day following this irradiation. The remaining five specimens of the first batch were tested the eighth day following irradiation. The last thirty specimens were tested according to the same scheme, that is, five at one day and five at eight days after irradiation.

V. RESULTS

The results, average value and standard deviation, of the tensile properties and Rockwell hardness tests are indicated in Table 1 through Table 4 according to the treatment, i.e., amount of irradiation and aging prior to testing, received by each group. The size of the group is not in all cases the same, with the exception of the hardness values. This is due to the fact that certain of the tensile tests did not produce results indicative of being truly representative of their respective group. The specimens not employed in computing their group average are indicated in Table 6. All specimens, however, were considered in the hardness test results. The values reported for the various properties were computed in accordance with their respective ASTM standard.

Table 1. Values of tensile strength

Integrated flux (nvt)	Irradiation to test (days)	Average value (psi)	Standard deviation (psi)	Specimens considered
0	control	9825	124	9 20 43 44
10^{11}	1	10045	178	5 8 33 39
10^{11}	8	10166	57	3 13 15
10^{12}	1	10006	745	27 37 40
10^{12}	8	10133	57	10 22 29
10^{13}	1	9510	174	2 4 19 28 38
10^{13}	8	10125	50	12 16 18 34
1.8×10^{14}	1	9846	145	6 17 21 31 41
1.8×10^{14}	8	9662	70	11 14 24 25 36

Table 2. Values of percentage elongation in two inches

Integrated flux (nvt)	Irradiation to test (days)	Average value (%)	Standard deviation (%)	Specimens considered
0	control	3.11	0.43	9 20 43 44
10^{11}	1	4.19	1.64	5 8 33 39
10^{11}	8	5.95	0.21	3 13 15
10^{12}	1	3.15	0.75	27 37 40
10^{12}	8	4.95	0.24	10 22 29
10^{13}	1	4.78	1.75	2 4 19 28 38
10^{13}	8	4.76	1.23	12 16 18 34
1.8×10^{14}	1	4.98	0.61	6 17 21 31 41
1.8×10^{14}	8	5.54	0.62	11 14 24 25 36

Table 3. Values of modulus of elasticity

Integrated flux (nvt)	Irradiation to test (days)	Average value (psi)	Standard deviation (psi)	Specimens considered
0	control	399,750	3304	9 20 43 44
10^{11}	1	420,000	18708	5 8 33 39
10^{11}	8	440,000	0	3 13 15
10^{12}	1	430,000	19365	27 37 40
10^{12}	8	431,666	18929	10 22 29
10^{13}	1	429,400	6268	2 4 19 28 38
10^{13}	8	478,750	81377	12 16 18 34
1.8×10^{14}	1	401,000	11401	6 17 21 31 41
1.8×10^{14}	8	424,000	16100	11 14 24 25 36

Table 4. Values of hardness (Rockwell M)

Integrated flux (nvt)	Irradiation to test (days)	Average value	Standard deviation	Specimens considered
0	control	89.00	1.66	9 20 43 44 45
10^{11}	1	90.70	1.72	5 8 23 33 39
10^{11}	8	92.17	0.98	3 13 15 32 42
10^{12}	1	91.00	0.83	1 27 30 37 40
10^{12}	8	91.63	1.12	10 22 26 29 35
10^{13}	1	89.90	0.99	2 4 19 28 38
10^{13}	8	91.93	1.38	7 12 16 18 34
1.8×10^{14}	1	88.77	1.38	6 17 21 31 41
1.8×10^{14}	8	90.20	0.84	11 14 24 25 36

The reactor power level and time at power used to obtain the reported integrated flux are listed in Table 5.

Table 5. Power level and time schedule

Integrated flux (nvt)	Power level (watts)	Time (min)	Date 1961
1.8×10^{14}	10,000	20	6- 1
10^{13}	1,000	11	6- 8
10^{12}	100	11	6-14
10^{11}	10	11	6-15

Composite stress-strain diagrams indicating average values of tensile strength and strain at fracture for the various specimen treatments including the actual fracture points of each specimen are found in Fig. 3 through Fig. 11. These diagrams were plotted using a composite of all values of stress and strain for the five specimens comprising each form of treatment, through which was drawn the best curve representing all of the specimens.

Fig. 3. Composite stress-strain diagram for unirradiated material (circles indicate actual specimen fracture points)

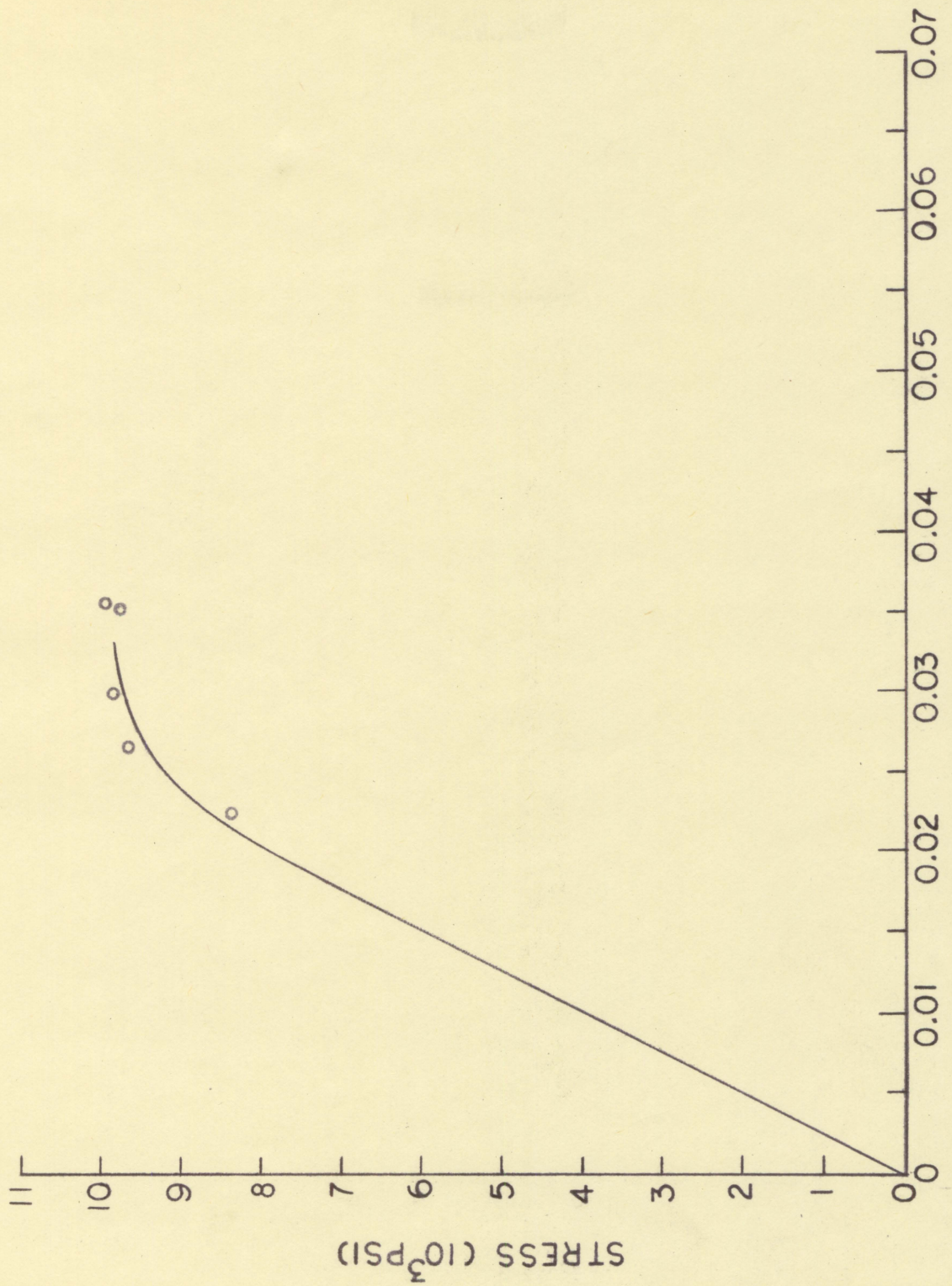

STRESS (10^3PSI)
0
1
2
3
4
5
6
7
8
9
10
11
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
STRAIN (IN/IN)

Fig. 4. Composite stress-strain diagram for material tested at 1 day after irradiation at 10^{11} nvt (circles indicate actual specimen fracture points)

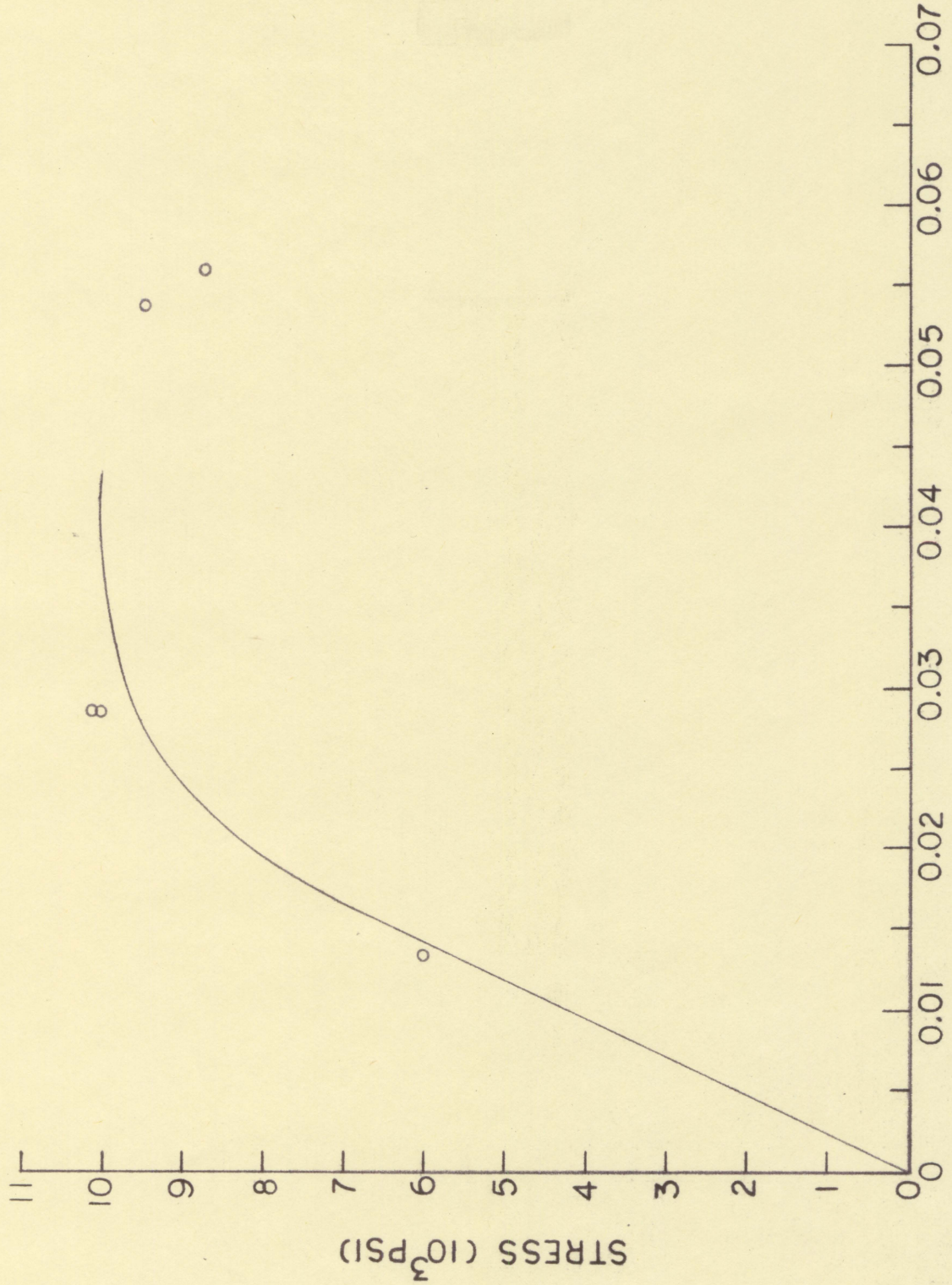

STRESS (10^3PSI)
STRAIN (IN/IN)
0
1
2
3
4
5
6
7
8
9
10
11
0.01
0.02
0.03
0.04
0.05
0.06
0.07

Fig. 5. Composite stress-strain diagram for material tested at 8 days after irradiation at 10^{11} nvt (circles indicate actual specimen fracture points)

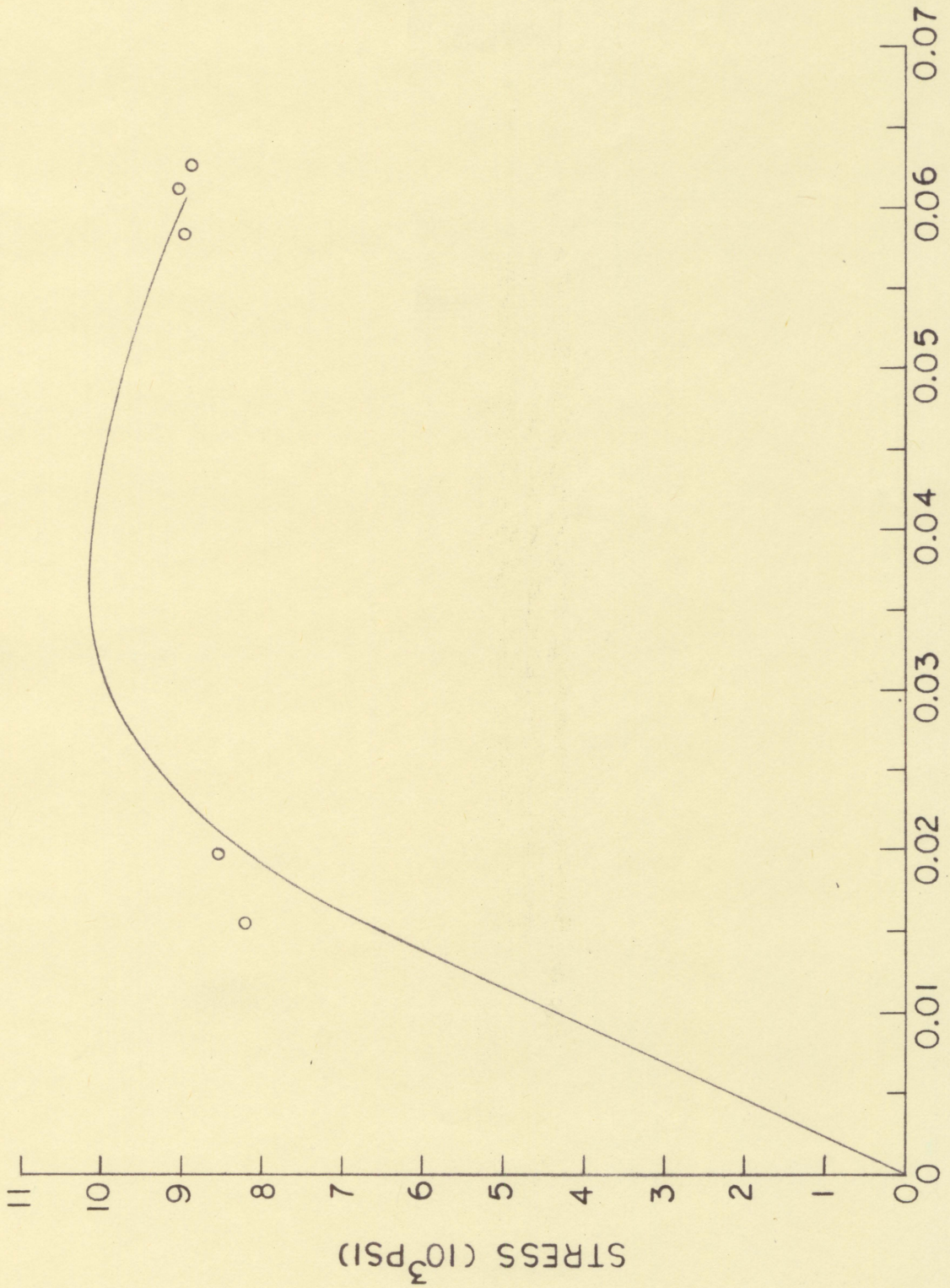

STRESS (10^3PSI)
STRAIN (IN/IN)
0
1
2
3
4
5
6
7
8
9
10
11
0.01
0.02
0.03
0.04
0.05
0.06
0.07

Fig. 6. Composite stress-strain diagram for material tested at 1 day after irradiation at 10^{12} nvt (circles indicate actual specimen fracture points)

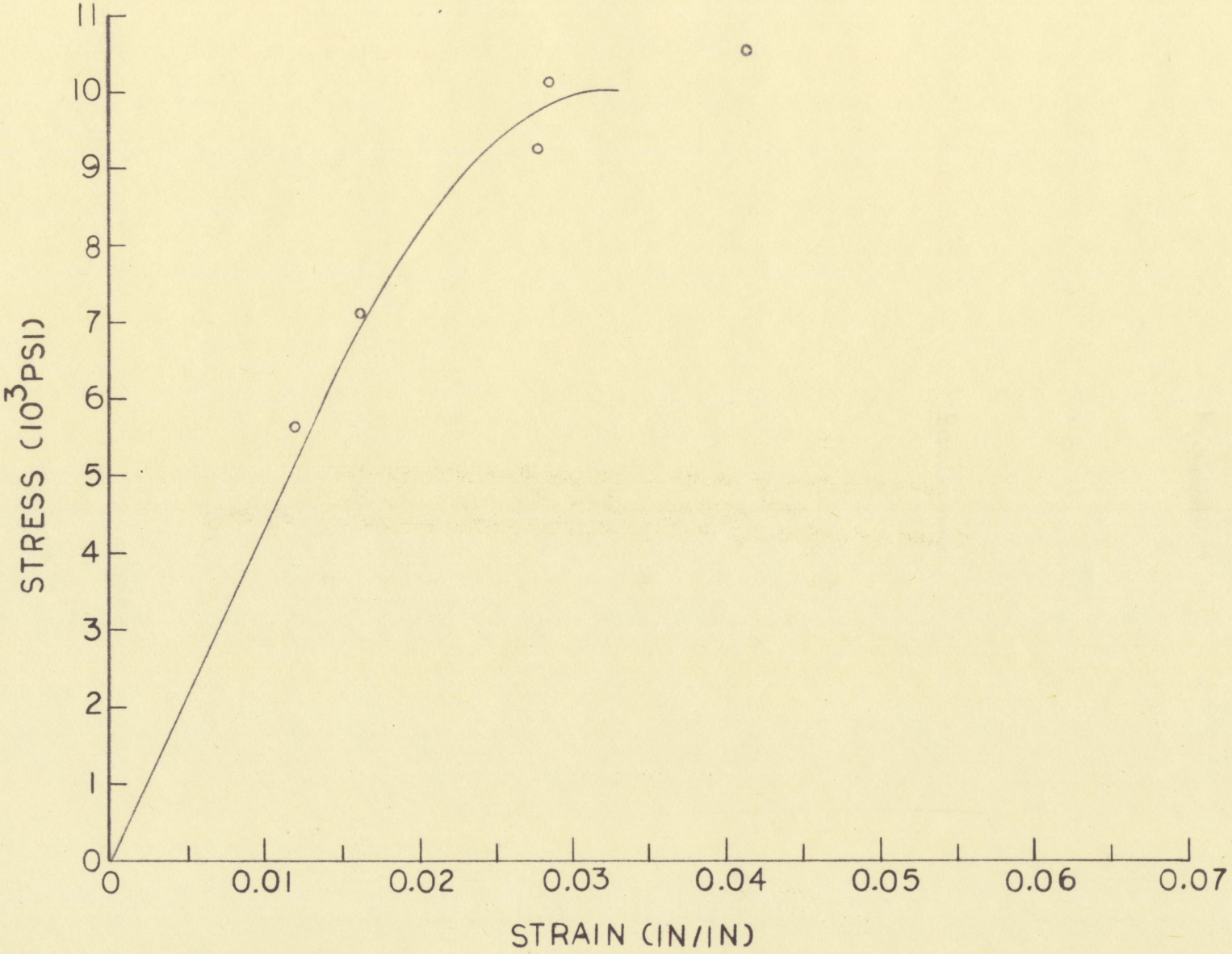

STRESS (10^3PSI)
11
10
9
8
7
6
5
4
3
2
1
0
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
STRAIN (IN/IN)

Fig. 7. Composite stress-strain diagram for material tested at 8 days after irradiation at 10^{12} nvt (circles indicate actual specimen fracture points)

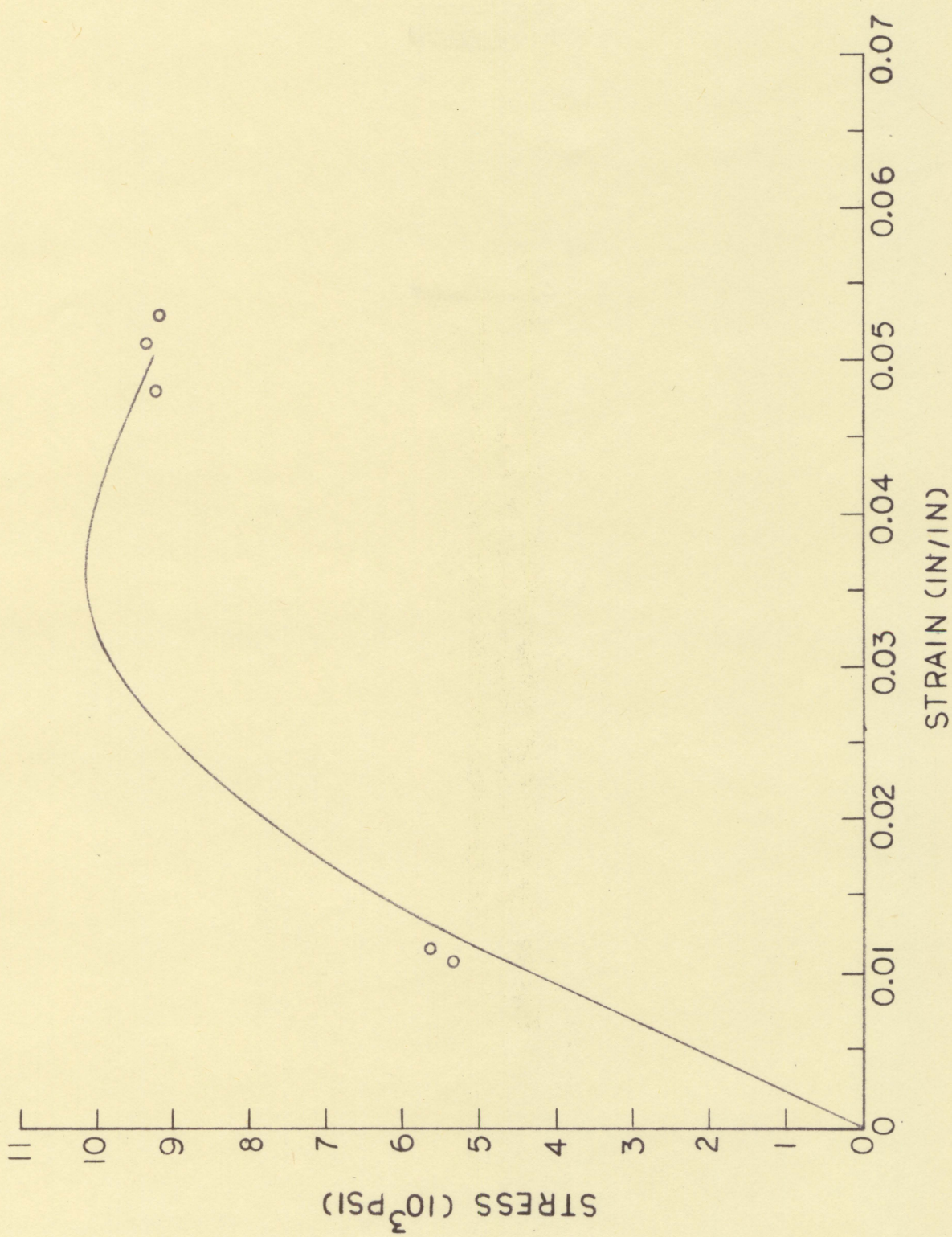

STRESS (10^3 PSI)
0
1
2
3
4
5
6
7
8
9
10
11
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
STRAIN (IN/IN)

Fig. 8. Composite stress-strain diagram for material tested at 1 day after irradiation at 10^{13} nvt (circles indicate actual specimen fracture points)

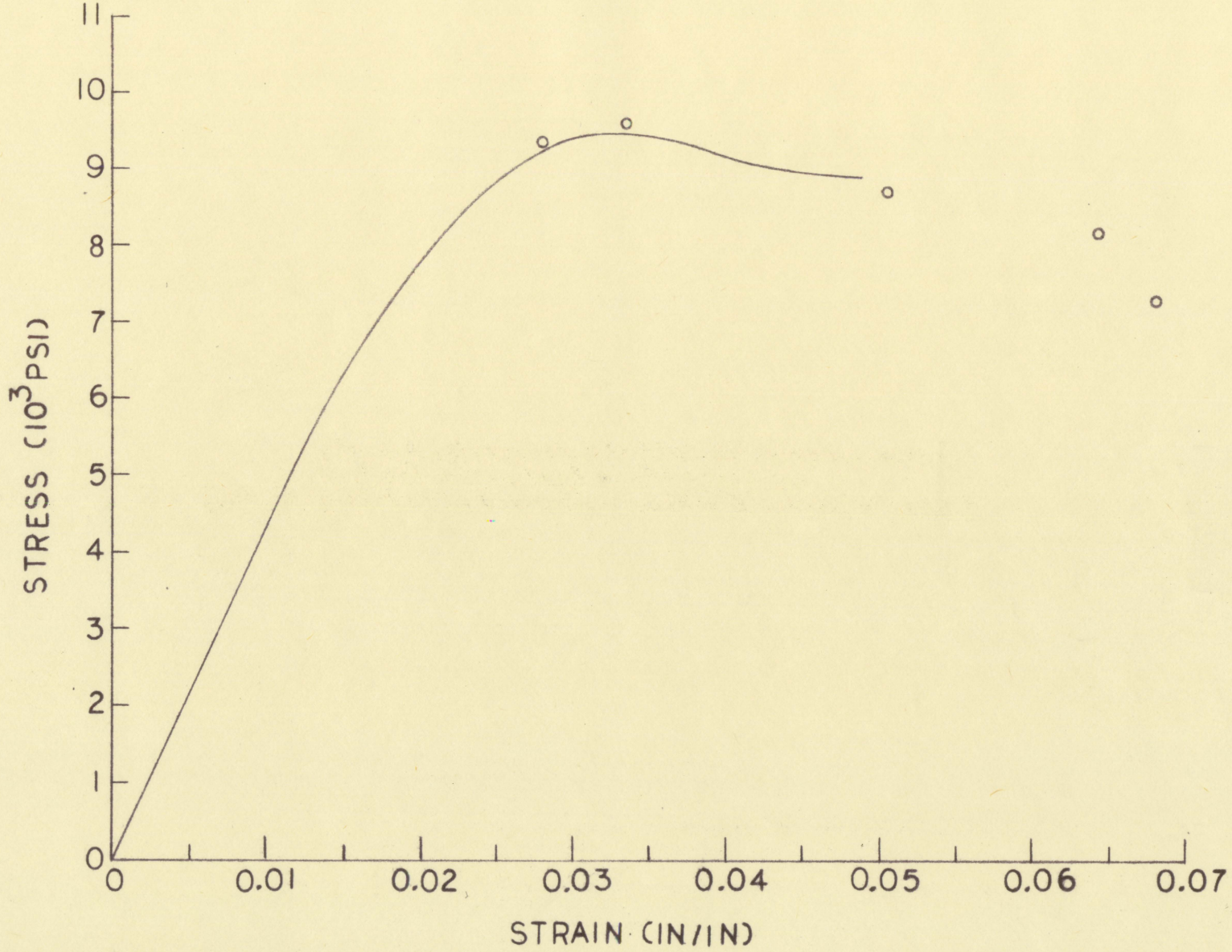

STRESS (10^3 PSI)
11
10
9
8
7
6
5
4
3
2
1
0
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
STRAIN (IN/IN)

Fig. 9. Composite stress-strain diagram for material tested at 8 days after irradiation at 10^{13} nvt (circles indicate actual specimen fracture points)

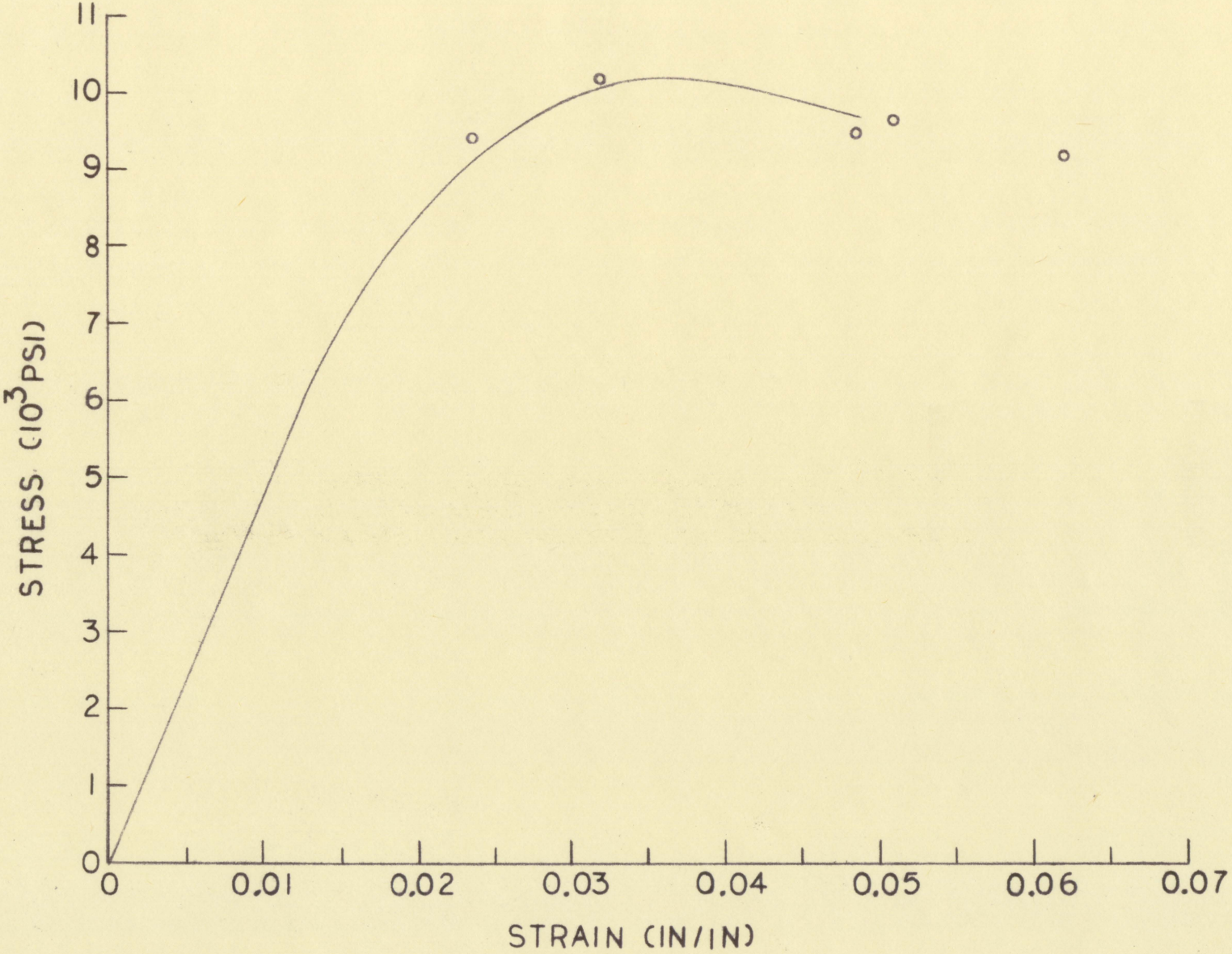

STRESS (10^3 PSI)
11
10
9
8
7
6
5
4
3
2
1
0
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
STRAIN (IN/IN)

Fig. 10. Composite stress-strain diagram for material tested at 1 day after irradiation at 1.8×10^{14} nvt (circles indicate actual specimen fracture points)

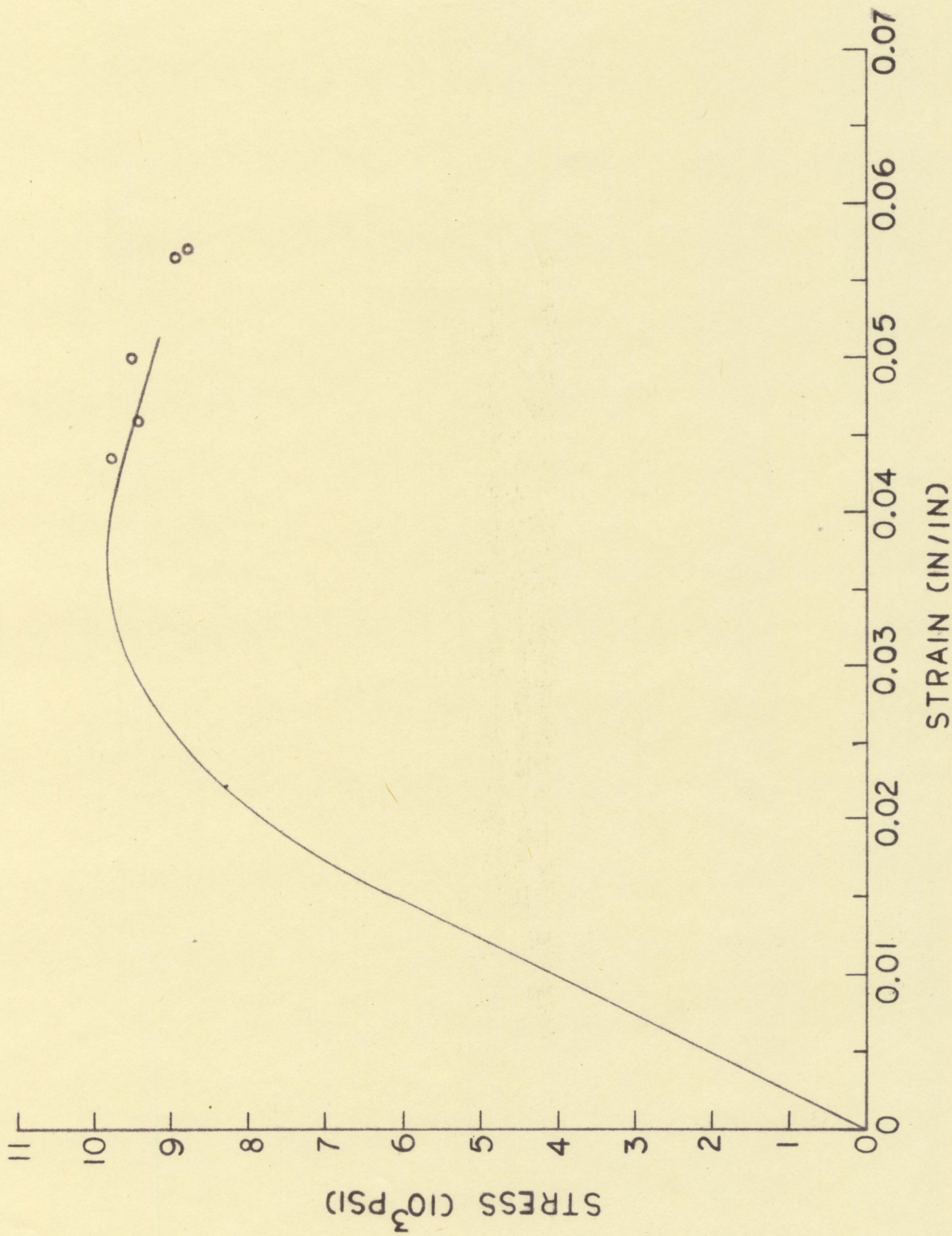
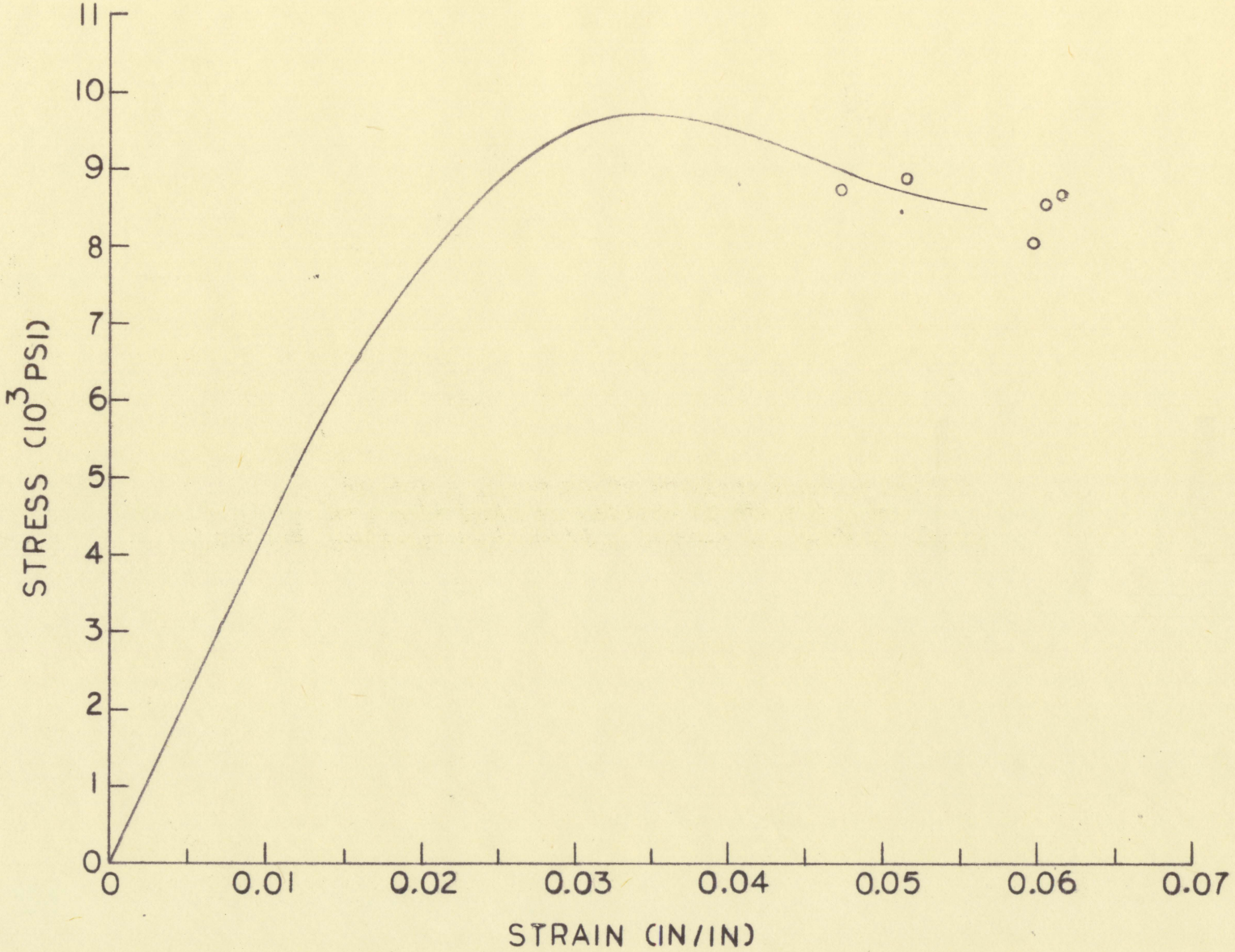

STRESS (10³PSI)
0
1
2
3
4
5
6
7
8
9
10
11
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
STRAIN (IN/IN)

Fig. 11. Composite stress-strain diagram for material tested at 8 days after irradiation at 1.8×10^{14} nvt (circles indicate actual specimen fracture points)


STRESS (10^3 PSI)
0
1
2
3
4
5
6
7
8
9
10
11
0
0.01
0.02
0.03
0.04
0.05
0.06
0.07
STRAIN (IN/IN)

VI. DISCUSSION

In general, the results indicated agreement with the effects of radiation reported for other polymers, that is to say, a slight improvement in the various properties followed by a degradation as the amount of exposure to radiation was increased. Before proceeding to an analysis of the results of the experiment, it may be beneficial to review the general effects of radiation on the mechanical properties tested as they are understood at the present time.

As previously stated, the predominant process of either crosslinking or degradation (scission; cleavage) will determine the overall effect. Radiation-induced crosslinking causes an increase in the tensile strength, modulus of elasticity, and hardness and a decrease in the percentage elongation of an organic material. The process of degradation reverses the preceding effects (14).

The analysis will be made in the order of increasing exposure. References to Fig. 12 through Fig. 15 may be of assistance in visualizing the situation.

The discussion will first be concerned with the tests made one day after irradiation. At the point of lowest exposure, 10^{11} nvt, there exists an indication of crosslinking by the increase in tensile strength as compared with the value of the unirradiated specimens. The next two points give evidence of a degradation process occurring through the slight decrease followed by a more pronounced one. An inconsistency appears to exist at the last point where a reversal of the previous trend takes place. However, this behavior is not necessarily inconsistent with

Fig. 12. Variation of tensile strength with radiation exposure and aging of irradiated material (circles indicate 1 day test above zero nvt; triangles indicate 8 day test)

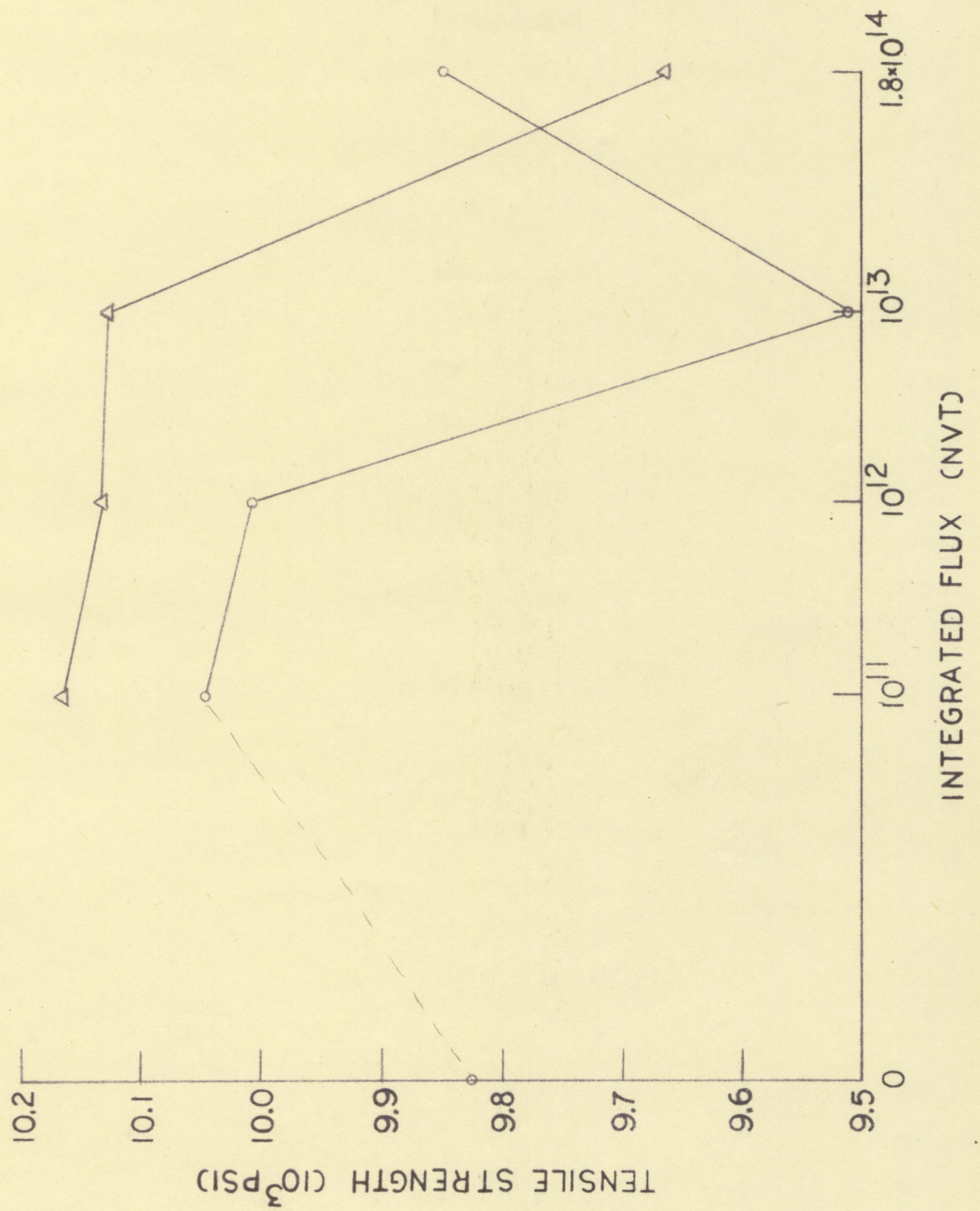

TENSILE STRENGTH (10^3 PSI)
10.2
10.1
10.0
9.9
9.8
9.7
9.6
9.5
0
10^{11}
10^{12}
10^{13}
1.8×10^{14}
INTEGRATED FLUX (NVT)

Fig. 13. Variation of percentage elongation with radiation exposure and aging of irradiated material (circles indicate 1 day test above zero nvt; triangles indicate 8 day test)

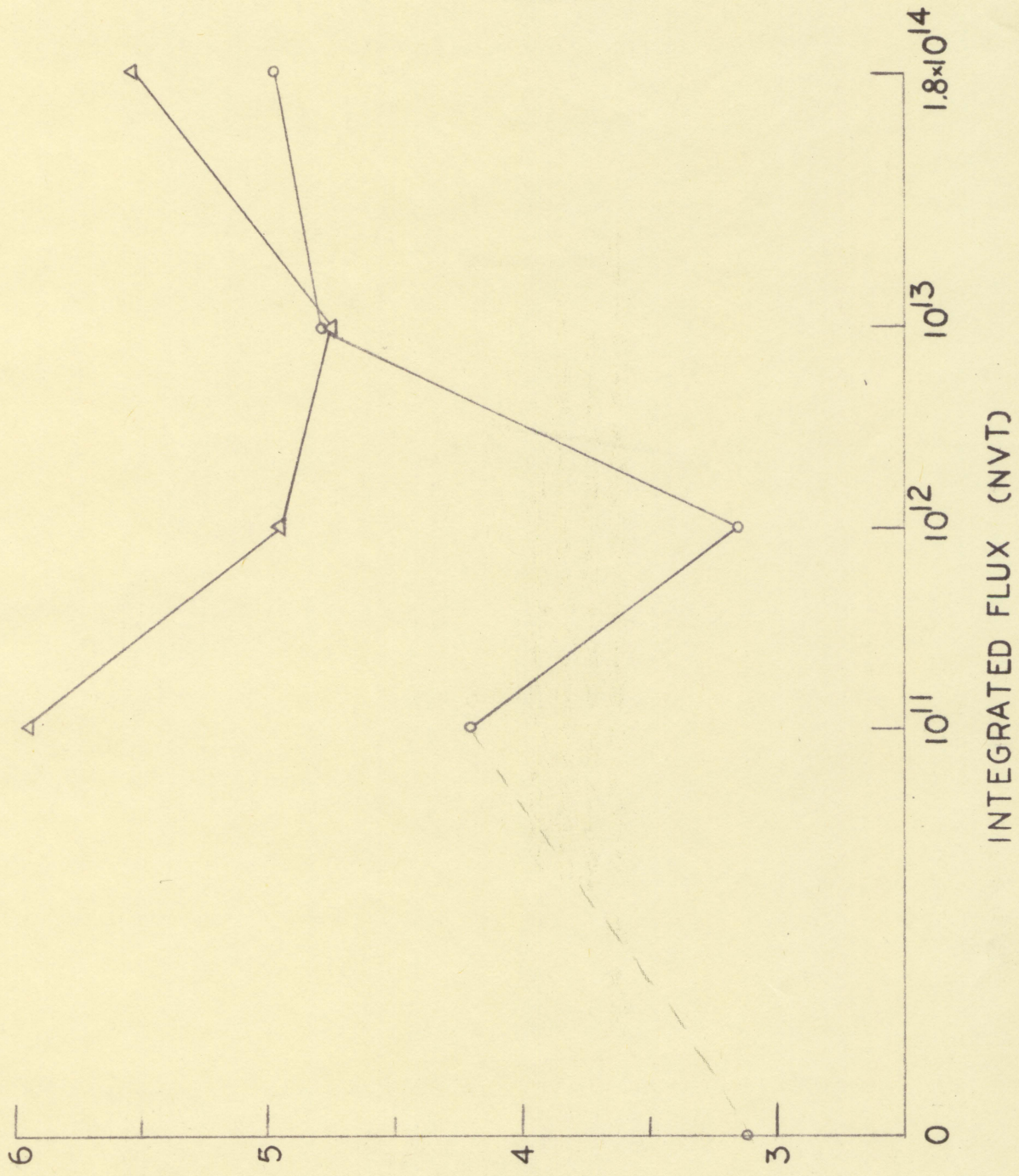

ELONGATION (%)
6
5
4
3
0
10^{11}
10^{12}
10^{13}
1.8×10^{14}
INTEGRATED FLUX (NVT)

Fig. 14. Variation of modulus of elasticity with radiation exposure and aging of irradiated material (circles indicate 1 day test above zero nvt; triangles indicate 8 day test)

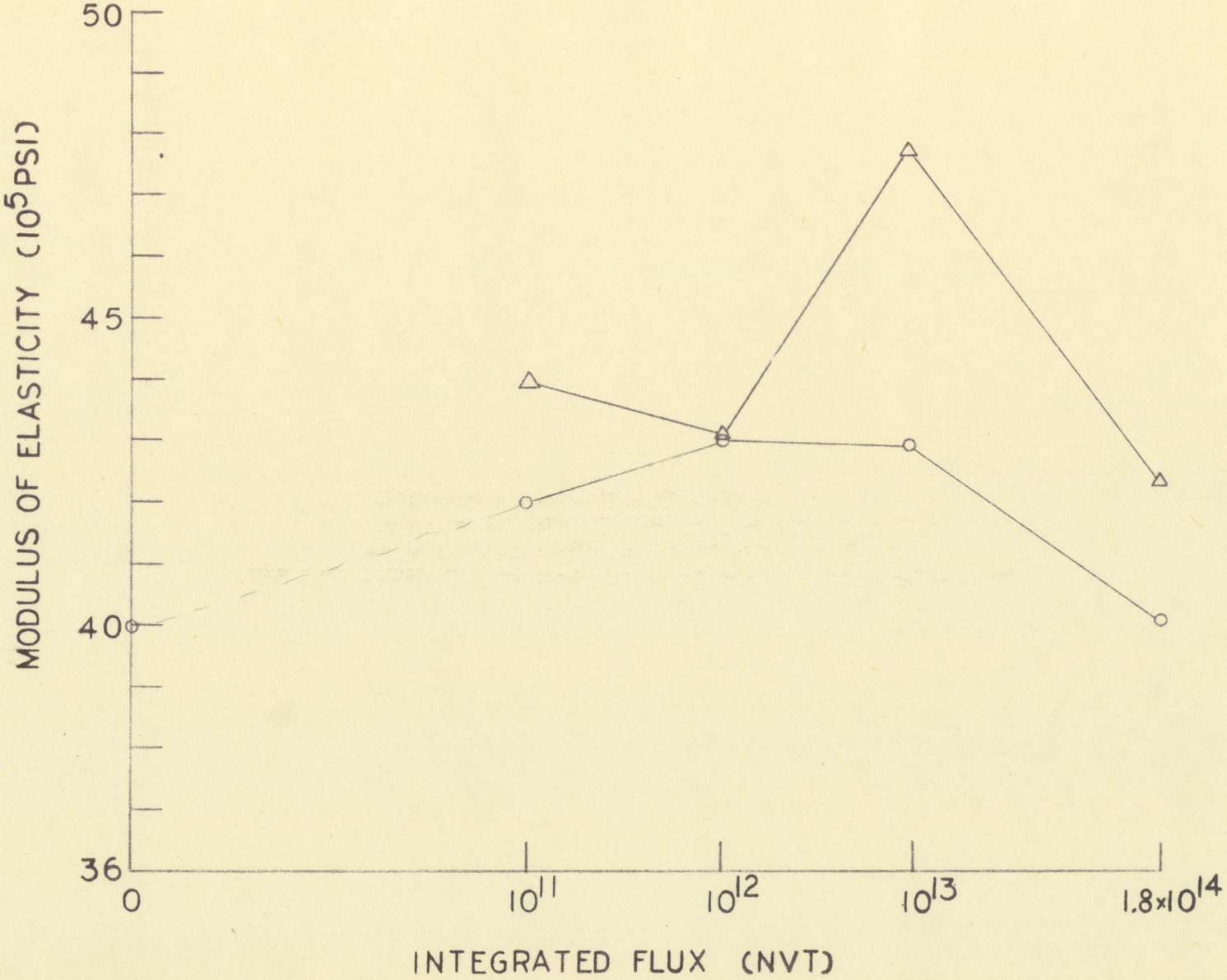
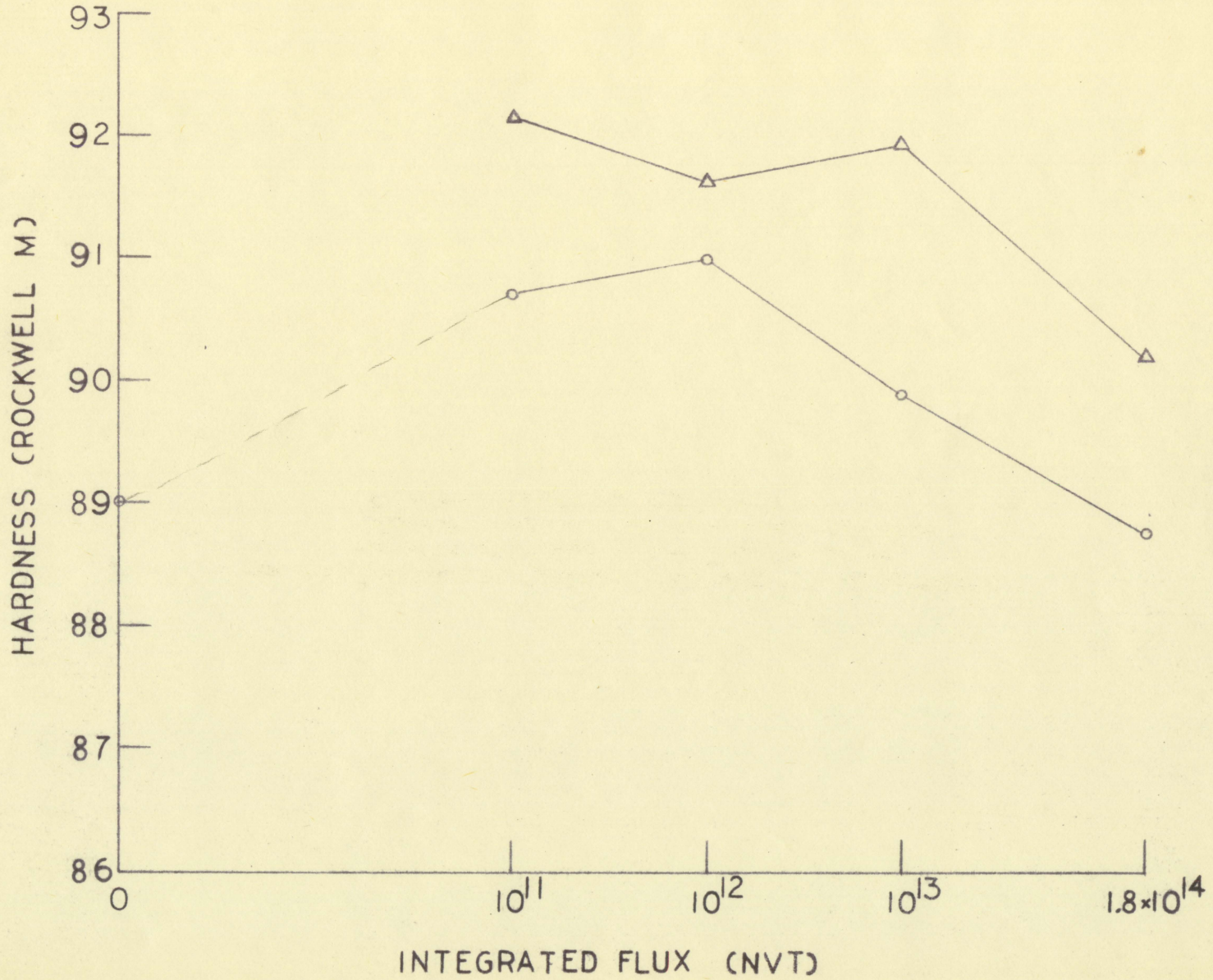

50
45
40
36
MODULUS OF ELASTICITY (10^5 PSI)
0
10^11
10^12
10^13
1.8×10^14
INTEGRATED FLUX (NVT)

Fig. 15. Variation of hardness (Rockwell M) with radiation exposure and aging of irradiated material (circles indicate 1 day test above zero nvt; triangles indicate 8 day test)


93
92
91
90
89
88
87
86
HARDNESS (ROCKWELL M)
0
10^{11}
10^{12}
10^{13}
1.8×10^{14}
INTEGRATED FLUX (NVT)

the idea of a single predominant process. Bovey (15) indicates that this situation often occurs in the instance of predominant crosslinking. It is a small segment of the big picture in which there is an initial rise to a maximum and then a decrease, which is followed by a final rise in strength to the point where the material reaches the brittle state. It is entirely possible that the initial maximum occurred at some point between zero and 10^{11} nvt, which would place all the experimental exposures in the "valley."

Elongation decreasing between 10^{11} and 10^{12} nvt suggests a crosslinking process. The increasing values of the following two points would be caused by a degradation. Thus, the intervals between 10^{11} to 10^{12} nvt and 10^{13} to 1.8×10^{14} nvt appear to be in contradiction with the explanation of the processes occurring in the tensile strength analysis.

The remaining tensile property tested, modulus of elasticity, shows an increase over the unirradiated value at 10^{11} nvt. It may be said, then, that crosslinking has taken place between these two points. The modulus continues to rise to the exposure of 10^{12} nvt, at which time it begins to drop off. The decrease is slow at first and more pronounced between 10^{13} and 1.8×10^{14} nvt. Here exists evidence of the same causes as were observed in the elongation.

Finally, it is seen that the same situation prevails with the hardness determinations. The only difference appears to be in the rate of decrease between the last two points. Thus, three out of the four properties seem to be in agreement as to indications of the processes which are occurring.

It may be well to review the sources of error in the two tests employed to determine the tensile properties and hardness prior to a re-examination of the tensile strength results. In the tensile test, the three crew members represent sources of human error. It so happens that the most probable error among these three exists in the following of the applied load, which is directly connected with the tensile strength determination. The other important bases of error include inaccurate readings and possible slippage of the specimen in the jaws of the testing machine and in the extensometer.

In contrast, the hardness test requires only one operator. True, he must read the stop watch and the hardness value at the same time upon the conclusion of each determination, but at that time the indicator travel is almost indistinguishable. The only time error is probable occurs when the indicator is near a scale division at the instant of a reading. This is infrequent. Thus, the hardness test appears to be the more reliable of the two.

The first inconsistency in the tensile strength occurs between 10^{11} and 10^{12} nvt. The difference in the average value of these points is thirty-nine. For the size of the specimen used, this amounts to approximately three pounds. It is possible for small errors in reading on the individual specimens to have been responsible. Also, it should be noted that the standard deviation for the 10^{12} nvt value is nearly four times as great as that of the preceding value.

A statistical analysis was made of all the results of this experiment by means of the "Student's" t test (17). At the five per cent level

of significance, the two points in question were found to be equal.

In view of the indications that the points at 10^{12} and 1.8×10^{14} nvt are in error, it would appear that crosslinking takes place up to an exposure of 10^{12} nvt, beyond which a process of degradation predominates.

Thus, the behavior of the properties can be explained in terms of processes known to occur in polymers subjected to radiation. However, one question still remains. If crosslinking has taken place up to the 10^{12} nvt exposure, how is it possible that the percentage elongation at 10^{11} nvt appears to be greater than the unirradiated value? Again, the statistical analysis shows the unirradiated, 10^{11}, and 10^{12} nvt values to be equal, with the increases beyond the 10^{12} nvt point significantly greater.

In general, the results of the tests made eight days after irradiation show an increase in the values of all the properties over the one-day test determinations.

If the two primary radiation effects are continuing to occur, an inconsistency results because of the increase of the percentage elongation due to aging of the irradiated material. Thus, some other reason for the aging effects must be found.

Here, notice is taken of the fact that a polymer in the unirradiated state contains both polycrystalline and amorphous regions. One effect of radiation on polymers is the destruction of crystallinity, as stated by Charlesby (2).

The possible recombination of fractured molecules and the return of portions of the solid to a crystalline structure would result in a

substance containing some polycrystalline regions. This mechanism might explain the observed aging effects since the crystalline structure could account for the increased percentage elongation along with the other properties by virtue of the properties of polycrystalline solids (18).

Studies made in England (19), (20) of irradiation effects on selected epoxy systems, without regard to aging, indicate the same general trend of effects although measured by means of changes in flexural strength.

VII. CONCLUSIONS

Conclusions drawn from the results of this investigation apply only to the specific composition of the material employed and the amount of reactor irradiation received. The poor statistics obtained, due to the small number of specimens, tend to cast doubt on the reliability of some of the data.

The value of the tensile strength is increased by exposures from 10^{11} to 10^{12} nvt, followed by a decrease occurring at 10^{13} nvt and continuing with increasing exposure to 1.8×10^{14} nvt. An increase takes place in the modulus of elasticity between 10^{11} and 10^{13} nvt. For this property there is no difference between the nonirradiated material and that receiving an exposure of 1.8×10^{14} nvt. The remaining tensile property, percentage elongation, is unchanged with exposures between 10^{11} and 10^{12} nvt, but increases gradually from 10^{12} to 1.8×10^{14} nvt. Hardness is increased between exposures of 10^{11} and 10^{13} nvt, and is unchanged from the value of this property in the nonirradiated material at 1.8×10^{14} nvt.

For those properties whose values are increased, the maximum value appears at the exposure of 10^{12} nvt.

The effect of aging on the irradiated material is to increase the values of all the properties investigated.

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IX. ACKNOWLEDGMENT

The author expresses his appreciation to Dr. Glenn Murphy and others for their assistance in preparing this thesis.

X. APPENDIX

Table 6. Data from tensile and hardness tests of reactor irradiated epoxy material

Specimen	Date irradiated 1961	Date tested 1961	Integrated flux (nvt)	Tensile strength (psi)	Elongation in 2 in. (%)	Modulus of elasticity (10^3 psi)	Hardness Rockwell M
1[a]	6-14	6-15	10^{12}	7100	1.54	422	90 92 91 90 91 90
2	6-8	6-9	10^{13}	9700	3.28	440	90 90 89 90 90 91
3	6-15	6-23	10^{11}	10200	6.14	440	89 91 92 91 92 92
4	6-8	6-9	10^{13}	9280	6.61	425	89 90 91 90 91 90
5	6-15	6-16	10^{11}	10000	5.74	415	89 91 92 90 89 91
6	6-1	6-2	1.8×10^{14}	9740	5.62	400	89 88 89 89 87 89
7[a]	6-8	6-16	10^{13}	9380	2.31	440	94 93 93 95 93 93
8	6-15	6-16	10^{11}	9880	5.47	400	86 87 88 89 89 90
9	N/A	6-2	N/A	9870	2.93	402	91 88 87 89 90 90
10	6-14	6-22	10^{12}	10100	4.70	440	90 93 92 91 90 91
11	6-1	6-9	1.8×10^{14}	9590	5.14	412	90 89 91 90 90 89
12	6-8	6-16	10^{13}	10200	4.77	600	92 91 91 90 91 90
13	6-15	6-23	10^{11}	10200	5.99	440	91 92 91 92 92 92
14	6-1	6-9	1.8×10^{14}	9780	5.96	420	89 90 92 90 90 91

[a]Specimen not included in average value of tensile properties.

Table 6 (Continued)

Specimen	Date irradiated 1961	Date tested 1961	Integrated flux (nvt)	Tensile strength (psi)	Elongation in 2 in. (%)	Modulus of elasticity (10^3 psi)	Hardness Rockwell M
15	6-15	6-23	10^{11}	10100	5.72	440	92 93 94 94 93 93
16	6-8	6-15	10^{13}	10100	3.13	425	93 93 94 92 91 93
17	6-1	6-2	1.8×10^{14}	9770	5.56	395	89 89 89 89 89 90
18	6-8	6-16	10^{13}	10100	5.02	445	90 93 92 90 90 92
19	6-8	6-9	10^{13}	9590	6.33	427	91 91 89 90 90 90
20	N/A	6-2	N/A	9780	3.45	395	91 89 91 90 89 87
21	6-1	6-2	1.8×10^{14}	9800	4.92	400	90 86 89 84 88 89
22	6-14	6-22	10^{12}	10100	4.99	410	90 90 90 91 93 90
23[a]	6-15	6-16	10^{11}	6090	1.24	470	93 92 91 92 91 92
24	6-1	6-9	1.8×10^{14}	9640	6.06	410	91 91 90 90 91 92
25	6-1	6-9	1.8×10^{14}	9640	4.65	450	90 91 90 89 90 90
26[a]	6-14	6-22	10^{12}	5630	1.07	535	92 93 92 93 93 92
27	6-14	6-15	10^{12}	10700	4.02	435	90 90 90 91 90 90
28	6-8	6-9	10^{13}	9600	4.97	425	90 89 90 89 89 89
29	6-14	6-22	10^{12}	10200	5.17	445	93 93 92 92 93 92
30[a]	6-14	6-15	10^{12}	5630	1.12	480	92 92 91 91 92 92

Table 6 (Continued)

Specimen	Date irradiated 1961	Date tested 1961	Integrated flux (nvt)	Tensile strength (psi)	Elongation in 2 in. (%)	Modulus of elasticity (10^3 psi)	Hardness Rockwell M
31	6-1	6-2	1.8×10^{14}	9820	4.52	390	89 89 90 87 88 88
32[a]	6-15	6-23	10^{11}	8570	1.89	445	93 93 92 92 93 92
33	6-15	6-16	10^{11}	10000	2.76	420	91 92 91 91 92 93
34	6-8	6-16	10^{13}	10100	6.11	445	92 91 93 90 92 91
35[a]	6-14	6-22	10^{12}	5330	0.99	470	91 93 91 91 91 91
36	6-1	6-9	1.8×10^{14}	9660	5.89	427	89 91 90 90 91 89
37	6-14	6-15	10^{12}	10100	2.76	440	90 92 91 92 90 92
38	6-8	6-9	10^{13}	9380	2.73	430	91 89 89 91 92 87
39	6-15	6-16	10^{11}	10300	2.78	440	91 92 90 91 92 93
40	6-14	6-15	10^{12}	9220	2.68	410	91 92 92 91 91 91
41	6-1	6-2	1.8×10^{14}	10100	4.27	420	89 89 90 91 91 90
42[a]	6-15	6-23	10^{11}	8210	1.47	470	92 92 92 93 93 92
43	N/A	6-2	N/A	9680	2.58	402	90 90 90 91 90 91
44	N/A	6-2	N/A	9970	3.48	400	87 89 90 90 87 89
45[a]	N/A	6-2	N/A	8390	2.19	397	89 90 85 87 87 86