

THE EFFECT OF NUCLEAR REACTOR RADIATION
ON THE ELECTRICAL AND MECHANICAL
PROPERTIES OF EPOXIDE POLYMERS

by

Charles V. Kincaid

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Name of Candidate: Charles Vernon Kincaid
Master of Science, 1965

Thesis and Abstract Approved: _____

Dick Duffey
Dr. Dick Duffey

Professor of Nuclear Engineering

Date approved: _____

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ABSTRACT

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on the Electrical and Mechanical Properties of Epoxide Polymers

Charles V. Kincaid, Master of Science, 1965

Thesis directed by: Dr. Dick Duffey, Professor of Nuclear
Engineering

The effect of nuclear reactor radiation on the volume resistivity, bulk compressibility, specific volume, and hardness of three epoxide polymers was studied. The polymers were thermally polymerized and then subjected to varying radiation doses in the enriched uranium, water moderated, heterogeneous nuclear reactor located at the University of Maryland.

Changes in the volume resistivity as a function of temperature for the various radiation doses was then determined by the use of an electrometer to measure the potential drop across the specimen. The effect of radiation on the bulk compressibility was determined by means of a special compressibility tester over the pressure range one to 8,000 atmospheres and temperatures 25°C to 250°C. The specific

volume and hardness were measured for each sample before and after irradiation using standard techniques.

The temperature dependence of the electrical volume resistivity was initially increased by exposure to 2.5 Mrads. Further irradiation up to 25 Mrads caused severe degradation of the temperature dependence of the electrical resistivity for all epoxide polymers studied.

The magnitude of the compressibility for the polymers was found to be relatively unaffected by irradiation up to 25 Mrads; however, determination of the pressure-induced glass transition yielded anomalous results.

No significant change in the hardness of the polymers was noted after varying amounts of radiation. The specific volume of an aromatic cured epoxide was not affected to any extent, but the aliphatic cured polymer showed a decreased specific volume.

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I

INTRODUCTION

Thermosetting, or crosslinked, polymers have come into increasing use in recent years. Some of the most widely used of the crosslinked polymers are the epoxides. These are used for industrial castings, potting of electrical and electronic components, high strength laminates and light weight foams. Extensive use is made of these polymers in space vehicles and solar cells in space satellites. Studies have also been made of epoxide polymers for use as shields to reduce permanent nuclear radiation damage.⁽¹⁾

Despite these widespread applications, a thorough literature search revealed surprisingly few reports concerning the properties of epoxide polymers after exposure to radiation. This investigation was undertaken to establish techniques for determining the degree of change caused by nuclear reactor radiation on certain properties of some epoxide polymers. Two epoxide systems were considered which had good radiation resistance and one which had somewhat less resistance. The properties investigated were electrical resistivity, bulk compressibility, hardness and specific

volume. These properties have been used by others to describe changes in polymers and can be correlated in some aspects with published work.

Organic materials are subject to damage from all types of ionizing radiation. Polymers, which are usually organic, are subject to such damage, or more correctly, change, due to radiation as well as being susceptible to extremes of temperature. Any tests conducted to determine changes due to radiation should also take into account the effect of temperature, if at all possible.

The primary tests run, those of electrical resistivity and mechanical compressibility, were made as a function of temperature, the hardness and specific volume measurements were not.

Electrical resistivity measurements have only recently been employed to study the properties and structure of cross-linked polymers, and are a new and useful research tool.^(2,3) Charlesby⁽⁴⁾ has investigated the radiation induced conductivity of various polymers, not including epoxides; however, he was concerned primarily with transient effects. A search of the literature revealed no work which has been done on the electrical resistivity of polymers after removal from the radiation flux. The simplicity of the techniques described in references 2 and 3 recommended them highly for

this investigation. Parameters obtained from these resistivity measurements are magnitude and temperature dependence of electrical resistivity, activation energy for the electrical conduction process, and the glass transition point or range.

The bulk compressibility of polymers has been studied by only a few investigators such as Bridgman,⁽⁵⁾ Weir,⁽⁶⁾ Matsuoka and Maxwell.^(7,8) These studies have considered several parameters of polymer systems such as change of volume with pressure and temperature and the consequent equations of state and glass-rubber phase diagrams. The glass transition range can be easily determined and could prove of value in comparison with that obtained from the electrical resistivity measurements for the same polymer.

Some polymers, such as polytetrafluoroethylene (teflon), exhibit a decrease in volume with increasing radiation dose up to 100 megarads (Mrads).⁽⁹⁾ Kline and Licht⁽⁹⁾ also showed a shift in the glass transition point to a lower temperature after irradiation. The magnitude of this change for epoxides, if large, could be compared with results obtained from the resistivity and compressibility measurements.

The hardness of polymers before and after irradiation was considered by Colichman and Strong to be a valuable indication of radiation resistance.⁽¹⁰⁾ Either an increase or a

decrease was observed by the authors, depending upon the epoxide system used. If valid, this could be useful in determining which polymer is the most resistant to radiation. The hardness was used merely as an indicator to corroborate findings from the previous measurements-- resistivity, compressibility, and specific volume.

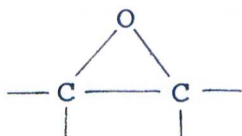
The results from these measurements should indicate the relative radiation resistance of aromatic amine cured epoxides and aliphatic amine cured epoxides. The glass transition provides a useful common factor to relate the results.



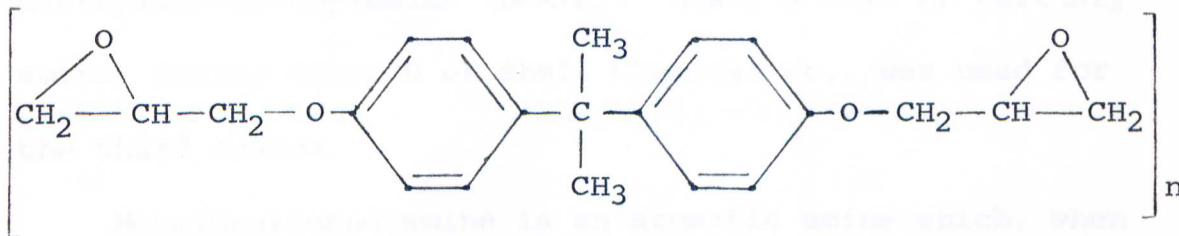
II

SAMPLE PREPARATION

A. Epoxide Resins. The epoxide resin employed in this investigation was EPON 828 (Shell Chemical Co.). The epoxide molecule is characterized by the reactive groups



which are the functional groups. The epoxide molecule, in its simplest form, can be represented by the diglycidyl ether of bisphenol A. (11)



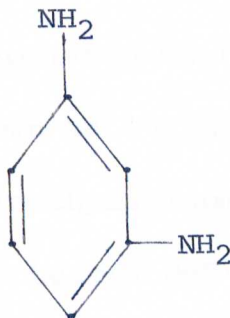
The very stable benzene ring contributes to the notable radiation resistance of all epoxide polymers. Some of the more important properties of the epoxide monomer are listed in Table 1, prepared from reference (11) and the manufacturer's literature.

The epoxide resins have the ability to transform readily from the liquid state to a hard, crosslinked solid. This hardness is accomplished by the addition to the liquid epoxide resins of a curing agent, sometimes called a hardener. The properties of the polymerized or hardened epoxide are dependent to a large extent upon the curing agent used. The resins in this investigation were polymerized into a cross-linked polymer by crosslinkage with the curing agent through various radicals.

This type of reaction is widely used and, when the crosslinking agent is an aromatic amine, also provides one of the most radiation resistant polymers, according to work done at Battelle Memorial Institute.⁽¹²⁾ For this study, the crosslinking agents were metaphenylenediamine (MPDA) and diethylaminopropylamine (DEAPA). Also, a salt of tertiary amine, Curing Agent D of Shell Chemical Co., was used for the third system.

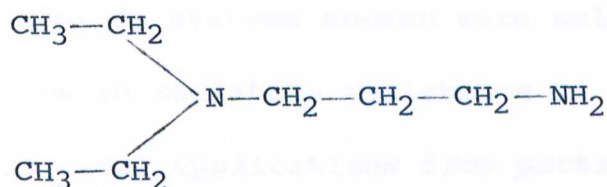
Metaphenylenediamine is an aromatic amine which, when used as a curing agent for EPON 828, provides a highly radiation resistant polymer. Aromatic amines also provide higher heat-distortion temperature than the aliphatic amines which, according to reference (12) is indicative of radiation resistance. This is likely due to the stable benzene ring being tightly crosslinked into the polymerized structure.

Metaphenylenediamine (MPDA) can be represented, ⁽¹¹⁾



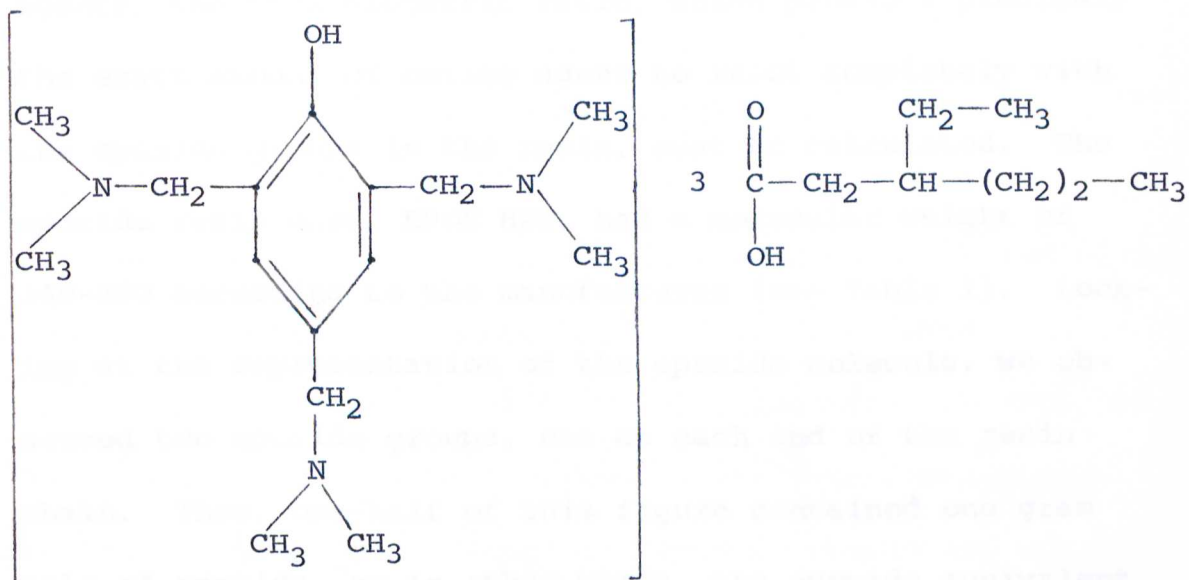
and is a light amber crystalline solid with a melting point of 60°C and a molecular weight of 108. It will be noted that MPDA has four active hydrogen ions capable of linking into the epoxide resin system.

Diethylaminopropylamine (DEAPA) is a pungent liquid with a room temperature viscosity of 1.9 centipoise and a molecular weight of 130. Its structural formula is ⁽¹¹⁾



DEAPA offers the advantage of a long pot life which is advantageous in many applications. The pot life is the time, after introduction of the curing agent, that the polymer remains in a liquid state and is able to be poured readily. Being an aliphatic amine, DEAPA is expected to be less resistant to radiation than is MPDA.

The tertiary amine salts have been used in applications where a long (6-hr) pot life is desired rather than the shorter (2-hr) pot life associated with DEAPA. The one chosen for this work is known as Curing Agent D by the Shell Chemical Co. and is tris(dimethylaminomethyl)phenol tri(2-ethylhexoate), commercially termed DMP-30. (11)



The three epoxide systems chosen were selected to represent a variation in radiation resistance as well as to have a variety of practical applications from potting compounds with a short pot life to a long pot life system for laying up reinforced plastic laminates for structural shapes.

The chemical formulae are not presented primarily for the chemistry involved in the polymerization, or crosslinking, process, but for the purpose of determining exactly what the compositions of the cured epoxide polymers were for

activation analysis after reactor irradiation. A prime requisite was to use a system that did not have any long-lived activation products which would create a radiation safety problem when handling the irradiated samples.

B. Mixing and Curing. When using the crosslinking agents, the stoichiometric ratio, which provides precisely the exact amount of curing agent to react completely with the epoxide groups in the resin, must be calculated. The epoxide resin used, EPON 828, had a molecular weight of 340-400 according to the manufacturer (see Table 1). Looking at the representation of the epoxide molecule, we observed two epoxide groups, one at each end of the resin chain. Thus, one-half of this figure contained one gram mole of epoxide, or in other words, the epoxide equivalent was 170. MPDA, it will be remembered, possessed four reactive hydrogens and a molecular weight of 108.

According to Lee and Neville,⁽¹¹⁾ in a crosslinking reaction one epoxide group reacts with one reactive hydrogen in the curing agent. Thus, we set up the relationship

$$\frac{340/2}{108/4} = \frac{100}{X}$$

to determine the parts per hundred (pph) of curing agent required to react exactly with 100 grams (g) of EPON 828.

Solving the above equation for X yielded approximately 15 g of MPDA for each 100 g of EPON 828. The commercially available resin, however, had an epoxide equivalent of 175-200 instead of 170 as calculated theoretically. Using this figure, we determined 14.5 parts MPDA to 100 parts of EPON 828. Expressed in per cent, this was 12.6.

Similar calculations for the other curing agents yielded values of 5.7 per cent for DEAPA and 13 per cent Curing Agent D.

The techniques for mixing the epoxide monomer and curing agent varied with the agent used. When using MPDA, the curing agent was melted at 65°C and mixed with the EPON 828 which had previously been warmed to the same temperature. An electrically driven mixer was used to completely mix the two compounds. It was found that many air bubbles were frequently entrapped in the process and had to be eliminated before curing. Air bubbles in the compressibility samples eliminated about 50 per cent of those cast. To remove air bubbles, the sample was placed in a beaker beneath a large bell jar which was carefully evacuated to eliminate any possibility of removing the fairly volatile curing agent. This technique resulted in better samples than other methods attempted. The resin was then poured into resistivity and compressibility molds.

DEAPA required no heating prior to mixing. However, to reduce the viscosity of the resin system and make it easier to cast, the EPON 828 was warmed to about 40°C prior to mixing in the DEAPA. The polymer was then mixed for 10 min by an electrical mixer, placed in a vacuum to remove any entrapped air bubbles, and cast into the compressibility and resistivity molds.

Curing Agent D is also a liquid, and the same procedure was used as in the case of DEAPA.

In all cases, 100 g of resin-curing agent systems were made up at a time. This was done to ensure that samples for all measurements, resistivity, compressibility, hardness, and specific volume, were of the same formulation and subjected to the same curing cycle.

Each of the three systems was polymerized at an elevated temperature to ensure that polymerization was as complete as possible.

The EPON 828 and MPDA samples were poured into the appropriate molds and cured 16 hr at 60°C, followed by 20 hr at 210°C.

The EPON 828 and DEAPA samples were cured for 16 hr at 60°C followed by 20 hr at 120°C.

Curing Agent D and EPON 828 samples were cured for 16 hr at 70°C, followed by 20 hr at 120°C.

In all cases, the temperatures of the post cure were

greater than the subsequent temperatures to which the samples were to be subjected during the resistivity or compressibility tests.

C. Molding of Samples. All samples prepared were designed to be simple and easily made.

The resistivity sample used in these tests was merely two electrodes, easily turned on a lathe from 2S aluminum, cast in the resin system to be investigated. A diagram of the resistivity sample is shown in Fig. 1. The material selected for the electrodes had to be chosen carefully to ensure a minimum of induced activity after irradiation by the thermal neutron flux of 1×10^{11} neutrons/cm²-sec in the reactor. Aluminum, in its relatively (greater than 99 per cent) pure form, 2S, was chosen. It has a thermal neutron absorption cross section of 0.21 barns and a half life of 2.3 min, allowing a minimum time before handling after irradiation. All machining needed on each electrode was done on a lathe. After machining, all electrodes were degreased by rinsing in methylethylketone (MEK) and stored in a clean bag.

A teflon mold was made in which to cast the specimens for the resistivity test. The epoxides, although remarkable adhesives, did not adhere to the mold and could be separated after curing without the use of a release agent which could

possibly contaminate the sample. This mold is shown in Fig. 2. The smaller diameter of the electrode was a press fit into the holes in the end caps of the mold, thus assuring the electrodes held their position during curing. The shoulder on each electrode was pushed firmly against the inside surface of each end cap, which established the $.080 \pm .002$ inch spacing between electrodes necessary to calculate the resistivity. Measurements made after cure by means of a "shadow-graph" confirmed that on all but two of the samples prepared, the spacing was maintained. During the initial post-cure, the samples remained in the mold. After they had hardened sufficiently to prevent breakage, the mold was disassembled and the sample removed. An 0.043 inch hole was drilled in each sample, as shown in Fig. 1, to accept a thermocouple lead.

The compressibility sample was prepared in a teflon coated mold $.250^{+.005}_{-.000}$ inch diameter and 8.25 inch long. Two compressibility samples could conceivably be obtained from each pour, but bubbles and imperfections generally reduced this to one. After the initial post-cure, the mold was disassembled and the sample carefully removed. The mold was generally heated to 40°C prior to any casting being made to reduce the chances of bubbles remaining in the sample during polymerization. The samples, after post-cure, were

cut to $3.00^{+.00}_{-.10}$ inch and faced off perpendicular to the 3-inch dimension.

Any roughness on the surface of the sample was removed with abrasive paper to ensure a tight fit in the cylindrical cavity of the compressibility tester.

The specimens for hardness and specific volume were obtained from the same mold as the compressibility samples using the same procedures.

All irradiations were carried out when the reactor was operating at 10 kilowatts to ensure known and reproducible radiation levels. The reactor core operates under approximately 17 ft of demineralized water, and the samples were placed on the upper face of the core in the same position for each irradiation, position D-4. This repositioned the samples in watertight polyethylene bottles, a procedure covered in Chapter IV.

The basic of the radioactivity measuring equipment was a Keithley Model 210 Electrometer with a Keithley Model 2000 Decade Switch. This equipment was used to measure the radioactivity of the samples after irradiation. The samples were placed in a lead container to shield the detector from the background radiation. The detector was a Geiger-Müller tube connected to the electrometer. The electrometer was calibrated with a known source of radioactivity. The radioactivity of the samples was measured by comparing the count rate of the samples to the count rate of the known source. The count rate of the samples was measured by counting the number of pulses from the detector over a period of time. The count rate of the known source was measured by counting the number of pulses from the detector over a period of time. The radioactivity of the samples was calculated by dividing the count rate of the samples by the count rate of the known source. The radioactivity of the samples was measured in units of disintegrations per minute (dpm). The radioactivity of the samples was measured in units of disintegrations per minute (dpm). The radioactivity of the samples was measured in units of disintegrations per minute (dpm).

III

EQUIPMENT

A. Nuclear Reactor. The nuclear reactor used for the irradiation was the University of Maryland Pool Training Reactor (UMR). Located on the University Campus at College Park, Maryland, the UMR is of the "swimming pool" type and is licensed to operate at 10 kilowatts (thermal). Some of the important characteristics of this reactor, according to the manufacturer⁽¹³⁾ are listed in Table 2.

All irradiations were carried out when the reactor was operating at 10 kilowatts to ensure known and reproducible radiation levels. The reactor core operates under approximately 17 ft of demineralized water, and the samples were placed on the upper face of the core in the same position for each irradiation, position D-4. This necessitated placing samples in watertight polyethylene bottles, a procedure covered in Chapter IV.

B. Resistivity Equipment. The basis of the resistivity measuring equipment was a Keithley Model 210 Electrometer with a Keithley Model 2008 Decade Shunt. This equipment was

used to monitor the d.c. current across the resistivity sample over the range 10^{-3} to 10^{-12} amperes. The voltage required was supplied by a 45 volt dry cell battery connected in series with the electrometer and sample as shown in Fig. 3.

A thermocouple was inserted in the hole previously drilled in the sample. The other end of the iron-constantan thermocouple wire was connected to a Leeds and Northrup Potentiometer and was used to determine the temperature of the sample during the resistivity measurement. (2,3)

The resistivity cell was prepared as described in the previous Chapter, and placed in the circuit. A photograph of the resistivity measurement equipment in an operating configuration is shown in Fig. 4. The resistivity cell was generally wrapped in fiberglass and placed in a can to reduce the rate of heat loss during the measurement. It is shown outside the can to illustrate the connections required. The principle of operation for the resistivity measurement was simply an application of Ohm's Law. Detailed instructions for the operation of the Keithley Model 210 electrometer can be found in reference 14.

C. Compressibility Equipment. The compressibility tester used was designed by Matsuoka and Maxwell⁽⁷⁾ and

improved upon by Warfield.⁽¹⁵⁾ The inner cylinder of the tester was made of hardened steel and had a cylindrical cavity to hold the specimen. The cylindrical cavity was lapped and polished to $0.250^{+.001}_{-.000}$ inch diameter. The inner cylinder was a shrink fit into outer steel jacket. Two case-hardened steel plungers 1.625 inch long and $0.250^{+.000}_{-.001}$ inch in diameter were inserted into the cavity as shown in Fig. 5.

Two electric heating bands were used to vary the temperature of the sample during compressibility measurements. The temperature was controlled over the range $25^{\circ}\text{C} - 250^{\circ}\text{C}$ ($\pm 1^{\circ}$) by means of a "VARIAC" and measured by two thermocouples placed in wells in the outer steel jacket.

The tester, shown in Fig. 6, was assembled with the specimen inside and placed on a Baldwin-Southwark Universal Test Machine (60,000 lb capacity). The Universal Test Machine was used in the compression mode with a rate of loading of 0.025 inch/min. The automatic stress-strain recorder plotted data continuously over the range 0-8000 lbs. Fig. 7 is a photograph of the assembled equipment.

D. Hardness Equipment. Hardness was measured before and after irradiation by means of a Rockwell Hardness Tester, Model 3JR, using the "M" scale. The flat machined end of the

compressibility specimen was used for the measurement.

Three readings were made and the average taken.

E. Specific Volume Equipment. Basically, the determination of the specific volume of the samples was made by first weighing the samples in air and then in water. The epoxide polymer was known to absorb less than .01 per cent by weight of water at room temperature. A "Gram-Atic" Balance, made by Fisher Scientific Co., was used for both the measurement in air and that in water. The specific volume was then given by $v_s = \frac{\text{Weight in air} - \text{Weight in water}}{\text{Weight in air} \times \text{Density of water}}$. The sensitivity of the balance was 0.0001 g. For simplicity, the compressibility specimens (0.250 inch diameter, 3.00 inch long) were used to determine specific volume.

IV

EXPERIMENTAL PROCEDURE

A. Irradiation. Two types of samples were irradiated, the resistivity cell and the compressibility specimen, both of which were described above. The irradiation location for all samples was position D-4 on the upper core face, as shown in Fig. 8. The core was located under approximately 17 ft of water. It was imperative, due to the effects of moisture on the epoxide system, observed by Kline,⁽¹⁶⁾ that the specimens be kept dry during the irradiations. To do this, all specimens were placed in polyethylene bottles with screw caps. The bottles were then sealed with melted paraffin and fitted with lead weights to sink them. Two lengths of stout nylon cord were knotted around the neck of the bottle beneath the cap and used to place the samples in the irradiation position. Two cords were used for added safety in case one cord broke or became loose. Figure 9 shows the samples in the irradiation position during a full power run.

Early in the test program it was thought best to place the specimens in the irradiation space ("glory hole") within

the reactor core so that a higher dose rate could be realized. However, this practice led to difficulties in inserting or withdrawing specimens and was discontinued. Therefore, although the small resistivity specimen was not irradiated in the "glory hole," this sample size was continued throughout the irradiation program in order to take advantage of the mold which was already constructed and the many cells cast.

Specimens, in the polyethylene bottles, were lowered to the irradiation position D-4 on the face of the reactor core. The attached nylon cords were connected on the other end to a fishing reel which facilitated raising and lowering. The time was noted when the specimens were placed on the core and the line and reel secured to the bridge structure.

After the selected times in the radiation field, the specimens were carefully raised to or near the pool surface and their activity measured. In all cases, immediately after irradiation the activity was large, about 100 milliroentgens/hr (mr/hr) and the specimens were placed in the fuel storage container on the tank bottom until the activity had declined enough to allow removal. The electrodes in the resistivity cells produced the isotope Al^{28} with a half life of 2.3 min and emitting two gamma rays. Although the

specimens usually remained in the storage containers about three days, some activity (less than one mr/hr) was still noted. This could be due to trace impurities in the aluminum with longer half lives. When the samples had reached a level of about .2 mr/hr, they were placed in a lead storage container and transported to the U.S. Naval Ordnance Laboratory, White Oak, in accordance with AEC licensing instructions. There they were stored until measured. After measurement, they were either returned to the UMR for further irradiation or held in storage until down to background. During and after measurements of irradiated specimens, the area was wiped and monitored using a U.S. Navy procured Count Rate Meter manufactured by Nuclear Corporation of America, Model CS-145.

B. Dose Rate Determination. In studies involving irradiation effects on materials, it is important to know the energy deposited in the sample from the radiation source. When a nuclear reactor is the radiation source, the flux conditions can be very complex since the radiation includes neutrons and gamma rays with a wide energy distribution. Fission fragments, beta, and alpha particles cannot reach the sample in any appreciable numbers because of their short range. The literature search produced two papers

concerning energy deposition in polymers from reactor radiation. Kline and Jacobs⁽¹⁷⁾ estimated the energy deposited in polyethylene by reactor radiation based on theoretical calculations. Jacobs and Kline⁽¹⁸⁾ reported experimental results of reactor radiation on various polymers, including polyethylene and epoxide, as well as a calculative method to substantiate those results. There appears to be only a small disparity in the estimation of energy deposited, depending upon which of the above methods is used.

Kline and Jacobs⁽¹⁷⁾ calculations were based on the use of the Pennsylvania State University Reactor (PSR) which is an enriched uranium, light water moderated, heterogeneous reactor similar to the UMR except that it was operated at 100 kilowatts. This paper, published in 1959, considered the reactor radiation to be divided into various components, namely: energy deposited from gamma radiation produced external to the sample; recoil energy deposited by the ${}_1\text{H}^2$ nucleus formed from the reaction ${}_0\text{n}^1 + {}_1\text{H}^1 \rightarrow {}_1\text{H}^2 + \gamma$; photon energy deposited from this same reaction; deuteron recoil energy deposited due to epithermal neutron flux; energy deposited from gammas produced by epithermal neutron absorption; and the recoil energy deposited from protons resulting from elastic scattering.

Epithermal, or fast (.4 ev to 10 Mev), neutrons may transfer all of their energy to a hydrogen atom, producing a high energy proton which is intensely ionizing. For carbon, the maximum amount of energy which can be transferred is only 28 per cent, and for oxygen only 22 per cent. (4) In polyethylene, the energy absorbed from epithermal neutrons is primarily from these collisions with hydrogen atoms. However, gamma radiation produced external to the sample is the largest contributor to energy deposited.

Using the PSR operating characteristics, this method yielded a total energy absorbed (E_a) of 1.09×10^9 ergs/g-hr for polyethylene. The rate of energy deposition is a function of the elemental constituents and relative density of hydrogen atoms and, as polyethylene and epoxide have approximately the same hydrogen density, it was possible to utilize the above value to estimate the energy deposited in the epoxides used in this study. However, the later experimental results by Jacobs and Kline (18) yielded values directly for energy absorbed in polyethylene and epoxides.

Jacobs and Kline, (18) in 1962, reported a series of experiments using the PSR to determine the energy deposited in polymers located on the core surface.

This method employed a cylindrical polymer specimen whose surface temperature was maintained uniform and

constant by means of a circulating water bath. Any flux gradient within the sample was eliminated by placing the .250 inch diameter, 2 inch long sample on the core face. The steady state temperature distribution then was dependent only upon the thermal conductivity, sample geometry, and rate of energy deposition. A thermocouple was placed at the center of the sample and the temperature difference between this point and the surface determined by means of a precision potentiometer. By use of the relationship⁽¹⁸⁾

$$E_a = 6.02 \times 10^{11} k \Delta T / d R^2 \quad \text{ergs/g-hr}$$

where E_a = energy deposited ergs/g-hr

k = thermal conductivity calories/cm-sec-°C

ΔT = temperature difference °C

d = density g/cm³

R = sample radius cm

the energy deposited was calculated. Jacobs and Kline presented this information graphically for several polymers. For polyethylene, the energy deposited was 1.5×10^4 ergs/g-hr-watt of reactor power. With the reactor operating at 100 kilowatts, the energy deposited would be 1.5×10^9 ergs/g-hr. This compares very favorably with the value of 1.09×10^9 ergs/g-hr calculated by Kline and Jacobs on a theoretical basis.

It was decided to use the results from the experimental work⁽¹⁸⁾ in lieu of the theoretical calculations⁽¹⁷⁾ because it gave values for the epoxide directly without any scaling from polyethylene results and also because it was more recent work. Based on these experimental results, the energy absorbed in a cylindrical epoxide polymer .250 inch in diameter and 2 inch long, placed on the core face, was 1.2×10^4 ergs/g-hr-watt of reactor power. With the UMR operating at 10 kilowatts, the energy deposited in the samples used in this investigation was 1.2×10^8 ergs/g-hr. This can also be expressed in the form 1.2 megarads/hr.

C. Resistivity Measurement. The equipment was set up as noted in Chapter III B, and the irradiated samples placed in an oven for 2 hr prior to the time of measurement to assure a stable temperature reading. The oven temperature was dependent upon the epoxide system to be studied. For EPON 828 and MPDA, the resistivity samples were raised to a temperature of $200^{\circ} \pm 10^{\circ}\text{C}$ in the oven; for EPON 828 and DEAPA, the temperature was $120^{\circ} \pm 10^{\circ}\text{C}$; and for EPON 828 and D system, the samples were conditioned at $175^{\circ} \pm 10^{\circ}\text{C}$. The temperatures selected were above the known glass transition region, a parameter discussed in the next Chapter. Prior to placing the samples in the oven, they were wrapped in fiberglass

fabric to retard heat loss during the resistivity measurements.

For the measurements, the Keithley electrometer was set at a full scale reading of 8 volts, and a current range of 10^{-7} or 10^{-8} amperes was set on the decade shunt.

The wrapped sample, after it reached the desired temperature, was removed from the oven and quickly placed in a can, the electrometer leads were snapped on and the thermocouple lead placed in the thermocouple well. This procedure took less than one minute. Temperature was measured in the Leeds and Northrup Potentiometer ($^{\circ}\text{F}$) and simultaneously the current corresponding to that temperature was read on the electrometer. This procedure was repeated, at least every 10°F , while the sample cooled down to room temperature. The rate of cooling was about $5^{\circ}\text{F}/\text{min}$. Table 3 is an example of the data obtained from one measurement. The temperature was first converted from $^{\circ}\text{F}$ to $^{\circ}\text{C}$ and then to the reciprocal of the absolute temperature for an Arrhenius plot. The current was read directly from the electrometer and decade shunt, and the voltage at that given current reading was determined by subtracting the reading on the electrometer from the impressed voltage, in this case 45 volts d.c. Using Ohm's Law, $R = E/I$, we obtained the resistance for a given current. The volume resistivity, ρ , was then calculated by means of

the relationship (20)

$$\rho = \left(\frac{A}{L} \right) R \quad \text{ohm cm}$$

where R was the resistance in ohms, A the surface area of material perpendicular to the potential gradient (area of the electrodes in cm^2), and L the current path length in the material (distance between electrodes in cm). A/L is also called the cell constant, and for these measurements was

$$\frac{A}{L} = \frac{\pi (1.97)^2}{4 (.2)} = 16 \text{ cm}$$

The computed data was then plotted as the logarithm of the electrical resistivity versus the reciprocal of the absolute temperature. This is known as an Arrhenius plot. From this plot can be calculated the activation energy of the system E_c , while the glass transition temperature, T_g , and magnitude and temperature dependence of resistivity can be obtained by inspection. These are shown in Figs. 10, 11, and 12. Two measurements were made of each irradiated sample to reduce the chance of error. In the case of the non-irradiated samples, two samples were made and cured under the same conditions. Existing data were available on the

non-irradiated temperature dependence of resistivity for the various systems. (20)

D. Compressibility Measurement. The compressibility tester, described in Chapter III, was placed on the fixed base of the Universal Test Machine and the specimen brought to the desired temperature by means of a "VARIAC" variable transformer. The movable head of the machine was brought down to contact the upper plunger, and the sensor for the automatic stress-strain recorder adjusted to just touch the undersurface of the movable head (see Fig. 7). The load was applied at the rate of 0.025 inch/min. It was found that at speeds greater than this, phenomena such as the glass transition cannot be determined, whereas slower speeds yielded no additional information. This procedure was repeated for each temperature desired. A continuous plot of stress versus strain was provided by the stress-strain recorder. The maximum load applied was usually about 8,000 lbs (equivalent in the .250 inch diameter compressibility sample to 11,000 atmospheres or 160,000 lbs/square inch). This was considered the maximum safe load, although a thick-walled iron casing was placed around the tester for safety.

It required about 6 hr to run each specimen, using 5 different temperatures, and the slow speed of 0.025 inch/

min head travel. The stress versus strain plots obtained were identical with those shown in Figs. 13, 14, and 15.

E. Hardness Measurement. The hardness of each sample before and after irradiation was measured on a Rockwell Hardness tester using the 'M' scale. The compressibility sample was placed on the plate of the Rockwell tester such that a flat machined face was presented to the "ball" doing the measuring. This was a non-destructive test. Three readings were made and an average taken. The readings before and after each irradiation for the three epoxide systems were plotted.

F. Specific Volume Determinations. For these measurements, a Fisher Gram-Atic Balance was used. This specimen was merely weighed in air, then suspended from a fine wire and submerged in a beaker of water to determine the weight in water. The difference in weight was calculated and this value was divided by the weight in air to get the specific volume.

Epoxide polymers of the type used absorbed less than .01 per cent of their own weight in water at room temperature. As the immersed time was only a matter of 2 min, much less than this was absorbed. As stated previously, the standard compressibility specimen was used for this measurement.

RESULTS AND DISCUSSION

A. Electrical Resistivity. Electrical resistivity versus the reciprocal of the absolute temperature plots were made for each epoxide polymer from measurements such as those given in Table 3. There were approximately ten measurements made for each of the three polymer systems, and Table 3 shows typical data. Such measurements were made both before and after irradiation. The extent of the irradiation to which the various samples were subjected is shown in Table 4.

Several parameters of a polymer system can be obtained from the temperature dependence of electrical resistivity. Such parameters are: the activation energy for the electrical conduction process; and the glass transition temperature, T_g .

A theoretical basis for calculating the activation energy of the electrical conduction process, E_c , was developed by Glasstone et al.,⁽²¹⁾ who stated that the concepts used in chemical kinetic studies can be applied to physical processes. According to Kallweit,⁽²²⁾ electrical conduction

in epoxide polymers is an ionic rate process. The largest source of ions in a polymer consists of impurities which are not part of the polymer structure. Thermal agitation also produces some ionic dissociation which increases with temperature. The radiation to which each sample was subjected also formed additional ions not present in the non-irradiated state.

The change in electrical resistivity of a polymer with temperature can be considered a rate process similar to those in chemical kinetics⁽²¹⁾ and the Arrhenius equation can be applied to calculate the activation energy for the electrical conduction process.

$$\rho = A_0 \exp (E_c/RT)$$

where ρ is the resistivity, A_0 is the temperature independent constant, R is the gas constant, 1.987 calories/degree mole, T is the absolute temperature, and E_c the activation energy for the conduction process.

The conduction depends not only on the number of ions present, but also on their mobility. The mobility of the ions present in a polymer subjected to an applied electric field is proportional to the reciprocal of the microviscosity.⁽²³⁾ The microviscosity becomes less at higher temperatures, and the mobility increases. Thus the electrical

conductivity increases and the electrical resistivity decreases at higher temperatures.

One of the parameters used for comparison in the various polymer systems was the glass transition temperature, T_g . The glass transition is the temperature range where the relaxation time, during which internal rearrangements are being made, is in the time scale of the experiment. That is, the measurements do not proceed at a rate too fast to detect the transition. At temperatures below T_g the polymer is in a hard glassy state and is an example of a solid not in configurational equilibrium. Certain internal degrees of freedom are "frozen in" and the polymer cannot easily adjust to changes in temperature or pressure. At temperatures above T_g , the polymer segments exhibit increased mobility resulting in increases in the free volume of the system.⁽²⁶⁾

The theory of the glass transition in crosslinked polymers is not well understood, and T_g is generally identified by some physical measurement. According to Eisenberg,⁽²⁴⁾ the glass transition is a phenomenon which occurs when a polymer is heated or cooled through a specific temperature range. Since, according to Ferry⁽²⁵⁾ the glass transition depends very strongly on the free volume of the system, it can be determined by studying some property dependent upon the free volume, such as the compressibility

or specific volume as a function of temperature.

Kauzmann⁽²⁶⁾ states that the glass transition is a relaxation phenomenon. This can be defined as follows, according to Davies⁽²⁷⁾: A system in equilibrium, when suddenly subjected to changes in the thermodynamic forces, will pass through a transient period before its thermodynamic coordinates attain a new equilibrium. During this interval the system is exhibiting relaxation. Pressure, temperature, and electric or magnetic fields are the thermodynamic forces, while the corresponding effects, dilatation, energy and electric or magnetic polarization are the thermodynamic coordinates.

Electrical resistivity measurements made on polymers in equilibrium, above T_g , usually exhibit a non-linear temperature dependence since changes in temperature result in progressive changes in the internal arrangement of the system. For temperatures below T_g , the system will exhibit a linear temperature dependence due to its highly rigid structure.

In the Arrhenius plots of resistivity versus the reciprocal of the absolute temperature, the glass transition can be determined from the change in slope as the polymer is slowly cooled from equilibrium to non-equilibrium conditions. The T_g obtained can then be compared with T_g values

found from other measurements such as specific heat.⁽²⁰⁾

No literature pertaining to the electrical resistivity of crosslinked polymers after irradiation was found. Ieda et al.⁽³²⁾ investigated the electrical resistivity after gamma irradiation for crystalline polyethylene and found considerable degradation after 2.8×10^7 rads. As stated in this paper, "although a number of investigations of the effect of ionizing radiation on physical properties of polymeric materials have been carried out, only a few investigations have been reported on the electrical conduction in polymers after irradiation." Kline⁽³³⁾ also suggested, "More electrical measurements data, including results as a function of temperature...." for epoxides both before and after irradiation.

The magnitude and temperature dependence of the electrical resistivity for the three polymer systems investigated are shown in Figs. 10, 11, and 12, and discussed in the following sections.

EPON 828 and MPDA (Epoxide Monomer cured with MPDA).

The effect of irradiation on the temperature dependence of the electrical resistivity for EPON 828 and MPDA is shown in Fig. 10. In the non-irradiated polymer the plot was linear over the range 80°C to 156°C. The magnitude and

slope of the curve compared favorably with that given by Warfield and Petree.⁽²⁰⁾ The glass transition temperature, T_g , for the non-irradiated sample was 156°C which agreed with Warfield and Petree's value of 158°C .

After 2.5 Mrads of irradiation, the resistivity exhibited higher values over the temperature range 80°C to 160°C . This portion of the plot appeared linear and approximately parallel to the non-irradiated plot. At temperatures above 160°C the resistivity plot became curved with a steeper slope which flattened out about 195°C . No sharply defined glass transition point was observed. However, the curve above 160°C departs radically from the slope of the linear portion of the plot.

Further irradiation produced a total of 5 Mrads of deposited energy and this plot differed radically from the previous one. The resistivity over the temperature range 130°C to 200°C followed essentially the same curve as that determined for the 2.5 Mrad sample. However, at temperatures below 130°C the resistivity values fell off rapidly until at 80°C it was an order of magnitude less than it was after the first irradiation and approximately what it was at that temperature for the non-irradiated sample. Again no well-defined T_g could be determined, although the region

above 160°C was quite different from the linear portion of the curve.

When exposed to a radiation dose of 16 Mrads, the resistivity showed a temperature dependence characterized by an almost continuous curve. No glass transition could be observed. The resistivity over the temperature range 80°C to 140°C exhibited a sharp decrease until at 80°C the value had decreased to a factor of 100 over the maximum observed.

The maximum radiation dose received by this system was 25 Mrads. The resistivity values fell approximately along the same curve as those for the 16 Mrad sample. At temperatures between 140°C and 200°C the resistivity was slightly lower than after 16 Mrads, but at temperatures between 80°C and 140°C it was essentially the same. Again no T_g could be observed.

EPON 828 and Curing Agent D. The effect of radiation on the temperature dependence of electrical resistivity of EPON 828 and Curing Agent D is shown in Fig. 11. For the non-irradiated polymer the plot was linear from 60°C to 73°C. From 73°C to 150°C the resistivity was non-linear with a decreasing slope over the range 110°C to 150°C. The magnitude and slope of this curve compared favorably with the published data,⁽²⁰⁾ and the glass transition at 73°C was only

slightly higher than Warfield and Petree's value of 66°C .

The first irradiation carried out in this system was 11 Mrads. The resistivity values increased approximately by a factor of 100 over the non-irradiated values at a given temperature over the range 90°C to 155°C . Below 90°C the resistivity departed from its linearity and became curved with constantly decreasing slope. At 72°C the resistivity value was the same as for the non-irradiated sample and at 55°C was one decade less. After this irradiation, no glass transition could be observed.

After 14.4 Mrads the resistivity decreased from its previous higher values and became a curve over the entire temperature range. At 55°C the resistivity was less than in the non-irradiated condition by a factor of almost 100.

Additional irradiation of 25 Mrads decreased the resistivity still further. It again followed a curved path and at 55°C assumed a value two decades less than the non-irradiated sample. Neither of these last two plots exhibited a detectable glass transition.

EPON 828 and DEAPA. This aliphatic amine cured system was expected to be affected more than the previous aromatic amine cured system. The initial resistivity plot compared favorably with the published Arrhenius plots⁽²⁰⁾

in both magnitude and temperature dependence. The glass transition occurred at 98°C as compared with a value obtained from specific heat measurements⁽²⁰⁾ of 106°C . The resistivity at 55°C was about 3×10^{16} ohm-cm.

After 7.2 Mrads the resistivity values were drastically reduced. The slope of the temperature-induced conductivity decreased sharply and at 55°C the resistivity was 1×10^{14} ohm-cm. No glass transition point could be determined.

A further decrease in electrical resistivity was observed after 21.6 Mrads of irradiation. The slope of the curve was more nearly horizontal and, while approximately the same at the higher temperatures, was a factor of about 100 less than 7.2 Mrad sample at 55°C . No T_g could be determined.

B. Compressibility. According to Eisenberg,⁽²⁴⁾ the glass transition in amorphous polymers is not only temperature dependent, but pressure and molecular weight dependent as well. In this investigation the temperature was held constant over each run and, as the same sample was used, the molecular weight was constant. The only remaining parameter of the three determining the glass transition was the pressure. Eisenberg considers the glass transition from the standpoint of pressure dependence and defines it as the

pressure at which a transition occurs, or glass transition pressure, P_g . Assuming the free volume theory of the glass transition is valid,⁽²⁵⁾ the increasing pressure "squeezes out" the free volume. At temperatures above the glass transition temperature, T_g , the effect is to cause the polymer to assume a glassy state after a certain critical point is reached in the free volume.

When this critical free volume is reached the compressibility characteristics change from those of a rubbery solid to those of a glassy solid and an inflection point is exhibited in the plot of the pressure versus $\Delta V/V$ plot. However, no change of compressibility characteristics will occur unless the temperature is above the T_g , regardless of the pressure.

If the temperature at which the compressibility is determined is plotted versus the pressure at which the inflection point occurs, a plot is obtained which shows the variation of T_g with pressure. A plot of this variation is the glass-rubber phase diagram.

Based on the above, Eisenberg concludes that the glass transition pressure is certainly an experimental fact.

The results of the bulk compressibility measurements are shown in Figs. 13-18. Plots, obtained under isothermal conditions, of the applied pressure in atmospheres versus

the per cent change in volume were made for each polymer as a function of temperature both before and after irradiation. The extent of the irradiation is shown in Table 4. The automatic stress-strain plot made on the Baldwin-Southwark UTM gave results of applied load versus strain in inches/inch. These were then converted to pressure versus per cent change in volume and presented as Figs. 13, 14, and 15. In several of the isotherms, changes in the slope of the curve resulted in an isotherm containing two curves. The inflection points, or changes in slope, are due to the pressure-induced glass transition, P_g , within the polymer. The pressure and temperature at which this P_g occurred were then used to prepare the plots shown in Figs. 16, 17, and 18. These figures are glass-rubber phase diagrams⁽¹⁵⁾ and were made for each polymer before and after irradiation. Crystalline phase diagrams have been prepared by Weir⁽⁶⁾ and Pistorius⁽²⁹⁾ for polytetrafluoroethylene.

After the pressure measurements were complete, the length of the sample was accurately measured and compared with the original length. In all cases the polymer returned to its original length, indicating that no observable permanent damage, such as the breaking of chemical bonds, had occurred due to the applied pressures.

Pressure versus strain plots were made commencing at about 25°C and at 25°C increments up to about 250°C. The load was applied at a rate of 0.025 inch/min until a maximum of 6,000 lbs, which is equivalent to about 8,000 atmospheres, was reached. This resulted in a series of isotherms for each polymer. Of the eight or nine isotherms obtained, only those made above T_g , usually four or five, could be expected to yield an observable P_g . Since many of the isotherms are superimposable, some of the data are omitted in Figs. 13, 14, and 15.

After each irradiation the above measurements were repeated. The isotherms thus obtained were not easily discernible from the isotherms of the non-irradiated specimens. For the sake of simplicity, no attempt was made to show the pressure versus $\Delta V/V_{25^\circ\text{C}}$ isotherms for each irradiated sample, on the same plot as the non-irradiated sample; and these results were plotted only in Figs. 16, 17, and 18. Thus, Figs. 13, 14, and 15 are merely typical pressure versus $\Delta V/V_{25^\circ\text{C}}$ plots showing the variation of P_g as a function of temperature.

The literature contains only one study⁽²⁸⁾ concerning the bulk compressibility of crosslinked polymers. Several references to studies on a few crosslinked polymers are in the literature,⁽²⁹⁾ but these studies were generally at low

pressures. The most noteworthy of these studies are those of Bridgman⁽⁵⁾ and Weir.⁽⁶⁾

EPON 828 and MPDA. This is a highly crosslinked polymer with a glass transition temperature determined by electrical resistivity measurements, of 156°C for the non-irradiated sample. The isotherms measured in the non-irradiated sample showed little temperature dependence of compressibility over the range 25°C to 251°C . In fact, the plots were so similar for the various temperatures that only the extremes, 25°C and 251°C , could be graphically portrayed in Fig. 13. The P_g shown on the 251°C isotherm occurred at 2,550 atmospheres. This data was then used to plot one point on the glass-rubber phase diagram, Fig. 16. P_g values were also obtained from the 234°C , 225°C , and 217°C isotherms. These values, with their corresponding pressures, were also plotted in Fig. 16. The non-irradiated temperature versus pressure phase diagram shown in Fig. 16 was plotted from these four points. The glass transition at one atmosphere was determined by extrapolating this line to intercept the temperature axis, as was done by Warfield.⁽³⁰⁾

The sample was subjected to a radiation dose of 2.5 Mrads and the measurements repeated. Again there was little temperature dependence over the temperature range 25°C to

234°C. Any difference in the compressibility isotherms between the irradiated and non-irradiated samples could not be discerned by the method of plotting used. However, P_g values were obtained from the 234°C, 224°C, 217°C, and 193°C isotherms. These were used to plot the curve shown in Fig. 16. This curve was approximately parallel to the non-irradiated curve and yielded a P_g of 175°C.

A further irradiation of 11 Mrads was conducted and the compressibility again measured. The stress-strain plots were very anomalous and only two exhibited any order at all, due to a mechanical failure in the test machine. The two valid isotherms, 246°C and 175°C, exhibited inflection points in the slope of the pressure versus $\Delta V/V_{25^\circ\text{C}}$ plot and these values were used in Fig. 16 to establish the phase diagram. The T_g for this sample appeared to be at 166°C.

A 14.4 Mrad irradiated sample was not measured due to the unavailability of a Baldwin Southwark test machine after a given date. This sample will be measured in the near future.

The magnitude of the compressibility was not affected to any degree by the radiation to which the samples were subjected. Between 25°C and 251°C the compressibility increased only from 6.2 per cent to 6.8 per cent at 5,000

atmospheres. This fact suggests an extremely rigid structure not easily affected by radiation, temperature, or pressure. However, the pressure-induced glass transition appears to decrease with increasing radiation.

EPON 828 and Curing Agent D. This is another aromatic cured epoxide with a glass transition of 73°C as determined by electrical resistivity measurement. For the non-irradiated sample, the pressure versus $\Delta V/V_{25^{\circ}\text{C}}$ plot is shown in Fig. 14. It was noted that this system exhibited a more noticeable temperature dependence of the compressibility than did the MPDA cured epoxide. Three isotherms could be plotted without superimposing one on another. Between 22°C and 185°C , the magnitude of the compressibility increased from 10.5 per cent to 15.5 per cent at 8,000 atmospheres. The increase of 163°C caused an increase of 5 per cent in the compressibility. However, it should be noted that the polymer at 185°C had undergone a change of phase, i.e., from a rubbery to a glass-like solid, whereas the polymer at 22°C was still below T_g . Isotherms exhibiting changes in the slope of the pressure versus $\Delta V/V_{25^{\circ}\text{C}}$ were 185°C at 3,900 atmospheres, 161°C at 2,900, 139°C at 2,350, 121°C at 1,850, 117°C at 1,300, 113°C at 1,250, and 90°C at 800 atmospheres. Some of these isotherms are not shown in

Fig. 14 as they would be superimposed. The phase diagram was prepared in the usual manner using the above data points and is shown in Fig. 17. The extrapolated value for T_g at one atmosphere was 70°C .

After irradiation of 7.2 Mrads the above procedure was repeated. The isotherms were not plotted in Fig. 14, for they did not differ sufficiently from the non-irradiated case to be discernible. Of the isotherms plotted by the automatic stress-strain apparatus, only five had a detectable P_g . These were 179°C at 2,760 atmospheres, 166°C at 2,450, 149°C at 2,050, 134°C at 2,020, and 114°C at 1,250 atmospheres. These data points were used to plot the phase diagram for the 7.2 Mrad sample shown in Fig. 17. The glass transition at one atmosphere appeared to drop to 63°C .

The above measurements were repeated after 14.4 Mrads. Again the isotherms were essentially the same as for the non-irradiated sample, only the inflection points differed slightly. Again five of the isotherms obtained from the plot of pressure versus $\Delta V/V_{25^{\circ}\text{C}}$ displayed a P_g . These data points were then used to plot the curve shown in Fig. 17. There was some scatter among the data points and the best straight line was drawn through these plotted points. The T_g thus obtained occurred at 94°C at one atmosphere.

The highest radiation dose received by an EPON 828 and Curing Agent D compressibility sample was 25 Mrads. The isotherms obtained from the pressure versus $\Delta V/V_{25^{\circ}\text{C}}$ plot indicated the following values for P_g : 176°C at 2,500 atmospheres, 164°C at 2,250, 148°C at 1,700, 135°C at 1,300, and 121°C at 1,250 atmospheres. These data points were plotted on the phase diagram in the usual manner. Again, the irregularity of the P_g coordinates precluded drawing a line through more than three of the points, and two had to be neglected. The three points chosen were those with the most well-defined P_g . This yielded a T_g of 68°C . If the P_g from the 164°C , 148°C , and 135°C isotherms had been used, the plot would have been nearly identical with that for the 14.4 Mrad sample.

The magnitude of the compressibility of this system was not affected by radiation up to 25 Mrads as no observable difference was noted in the 22°C and 185°C isotherm after irradiation. The pressure-induced glass transition displayed quite noticeable changes after irradiation and appeared to vary from a straight line function.

EPON 828 and DEAPA. This aliphatic amine cured system was more susceptible to changes due to irradiation than the previous systems, according to the electrical

resistivity measurements. Warfield⁽³⁰⁾ had previously attempted a study of the compressibility of this polymer but the anomalous results obtained from a non-irradiated sample led to abandonment of the work.

The initial series of isotherms, shown in Fig. 15, indicate that this system exhibits little temperature dependence of the compressibility over the temperature range 25°C to 203°C. Between 25°C and 203°C, the magnitude of the compressibility increased from 10.2 per cent to 11.2 per cent at 8,000 atmospheres. Three of the isotherms, 203°C, 178°C, and 161°C (not shown) exhibited pressure-induced glass transition. A phase diagram for this system was prepared and is shown in Fig. 18. The data were not satisfactory for plotting a phase diagram using the points from the isotherms just mentioned, and a dotted line is shown to indicate the curve described by these points.

The compressibility of the sample exposed to 7.2 Mrads was then measured. Only three of the isotherms generated exhibited any P_g , and these were almost identical with the non-irradiated sample. An attempt to construct a phase diagram of this sample proved futile. The values of the P_g from the isotherms, 205°C at 2,300 atmospheres, 190°C at 2,500, and 178°C at 2,400, are shown with a dotted line to indicate an apparent curve.

A sample exposed to an irradiation of 12.3 Mrads was then measured. The isotherms had an observable P_g as follows: 214°C at 2,520 atmospheres, 206°C at 2,460, 193°C at 2,300, 178°C at 2,110, and 163°C at 1,750. A phase diagram was also plotted for this sample, but again the curve produced was difficult to interpret. This is shown in Fig. 18.

A sample, irradiated to 25 Mrads, was not measured due to unavailability of the Baldwin-Southwark test apparatus. For the non-irradiated sample, the magnitude of the compressibility increased from 10.1 per cent to 11 per cent at 8,000 atmospheres between 25°C and 203°C.

This polymer, EPON 828 and DEAPA, yielded compressibility test results which are anomalous and difficult to interpret. There was no order to the phase diagram either before or after irradiation, and it can only be concluded that interpretation of the results must await an extensive study of the compressibility of the system.

In all the measurements made, the polymers exhibited a non-linear pressure dependence with the polymer becoming less compressible at the higher pressures. The mechanism of the compressibility of polymers is not clear. It would seem logical that the highly crosslinked polymers, such as used in this investigation, would exhibit less compressibility than would the linear polymers. However, Warfield⁽²⁸⁾ has

found no significant difference between linear and cross-linked polymers at a given temperature and pressure. His results indicated that efficient packing, i.e., crystallinity, appears more important in determining the magnitude of the compressibility than the type of polymeric bonding. While there is no unanimous agreement on the nature of the compressibility, it appears that at pressures below 10,000 atmospheres the compressibility results from the "squeezing out" of free volume, defects, or holes in the polymer and is temperature dependent. At pressures greater than this, another phenomenon, the shortening of the equilibrium positions of the molecules, is predominant. (28)

C. Hardness Measurement. The hardness of the polymers studied was either increased or decreased after irradiation, depending upon the curing agent used. Each polymer investigated, and the effects of radiation on its hardness, is discussed below and shown in Fig. 19.

EPON 828 and MPDA. The hardness of this polymer system was relatively unaffected by radiation dosage up to 14 Mrads. At room temperature, and in non-irradiated condition, this polymer had a hardness of 108 on the Rockwell "M" scale. After an irradiation of 2.5 Mrads, the hardness had dropped somewhat to 106, and after 7.2 Mrads to 104. After

14.4 Mrads, the hardness was 106.

These variations are within the experimental error and the total decrease, 108 to 104, is not significant.

EPON 828 and Curing Agent D. As was expected from an aromatic amine cured polymer, this system also proved relatively unaffected by radiation up to 25 Mrads. At room temperature the non-irradiated sample was the hardest of the three polymers tested, having a Rockwell "M" hardness of 110. Irradiated samples were measured for hardness after 7.2 Mrads, 14.4 Mrads, and 25 Mrads. The hardness noted was, respectively, 108, 108 and 107. As with the MPDA cured system, it appeared that the hardness decreased with radiation dose; but the slight decrease could certainly be attributed to experimental technique.

EPON 828 and DEAPA. It was expected that this aliphatic amine cured system would display the greatest variation in hardness as, from both the experimental work described previously and literature cited, the aliphatic cured polymers were considered to be more susceptible to radiation. However, it too, proved relatively unaffected by 25 Mrads. At room temperature, and non-irradiated, the Rockwell "M" hardness was 96. After 7.2 Mrads, the hardness was 98; after 12.3 Mrads, 97; and after 25 Mrads, 99. The

slight variation seems to indicate an increase in hardness.

The results of the hardness measurements appear to be different than would be expected from the work of Colichman and Strong⁽¹⁰⁾ who investigated the hardness, heat distortion temperature, and compressive strength of nine different epoxide compositions after gamma irradiation up to 10^8 roentgens. They stated that hardness properties varied the greatest amount of the properties studied and could be used as a measure of radiation resistance. However, the only polymer studied by Colichman and Strong, which was the same as was used in this investigation, was EPON 828 and MPDA. This they stated was the most stable system studied and the hardness exhibited little or no change after irradiation. Curing Agent D, being aromatic, could be expected to have a similar resistance. DEAPA cured EPON 828 was not studied by these investigators; but another system, EPON 828 with an aliphatic reactive diluent, allyl glycidyl ether, and methylene dianiline, was used and gave increased hardness after irradiation. The increased hardness was explained as being due to the methylene groups forming rigid cross links between polymer chains. The increase noted in the DEAPA system cannot be due to the same action.

Based on the hardness measurements, the use of this property to measure the radiation resistance up to 25 Mrads

of the three polymers studied is not promising.

D. Specific Volume. The specific volume, v_s , was measured for each of the three polymers after varying irradiations up to 25 Mrads. Licht and Kline⁽⁹⁾ observed that the specific volume of polytetrafluoroethylene decreased with increasing dose up to 100 Mrads. It was the intention of this investigation to study the effect of irradiation on the specific volume of epoxide polymers at doses up to 25 Mrads.

EPON 828 and MPDA. The variation of specific volume with irradiation for this polymer is shown in Fig. 20. After 2.5 Mrads, v_s showed no observable change. Further irradiation of 11 Mrads caused a decrease in specific volume from .825 to .821 cm³/g. The final irradiation, 14.4 Mrads, produced an additional decrease to .818 cm³/g. The decrease in v_s , while slight, is also constant for this polymer.

EPON 828 and Curing Agent D. This polymer also exhibited a decrease in specific volume with radiation. Initially, it had a v_s slightly greater than the MPDA cured epoxide, but after 7.2 Mrads, it was slightly less. After 14.4 Mrads, the v_s for the two polymers, MPDA cured and

D cured, is essentially the same and the rate of decrease for this polymer has leveled off. Additional irradiation to 25 Mrads did not appreciably decrease the v_s further.

EPON 828 and DEAPA. This system had the highest specific volume initially; but after 2.5 Mrads, the v_s value had decreased from .847 to .819 cm^3/g . After irradiation to 7.2 Mrads, the v_s decreased further to .811 cm^3/g . No appreciable change was noted after 11 Mrads; and after 25 Mrads, the v_s was 0.805 cm^3/g .

The above results were in accordance with the previous experiments and the literature cited. That is, the aliphatic amine cured polymer exhibits greater change than the aromatic. However, the specific volume was expected to decrease for all polymers and the EPON 828 and MPDA polymer showed very slight change. According to Licht and Kline,⁽⁹⁾ the specific volume appears to be primarily dependent upon three factors: average molecular weight, per cent crystallinity, and void content. As these parameters can be expected to vary from sample to sample depending upon sample fabrication, the v_s can be expected to vary.

The epoxides studied are not crystalline and the void content can reasonably be expected to vary indiscriminately between samples. The consistent decrease in specific volume

could probably be due to chain scission in the polymer when irradiated in the presence of oxygen.⁽⁹⁾ This would have to be confirmed by further investigations.

VI

CONCLUSIONS

Based on these investigations, it appears that the electrical volume resistivity is a more sensitive parameter to detect changes due to nuclear reactor radiation than are the other properties: bulk compressibility, hardness, and specific volume.

The validity of the use of electrical resistivity measurement to describe changes in a polymer system caused by external forces has also been proven experimentally by the investigators referenced earlier. A theoretical corroboration that the electrical conduction process is ionic in nature and adheres to Ohm's Law is contained in a paper by Barker and Thomas.⁽³¹⁾ Although no literature was found concerning any previous measurements of the electrical resistivity of crosslinked polymers after irradiation, Ieda et al.⁽³²⁾ investigated this property for crystalline polyethylene.

The results of the electrical resistivity investigation before and after irradiation suggest an initial increase in crosslinking as evidenced by the initial

increased resistivity. Radiation induced crosslinking has also been noted by Kline and Sauer⁽³⁴⁾ with polyethylene terephthalate, and Charlesby⁽⁴⁾ on many polymers. Additional irradiation appears to degrade the polymer, especially at the lower temperature region. Warfield⁽³⁵⁾ noted a similar decrease of the electrical resistivity at the lower temperature during thermal degradation studies. As both reactor radiation and heat are forms of radiation, the effect upon the polymer could be similar.

The magnitude of the compressibility does not appear to be sensitive to radiation for the dose range investigated. The pressure versus per cent change in volume curves did not evidence any appreciable change due to radiation, and the phase diagrams were all rather inconclusive. The pressure-induced glass transition temperature decreased with increased radiation but also showed considerable disorder, especially in the DEAPA cured sample. Much more basic work will be needed in this field before the results from the phase diagrams can be correlated.

However, the results for the phase diagrams may not be as inconclusive as they appear. Eisenberg⁽²⁴⁾ has shown that the pressure-induced glass transition of a solid composed of two species can exhibit non-linear behavior. After irradiation, it is conceivable that the structure of the

polymer is so changed that it behaves as two different species of the same material. The non-linear phase diagrams, after irradiation, could be due to this phenomenon.

The hardness measurements did not show any significant indication of change due to radiation up to 25 Mrads. Hardness is a surface phenomenon and will probably not show any definite change until mechanical degradation of the polymer begins. The damage threshold for the mechanical properties of epoxide polymers is about 9.5×10^8 rads, according to Battelle Memorial Institute findings. (12)

Results of the specific volume investigations indicate a decrease in the specific volume with increasing radiation dose. However, some polymer systems display a greater percentage decrease than others.

VII

RECOMMENDATIONS FOR FURTHER STUDY

It is recommended that further study be given to the following problem areas associated with this investigation:

1. An investigation should be undertaken of the rate of energy deposition in various polymers due to nuclear reactor radiation. Techniques similar to those employed by Jacobs and Kline⁽¹⁸⁾ could serve as basis for this work.
2. A systematic study should be made of various polymers (i.e., crosslinked as well as crystalline) to determine the effect of radiation on their temperature dependence of electrical resistivity. Radiation damage can be induced using flux levels available with the UMR, and irradiations should be considered up to 1,000 Mrads.
3. The study of the compressibility of crosslinked polymers should be broadened to include other polymer systems and the interpretation of the phase diagrams should be explored.

4. The specific volume of various polymers should be investigated as a function of temperature and irradiation. This should enable a glass transition temperature to be determined which could be compared to that obtained from the electrical resistivity measurements.
5. An investigation should be undertaken to determine other properties of polymers which might indicate changes due to radiation. Electrical properties should include a.c. resistivities and dielectric strength. Mechanical properties should include investigations of tensile strength⁽³⁶⁾ and behavior at extremely low pressures and temperatures.

TABLE 1

Properties of Epoxide Monomer

Melting point	Liquid
Color (25°C)	Amber (12 Gardner)
Viscosity at 28°C, centipoise	10-20,000
Average molecular weight	340-400
Epoxide equivalent	175-210
Hydroxyl equivalent	85
Density, lbs/gallon	9.7

TABLE 2
University of Maryland Reactor (UMR) Characteristics

Normal Operating Power Level	10 kw
Thermal Neutron Flux, maximum	2.5×10^{11} n/cm ² -sec.
Thermal Neutron Flux, Core Face	1.0×10^{11} n/cm ² -sec.
Epithermal Neutron Flux, average	4.4×10^{10} n/cm ² -sec. (20)
Fast Neutron Flux, maximum	3.5×10^{11} n/cm ² -sec.
Fast Neutron Flux, average	1.5×10^{11} n/cm ² -sec.
Critical Mass U-235	2.7 kg of U ²³⁵
Cooling System	
coolant flow rate	15 gpm
heat removal capacity	34,150 BTU/hr
Core Geometry	An array of 19 fuel elements in roughly a square, reflected on most of three sides by canned graphite reflector pieces, and on fourth side by the thermal column.
Fuel Elements	
type	flat plate, 16 g (± 0.2 g) enriched Uranium
composition	Uranium-Aluminum alloy
enrichment in U-235	93.5%
number of elements in core	Thirteen 10 plate, three 6 plate (E-4, E-6, C-7), one 5 plate containing "glory hole" (D-6), one 4 plate on front side of core (B-4), one 9 plate near "glory hole" (C-4)
Moderator and Coolant	Demineralized water
Control	One regulating and two shim-safety rods

TABLE 3

Electrical Resistivity Data

Specimen - EPON 828 and MPDA

Condition - Irradiated 2.5 Mrads

Date - 4 Nov. 1964

T ^{°F}	T ^{°C}	$\frac{10^3}{\sigma_K}$	V _B	I	E	R	A/L	ohm-cm
390	199	2.12	45	$.8 \times 10^{-7}$	44.2	55.2×10^7	16	8.8×10^9
385	196	2.13	45	$.5 \times 10^{-7}$	44.5	89.0×10^7	16	1.4×10^{10}
380	193	2.14	45	5.0×10^{-8}	40	9.0×10^8	16	1.5×10^{10}
377	192	2.15	45	4.4×10^{-8}	40.6	10.1×10^8	16	1.6×10^{10}
374	190	2.16	45	3.8×10^{-8}	41.2	12.2×10^8	16	1.9×10^{10}
371	188	2.17	45	3.2×10^{-8}	41.8	14.6×10^8	16	2.3×10^{10}
369	187	2.17	45	2.8×10^{-8}	42.2	16.9×10^8	16	2.7×10^{10}
363	184	2.19	45	2.2×10^{-8}	42.8	21.7×10^8	16	3.5×10^{10}
359	182	2.20	45	1.7×10^{-8}	43.3	25.5×10^8	16	4.1×10^{10}
353	178	2.21	45	1.2×10^{-8}	43.8	36.5×10^8	16	5.8×10^{10}

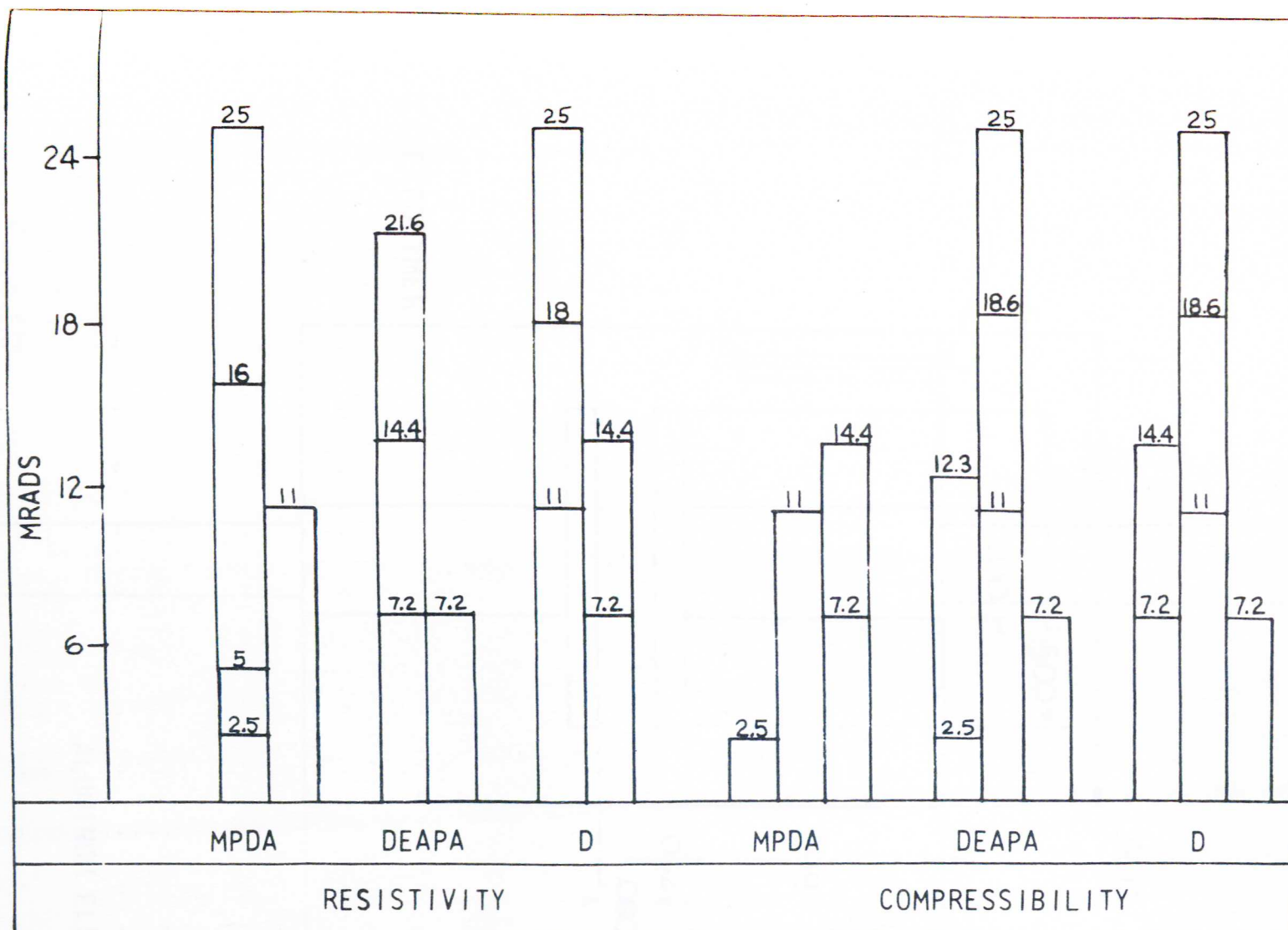
TABLE 3 (continued)

$T^{\circ}\text{F}$	$T^{\circ}\text{C}$	$\frac{103}{^{\circ}\text{K}}$	V_B	I	E	R	A/L	ohm-cm
348	176	2.23	45	$.9 \times 10^{-8}$	44.1	49.0×10^8	16	7.8×10^{10}
341	172	2.25	45	6.0×10^{-9}	39	6.5×10^9	16	1.0×10^{11}
335	168	2.27	45	3.8×10^{-9}	41.2	10.8×10^9	16	1.7×10^{11}
329	165	2.28	45	2.4×10^{-9}	42.6	17.7×10^9	16	2.8×10^{11}
321	161	2.30	45	1.5×10^{-9}	43.5	29.0×10^9	16	4.6×10^{11}
315	157	2.33	45	1.0×10^{-9}	44	44.0×10^9	16	7.0×10^{11}
312	156	2.33	45	6.4×10^{-10}	38.6	6.0×10^{10}	16	$.9 \times 10^{12}$
307	153	2.35	45	5.2×10^{-10}	39.8	7.7×10^{10}	16	1.2×10^{12}
303	151	2.36	45	4.2×10^{-10}	40.8	9.7×10^{10}	16	1.5×10^{12}
300	149	2.37	45	3.8×10^{-10}	41.2	10.8×10^{10}	16	1.7×10^{12}
287	142	2.41	45	2.0×10^{-10}	43	21.5×10^{10}	16	3.4×10^{12}
282	139	2.43	45	1.6×10^{-10}	43.4	27.1×10^{10}	16	4.3×10^{12}
276	136	2.44	45	1.1×10^{-10}	43.9	39.9×10^{10}	16	6.0×10^{12}

TABLE 3 (continued)

$T^{\circ}\text{F}$	$T^{\circ}\text{C}$	$\frac{103}{^{\circ}\text{K}}$	V_B	I	E	R	A/L	ohm-cm
271	133	2.46	45	1.0×10^{-10}	44	40.0×10^{10}	16	6.4×10^{12}
264	129	2.49	45	$.5 \times 10^{-10}$	44.5	89.0×10^{10}	16	1.4×10^{13}
252	122	2.53	45	3.5×10^{-11}	41.5	11.8×10^{11}	16	1.9×10^{13}
246	119	2.55	45	2.6×10^{-11}	42.4	16.3×10^{11}	16	2.6×10^{13}
240	116	2.57	45	2.0×10^{-11}	43	21.5×10^{11}	16	3.4×10^{13}
230	110	2.61	45	1.0×10^{-11}	44	44.0×10^{11}	16	7.0×10^{13}
222	106	2.64	45	$.5 \times 10^{-11}$	44.5	44.5×10^{11}	16	7.1×10^{13}
205	96	2.71	45	2.8×10^{-12}	42.2	15.0×10^{12}	16	2.4×10^{14}
200	93	2.73	45	2×10^{-12}	43	21.5×10^{12}	16	3.4×10^{14}
195	91	2.75	45	1.4×10^{-12}	43.6	31.1×10^{12}	16	4.9×10^{14}
190	88	2.77	45	1.2×10^{-12}	43.8	36.0×10^{12}	16	5.8×10^{14}
183	84	2.80	45	$.5 \times 10^{-12}$	44.5	89.0×10^{12}	16	1.4×10^{15}

TABLE 4
IRRADIATION HISTORY



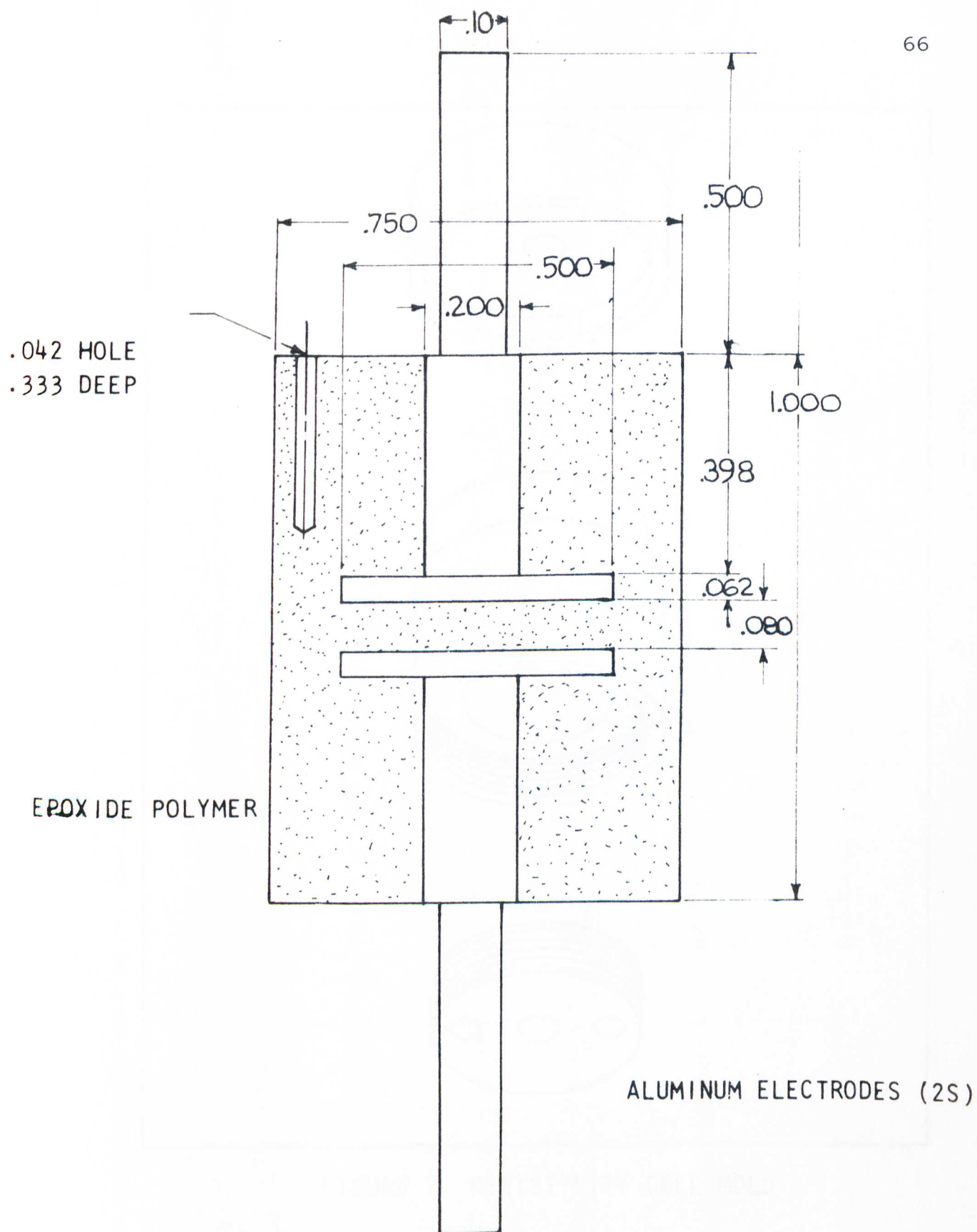


FIGURE 1 - RESISTIVITY CELL

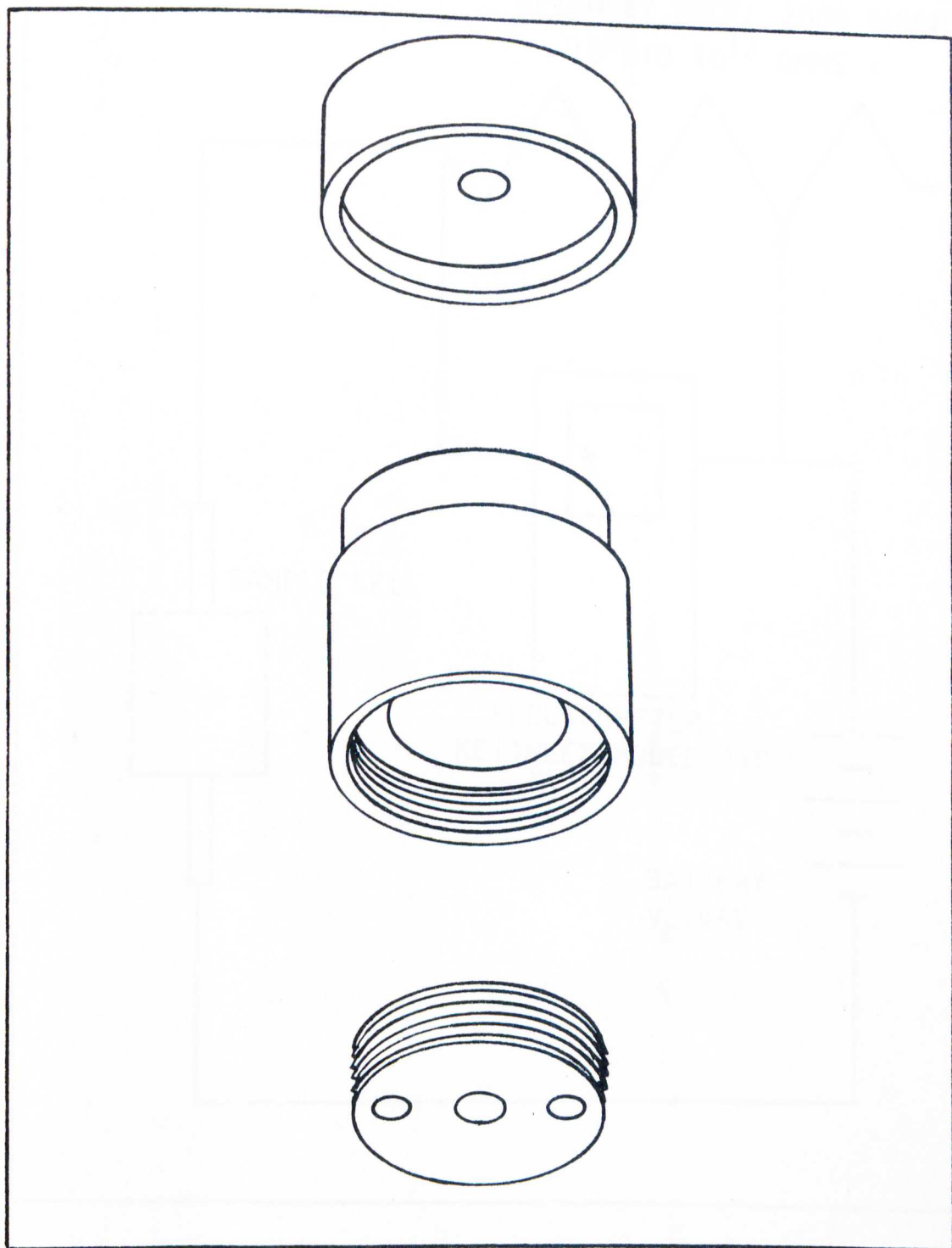


FIGURE 2 RESISTIVITY CELL MOLD

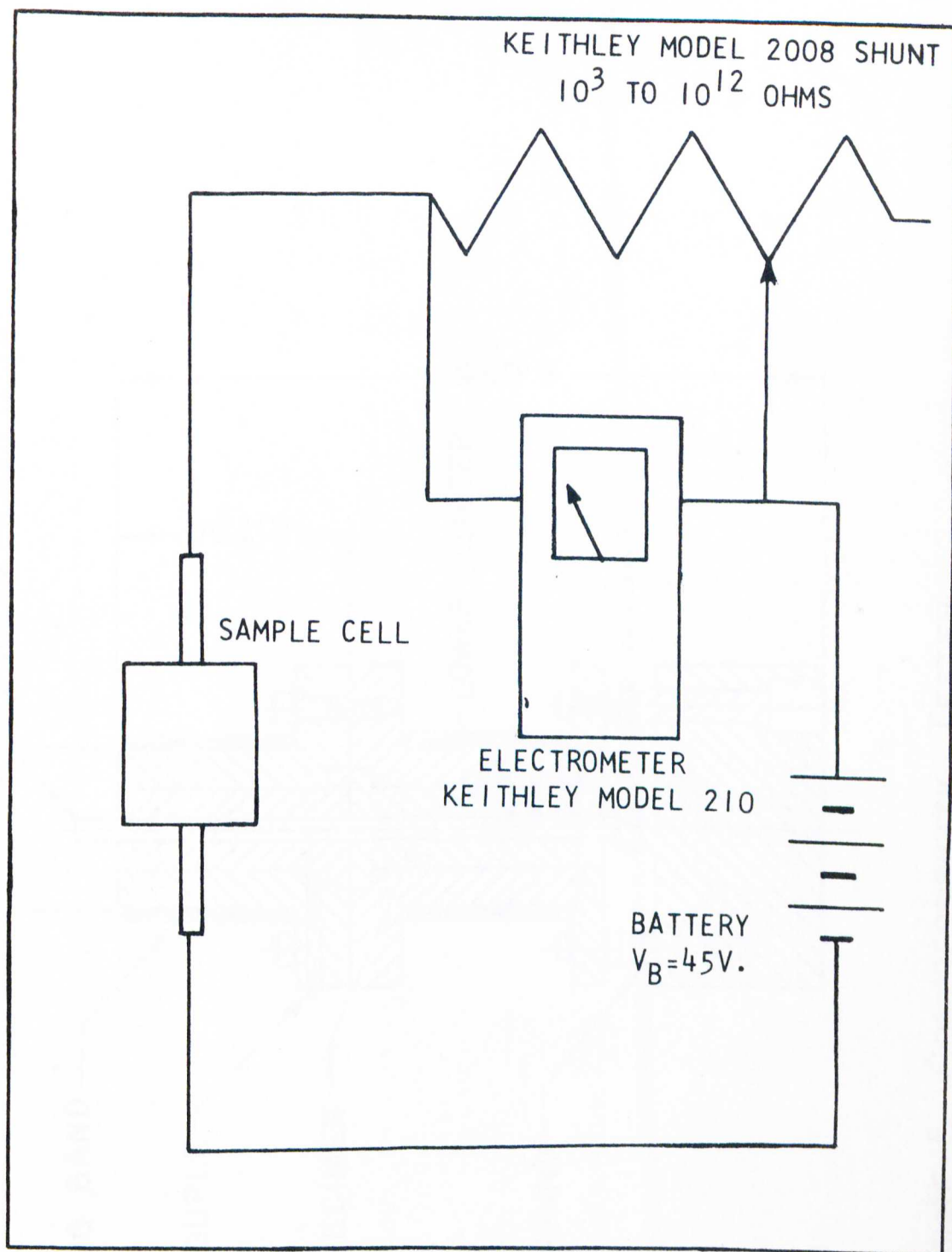


FIG. 3. ELECTRICAL CIRCUIT - RESISTIVITY

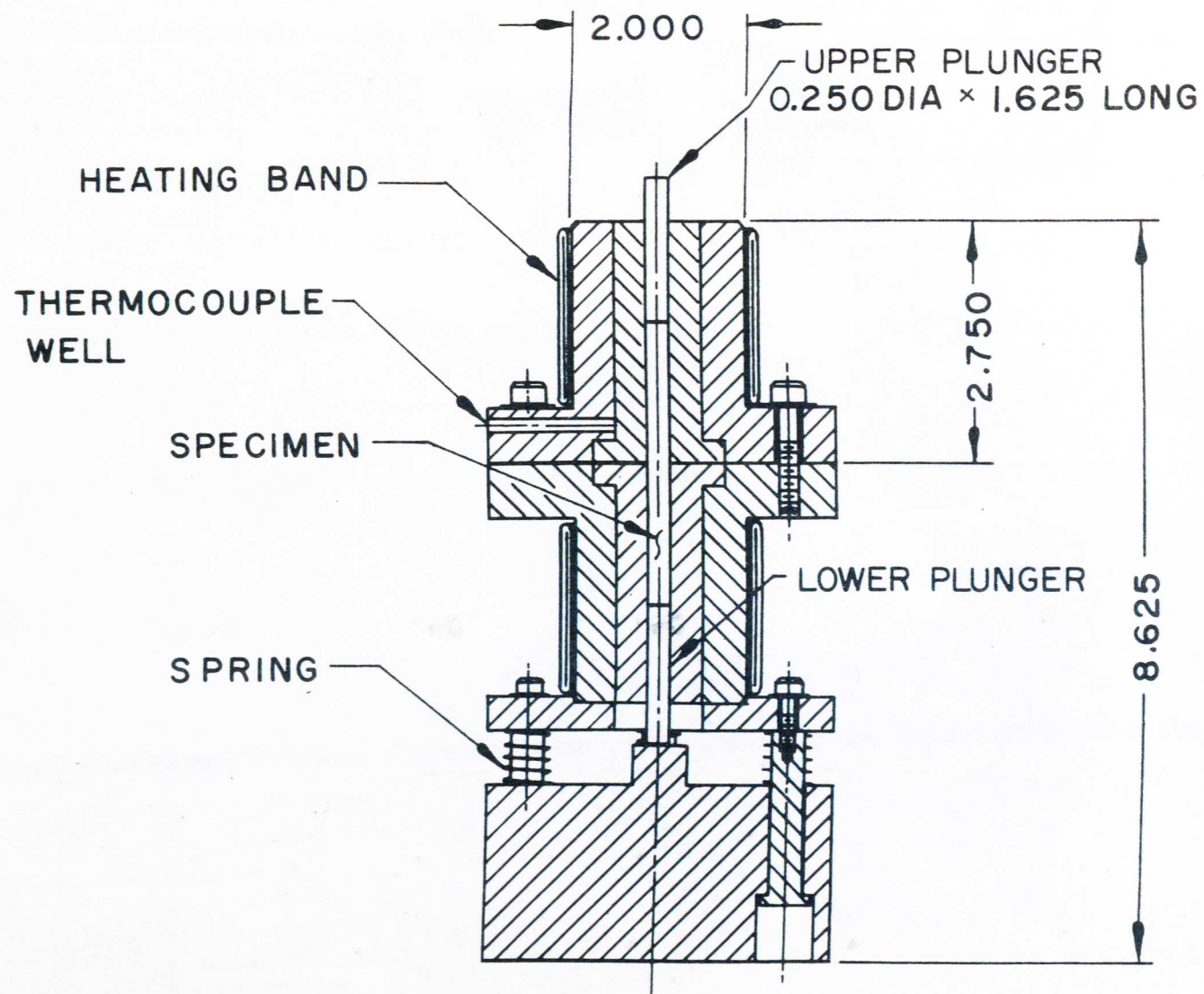


FIGURE 5. COMPRESSIBILITY TESTER

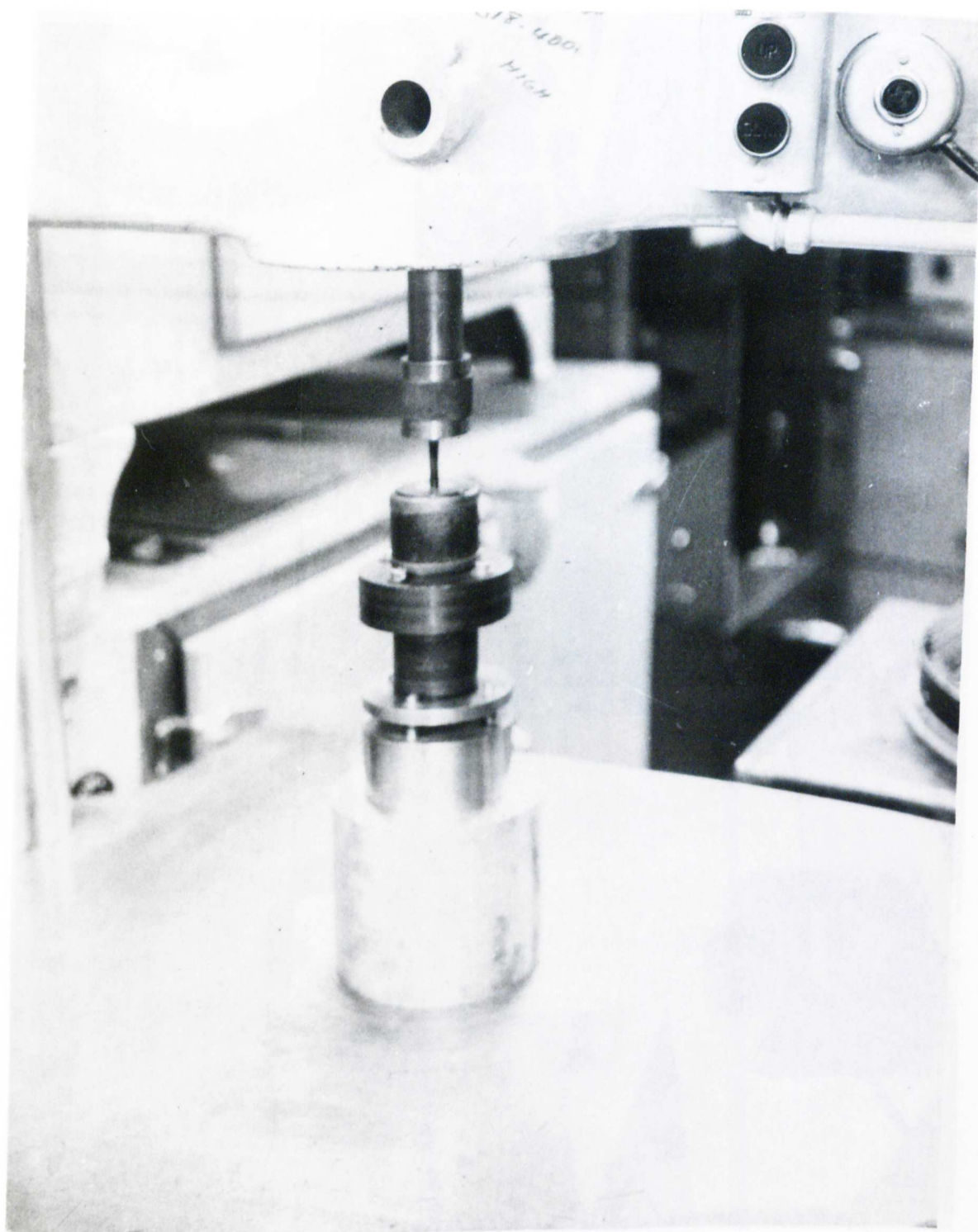


FIG. 6. COMPRESSIBILITY TESTER ON TEST MACHINE

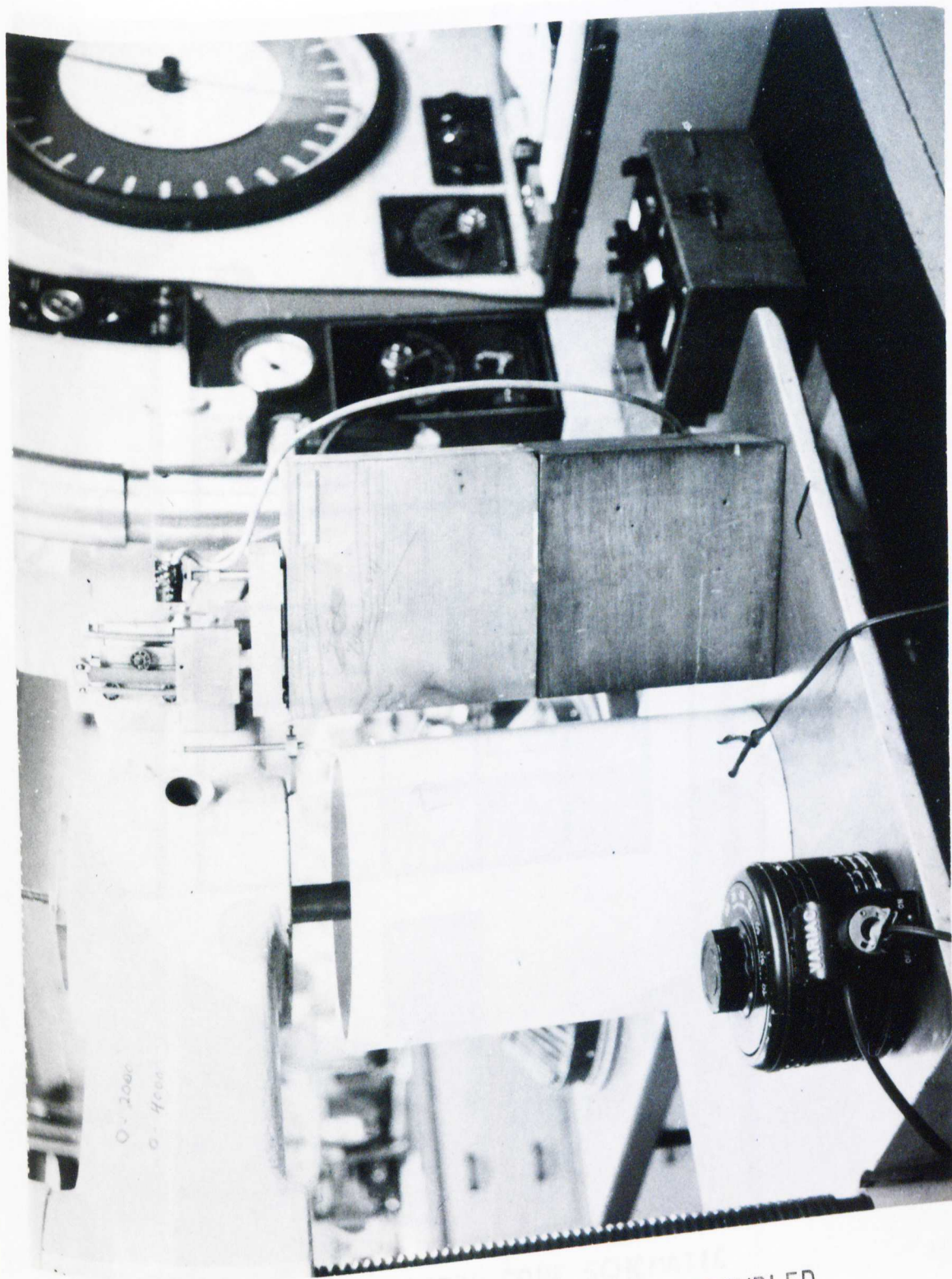


FIG. 7. COMPRESSIBILITY EQUIPMENT ASSEMBLED

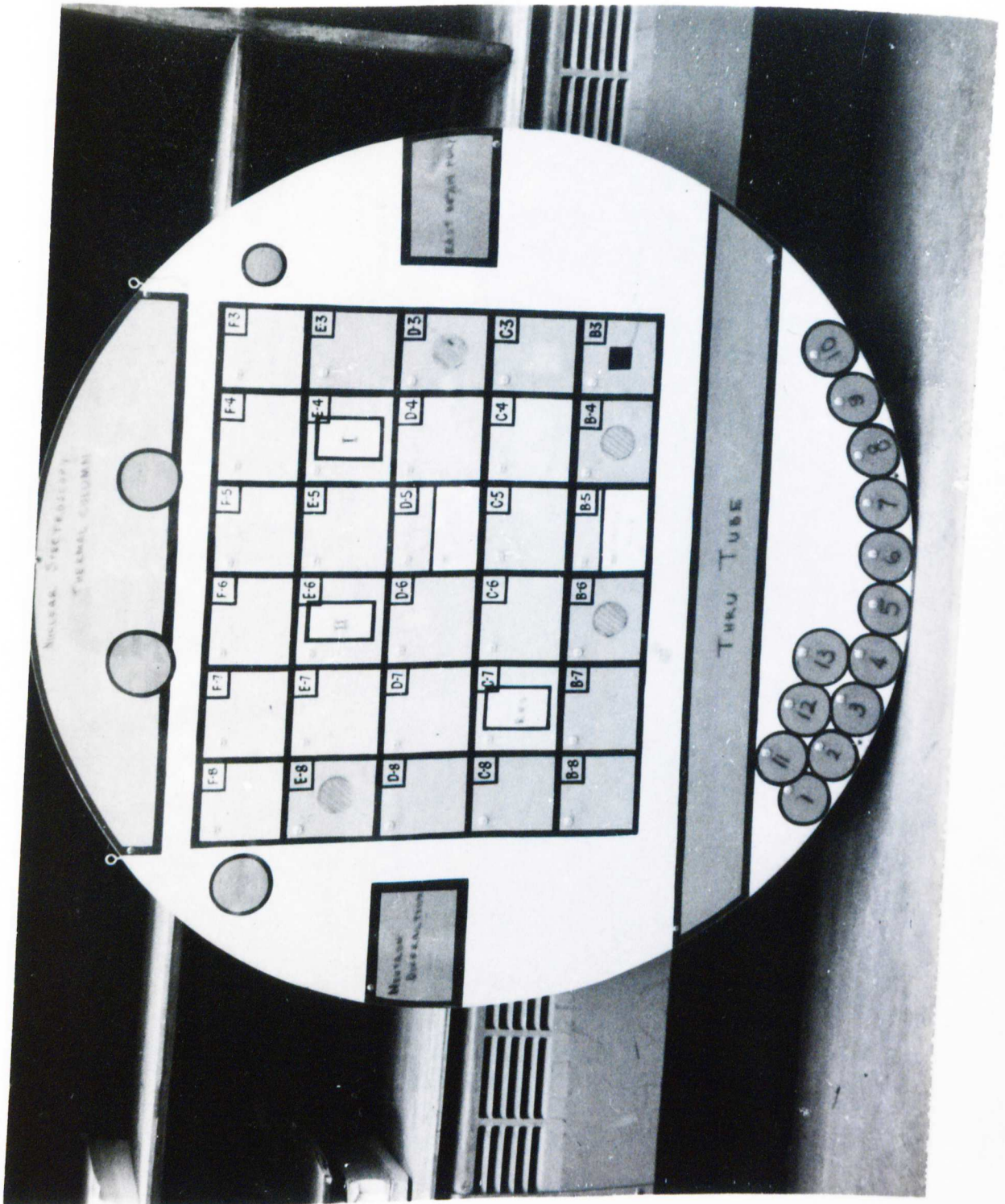


FIG. 8. REACTOR CORE SCHEMATIC

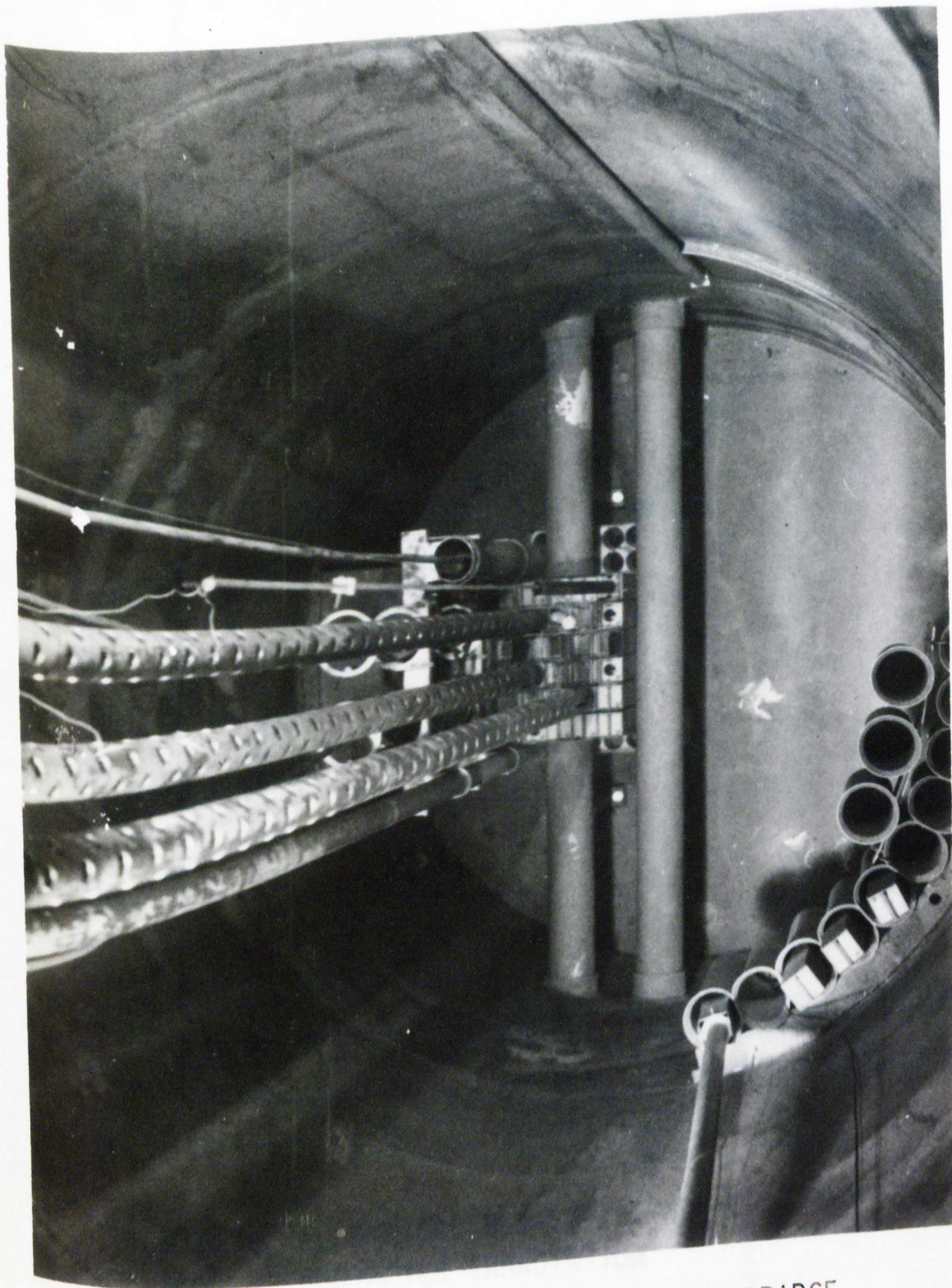


FIG. 9. NUCLEAR REACTOR CORE VIEWED FROM BRIDGE

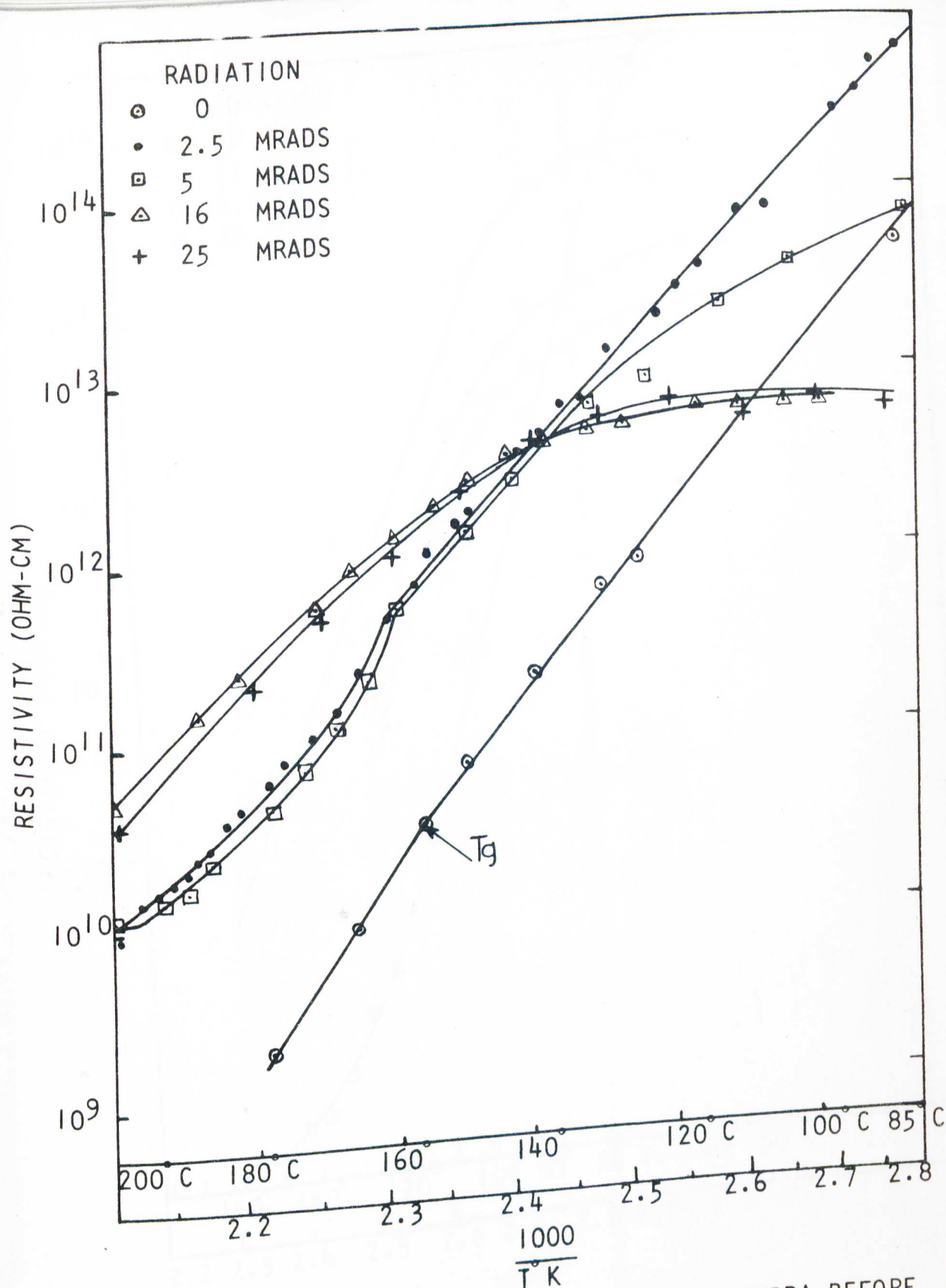


FIG. 10. ELECTRICAL RESISTIVITY OF EPON 828+MPDA BEFORE AND AFTER IRRADIATION

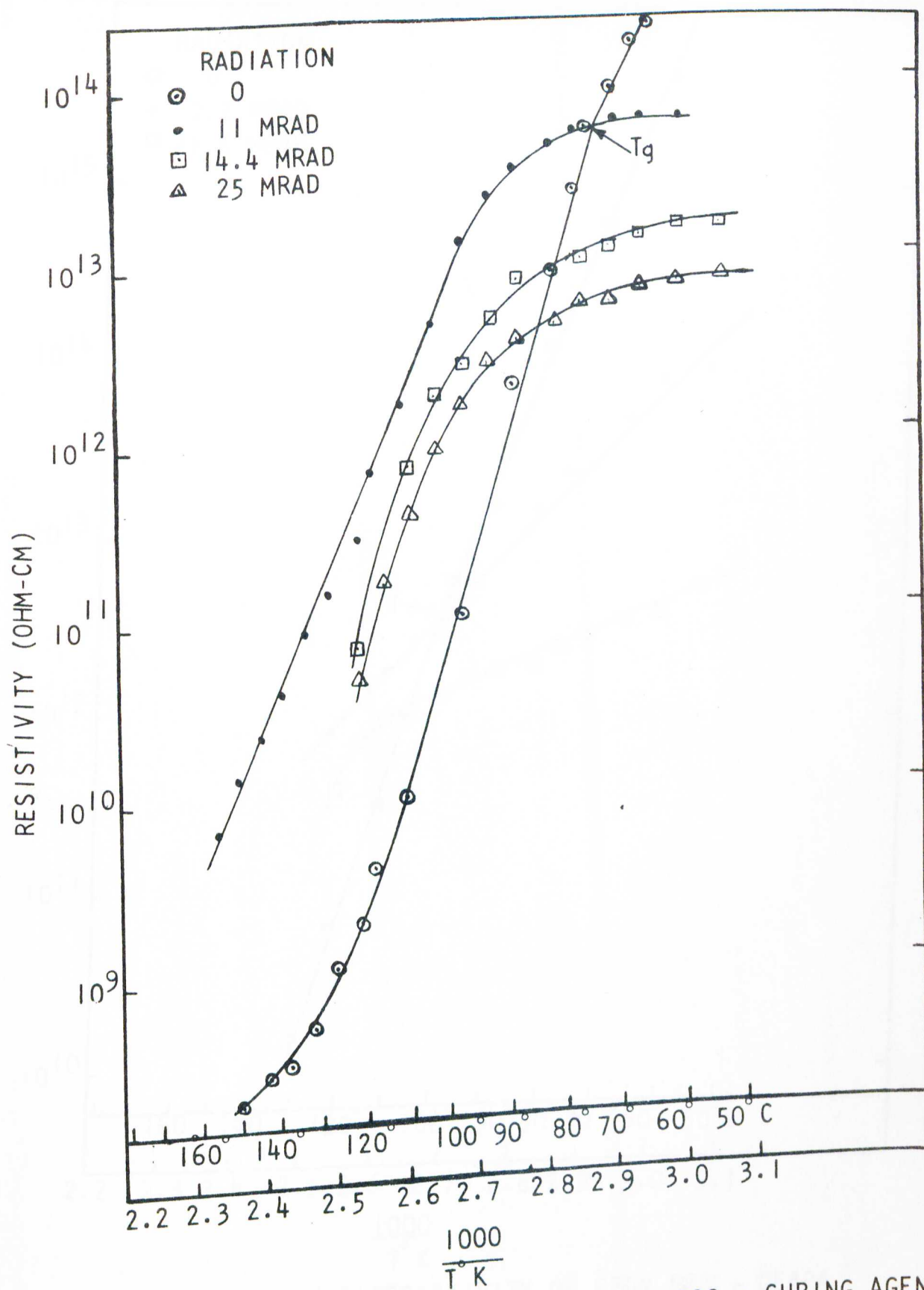


FIG. 12. ELECTRICAL RESISTIVITY OF EPON 828 + CURING AGENT D BEFORE AND AFTER IRRADIATION

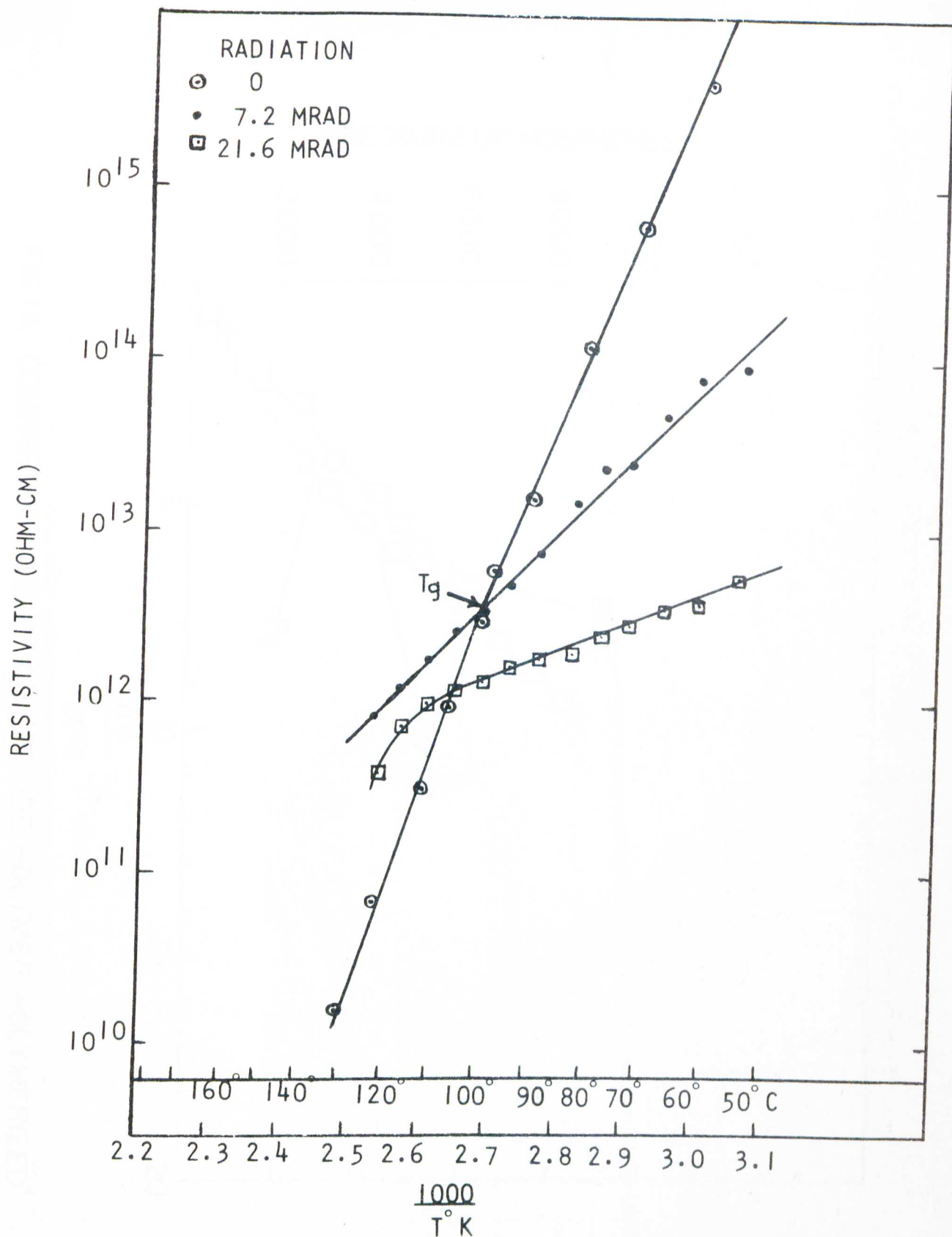


FIG. 12. ELECTRICAL RESISTIVITY OF EPON 828 + DEAPA BEFORE AND AFTER IRRADIATION

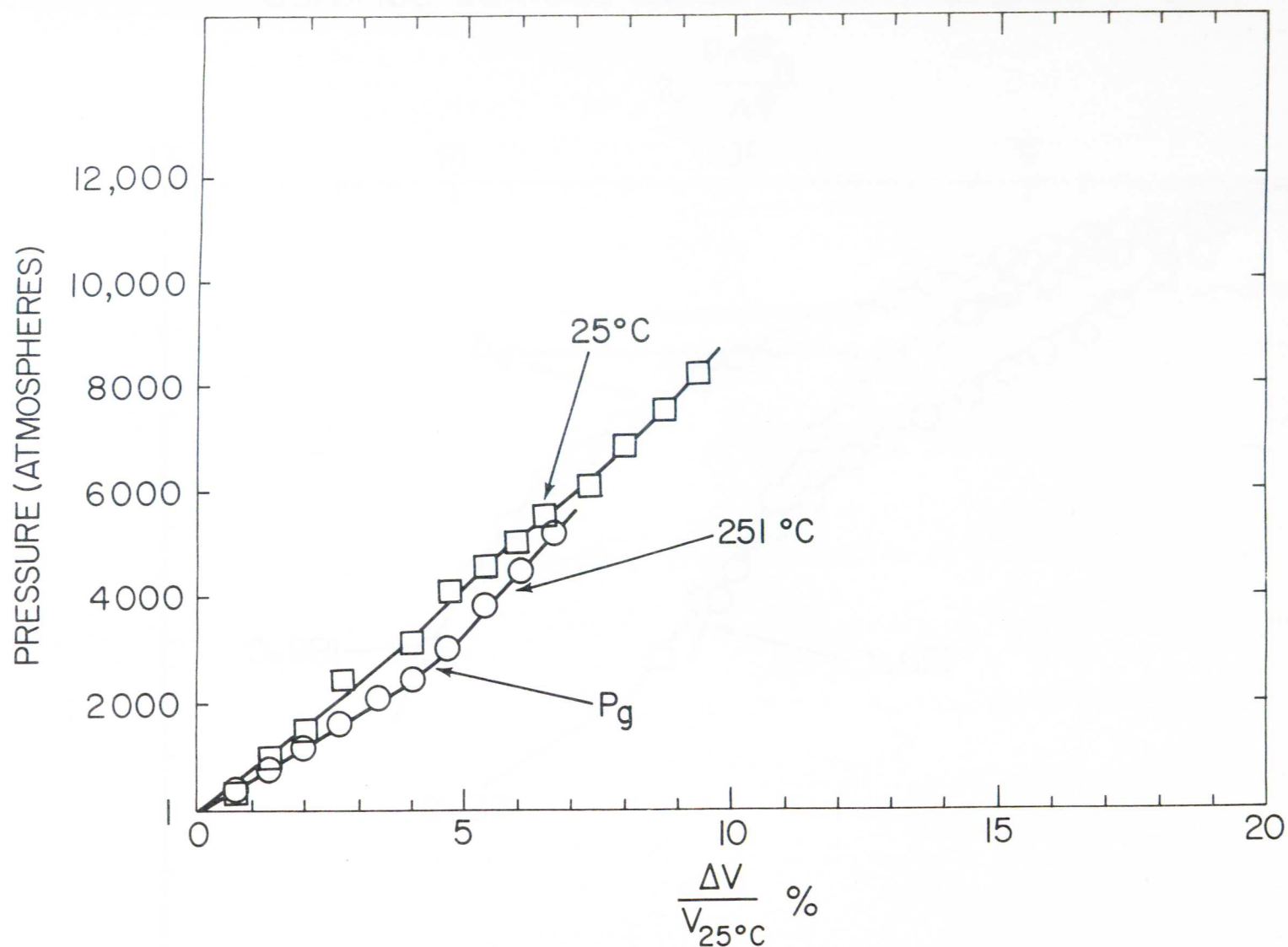


FIG.13. COMPRESSIBILITY OF AN EPOXIDE POLYMER POLYMERIZED WITH *m*-PHENYLENE DIAMINE

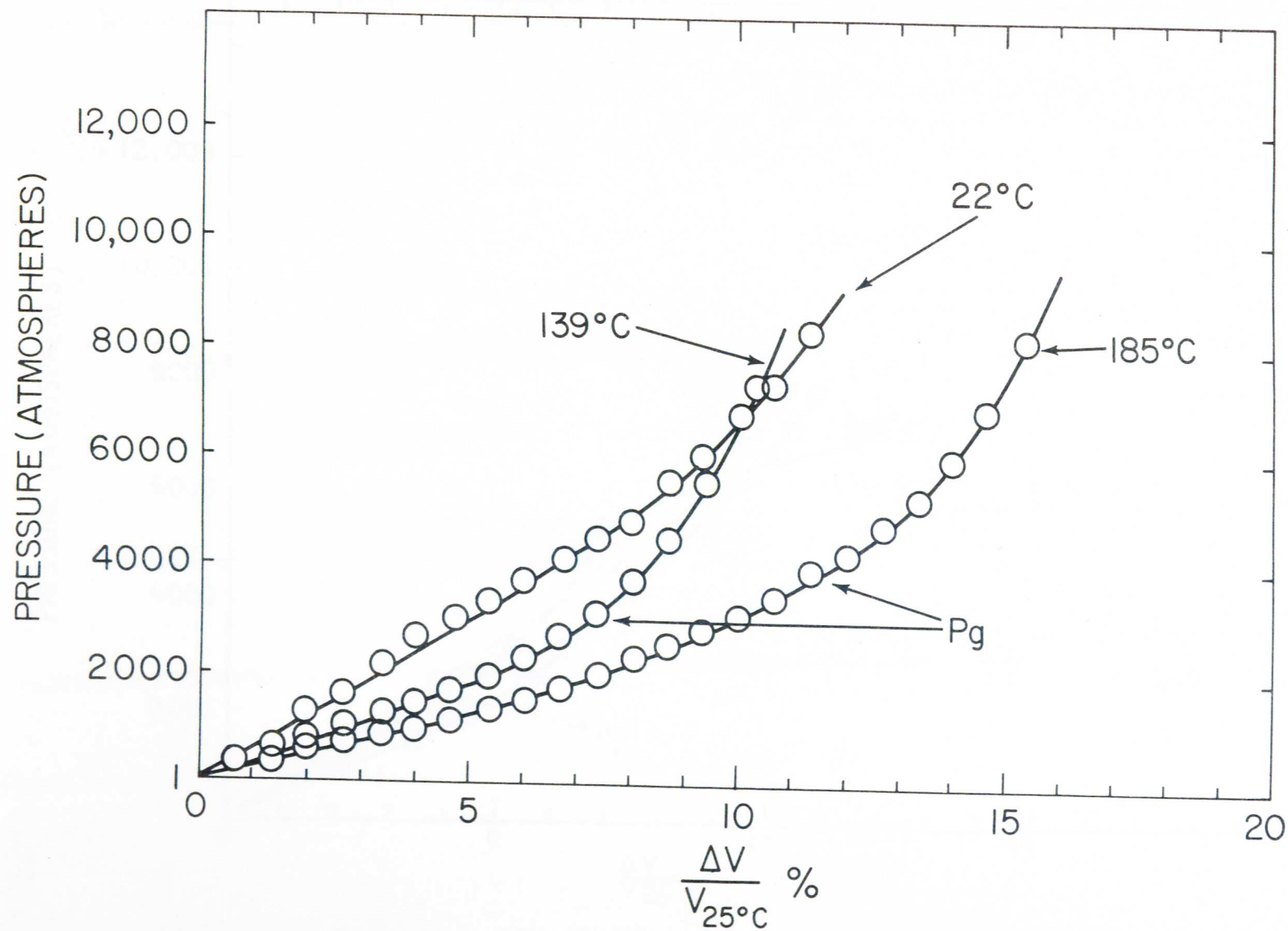


FIG.14 COMPRESSIBILITY OF AN EPOXIDE POLYMER WITH HARDENER D.

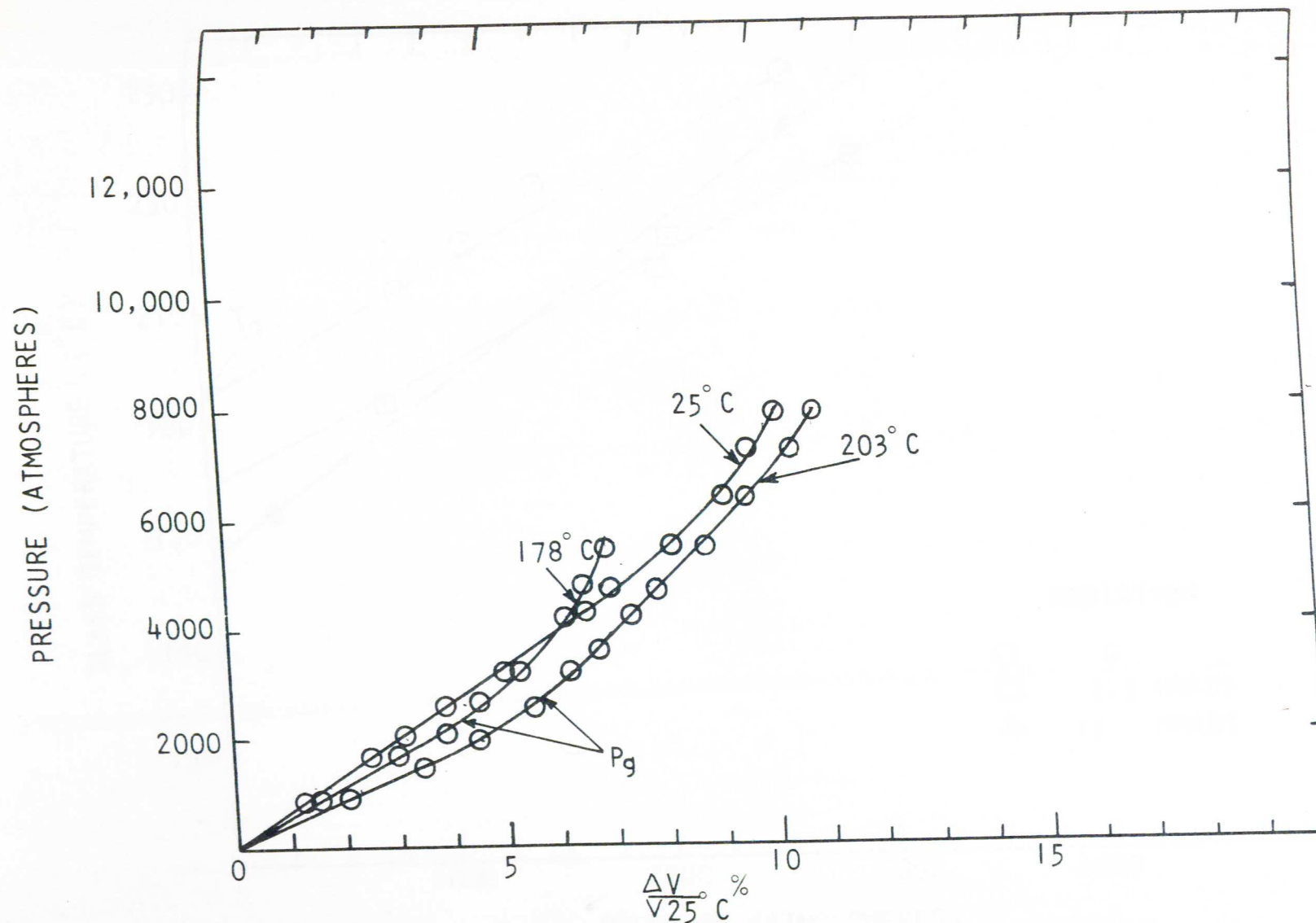


FIG. 15. COMPRESSIBILITY OF AN EPOXIDE POLYMER
POLYMERIZED WITH DEAPA

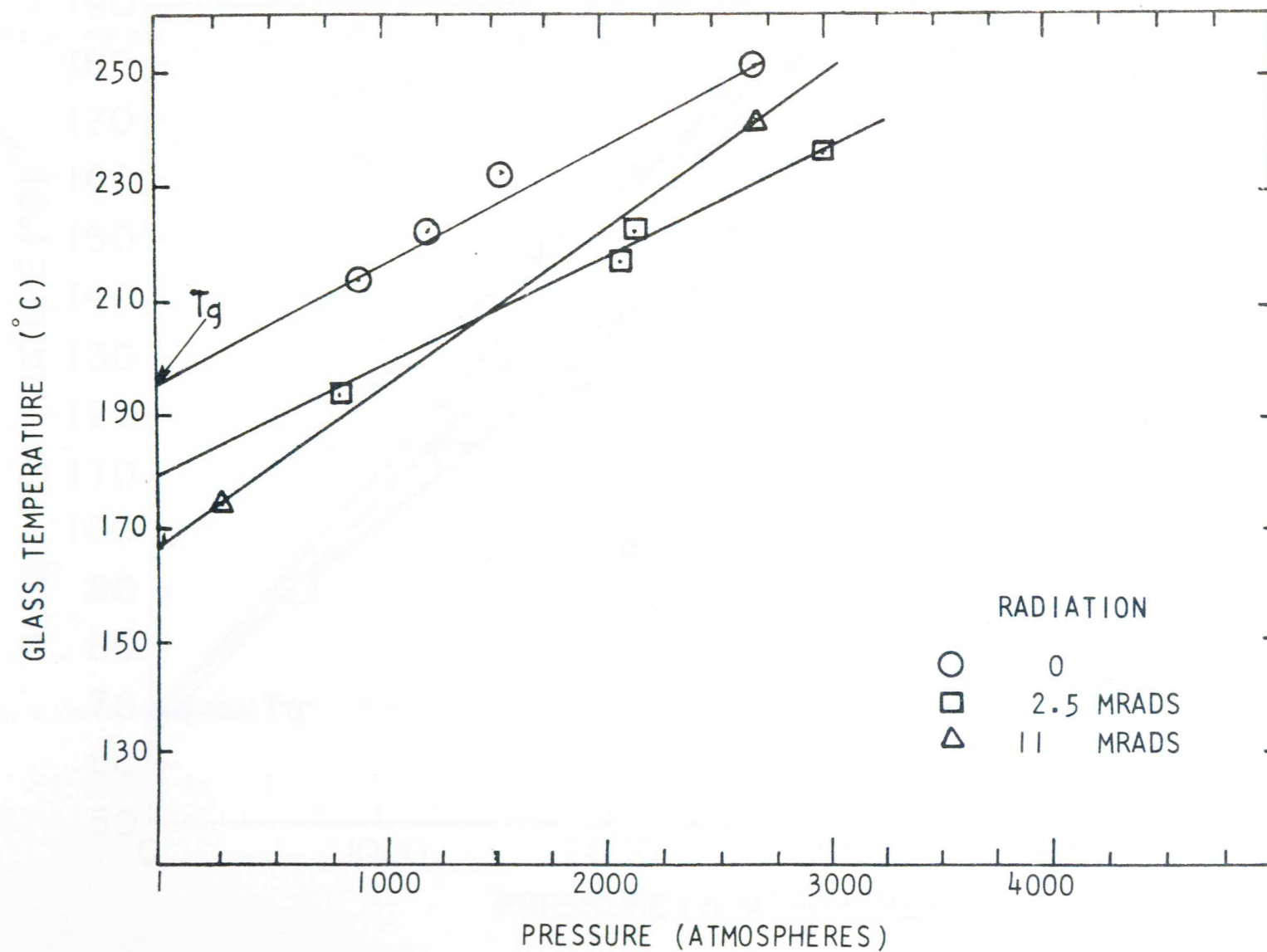


FIG. 16. PHASE DIAGRAM FOR EPON 828 + MPDA

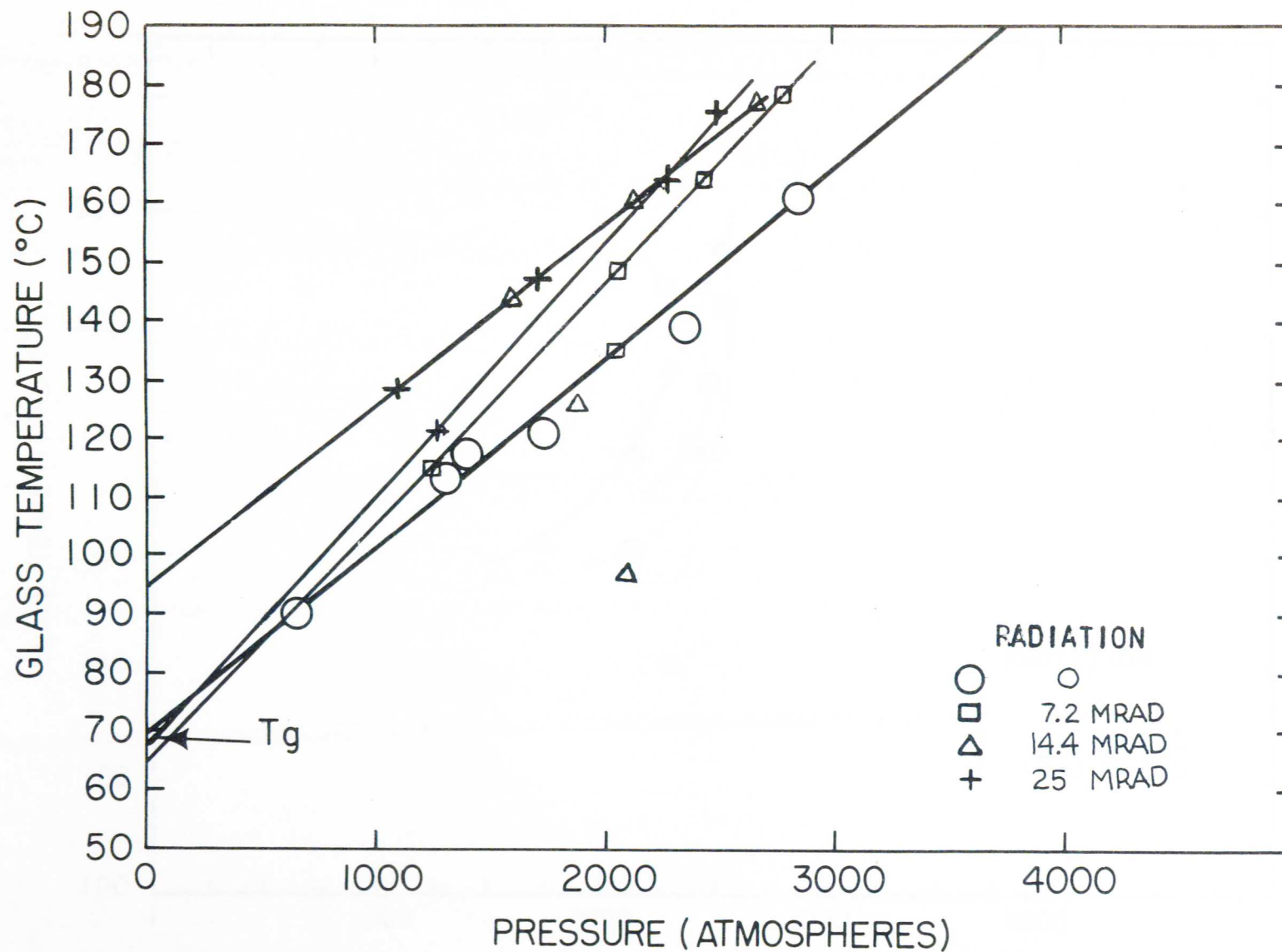


FIG.17. VARIATION OF GLASS TEMPERATURE
WITH PRESSURE FOR EPON 828 + D

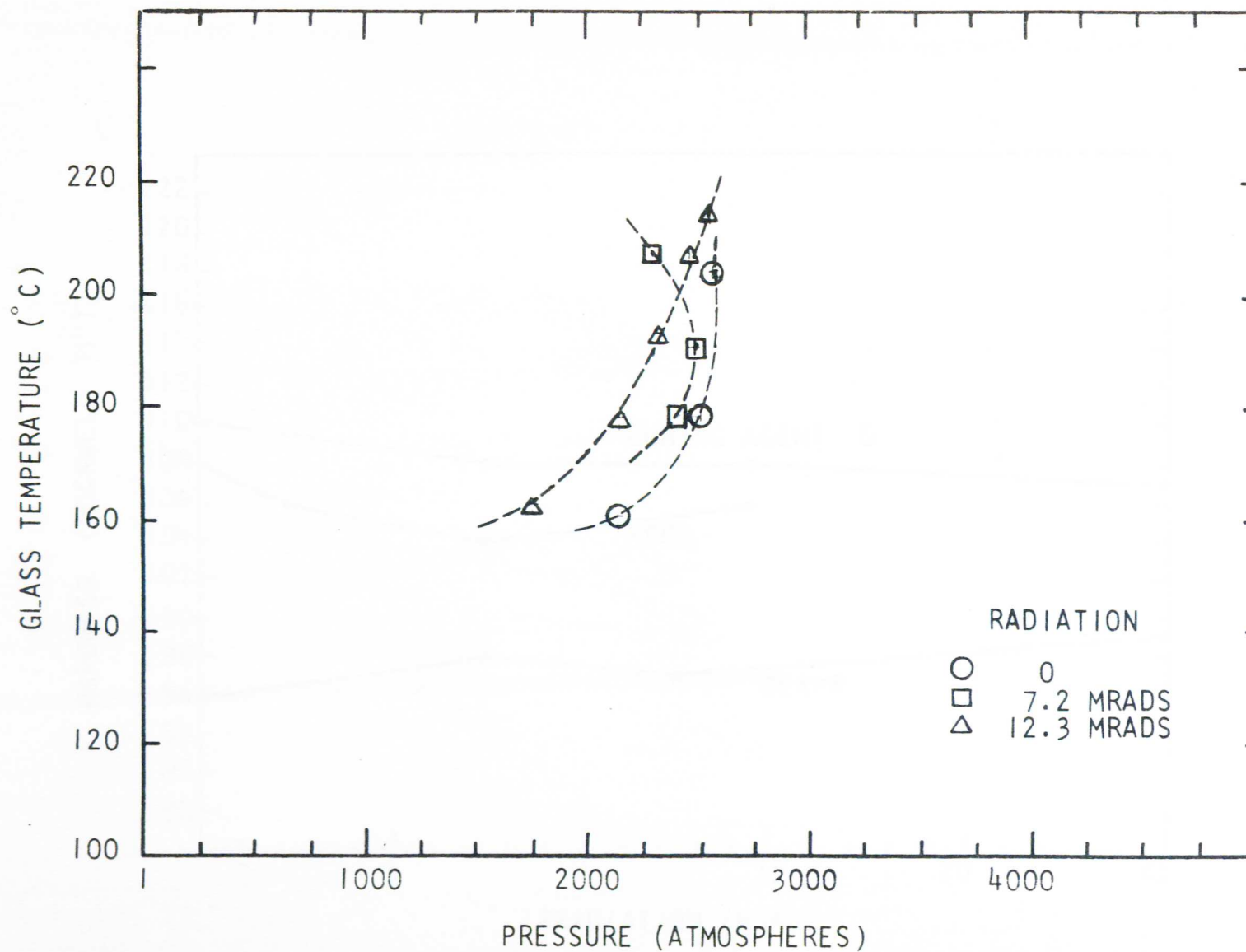


FIG. 18. PHASE DIAGRAM FOR EPON 828 + DEAPA

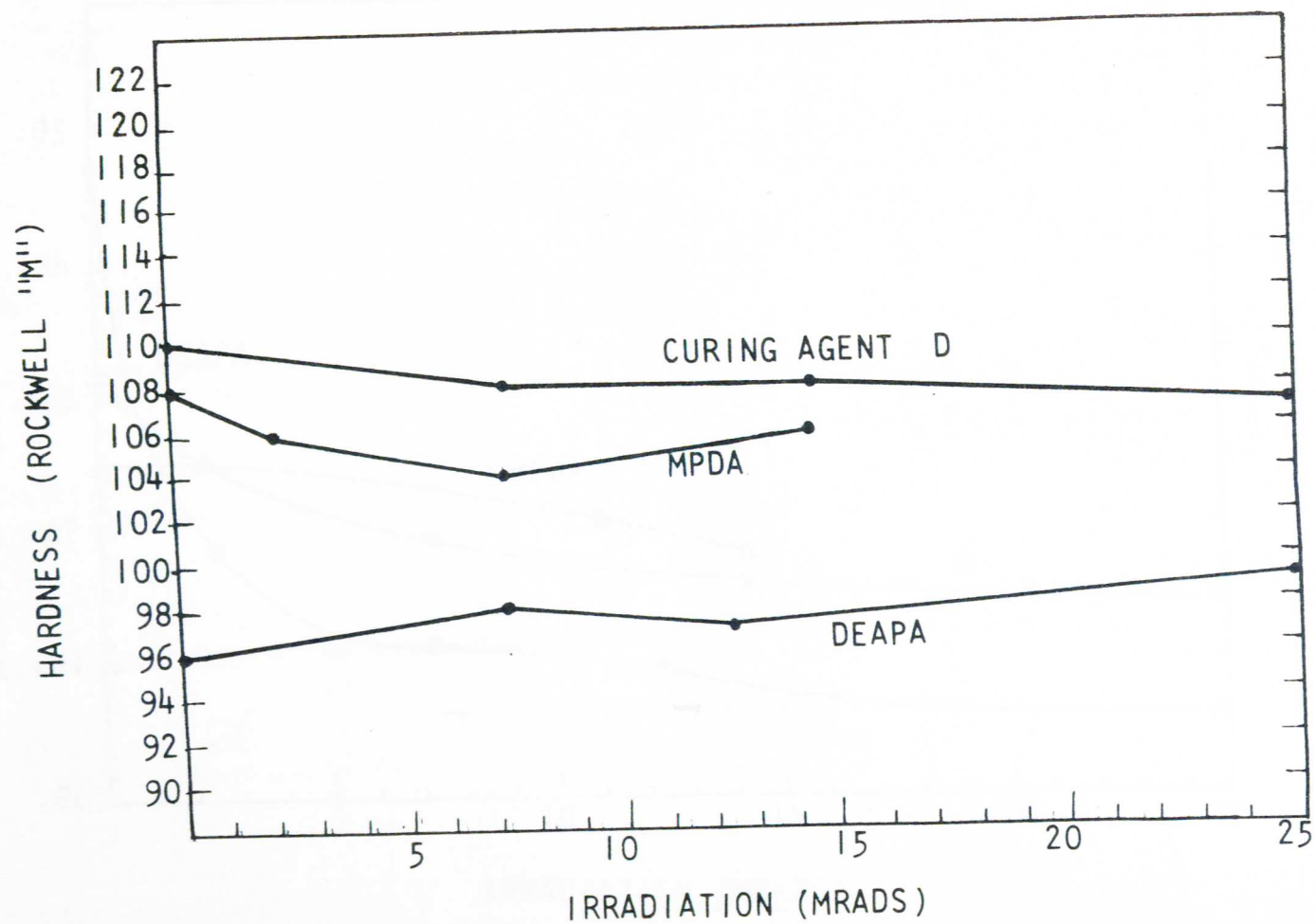


FIG. 19. HARDNESS VS. IRRADIATION FOR EPOXIDE POLYMERS

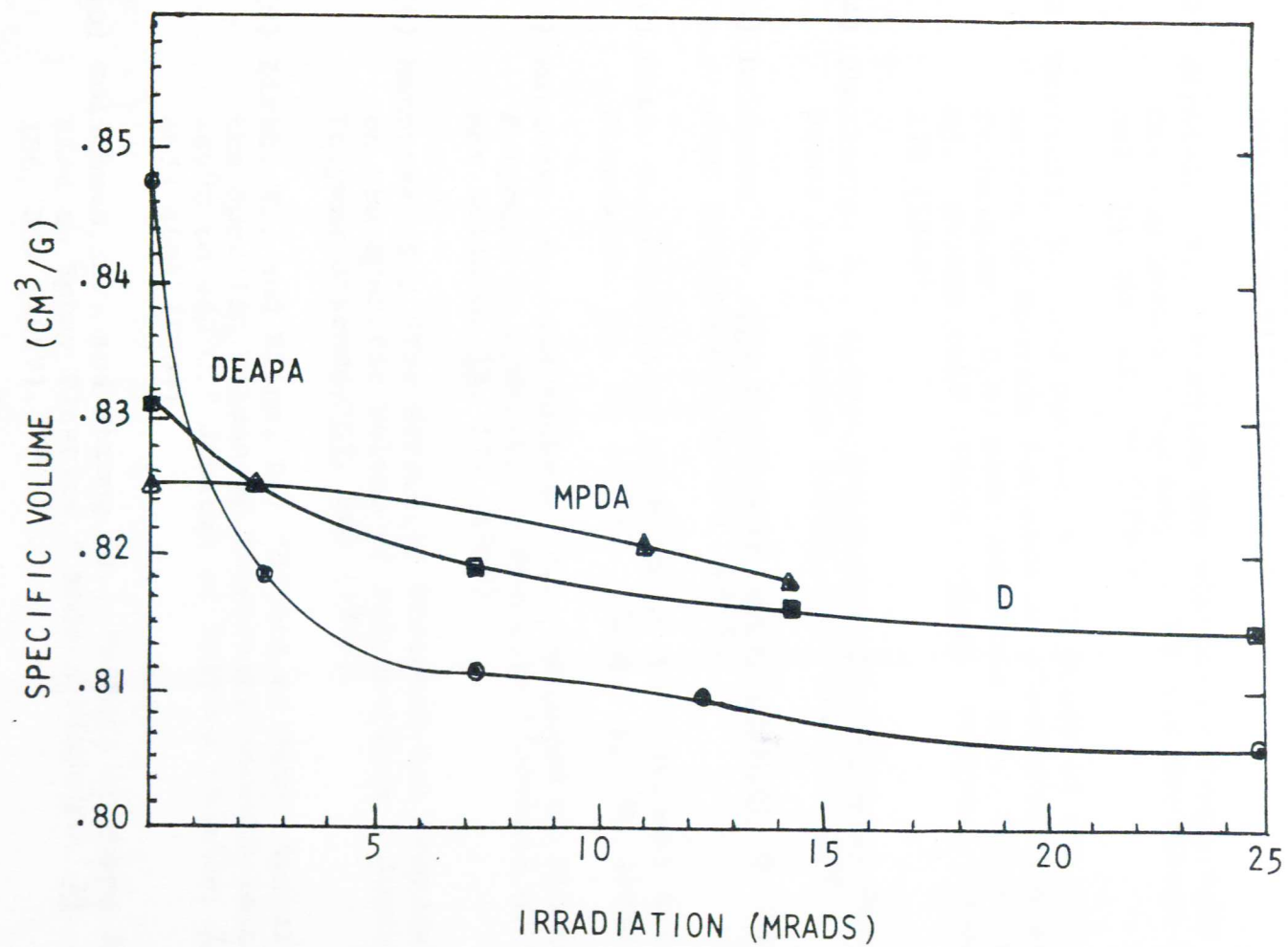


FIG. 20. SPECIFIC VOLUME VS. IRRADIATION FOR EPOXIDE POLYMERS

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Place of Birth: Silver Spring, Maryland.

Degrees and Date of Completion: B.S., 1953

Date of Birth: January 11, 1930

Place of Birth: Silver Spring, Maryland.

Secondary Education: Baltimore Polytechnic Institute
Baltimore, Maryland
June 1949

College Institution	Dates	Degree	Date of Degree
University of Maryland	1953-1957	B.S.	1957
University of Maryland	1957-1958	M.S.	1958

Major: Nuclear Engineering.

Minor: Physics.

Positions held: Mechanical Engineer
U.S. Naval Ordnance Laboratory
White Oak, Maryland
1955-1962

Physical Science Coordinator
U.S. Naval Ordnance Laboratory
U.S. Ordnance
London, England
1962-1964.

General Engineer
U.S. Naval Ordnance Laboratory
White Oak, Maryland
1964-Present.