# ACTION OF IONIZING RADIATION ON EPOXY RESINS*

(Sects. 3-6 of CERN report 70-10 by M. E. Van de Voorde, Geneva 1970)

## 3. ACTION OF IONIZING RADIATION ON EPOXY RESINS

### 3.1 Current state of knowledge of effects of radiation on epoxy resins

At present there is much interest in the effects of nuclear radiation on the physical properties of reticulated resins. Relatively few studies have been published in this field. For example, in his work on the basis of radiation effects on polymers, Charlesby [59] devoted only a brief chapter to the reticulated polymers and did not even mention the polyepoxide systems.

In general, the literature is lacking in publications on the effects of radiation on the polyepoxide systems. The first publications on modifications undergone by epoxide resins exposed to radiation date from 1957 [60, 61]. They are observations made by the builders of atomic piles [62] and accelerators [63-68] who had to choose between materials that were resistant and non-resistant to the radiation from reactors, accelerators, or related installations. However, most often, these reports make no important contributions to our basic knowledge on the subject. Several years passed before more systematic studies appeared [69-74], but until now no basic research on structural variations in the molecules of epoxide resins seem to have been made.

In the following pages we propose hypotheses on the mechanism of degradation of certain irradiated epoxide resins and attempt to establish a relation between chemical structure and physical properties of irradiated epoxy resins.

### 3.2 Effect of nuclear radiation on organic materials

We may classify the different types of nuclear radiation into three categories: (1) charged particles, (2) neutral particles, and (3) electromagnetic radiation. The interactions caused by the radiations differ in detail, but the effect of all is ionization and excitation of the organic molecules [75-77].

The ionization is caused by loss of an electron when the molecule collides with a high-energy particle:

$$RX \xrightarrow{\sim\sim} \underset{\text{cation}}{RX^+} + \underset{\text{high-energy electron}}{e^-} \qquad (3.1)$$

The symbol $\xrightarrow{\sim\sim}$ indicates the change which follows the irradiation. To obtain this reaction, 12 to 15 eV is necessary.

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*Translated from the French by Martha Gerrard, Office of Language Services, Oak Ridge National Laboratory, Oak Ridge, Tenn.

In the case of excitation, an electron receives energy by collision and goes into a higher-energy orbit,

$$RX \longrightarrow RX^* \text{ (excited molecule)} \qquad (3.2)$$

The high-energy electrons produced by ionization collide with other molecules until their energy is consumed. The thermal electron will then be absorbed by an ion,

$$RX^+ + e^- \text{ (thermal electron)} \longrightarrow RX^* \text{ (excited molecule)} \qquad (3.3)$$

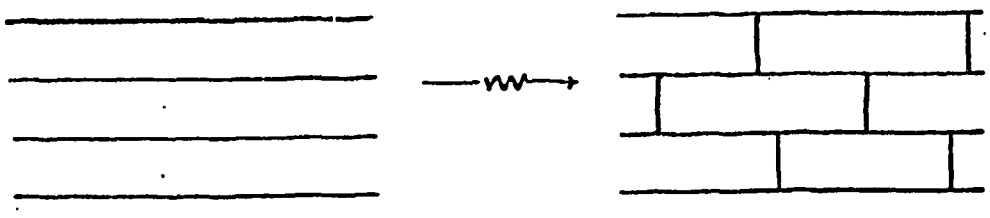
The energy imparted to the molecule RX* is equal to the energy necessary to ionize it. The excited molecule RX* produced either in reaction 3.3 or directly in reaction 3.2 is brought to an energy state sufficient to rupture one or more homopolar bonds in the molecule network, causing formation of free radicals,

$$R^* \longrightarrow R\cdot + X\cdot \qquad (3.4)$$

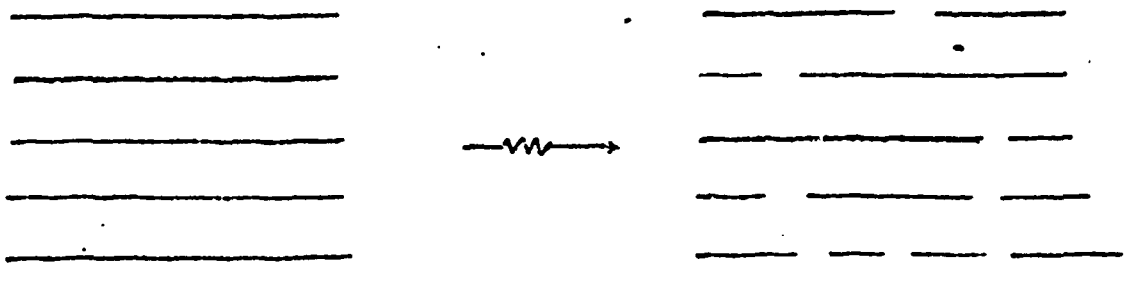
(free radicals)

These free radicals are very active and can react among themselves or with surrounding molecules, causing irreversible chemical modifications.

We observe in general that the irradiation causes a reticulation or a degradation. The reticulation is the formation of new transversal bonds between the polymer molecules. They are manifested by an increase in the average molecular weight, resistance to traction, hardness, etc., and a decrease in the rupture elongation, elasticity, etc. This reaction may be shown schematically,



Degradation, on the other hand, is a rupture of the primary bonds of the polymer chain. It is manifested by a decrease in average molecular weight, and may be shown schematically,

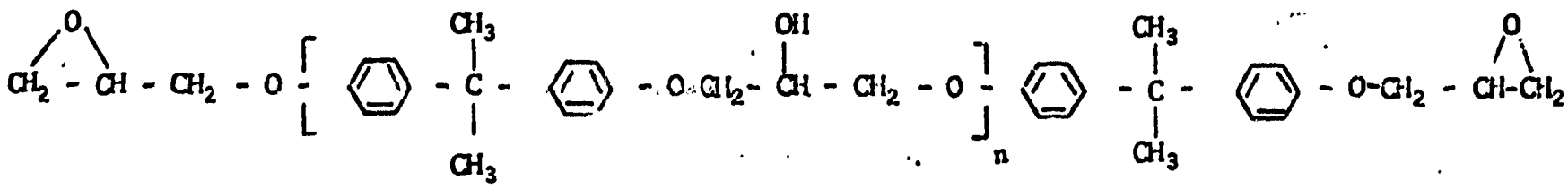


When a polymer is exposed to radiation, reticulations and degradations go on simultaneously and concurrently, but in general one or the other predominates and determines the changes in mechanical, electrical, and physical properties of the product [78].

## 3.3 Effect of nuclear radiation on epoxy resins

### 3.3.1 Non-hardened epoxy resins

We have studied the changes in molecular structure that occur in epoxy resins exposed to ionizing radiation. The studies were made on synthetic epoxy resins with an epichlorhydrin and diphenolpropane base. The resin DGEBA is a liquid at ambient temperature and has an epoxy equivalent between 180 and 190. The resin DGEBA/B is solid at ambient temperature and has an epoxy equivalent of 370-400. The structure of resins of this type is indicated by the scheme



where $n \approx 0$ for the liquid (DGBA) and $> 1$ for the solid (DGBA/B).

#### 3.3.1.1 Experimental study

The crude products were purified by distillation in toluene, followed by precipitation with distilled water. The volatile products were eliminated by vacuum distillation.

The resins were irradiated in air and in a vacuum at ambient temperature by gamma radiation from spent fuel elements. A bicapillary pyknometer was used for determining density [79] and a Ubbelohde viscosimeter for viscosity measurement [80]. The measurements were made with a precision of 0.1% for the density and ±1.5% for viscosity. The epoxy group content was determined chemically [81] with a precision of about 5%.

The nature of the materials produced by radiolysis of the epoxy compounds was studied by mass spectrometric analysis and infrared spectroscopy. Mass spectrometry was also used to determine the gaseous product content. The infrared spectra were measured with a Perkin Elmer spectrometer (NaCl prism) in the 4000 - 400 $cm^{-1}$ region. For the spectrum measurements, tablets were prepared by compression with KBr. The mass analysis was made with an AEI gas analyzer, model MS10. The pressure limit in the analyzer was around $1 \times 10^{-8}$ Torr.

#### 3.3.1.2 Results

i. Density. The density of the DGEBA resin increased with radiation dose at different temperatures (Figs. 3.1, 3.2). The change did not depend on whether the irradiation was made in air or vacuum. The increase is caused by formation of nets which increase the reticulation density of the epoxy molecules.

ii. Viscosity. The viscosity of the resin DGEBA also increased with radiation dose at different temperatures (Fig. 3.2). An increase in viscosity is usually related to an increase in molecular weight of the molecules. The experiments show that beyond a dose of $1 \times 10^9$ rads, the liquid resin solidifies due to formation of a complete network of bonds in three dimensions.

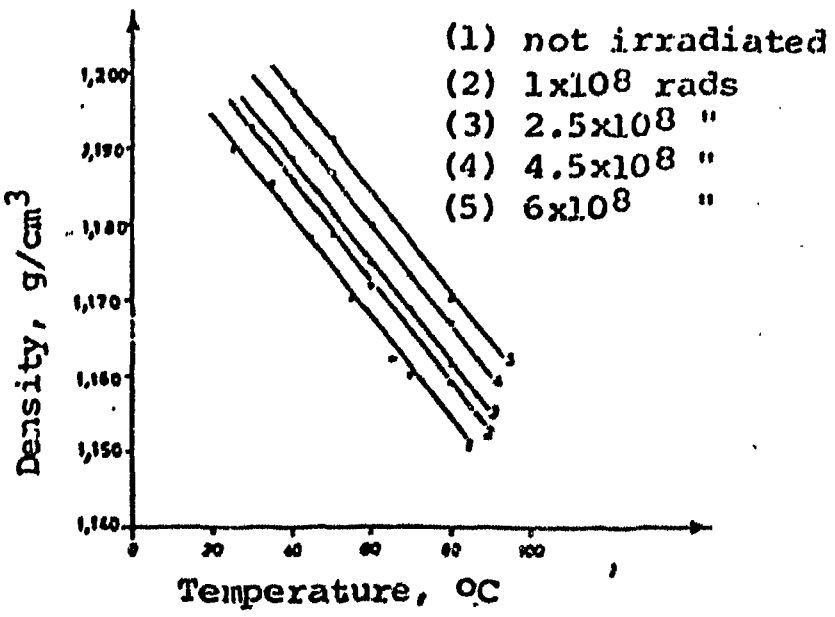



Fig. 3.1. Change in density of resin DGEBA as a function of temperature.

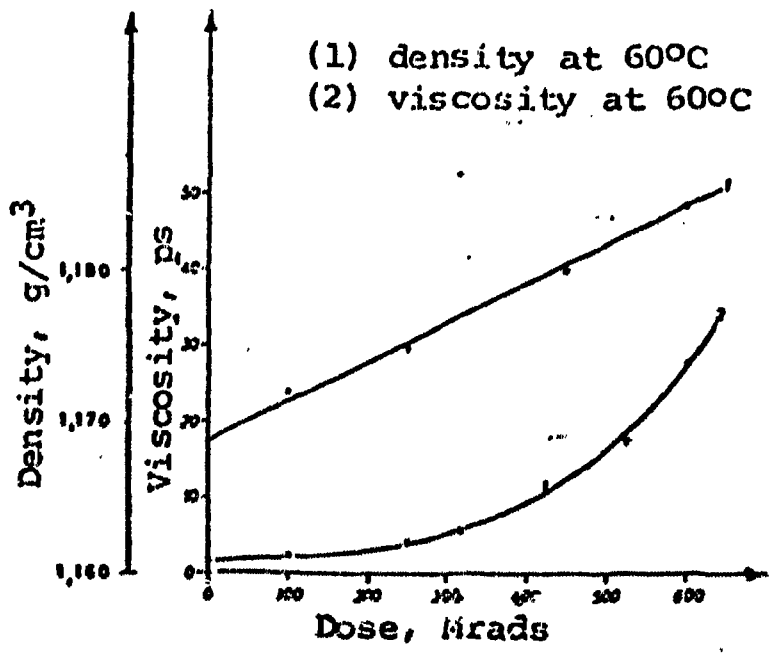



Fig. 3.2 Change in density and viscosity if resin DGEBA as a function of absorbed dose at different temperatures [sic].

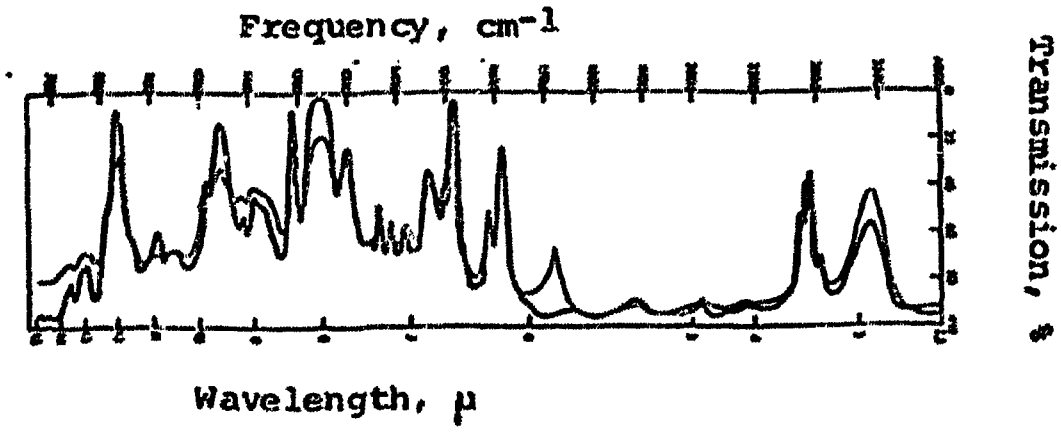



Fig. 3.3. Infrared spectra of DGEBA/B resin without hardening. Heavy line is for non-rradiated resin, light line for irradiation to a dose of 200 mrads [sic] in vacuum.

ii). Epoxy group content. Upon irradiating DGEBA resin to a dose of $2\times10^8$ rads, a decrease in the epoxy group content of about 3 groups per 100 eV of energy was estimated; the G value thus is given by

$$G_{-\left(-\underset{O}{C}-C\right)} = 3$$

iv. Infrared spectra. Non-irradiated epoxy resin spectra coincided with those indicated in published work [82, 83]. In the spectra (Fig. 5.3) of the irradiated epoxy resins (DGEBA/B) the following modifications are seen:

A decrease in the intensity of the 864 and 915 $cm^{-1}$ radiations (vibrations corresponding to the epoxy group [83]),

Decrease in the intensity of the 1040 and 1245 $cm^{-1}$ rays (ether bond) [82, 84].

Decrease in intensity of the 1370 and 1390 $cm^{-1}$ doublet ($CH_3$ deformation vibrations) [82, 85, 86].

Appearance of a new peak at 1720 $cm^{-1}$ (carbonyl group vibrations) and increase in 3420 $cm^{-1}$ ray (hydroxyl group valence vibration) [82, 84].

v. Mass spectrometric analysis. The results of mass spectrometric analysis of products released when epoxy resins are irradiated show that besides liberation of $H_2$, $CH_4$, $C_2H_2$, and $C_3H_8$, heavier products (50 to 120 and greater) begin to appear in the mass spectrum. The average results of five experiments are given in Table 3.1.

Table 3.1 Amount of gas formed in radiolysis of epoxy resins

| Product<br>~~Produit formé~~ | Dose of radiation | |
|---|---|---|
| | $5.10^7$ rad | $2.10^8$ rad |
| $H_2$ | 91,0 % | 75 % |
| $CH_4$ | traces | 2,5 % |
| $C_2H_6$ | 4,0 % | 15 % |
| ~~Masses lourdes~~<br>Heavy masses | 3,0 % | 1,5 % |

The release of heavy substances in the off-gas is observed only after the sample has been heated. These are probably by-products of the destruction of the epoxy resins.

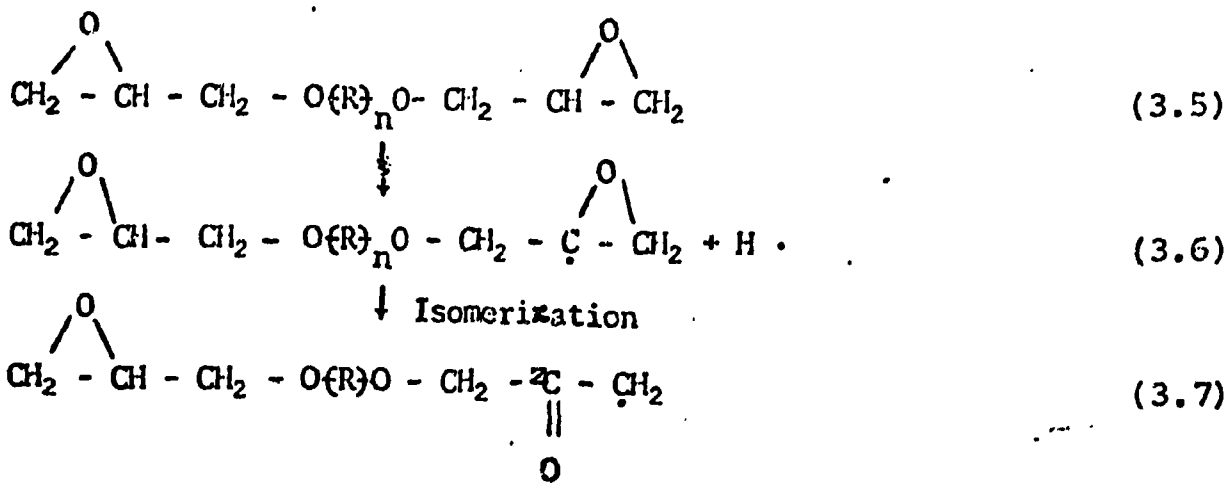
vi. We were also able to show that the solubility of epoxy resins in acetone decreases as a function of dose. At $10^9$ rads the resin DGEBA is no longer soluble in acetone.

### 3.3.1.3 Interpretation of Results

The above statements indicate that ionizing radiation causes a rupture of the chain in epoxy resins, followed by reticulation and degradation of the epoxy resins with formation of gas.

i. Reticulation. For the reticulation, the following mechanisms may be proposed:

1. The primary effect of the action of radiation on epoxy resins seems to be to detach the hydrogen atom from the beta carbon of the epoxy ring (as in the case of peroxide reaction with these compounds, with consecutive isomerization of the radical obtained to form a ketone radical) [87, 88]:

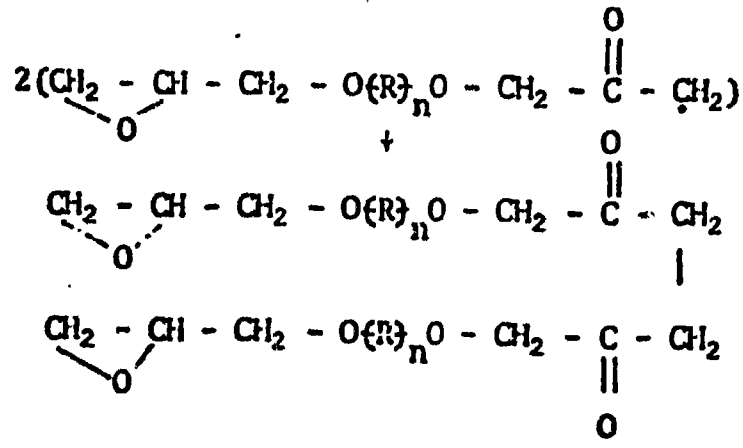


(3.5)

(3.6)

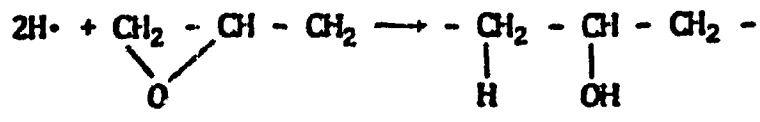
(3.7)

2. The radicals formed in reactions 3.5-3.7 can then enter into a reticulation reaction:



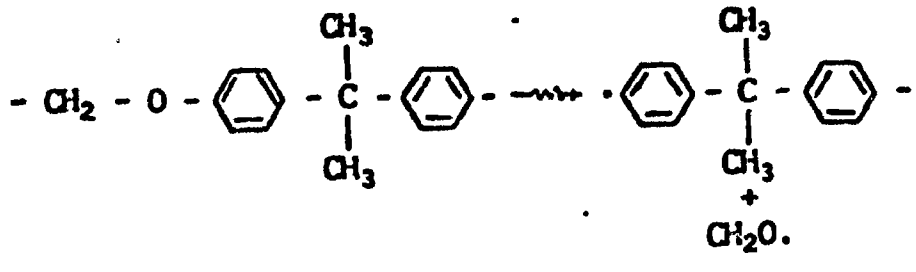
(3.8)

3. The hydrogen formed in reaction 3.6 may act like the reducing agents used for hardening epoxy resins, causing rupture of the epoxy ring:



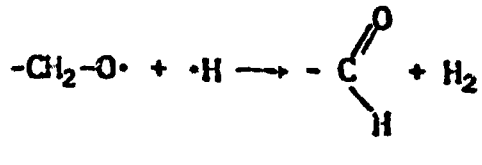
(3.9)

ii. Degradation. Degradation is probably explained by rupture of the ether bonds,



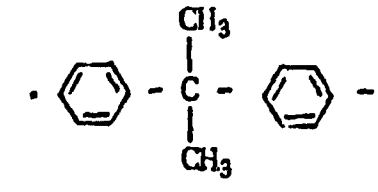
(3.10)

followed by isomerization of the $CH_2O$ radical,



(3.11)

On the other hand, the radical



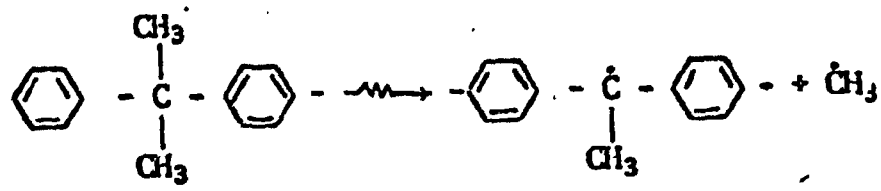
combines with hydrogen or other radicals. This would explain the decrease in intensity of the line corresponding to the ether bond and the appearance of a line of 1720 $cm^{-1}$ (C=O). This reaction mechanism corresponds to that proposed by Neimann [89] in the study of pyrolysis of epoxy resins.

iii. Formation of gas. The presence of hydrogen, methane, and ethane in the product used for mass spectrometric analysis corresponds to the following in the proposed mechanism:

Recombination of the protons formed according to 5.2,

$$H\cdot + \cdot H \longrightarrow H_2 \uparrow \qquad (3.12)$$

The action of the radiation may also cause detachment of the methyl group and formation of a radical,



(3.13)

This has also been observed in thermal destruction of epoxy resins with a quaternary carbon atom tracer [90]. The methyl radicals formed can react with the protons or among themselves,

$$CH_3\cdot + \cdot H \longrightarrow CH_4 \uparrow \qquad (3.14)$$

$$CH_3\cdot + \cdot CH_3 \longrightarrow CH_3 - CH_3 \uparrow \qquad (3.15)$$

### 3.3.1.4 Conclusions

1. The action of ionizing radiation on epoxy resins is probably similar to that of chemical hardeners in the sense that they open up the epoxy rings and cause formation of hydroxyl groups.

2. Exposure to nuclear radiation may be considered to be similar to pyrolysis at low temperature [91-95].

## 3.3.2 Hardened resins

### 3.3.2.1 Experimental study

The infrared spectra and mass analyses of hardened epoxy resins have been measured before and after irradiation in order to get some idea of changes in molecular structure due to the irradiation. The measurements

after irradiation were made on seriously damaged samples. The infrared spectra were made with a Perkin-Elmer model 221 spectrophotometer in the region 2.5-15 μ, using a NaCl prism. The samples were suspended in paraffin. The mass analyses were made with an AEI gas analyzer, type MS10. The de-gassing rate was determined by measuring the increase in pressure at constant volume.

The irradiations were made in the ASTRA nuclear reactor, position 1, in a vacuum and at ambient temperature. The resins studied were

EPN + DADPS

DGEBA/B + AP

DGEBA + MDA + $A\ell_2O_3$

DGEBA + DDSA + BDMA + PoGℓ

### 3.3.2.2 Results

1. Infrared spectra: Most of the infrared spectra were practically identical with those of the nonirradiated (spectra 2-4). Only a few minor differences were noted in the resin EPN + DADPS (spectrum 1): disappearance of the 915-$cm^{-1}$ line (epoxy group), decrease in intensity of the 1185-$cm^{-1}$ line (ether bond), and appearance of the 1720-$cm^{-1}$ peak (carbonyl group vibration). The measurements and the sample irradiations were repeated several times. Similar results were obtained by Mixer et al. [61].

2. Mass spectrometric analysis: Mass analysis showed that, among the gaseous decomposition products, hydrogen was the most important (90%). The other components were CO, $CH_4$, $C_2H_6$, and $H_2O$. The factor $G_{gas}$ varied between $10^{-2}$ and $5\times10^{-1}$ for epoxy resins irradiated to $5\times10^8$ rads.

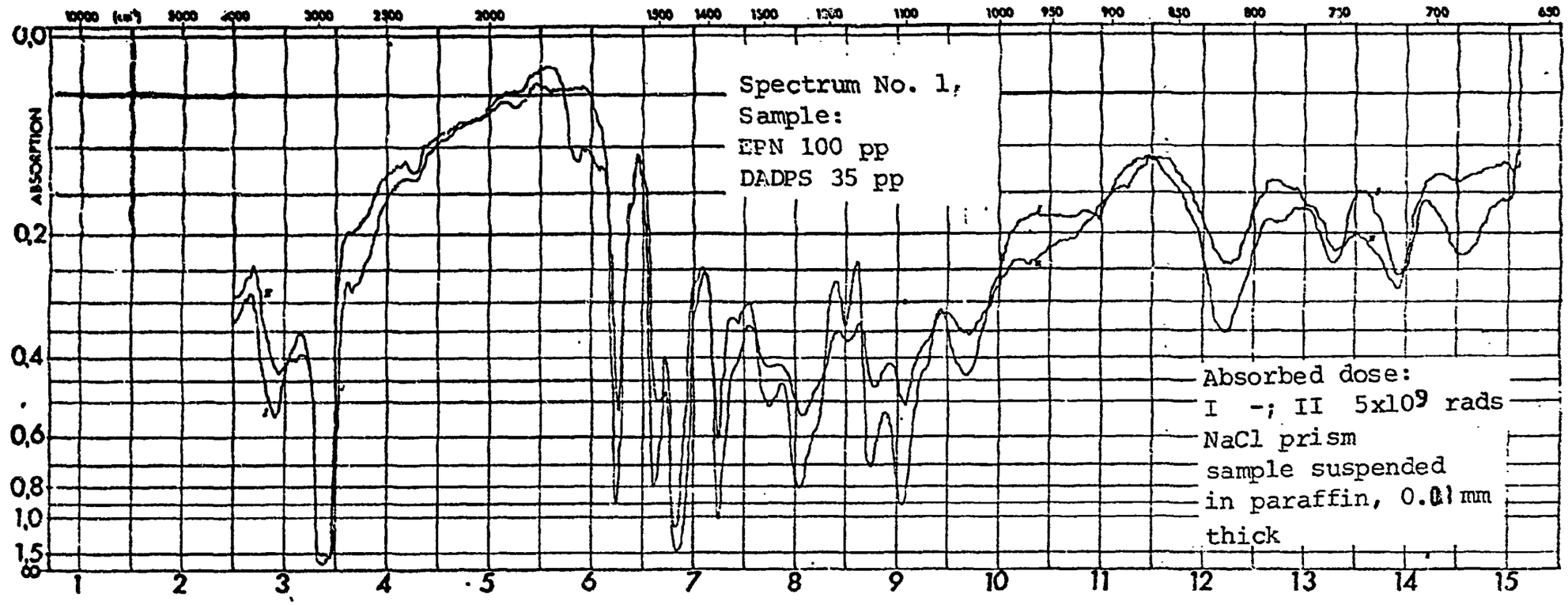
### 3.3.2.3 Conclusions

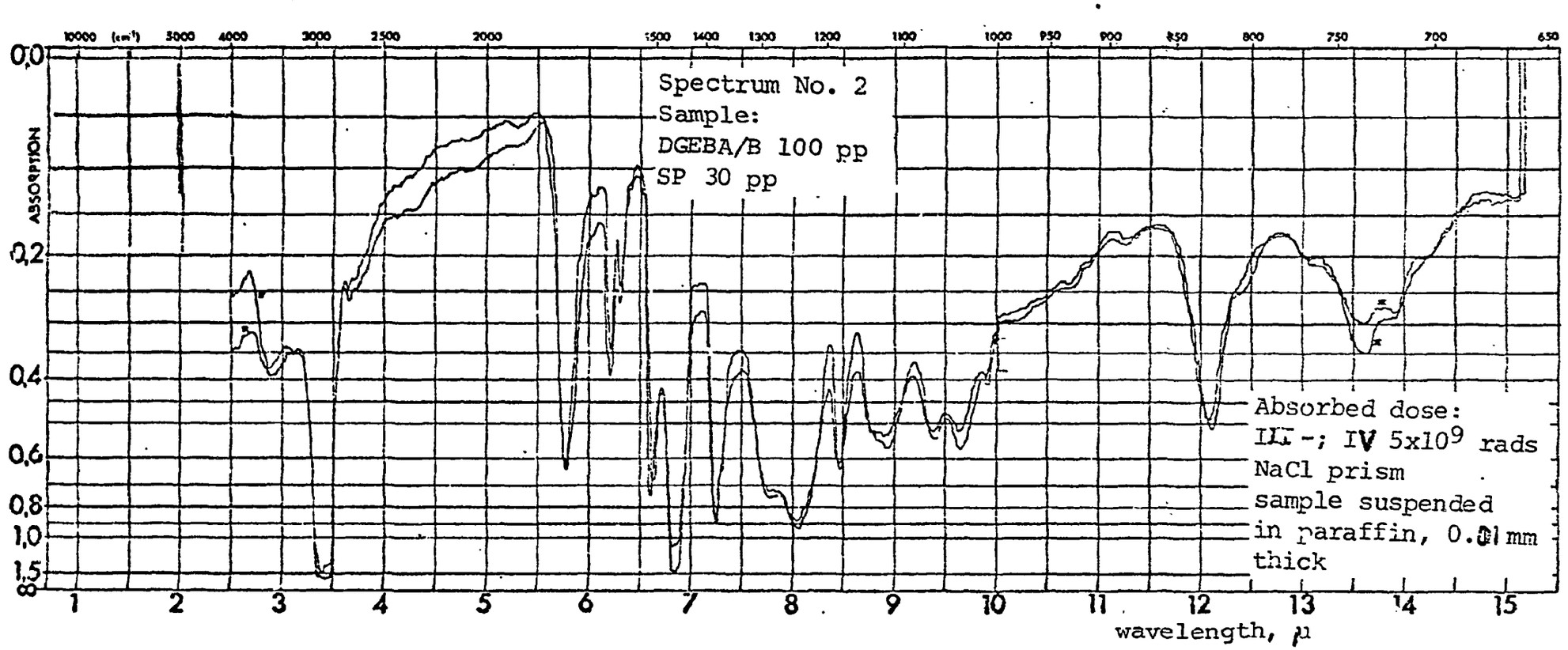
1. The absence of changes in most of the spectra (Nos. 2-4) before and after irradiation may be explained by the fact that minimum changes in chemical structure may cause significant changes in mechanical properties. The minor changes in spectrum No. 1 may be explained by a post-polymerization of epoxy groups due to the irradiation (see 3.3.1.3).

2. The amount of gas formed during the irradiation of the epoxy resins is less in comparison with other polymers; e.g., the value of $G_{gas}$ for polyethylene is around 3 [94].

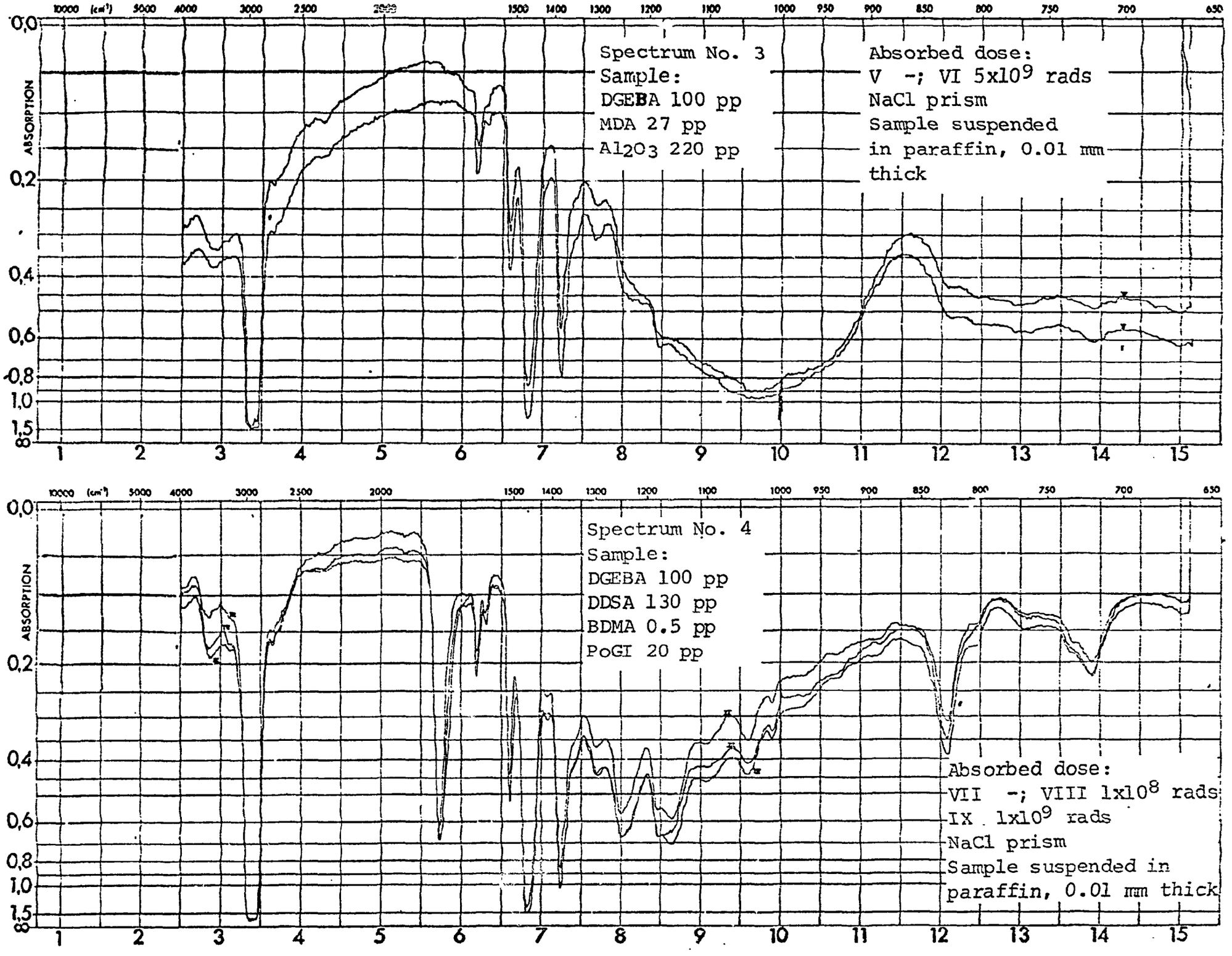
3. The radiation resistance of epoxy resins can be explained by their structure. The radicals formed in the broken chains probably can react among themselves to form new structures as radiation resistant as the first. This is probably the reason for most of the hardened resins being still very radiation resistant to $10^9$ rads.

Frequency, $cm^{-1}$



Frequency, $cm^{-1}$




Wavelength, $\mu$

# 4. PROPERTIES OF EPOXY RESINS AFFECTED BY RADIATION

Because of modifications produced in the chemical composition, the reticulation density, molecular weight, etc., of an irradiated epoxy resin, the irradiated sample shows a corresponding change in physical properties.

## 4.1 Mechanical properties*

### 4.1.1 Interpretation of results

Some of the most spectacular changes in epoxy resins exposed to radiation are those which affect their mechanical properties. Especially from the engineer's standpoint, these often are the most important alterations.

Figures 4.1 to 4.7 show, on examples of epoxy resins, the modification of different mechanical properties as a function of the absorbed dose. All the results are expressed in percentage of initial values, with indication of the average value and the dispersion. Some photographs (4.1 to 4.4) are presented to show better what happens during the irradiation. We may deduce that:

An increasing dose affects the mechanical properties of epoxy resins differently, depending on the type.

Resistance to bending, pulling, heat, and shock of most of the resins begins by increasing proportionally to the dose up to a maximum after which it decreases with increasing dose. The initial increase has been attributed to the predominance of the reticulation during the first phase. When the transverse bonds have become sufficiently numerous that the chain segments are immobilized, the chain ruptures begin to predominate, which explains the decrease of the resistance in the second phase.

The deflection and the extension at rupture decrease rapidly and very uniformly with increasing dose. The result is attributed to the predominance of reticulation in these resins.

The modulus of elasticity and the hardness are very little affected by the irradiation.

The absorption of water increases progressively with the absorbed dose, and this increase is pronounced from the moment that the other mechanical properties are attacked; the material has become porous (photos 4.1-4.2).

For sufficiently high doses, the presence of gas creates, in the substance, from internal tensions which can significantly contribute to the deterioration of mechanical properties (photos 4.1-4.2).

In general, we conclude from these figures that epoxy resins are radiation resistant compared with other polymers [95]; they are almost not affected by doses of $1 \times 10^8$ rads or less.

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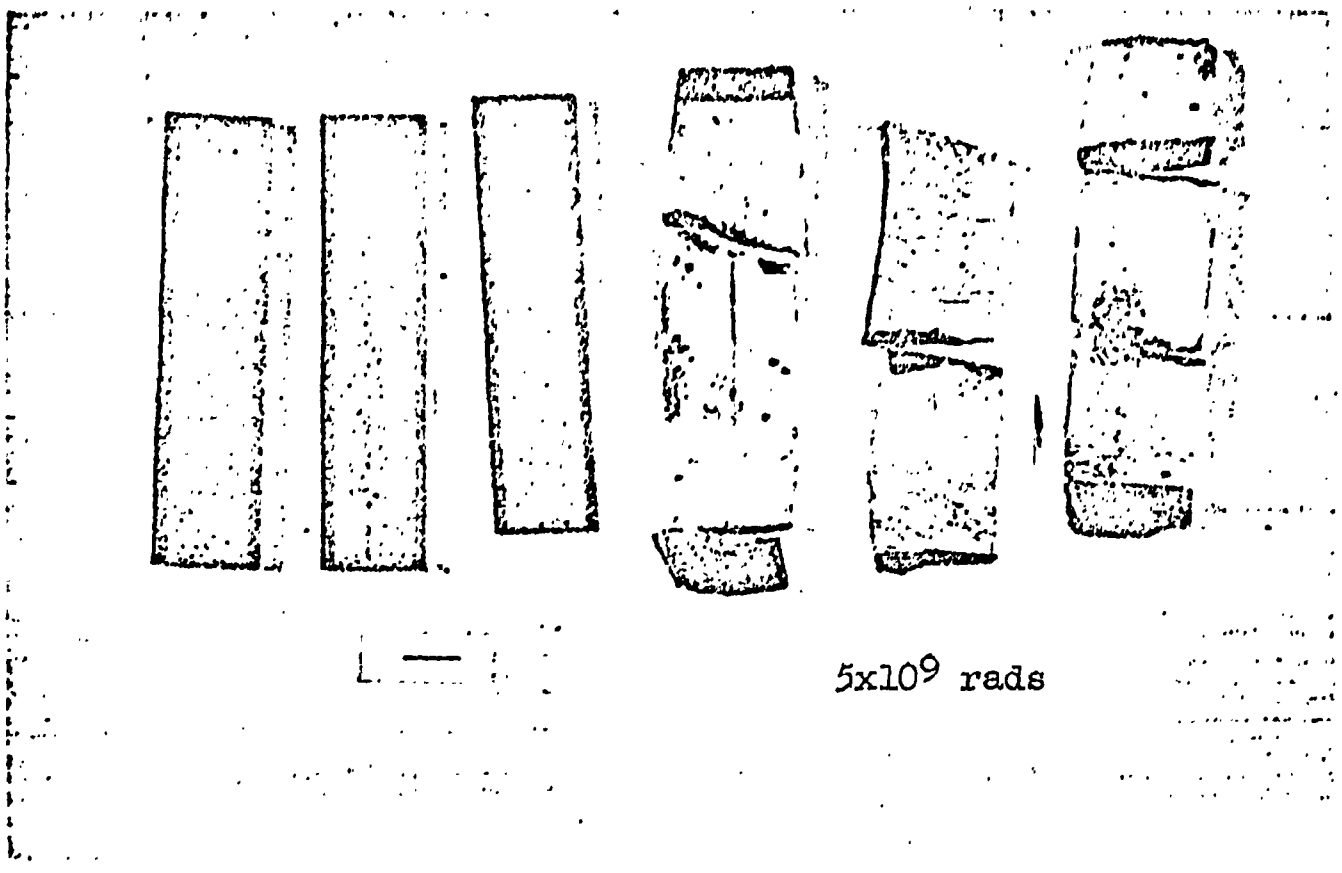
* All irradiations were made in the ASTRA nuclear reactor.

Photo 4.1 Change in appearance of DGEBA - DADPS as a function of absorbed dose.



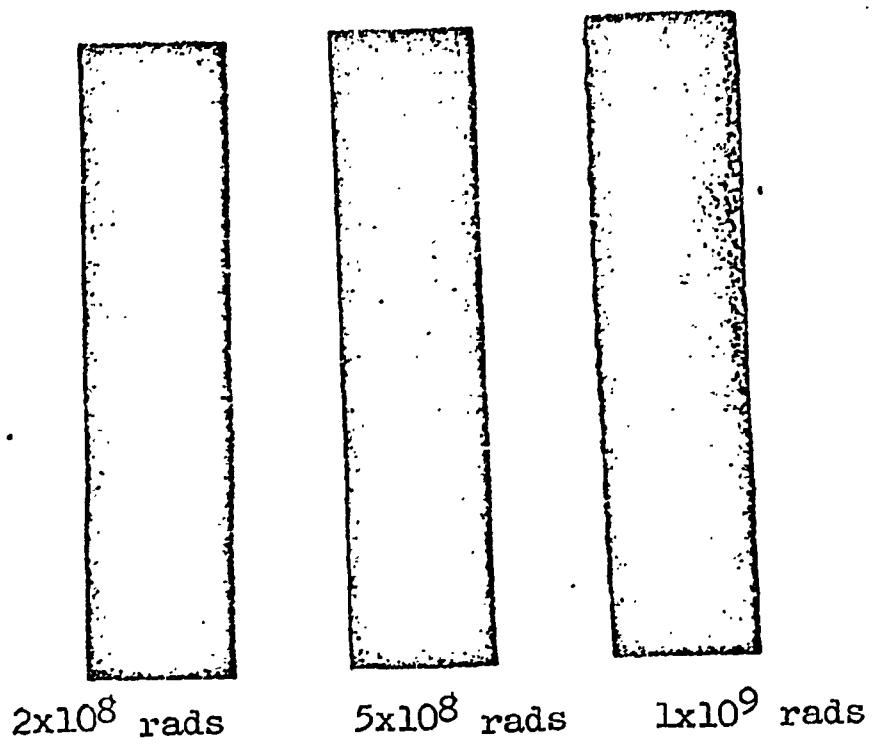
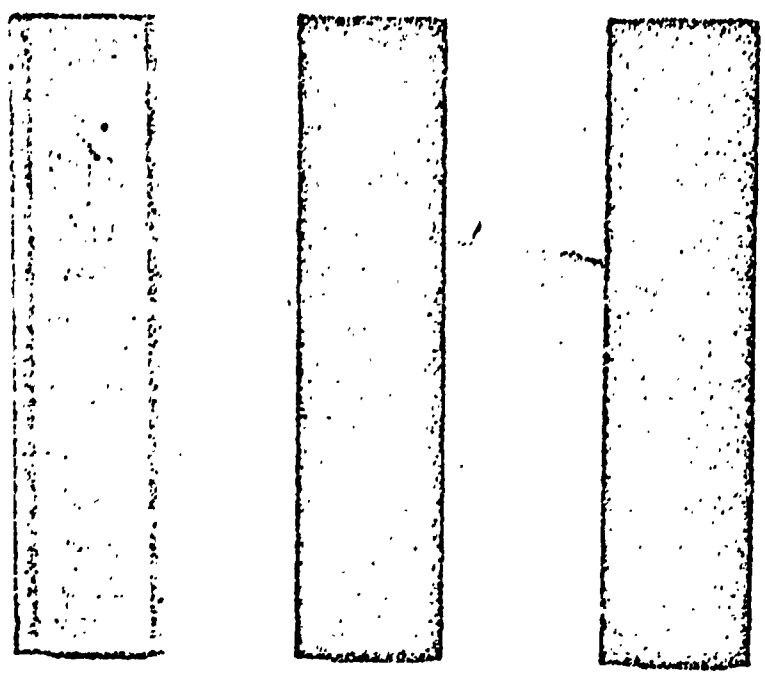
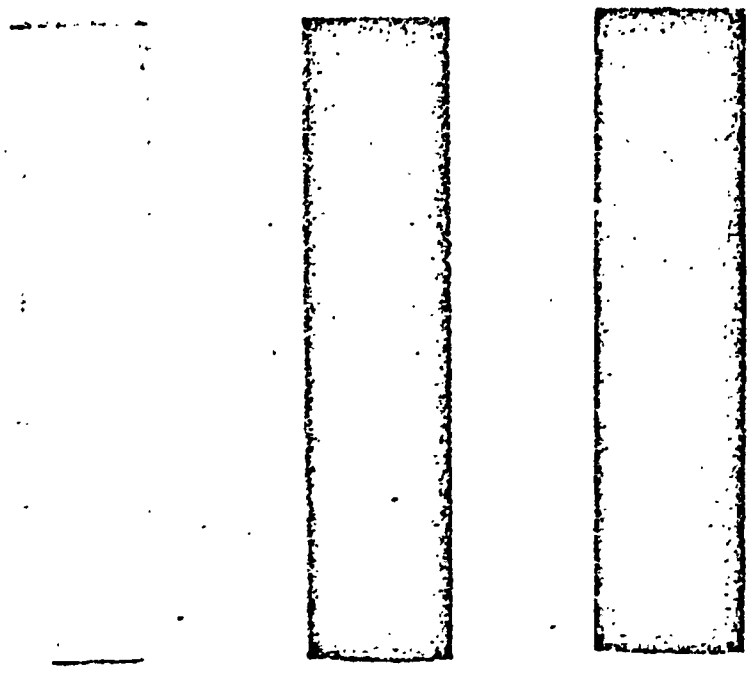




Photo 4.2 Change in appearance of VCD - MA - BSMA as a function of absorbed dose.

Photo 4.3 Change in appearance of EPN - DADPS as a function of absorbed dose.



$5x10^8$ rads $2x10^9$ rads

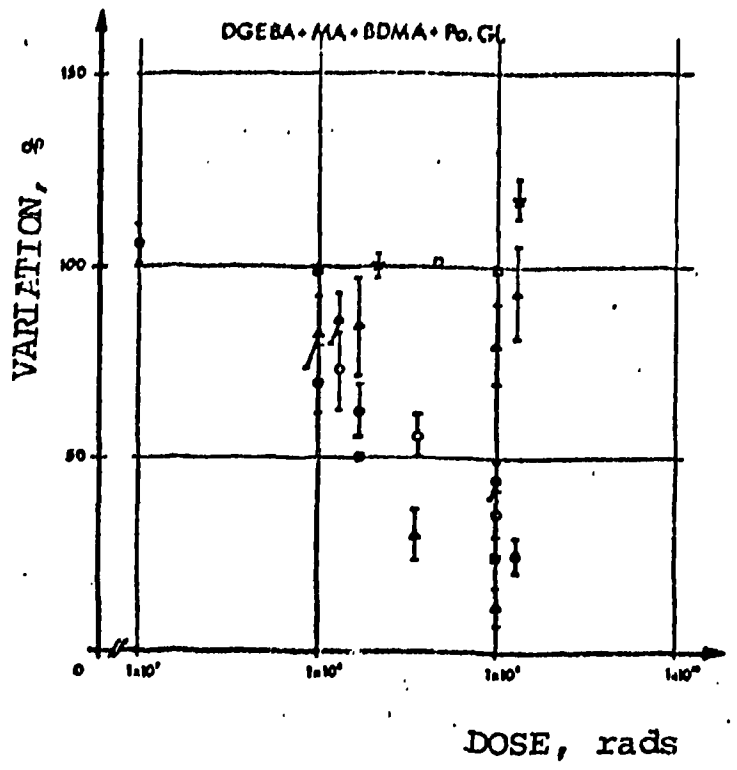


$5x10^8$ rads $2x10^9$ rads

Photo 4.4 Change in appearance of DGEBA - MDA as a function of absorbed dose.

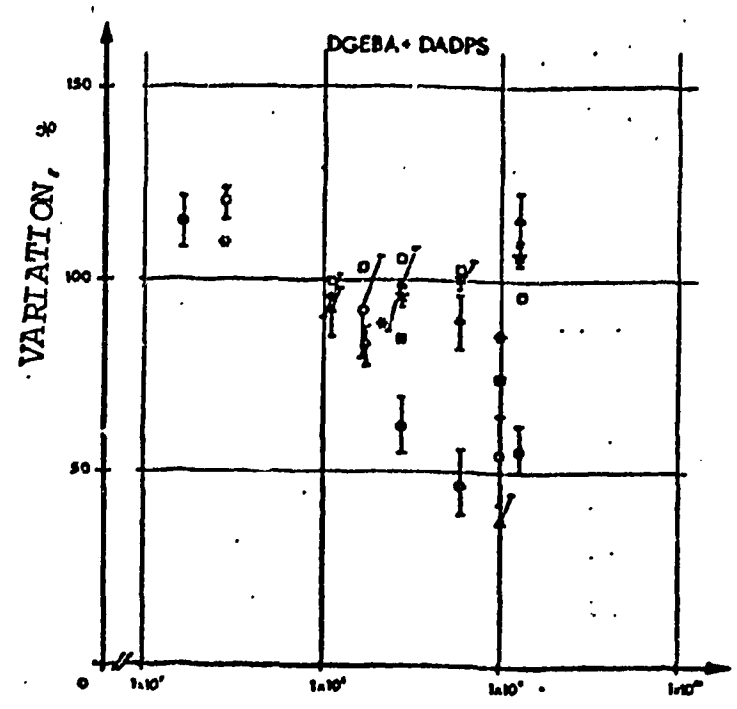
Figs. 4.1-4.7

Note: On all seven of the graphs in this group, the numbers on the ordinate run from 0 to 150 and on the abscissa, from $1x10^7$ to $1x10^{10}$

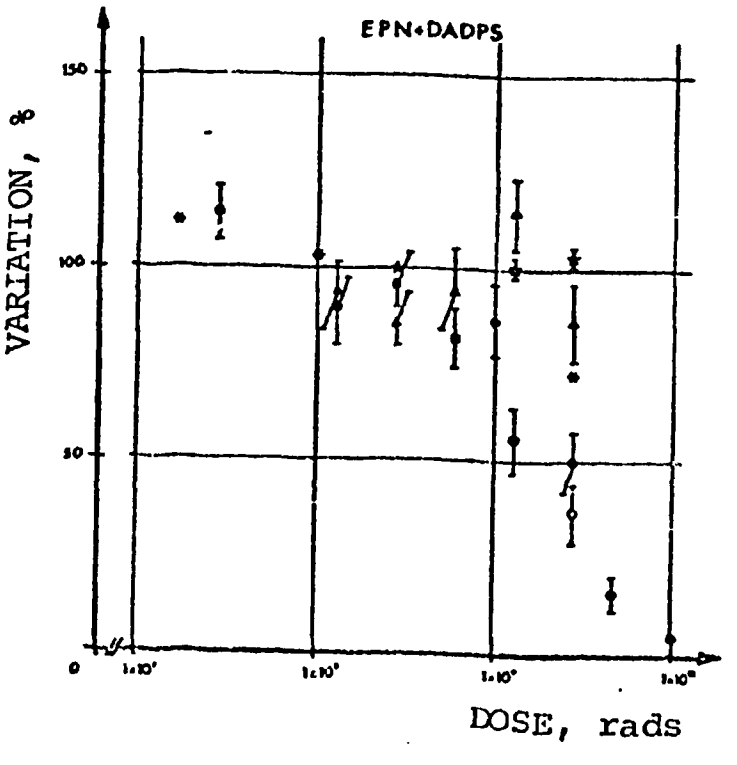



Modification of mechanical properties of epoxy resin as a function of absorbed dose

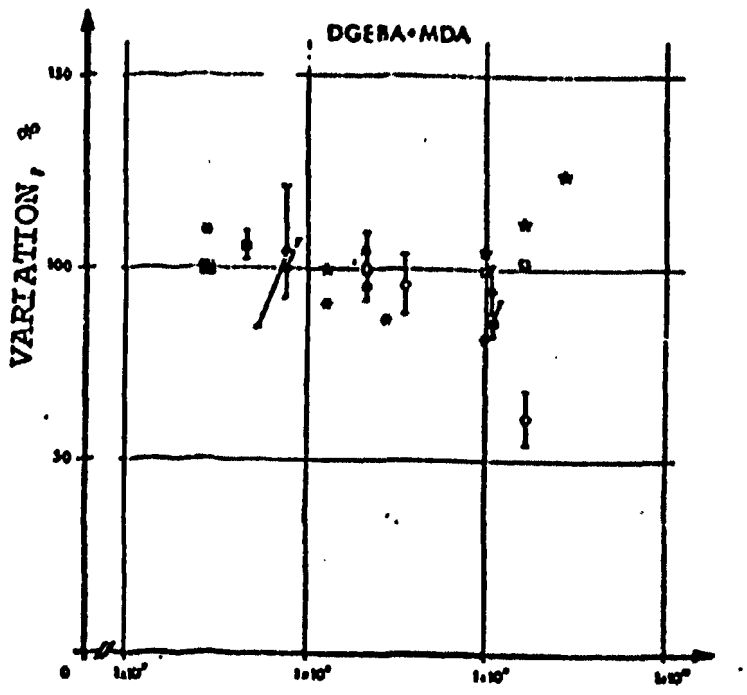
| | | | |
|---|---|---|---|
| ● | 1 Resistance to bending | 12.3 | $kg/mm^2$ |
| ◇ | 2 Resistance to traction | 6 | $kg/mm^2$ |
| ▲ | 3 Modulus of elasticity | 283 | $kg/mm^2$ |
| △ | 4 Elongation at rupture | 2.5 | mm |
| ■ | 5 Resistance to shock | 14 | $kg-m/cm^2$ |
| □ | 6 Hardness | 87 | Shore D |
| ★ | 7 Water absorption, 25°C (4 days) | 0.4 | % |
| ✱ | 8 Point of yielding to heat | | °C |




| | | | |
|---|---|---|---|
| ● | 1 Resistance to bending | 15.6 | $kg/mm^2$ |
| ◇ | 2 Resistance to traction | 6.8 | $kg/mm^2$ |
| ▲ | 3 Modulus of elasticity | 221 | $kg/mm^2$ |
| △ | 4 Elongation at rupture | | mm |
| ■ | 5 Resistance to shock | 15 | $kg-m/cm^2$ |
| □ | 6 Hardness | 88 | Shore D |
| ★ | 7 Water absorption, 25°C (4 days) | 0.8 | % |
| ✱ | 8 Point of yielding to heat | 185 | °C |

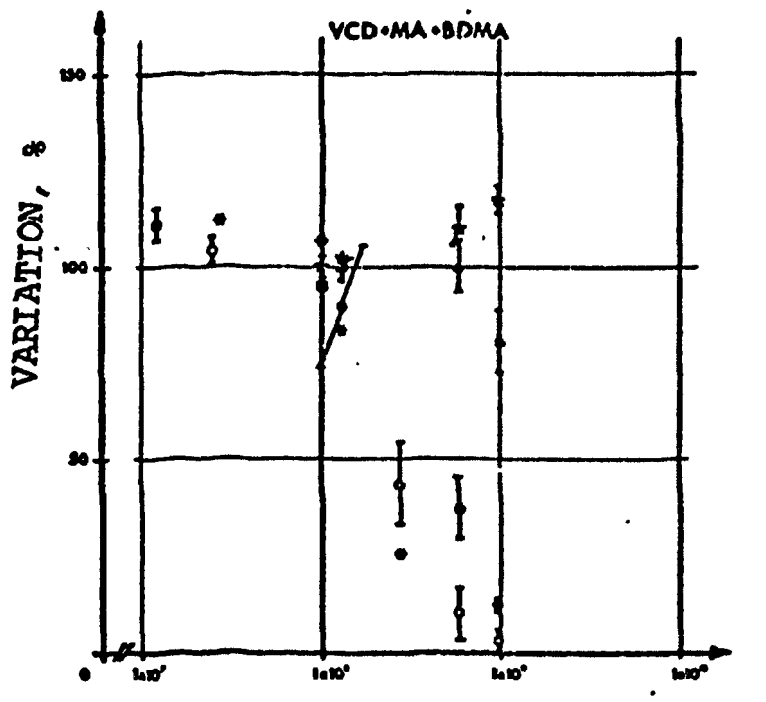



| | | | |
|---|---|---|---|
| ● | 1 Resistance to bending | 14.5 | $kg/mm^2$ |
| ◇ | 2 Resistance to traction | 9.1 | $kg/mm^2$ |
| ▲ | 3 Modulus of elasticity | 245 | $kg/mm^2$ |
| △ | 4 Elongation at rupture | | mm |
| ■ | 5 Resistance to shock | | $kg-m/cm^2$ |
| □ | 6 Hardness | | Shore D |
| ★ | 7 Water absorption, 25°C (4 days) | 0.5 | % |
| ✱ | 8 Point of yielding to heat | 216 | °C |



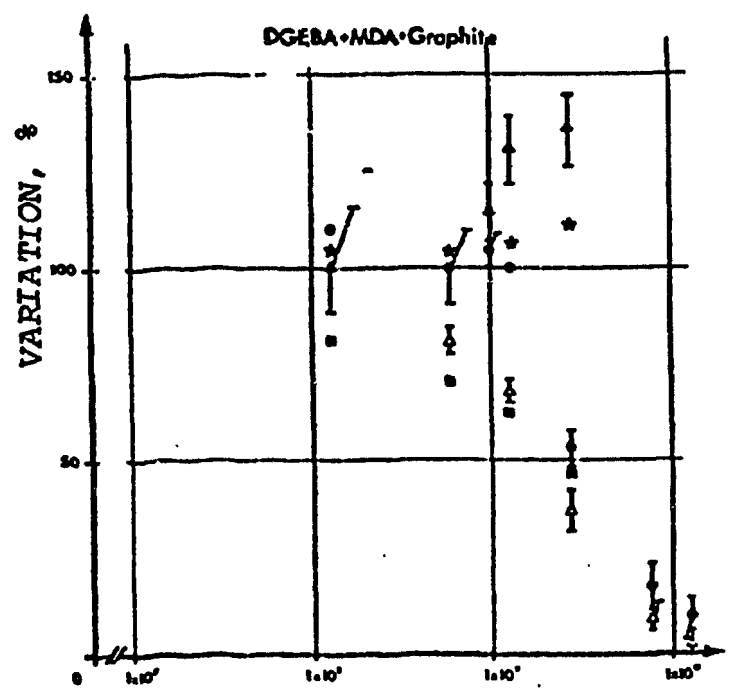

DOSE, rads

| | | | |
|---|---|---|---|
| ● 1 | Resistance to bending | 17 | kg/mm² |
| ○ 2 | Resistance to traction | 7.2 | kg/mm² |
| ▲ 3 | Modulus of elasticity | 325 | kg/mm² |
| △ 4 | Elongation at rupture | | mm |
| ■ 5 | Resistance to shock | 25 | kg-m/cm² |
| □ 6 | Hardness | 86 | Shore D |
| ★ 7 | Water absorption, 25°C (4 days) | 0.6 | % |
| ✱ 8 | Point of yielding to heat | 158 | °C |



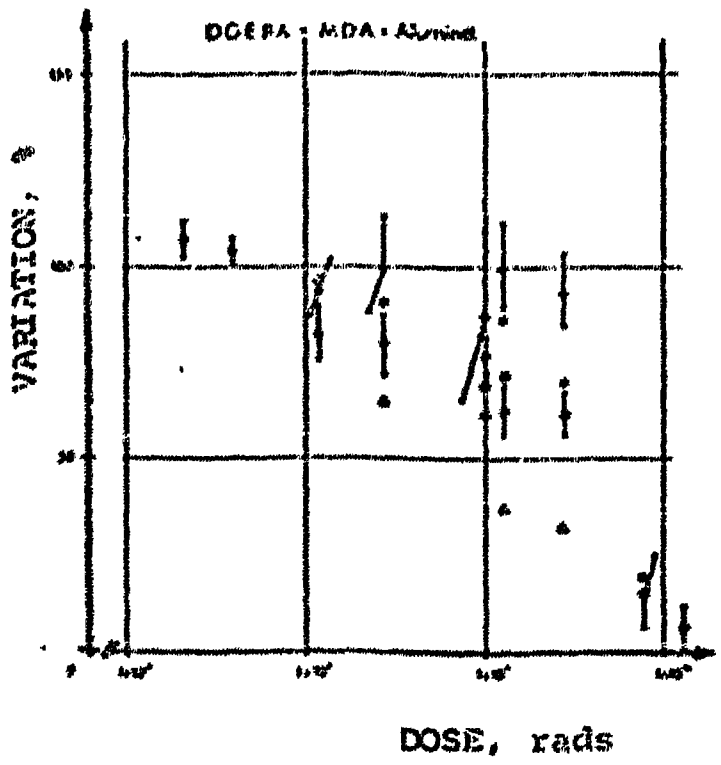

DOSE, rads

| | | | |
|---|---|---|---|
| ● 1 | Resistance to bending | 4.8 | kg/mm² |
| ○ 2 | Resistance to traction | 2.7 | kg/mm² |
| ▲ 3 | Modulus of elasticity | 250 | kg/mm² |
| △ 4 | Elongation at rupture | | mm |
| ■ 5 | Resistance to shock | 2.6 | kg-m/cm² |
| □ 6 | Hardness | | Shore D |
| ★ 7 | Water absorption, 25°C (4 days) | 0.8 | % |
| ✱ 8 | Point of yielding to heat | 186 | °C |




DOSE, rads

| | | | |
|---|---|---|---|
| ● 1 | Resistance to bending | 6.3 | kg/mm² |
| ○ 2 | Resistance to traction | | kg/mm² |
| ▲ 3 | Modulus of elasticity | 423 | kg/mm² |
| △ 4 | Elongation at rupture | 2.8 | mm |
| ■ 5 | Resistance to shock | 6.8 | kg-m/cm² |
| □ 6 | Hardness | | Shore D |
| ★ 7 | Water absorption, 25°C (4 days) | 0.11 | % |
| ✱ 8 | Point of yielding to heat | | °C |




| | | | |
|---|---|---|---|
| ● 1 | Resistance to bending | 11.4 | kg/mm$^2$ |
| ○ 2 | Resistance to traction | | kg/mm$^2$ |
| ▲ 3 | Modulus of elasticity | 541 | kg/mm$^2$ |
| △ 4 | Elongation at rupture | 2.1 | mm |
| ■ 5 | Resistance to shock | 7 | kg-m/cm$^2$ |
| □ 6 | Hardness | | Shore D |
| ★ 7 | Water absorption, 25°C (4 days) | ... | % |
| ✱ 8 | Point of yielding to heat | 152 | °C |

Note: By definition, the radiation sensitivity of a substance to an ionizing radiation is measured by the dose of the radiation that causes deterioration, to 50% of its initial value, of at least one physical parameter of the substance.

4.1.2 Measurements

All tests were made using the VSM, ASTM, and DIN standards but modified in such a way as to be suitable for irradiated epoxy resins. (VSM = Vereins Schweizerischer Maschinenindustrieller; ASTM = American Society for Testing and Materials; DIN = Deutsche Industrie Normen.)

1. Flexion test (ASTM-D 790-61). This test is made with a tensiometer equipped with apparatus for measuring deviations. To obtain reproducible results, the punch should descend at a constant rate of about 2 mm/min. The modulus of elasticity is calculated from

$$E = \frac{m.L^3}{4w.t^3} \quad (\text{kg.force} \times \text{cm}^{-2})$$

where L is the distance between supports, (7.5 cm); w is the width of the test piece (2.0 cm); t is the thickness of the test piece (0.6 cm); and m is the slope at the origin of the tangent to the pressure-deflection curve (kg/cm). The resistance to bending, S (kg/cm$^2$), is calculated by

$$S = \frac{3}{2} \frac{P_b \cdot L}{w \cdot t^2}$$

where $P_b$ is the load (kg) at rupture.

2. Traction test (D 638 - 61 T). The test is made at 20 ± 5°C. The

average width and thickness of the thinner zone of the sample were determined with a precision of 0.03 mm. The enlarged ends of the sample were held in the clamps, and its principal axis was in the direction of the traction. The sample was drawn out by varying the clamps at a practically constant rate so that the rupture was produced in 1 to 2 min. The load at rupture is about 1% of the true value. The resistance of the resistance of the sample to traction is calculated from the load at rupture and the initial cross-section of the sample.

3. Elongation at rupture test (D 638-61 T). Two parallel marks are traced on the thin part of the sample, 25 mm apart. The material used for marking should not have any effect on the material of the sample, and the lines are drawn as narrow as possible. The use of a marker with parallel printed scales is recommended, but it is necessary to ensure that the marker does not harm the sample.

The sample is mounted on the machine and tested as in the traction test. The load at rupture and the distance between the reference lines at rupture are noted. The distance between the reference lines is measured with a precision of ±5%. The sample broken outside the reference lines is rejected.

4. Flexion by impact test (VSM 77.105. The Charpy driver-pendulum is used. The sample bars, supported at their ends, are struck in the middle by the mass of the pendulum. The samples are 60 x 10 x 4 mm with intact edges and faces without scratches.

The resistance to flexion on impact, $a_k$, is the quotient of the work, $A_s$, supplied to break the bar divided by the section, $F_o$, of this latter, measured with a precision of 0.03 mm:

$$a_k = \frac{A_s}{F_o} \text{ kg cm/cm}^2$$

5. Hardness (DIN 53.505). The test is made with a hardness meter, Shore type D. The test pieces are 30-mm-dia disks, 2 mm thick. Five different points are measured by applying the same pressure for 3 seconds.

6. Test for bending with heat (ASTM D648-56). The principle of this test is to determine the temperature for a deflexion of the test piece of 0.25 mm. The test piece is heated in a mineral oil bath with a temperature increase rate of 2°C/min and subjected at the same time to a load of 500 g in the middle. The sample dimensions are 120 x 12 x 6 mm measured with a precision of 0.03 mm.

7. Water-absorption test (ASTM D570-59). The samples are in the form of a 50-mm-dia disk, 3 mm thick, measured with a precision of 0.03 mm. They are weighed before and after immersion in water at 25°C for 4 days, using an analytical balance.

## 4.2 Optical properties

Under the effect of radiation, all the epoxy resins undergo color changes. They turn brown or brownish black, depending on the absorbed dose (Photos 4.1-4.4). The minimum dose at which the color change becomes

perceptible is very variable and depends on the chemical composition of the resin.

The origin of the coloration or the optical absorption bands is probably due to two causes:

a) The absorption due to the formation of double bonds in the molecular network [96], as is the case with other irradiated polymers [97, 98].

b) The absorption due to the presence of radical centers, with the nonpaired electron behaving as a color center similar to those which can be produced in alkali halides [99, 100] and detectable by electron paramagnetic resonance [101]. Photographs 4.1-4.4 show the coloration of the different epoxy resins.

## 4.3 Electrical properties

The chief electrical properties determining the behavior of an epoxy resin as an insulator are the electrical conductivity and the electrical rigidity. These properties depend on the chemical structure, the reticulation density, the number and mobility of the free charge carriers, and the number of captive electrons, and the distribution of the energy to the places where they are found, etc. We consider that the free charges (ions and electrons) produced by radiation exposure can change the electrical properties, especially during and immediately after the irradiation, but this effect is transitory.

With regard to radicals, their chemical activity, in particular their affinity for recombining among themselves, is such that if two radicals are formed on neighboring chains, they tend to be neutralized by forming a reticulation or even a nonsaturated bond and gas. These structural modifications in the resin change the number and mobility of the charge carriers such that they affect the electrical properties. This effect is permanent.

### 4.3.1 Transitory modifications

One of the principal transitory effects, very characteristic and pronounced, is the considerable decrease in the volumetric resistivity in the resin during and immediately after irradiation.

Figure 4.8 shows the variation in the volumetric resistivity of resin DGEBA as a function of the time after irradiation, at ambient temperature, in a $2 \times 10^6$-rad/hr $^{60}Co$ source. These measurements were made about 15 min after the irradiation. From the results we see that:

The resistivity increases enormously after the measurement
The initial value ($3 \times 10^{16}$ ohm-cm) is again the value almost always 24 hr after the irradiation
Values lower than $5 \times 10^{14}$ ohm-cm are found at the beginning of the measurement

The electrical conductivity observed 15 minutes after the irradiation

is undoubtedly proportional to the electrons and mobile ions created by the absorbed radiation. The persistence of the effect for a long time after the exposure to radiation is attributed to the fact that some of the electrons are trapped at the spots of least potential. These electrons escape little by little to rejoin the cations of opposite charge.

Figure 4.8 shows also that the volumetric resistivity is larger than the initial value for resins irradiated with low doses. For example, 24 hr after the irradiation, the volumetric resistivity, for a resin hardened for 5 hr at 80°C, is of the order of $7 \times 10^{16}$ ohm-cm. This phenomenon is probably due to a post-hardening of the resin. For resins irradiated with doses at which the mechanical properties are degraded, $3 \times 10^{9}$ rads, the volumetric resistivity does not attain the initial value. Nevertheless, it is always found that the resistivity measured 15 minutes after the irradiation is always less than that measured a little later.

Analogous phenomena are found for dielectric rigidity. About 15 minutes after the irradiation, the value is less than the initial value. A decrease of about 20% is reported in the residual conductivity created by the radiation. Measurements made a little later give equal, lower, or higher values than the initial value depending on the dose absorbed by tne resin. (Table 4.1).

Table 4.1 Change in dielectric rigidity (kV/mm) of the resin DGEBA as a function of time after irradiation (hardened 5 hr at 80°C)

| | 15 min | 1 hr | 8 hr |
|---|---|---|---|
| nonirrad. | 21,2 ± 0,8 | 21,2 ± 0,8 | 21,2 ± 0,8 |
| $2,5 \cdot 10^{8}$ rad | < 15 | 20,1 ± 0,8 | 22,8 ± 0,8 |
| $1 \cdot 10^{9}$ rad | < 15 | 16,2 ± 0.8 | 17,7 ± 0,8 |

### 4.3.2. Permanent modifications

Permanent changes were measured by the difference between the properties measured before and long after irradiation in the ASTRA nuclear reactor. At high radiation doses, ionization and excitation of the epoxy resin subjected to bombardment cause a series of complex chemical modifications which are translated to permanent alterations in the resin. We can also expect permanent deterioration of some properties such as the volumetric resistivity and the dielectric rigidity. These effects are very important since they determine the length of time the resin can be used as an insulator.

#### 4.3.2.1 Volumetric resistivity

All the curves in Figs. 4.9-4.11 show a decrease as a function of the

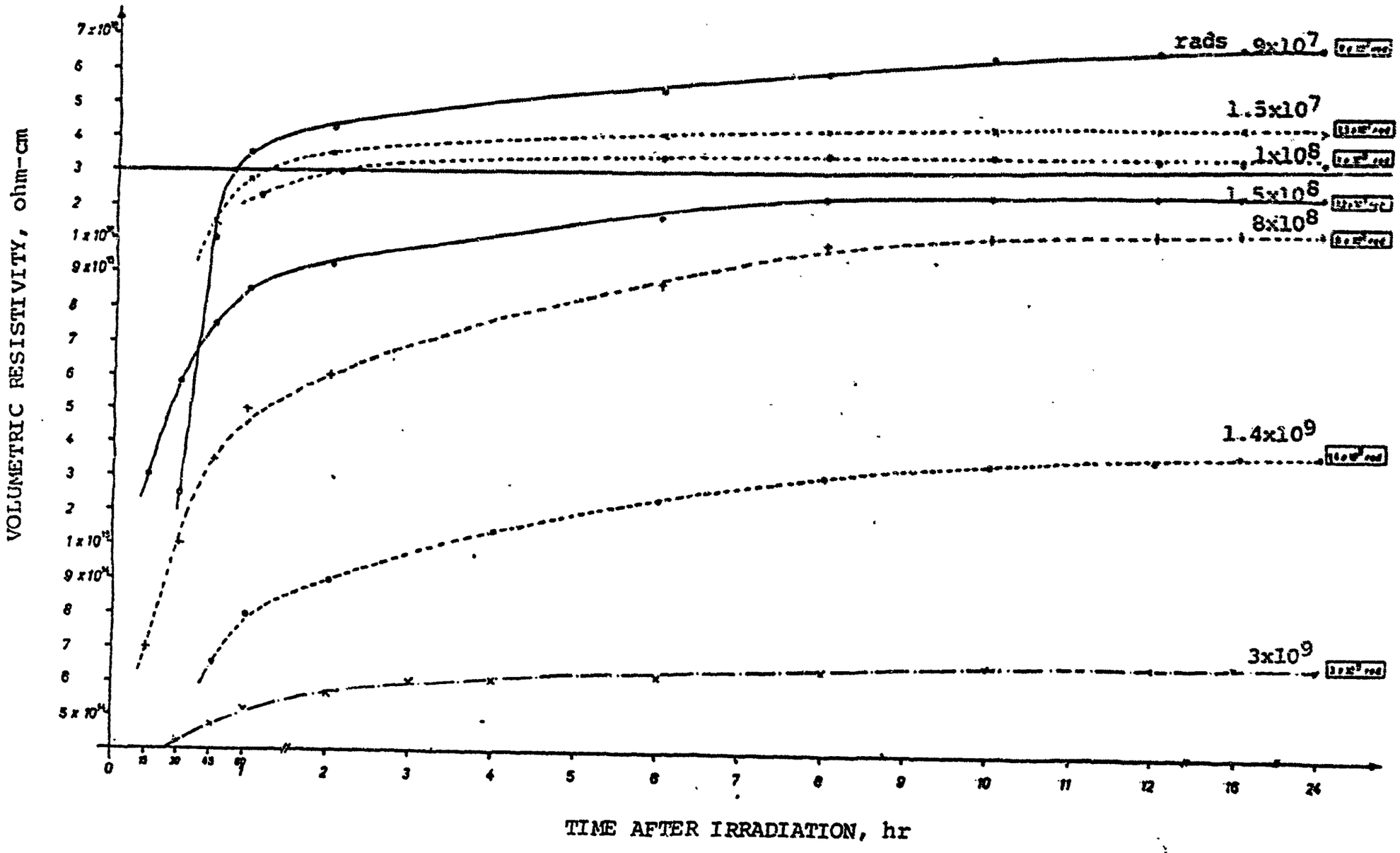



Fig. 4.8 Change in volumetric resistivity of resin DGEBA + MDA as a function of time after irradiation. Hardening conditions: 5 hr at 80°C; temperature during measurement: 20°C.

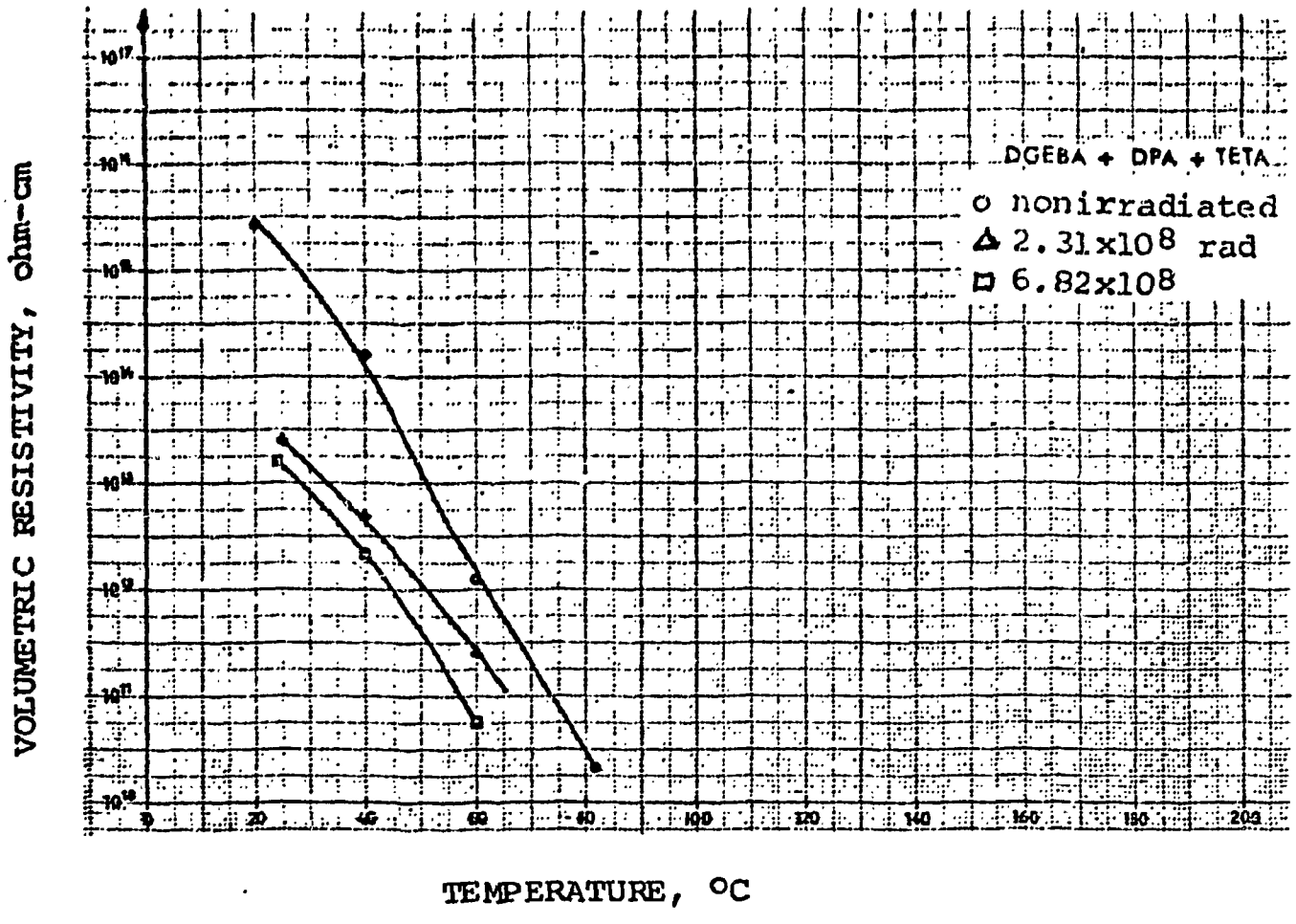



Fig. 4.9 Volumetric resistivity vs. temperature for irradiated epoxy resins (numbers on abscissa run from 0 to 200; on ordinate, from $10^{10}$ to $10^{17}$).

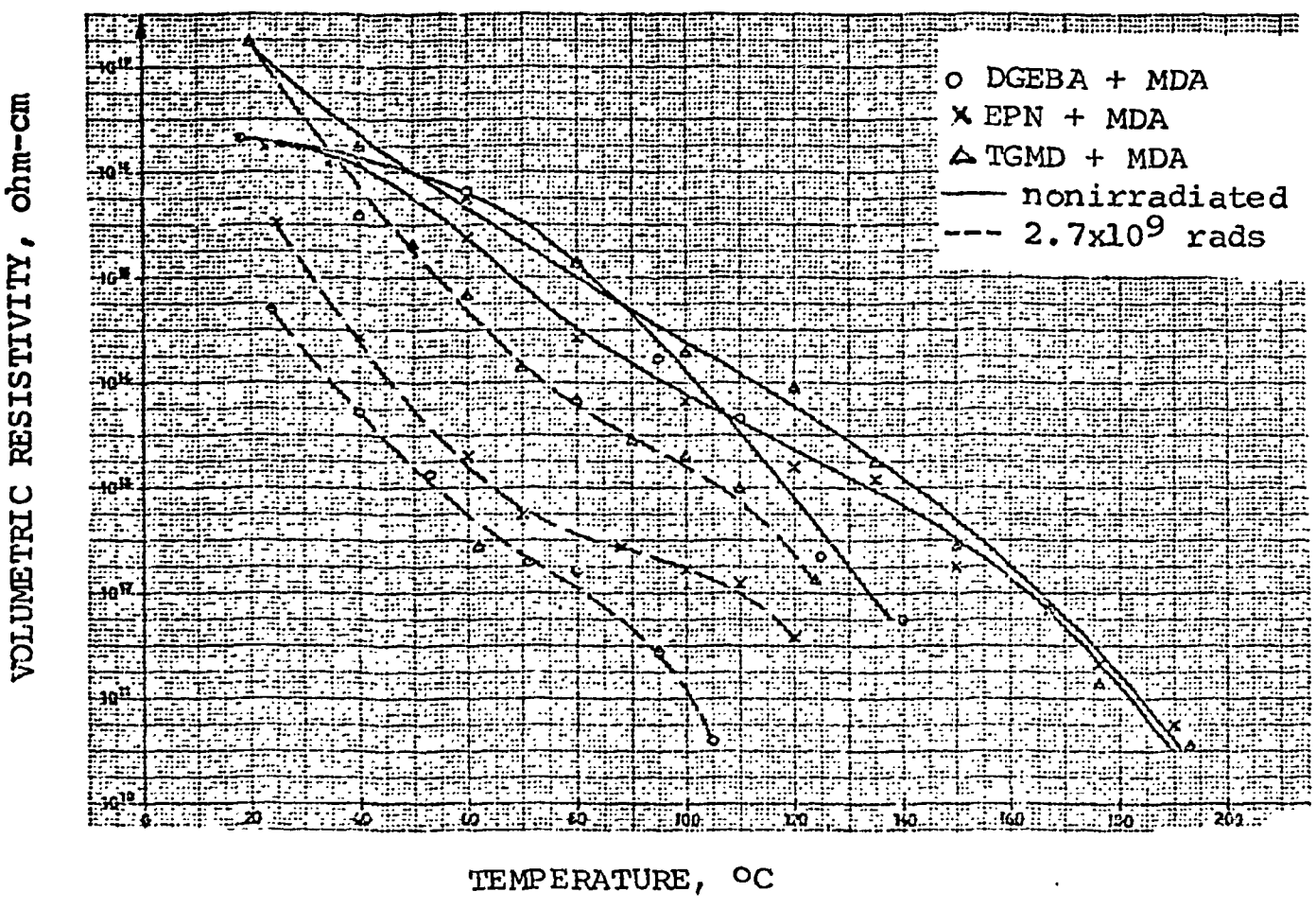



Fig. 4.10 Volumetric resistivity vs. temperature for irradiated epoxy resins. (nombers on ordinate and abscissa same as in Fig. 4.9.)

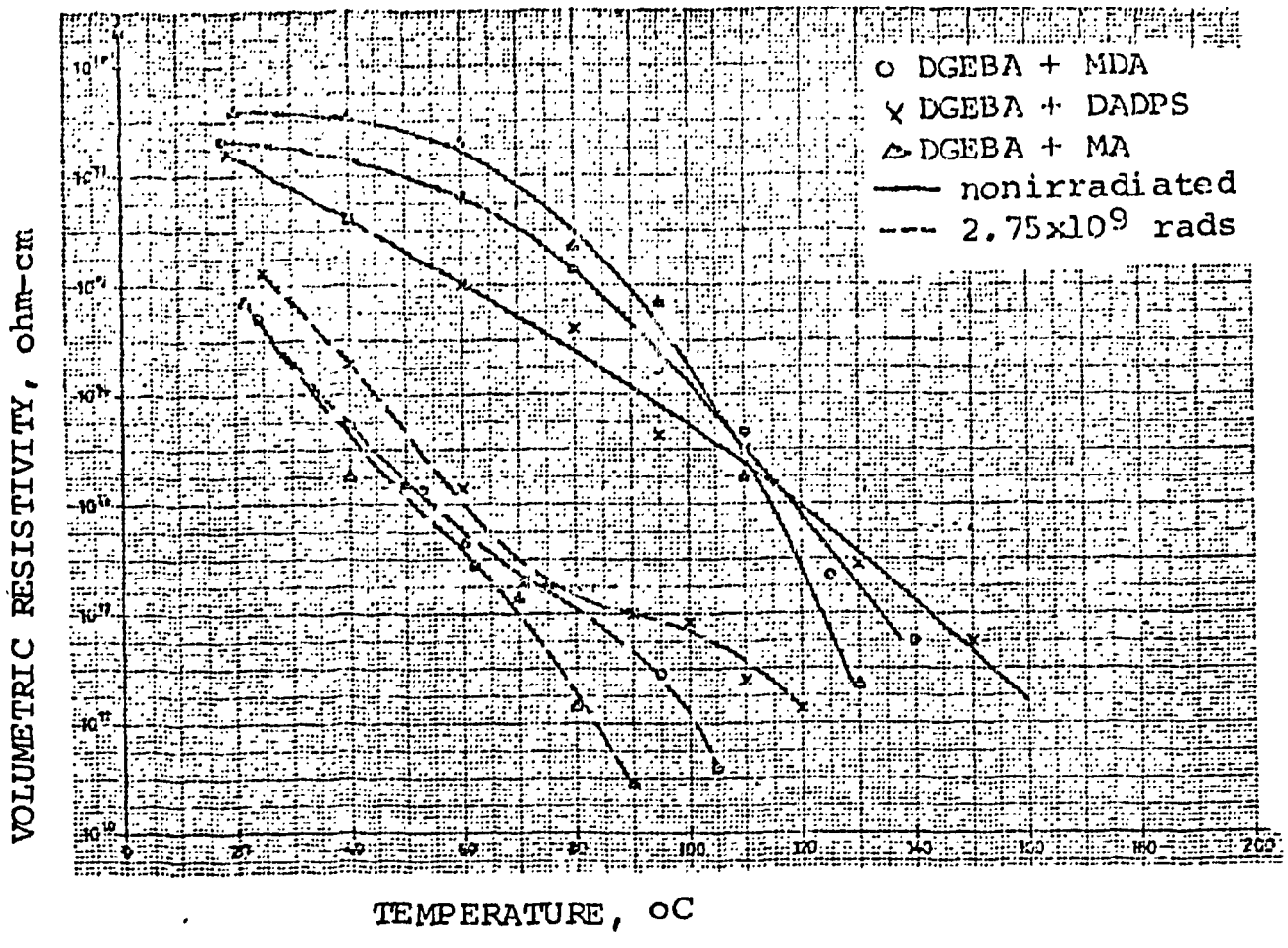



Fig. 4.11 Volumetric resistivity vs. temperature for irradiated epoxy resins (numbers on ordinate and abscissa same as in Fig. 4.9).

absorbed dose, at ambient temperature, and as a function of the temperature. It is well known that the constituents with a relatively low molecular weight are formed during radiation exposure with high doses. These substances, once charge carriers, can be displaced more easily in the resin than in a tridimensional-structure substance. In addition, an increase in the temperature increases the energy available and facilitates the displacement of charge carriers, which causes an increase in the conductivity of the epoxy resins.

The resistivity at ambient temperature of nonirradiated epoxy resins is of the order of $10^{16}$ ohm-cm. We note only slight variations at $2x10^9$ rads and at ambient temperature for the systems that are mechanically the most resistant to radiation (Figs. 4.10 and 4.11).

The resin DGEBA-DBP-TETA is sensitive to radiation under atmospheric conditions and has a resistivity of only $10^{13}$ ohm-cm at $6.8x10^8$ rads. It should be noted that this resin also has a low resistance to radiation from the point of view of its mechanical properties.

The resin DGEBA hardened with aromatic amines or anhydrides gives essentially the same results.

4.3.2.2 Dielectric rigidity (Table 4.2)

In general, it is observed that a decrease in the dielectric rigidity occurs as a function of the absorbed dose. The increase observed with low doses

on the resin TGMD + MDA agrees well with the observation that this resin shows a supplementary polymerization under irradiation. The larger molecules formed by the irradiation support larger differences in potential than the smaller molecules obtained by the normal hardening processes.

All the resins hardened at higher temperatures have about 90% of their initial value at $1x10^9$ rads. The resin DGEBA-DBP-TETA, hardened at ambient temperature, keeps only 84% of its initial value at $6.8x10^8$ rads. A $1x10^9$-rad dose damages it mechanically, and its dielectric rigidity cannot be measured.

4.3.3 Measurements

All the tests were made with application of ASTM standards, modified for adaptation to irradiated epoxy resins.

1. Volumetric rigidity. (ASTM, D 257-61). The measurements were made under atmospheric pressure of 740 mm Hg and at 45% humidity. A megohm bridge was used for the conductivity measurements under a continuous potential of 1000 V.

The dielectric samples for studying the volumetric resistivity had the shape of leaves of 150 by 150 by 2 mm with an effective surface of 80 $cm^2$, the thickness being always measured to 0.01 mm, the samples were cleaned mechanically and chemically before the test, and four samples were used for each level of radiation.

The volumetric resistivity was determined as a function of the temperature. The method used was an increase in the temperature by steps (15°C in 30 min) to the point of bursting.

Since the volumetric resistivity of an epoxy resin increases with time for a given electric field, the measurements were not recorded more than a minute under tension. The dispersion of these resistivity measurements was of the order of 10%.

2. Dielectric rigidity (ASTM, 149-61).

The measurements were made at ambient temperature (22-26°C) under normal atmospheric pressure (740 mm Hg) and with a frequency of 50 Hz, the samples to be tested being immersed in transformer oil to prevent bursting on the surface.

The method of increasing the potential by steps, 2 kV/min, until bursting was produced was used. An electrostatic voltmeter was used as the measuring instrument. The steel electrodes were spherical, 50 mm dia, and rested on the large faces of the sample. One electrode was fixed and the other could be adjusted by a permanent spring which regulated the pressure.

These tests were made with leaves of 150 by 150 by 2 mm. The thickness was measured to 0.01 mm since this dimension is very important for calculating the dielectric rigidity from the measurement of the rupture tension.

Table 4.2 Dielectric rigidity

| Composition of resin | Dielectric rigidity (kV/mm) for various doses (rads) | | | | | | |
|---|---|---|---|---|---|---|---|
| | - | $2{,}31 \times 10^8$ | $5{,}61 \times 10^8$ | $6{,}82 \times 10^8$ | $1{,}21 \times 10^9$ | $1{,}24 \times 10^9$ | $2{,}75 \times 10^9$ |
| 1) DGEBA + MDA | 21,2 ± 0.8 | | | | 17,7 ± 0,8(83,5)* | | 16,1 ± 0,8(76) |
| 2) DGEBA + DADPS | 21,4 " | | | | 18,5 " (86,5) | | 17,5 " (82) |
| 3) DGEBA + MA | 19,0 " | | | | 18,2 " (96) | | 17,8 " (93,5) |
| 4) DGEBA/B + AP | 18,1 " | | | | 17,4 " (96) | | 14,5 " (80) |
| 5) DGEBA + DPA + TETA | 19,6 " | 19,5 ± 0,8(100) | | 16,5 ± 0,8(84) | 0 | | |
| 6) EPN + MA + BDMA | 22,5 " | | 21,0 ± 0,8(93,5) | | | 20,0 ± 0,8(89) | |
| 7) EPN + MDA | 19,1 " | | 20,0 " (105) | | | 18,5 " (97) | |
| 8) TGMD + MA + BDMA | 20,1 " | | 18,7 " (93,5) | | | 18,0 " (90) | |
| 9) TGMD + MDA | 23,4 " | | 23,3 " (100) | | | 25,2 " (108) | |

*Numbers in parentheses indicate percentages of initial values.

No special attention was paid to preparation of the sample, and four specimens were used for each level of radiation. The dispersion of the measurements was around 8%.

## 5. FACTORS THAT AFFECT THE IRRADIATION EFFECTS

The experimental study of the irradiation of epoxy resins permits the conclusion that the radiation resistance of these resins depends especially on (1) the molecular structure and the bonding force, (2) the chemical composition, and (3) the irradiation conditions.

### 5.1 Molecular structure and bonding force

The effect of the molecular structure and the bonding force drops because the energy of the irradiation is absorbed and dissipated in a given volume rather than at the point of impact. In the resins, the energy is distributed along a definite segment of molecules.

i. The epoxy resins of aromatic structure are more resistant than the aliphatic (see Figs. 5.1 and 5.2 and compare also Fig. 5.3 with 5.4 and 5.5). This phenomenon has also been observed in the study of electron magnetic resonance [102] of irradiated epoxy resins. It has been shown that the concentration of carriers of mobile charge is higher in the aliphatic resins. The molecules in the aromatic rings are dispersed homogeneously and are very radiation resistant (Fig. 5.6). The more resistant resins seem to be obtained when, in the chain, the aromatic groups alternate with about six atoms (Figs. 5.7-5.8), e.g. DGA + MPDA.

In the neighborhood of the aromatic rings, the stability of a chain under the impact of a nuclear particle or radiation is due to the fact that (a) the energy received in the irradiation is displaced along the chain, and that (b) the aromatic ring absorbs the energy acquired in passing by the resonance structures. The resonance* energy of a benzene core is such that the vibration-rotation energy imparted to it at the time of impact is dissipated in heat without causing chemical bond rupture in the molecule. The molecules that have the highest resonance energy are the most radiation resistant.

The aliphatic resins do not have a resonance character, which explains their lower resistance to radiation than the aromatics. Further, the chemical bonds between the carbon atoms in the aromatic molecules are stronger than those between the carbon and hydrogen atoms; the reverse is true of the aliphatic chains [103]. The result is that in the aliphatics the rupture is produced in the principal chain (degradation), while in the aromatics it is rather in the secondary groups (reticulation).

ii. The cycloaliphatic epoxy resins are more resistant than the linear aliphatics (Fig. 5.4). This is probably due to the fact that the cycloaliphatics

*While it is possible to establish two or more electron structures of the molecule for almost identical energies, this indicates that this molecule also has an intermediary structure with an energy lower than the established structures. This supplementary factor of stability is called "resonance energy."

Note: In all figures in this group the ordinate runs from 0 to 150 and the abscissa from $1x10^7$ to $1x10^{10}$.

EFFECT OF HARDENERS ON EPOXY RESINS AS A FUNCTION OF RADIATION DOSE

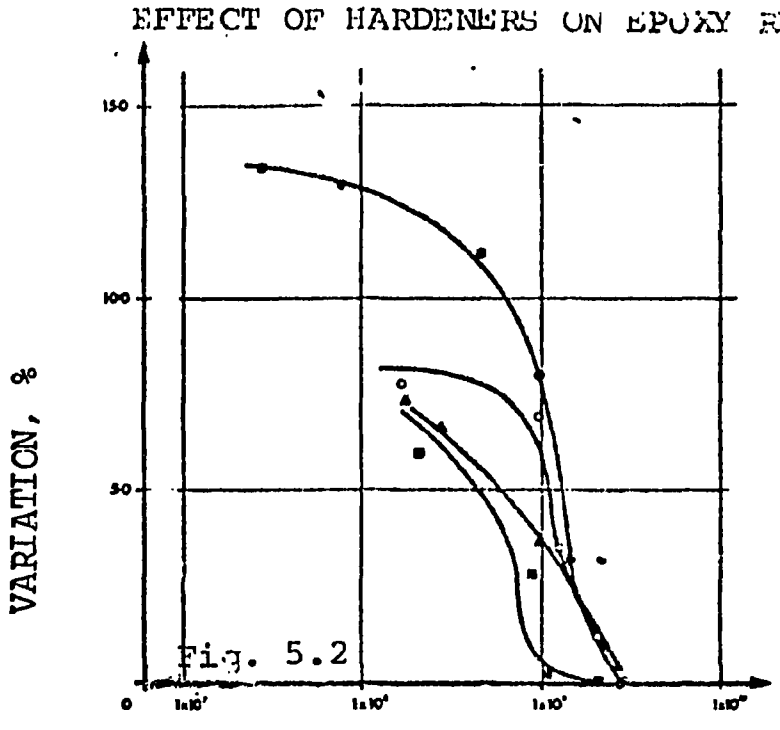



Fig. 5.2

DOSE, rads

Flexion resistance, kg/mm²

| | |
|---|---|
| ● DGEBA+AP | 13 |
| ○ DGEBA+MA+BDMA | 12.3 |
| ▲ DGEBA+NMA+BDMA | 11.8 |
| ▣ DGEBA+DDSA+BDMA | 9 |

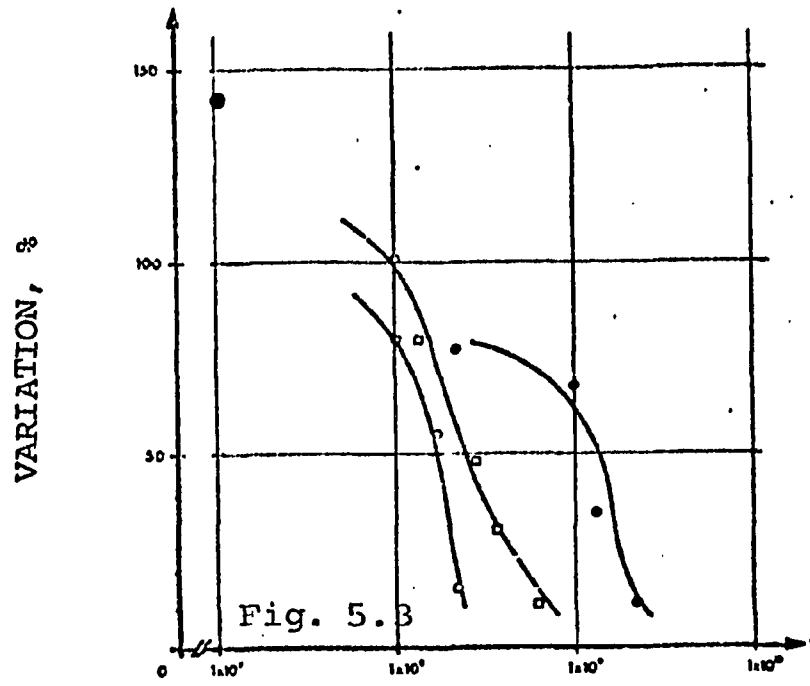



Fig. 5.3

DOSE, rads

Flexion resistance, kg/mm²

| | |
|---|---|
| ○ EDBAH+MA+BDMA | 8.8 |
| ⊠ BECP+MA+BDMA | 7.4 |
| ◐ DGEB+MA+BDMA | 12.3 |

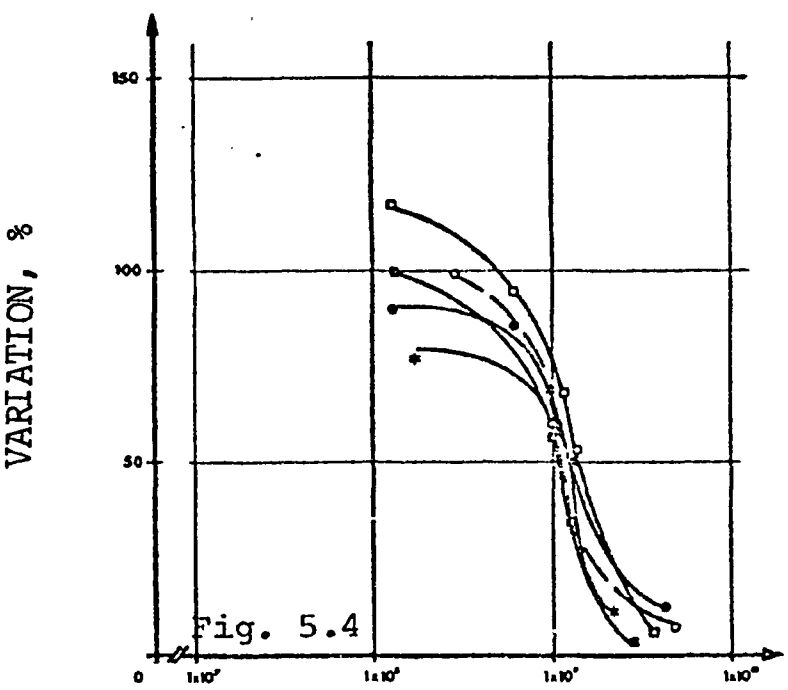



Fig. 5.4

DOSE, rads

Flexion resistance, kg/mm²

| | |
|---|---|
| * DGEBA+MA+BDMA | 12.3 |
| ○ TGTPE+MA+BDMA | 10.5 |
| ◉ TGMD+MA+BDMA | 6.9 |
| ▣ EPN+MA+BDMA | 10 |
| □ DGPP+MA | 8.5 |

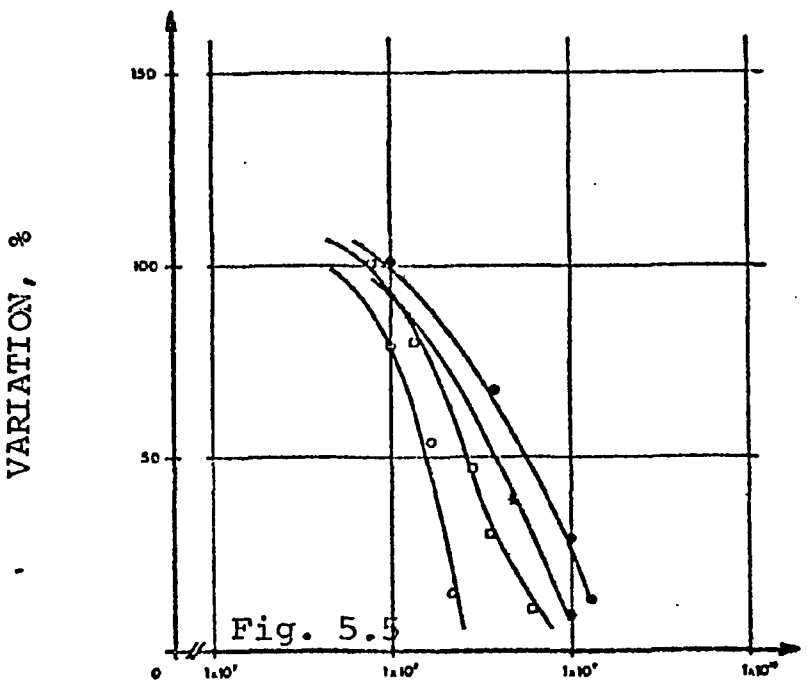



Fig. 5.5

DOSE, rads

Flexion resistance, kg/mm²

| | |
|---|---|
| ◉ DADD+MA | 4.8 |
| * VCD+MA+BDMA | 4.8 |
| ○ EDBAH+MA | 8.8 |
| ⊏ BECP+MA | 7.4 |

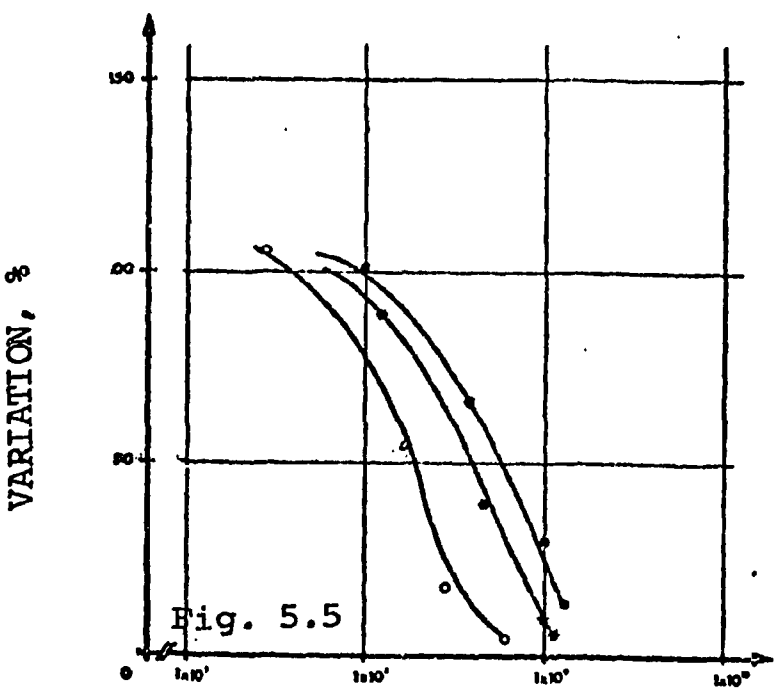



Fig. 5.5

Flexion resistance, kg/mm$^2$

| | |
|---|---|
| ● DADD+MA | 7.4 |
| * VCD+MA+BDMA | 4.8 |
| o ECC+MA | 6.1 |

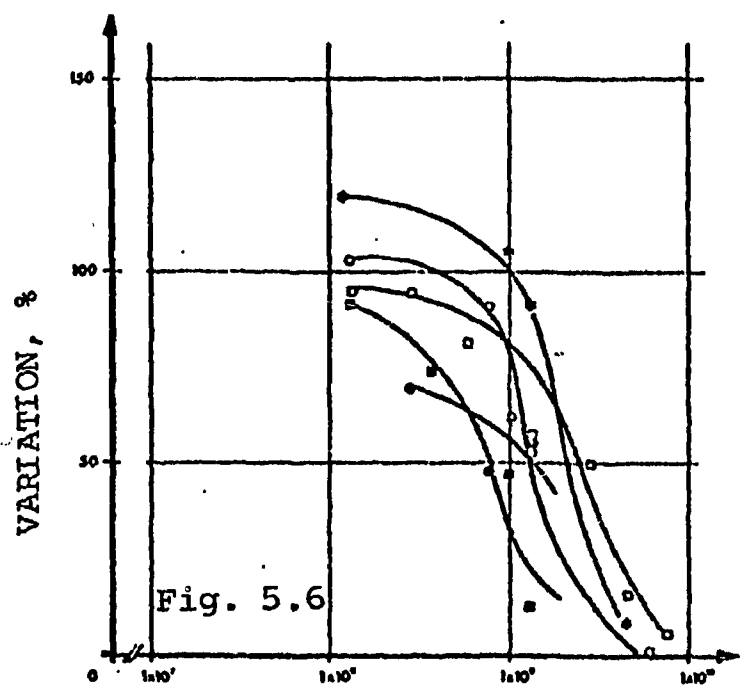



Fig. 5.6

Flexion resistance, kg/mm$^2$

| | |
|---|---|
| ● DGEBA+DADPS | 15.4 |
| o TGTPE+DADPS | 7.1 |
| * TGMI+DADPS | 9.1 |
| □ EPN+DADPS | 14.5 |
| ■ DGPP+DADPS | 9.5 |

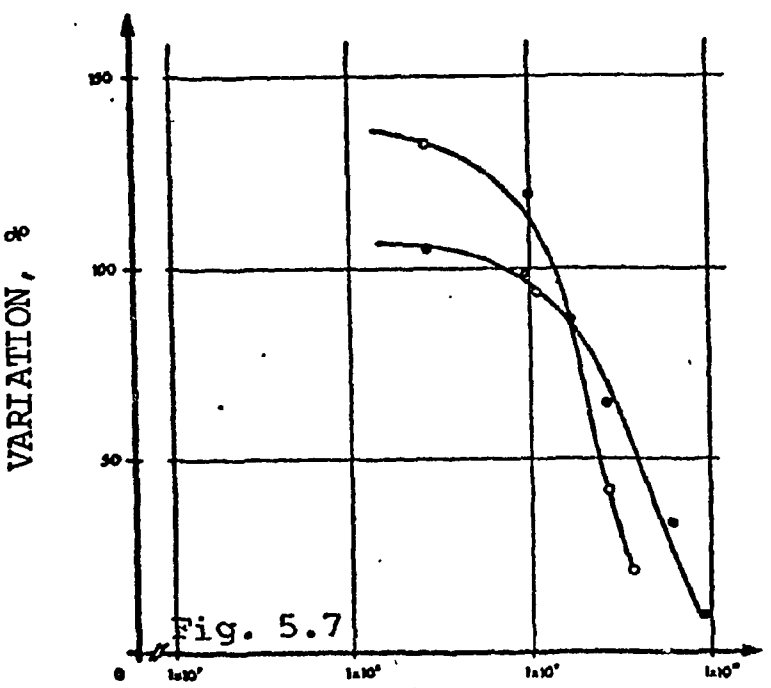



Fig. 5.7

Flexion resistance, kg/mm$^2$

| | |
|---|---|
| DGEBA+MPDA | 12 |
| DGA+MPDA | 9 |

[symbols missing on original]

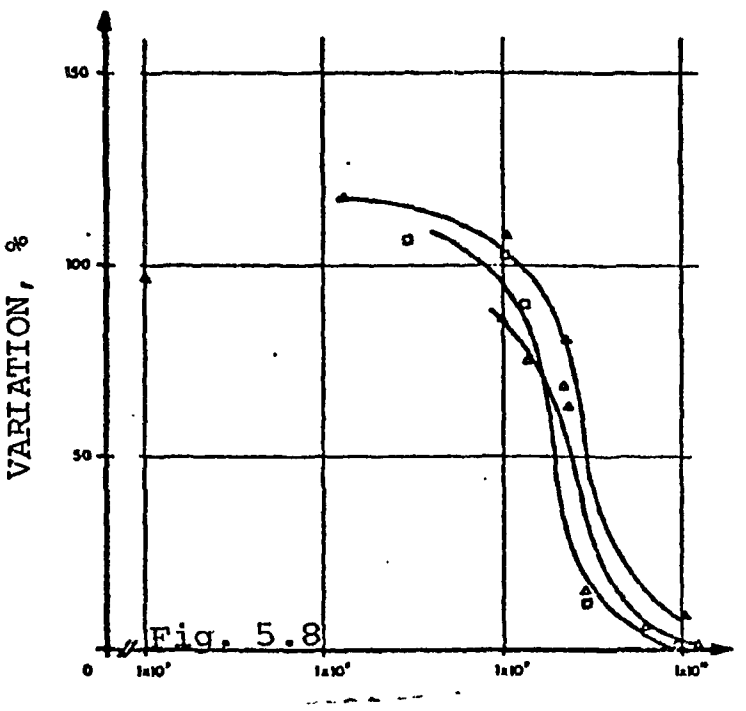


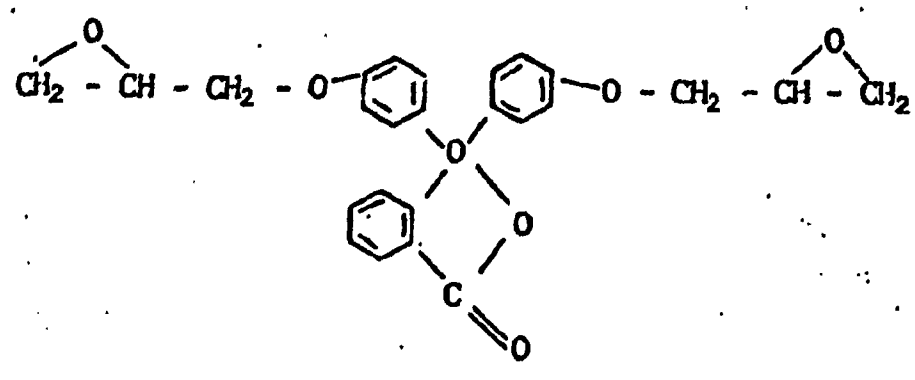

Fig. 5.8

Flexion resistance, kg/mm$^2$

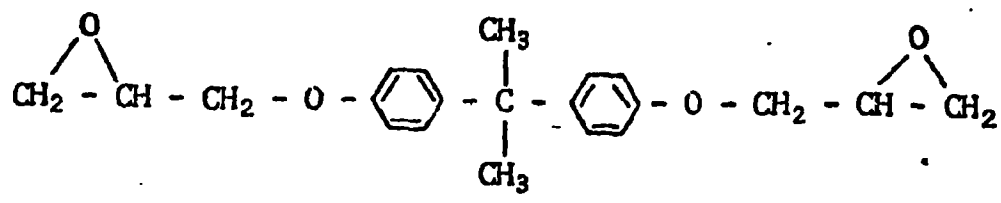
| | |
|---|---|
| ▽ TGMD+NMA+BDMA | 8.5 |
| △ TGPAP+NMA | 13.6 |
| ▲ DGA+NMA | 10.3 |

are capable of forming very rigid epoxy structures. It is probable that a rupture in a cycloaliphatic resin is followed by a recombination of the ruptured bond. The product will be attacked only by absorption of a higher amount of energy.

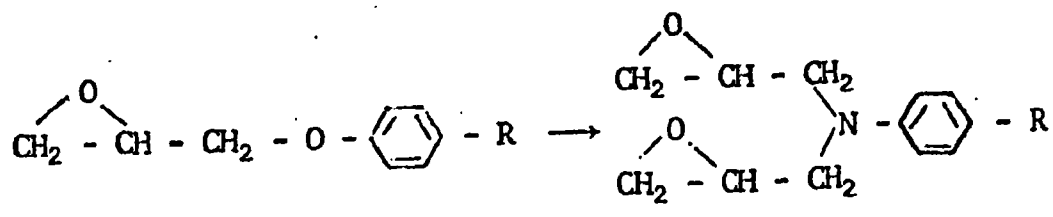
iii. A high local concentration of benzene groups risks steric disarrangements in the epoxy resin. These resins are also not so resistant as we would expect (Fig. 5.6).



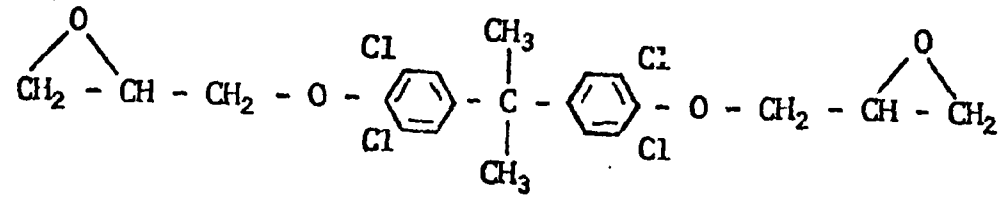
iv. The quaternary carbon atoms always have weak points ~~to~~ *in* the irradiation. They are easily attacked by the radiation. The same phenomenon has been observed in studies of thermal resistance of polymers (Figs. 5.3-5.6) [104].



v. The presence of ether groups in the epoxy resins seems to be a weakness. A good solution consists in replacing these groups by amines or in suppressing them completely (Figs. 5.1, 5.7, 5.8, Chap. III).



vi. The presence of chlorine in the aromatic ring of the resin does not seem to decrease its resistance to radiation very much although the chlorine atom has a tendency to capture thermal neutrons, producing high-energy (0.62 MeV) protons (Fig. 5.9).



vii. Resins with basic groups seem more resistant than those with acid groups (Fig. 5.10). There could be two reasons for this:

a) The epoxy resins hardened by anhydride type hardeners have - C - O - groups in their structure, which are known to be sensitive to radiation.

b) The basic groups in resins hardened by amines can react with hydrogen ions, generally formed by the action of radiation on epoxy resins, and this reaction could interfere with structure changes.

viii. Resins with a large number of epoxy groups well distributed in their molecules give more radiation resistant products than those with a small number of epoxy groups. The first are capable of forming denser and more rigid structures. The reticulation density has been measured by the HDT method [105]. It should be noted that the resins with a high HDT value are also very radiation resistant (Table 5.1). In addition, an epoxy equivalent lower than 200 is a condition for good radiation resistance of aromatic resins.

TABLE 5.1

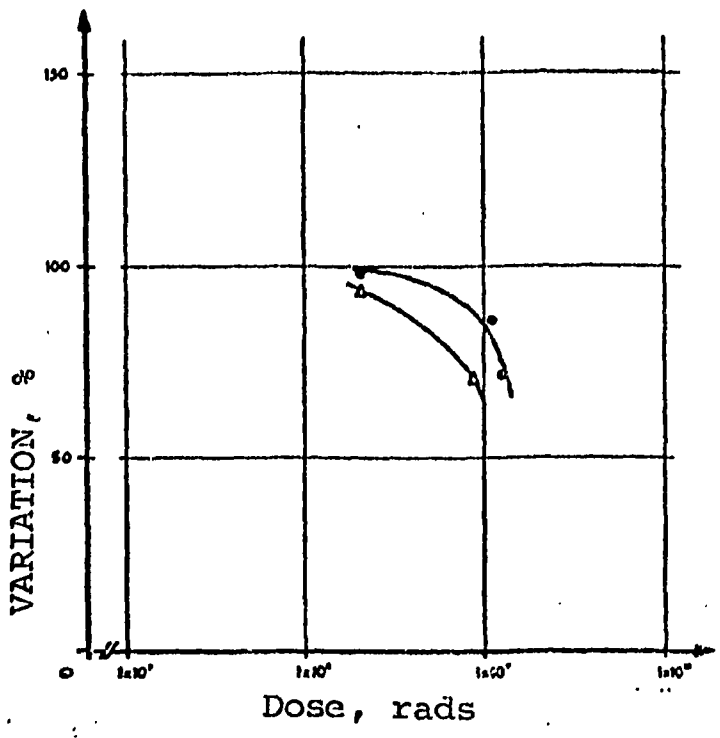
| Composition of resin | epoxy equivalent | HDT °C | Resistance to radiation (threshold) (rad) |
|---|---|---|---|
| DGEBA + MDA | 180 | > 150 | > $1.10^9$ |
| DGEBA + DBP + TETA | 400 | ∿ 60 | ∿ $10^7$ |
| EPN + MDA | 180 | > 200 | > $2.10^9$ |

## 5.2 Chemical Composition

All the elements composing the epoxy resins play their part in determining the radiation resistance. Let us look at them point by point:

### 5.2.1 Resins

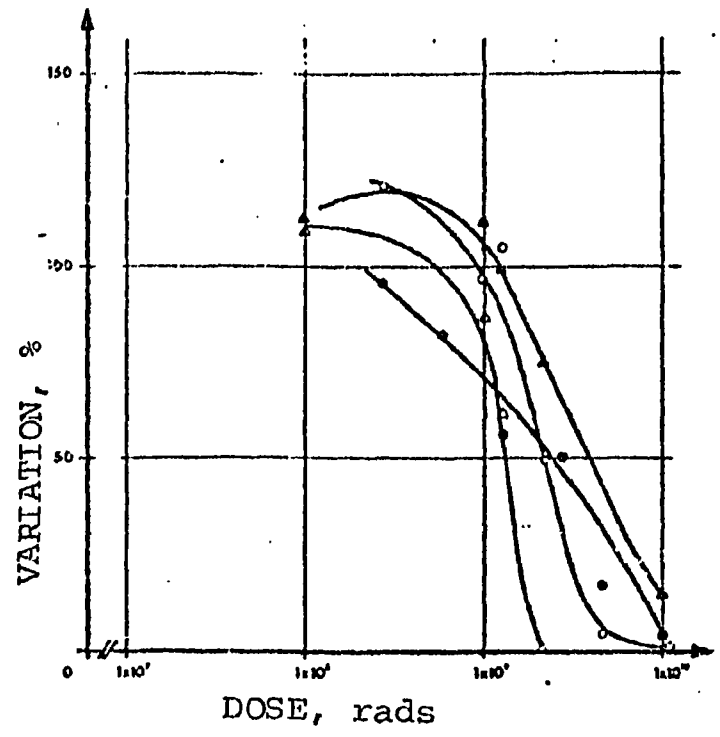
Figures 5.3, 5.6-5.8 demonstrate the effect of a given hardener on different types of aromatic epoxy resins as a function of the irradiation, while Figs. 5.1, 5.4, 5.5 show the effect of a given hardener on different types of aliphatic resins. It can be determined that almost all the aromatic compositions are radiation resistant up to $1x10^9$ rads. The composition DGA + MPDA still has 10% of its initial mechanical properties at $1 \times 10^{10}$ rads. On the other hand, most of the aliphatic resins begin to deteriorate at $2x10^8$ rads.




Resistance to Flexion

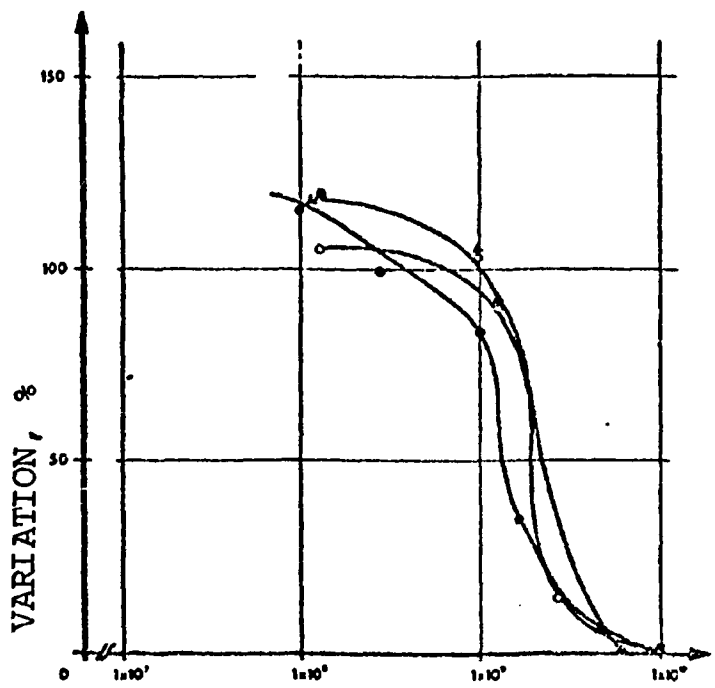
- ● DGEBA + MDA 16 kg/mm$^2$
- △ EDTC + MDA 11.2 "

Fig. 5.9 Effect of a given hardener on epoxy resin resistance to radiation.




- ● EPN + DADPS 14.5 kg/mm$^2$
- o EPN + NMA + BDMA 6.9
- ▲ EPN + MDA 7.9
- △ EPN + HPA + BDMA 15.6

Fig. 5.10 Effect of different hardeners on resistance of epoxy resins exposed to radiation. (experimental resins).




- ● TGMD + MA + BDMA 6.9 kg/mm$^2$
- o TGMD + NMA + BDMA 13.3
- ▲ TGMD + DADPS 9.1

Fig. 5.11 Effect of different hardeners on resistance of epoxy resins exposed to radiation. (experimental resins)

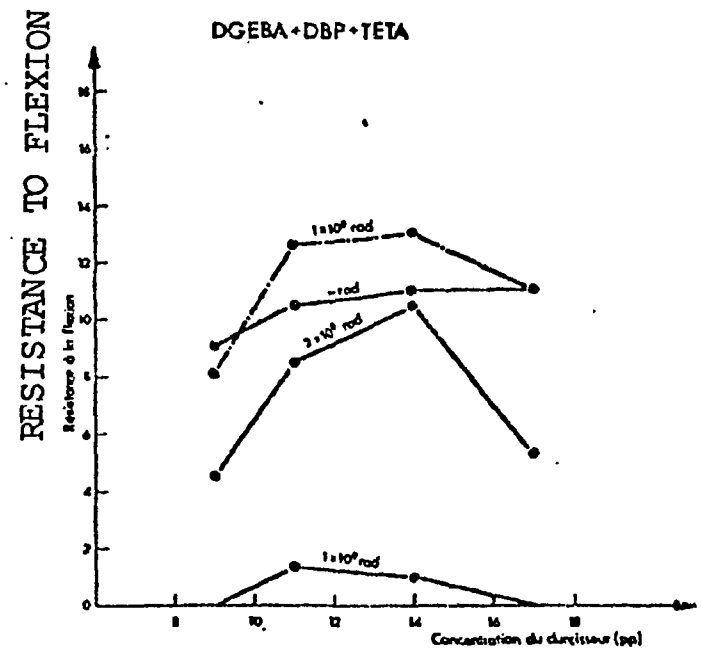



Fig. 5.12 Effect of different concentrations of hardeners on resistance of epoxy resins to radiation.

### 5.2.2 Hardeners

The effect of different hardeners on the resistance of epoxy resins to radiation is shown in Fig. 5.2 for standard resins and in Figs. 5.10 and 5.11 for experimental resins. It may again be seen that the aromatic amines give the most radiation-resistant compositions. From Figs. 5.12 and 5.13 it may be seen that the concentration of the hardener used is important. The best results were obtained with a concentration equal to the stoichiometric value.

### 5.2.3 Charges

Charged resins may be divided into two categories: those charged with powder and those that are stratified.

#### 5.2.3.1 Resins loaded with powder

Resins filled with mineral loads are in general more radiation resistnat than the non-loaded ones, but the latter are in turn more resistant than those loaded with organic materials (paper, etc.) (Fig. 5.14) [102]. The resistance increases with the size of the load (Fig. 5.15). The size of the grains also plays a role: the largest seem the most radiation resistant (5.16). The choice of hardener is not affected by the presence of a charge (Fig. 5.17).

#### 5.3.3.2 Resins layered with glass or silica fabric

These are the most radiation resistant (Fig. 5.18). All systems studied resisted more than 20 kg/mm$^2$ at $5 \times 10^9$ rads (Fig. 5.19, 5.20). From these figures it may be seen that the resins layered in silica fabric are more radiation resistant than those reinforced with glass fabric. The explanation may be found in the fact that the glass contains several percent boron oxide, where the element boron has a high effective capture cross-section ( $\sigma_o = 755$ barns) for thermal neutrons. The energy stored by this process in the glass fabric may reach 30% of the total energy received for radiations made in position 1 of the ASTRA reactor. The capture reaction may be written as follows:

$$^{5}_{9}B + ^{0}_{1}n \rightarrow ^{3}_{7}Li + ^{2}_{4}He$$

The alpha particle produced has a trajectory in the material that is so short that we can estimate that all its energy, E, liberated by the reaction is absorbed in the irradiated sample, causing supplementary damage in the resins layered with glass fabric.

The amount of energy deposited, by irradiation, in the layers due to the presence of boron in the glass can be evaluated as follows: The layers contain at least 50 wt % glass, which contains a maximum of 8% $B_2O_3$.
Then the boron content $= 0{,}50 \times 0{,}08 \times \frac{21{,}64}{69{,}64}$ g/g of layer $= 0{,}0124 \times \frac{6{,}025 \times 10^{13}}{10{,}82}$

$= 6{,}9 \times 10^{20}$ atoms of natural B per g of layer.

With a reactor flux of $5 \times 10^{10}$ n/cm$^2$.sec, the number of neutrons captured per second will be $6{,}9 \times 10^{20} \times 5.10^{10} \times 755.10^{-24} = 2{,}6 \times 10^{10}$. Each capture reaction emits an alpha particle with an energy of 2.57 MeV. The energy deposited is then

$$= 2{,}6 \times 10^{10} \times 2{,}57 \times 10^{6} \times 1{,}6 \times 10^{-12} \times 10^{-2} \text{ rad/s}$$

$$= 1 \times 10^{3} \text{ rad/s or } 3.6 \times 10^{6} \text{ rad/h.}$$

### 5.2.3.3 Hypotheses on the role of the charge

#### 1. Effect of dilution

A loaded resin may be considered as a resin diluted with mineral products (alumina, silica, etc.) or with organic products (paper, cotton, etc.). In such a resin, only a fraction of the energy will be absorbed by the resin and the rest by the charge.

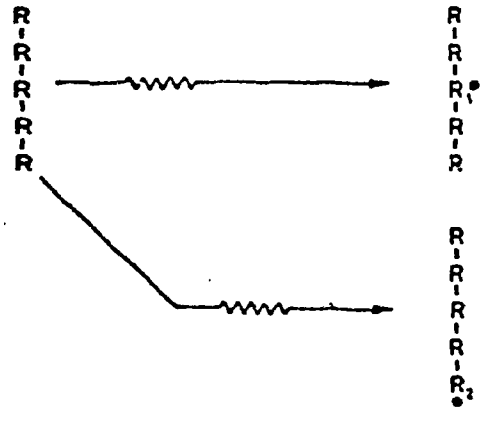
The mineral charges being more radiation resistant than the resins, the resins containing minerals will be more radiation resistant than pure resins. The reverse is true for resins loaded with paper, cotton, etc.

#### 2. Fixation of free radicals

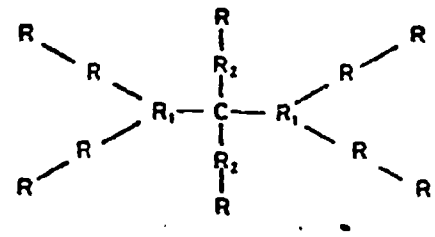
The effects of radiation are often the result of secondary reactions, for example, a radical formed in the system reacts with another molecule, causing the changes observed. The charge may then capture the radicals and thus hinder the secondary reactions. In this case, a bond between the radicals of the resin and the radicals on the surface of the charge will be made. For carbon black, this hypothesis is valid because the epoxy resins containing graphite have a very high concentration of radicals before irradiation [102]. It has been possible to show by a chemical method [106] and by electron paramagnetic resonance [107] the radical nature of carbon black.

The mechanism of the reaction between the organic chains and the carbon black may be described as follows:

Reaction of deterioration



Reaction of repair



$R_1$ and $R_2$ are radicals
R = aromatic groups
C = carbon black

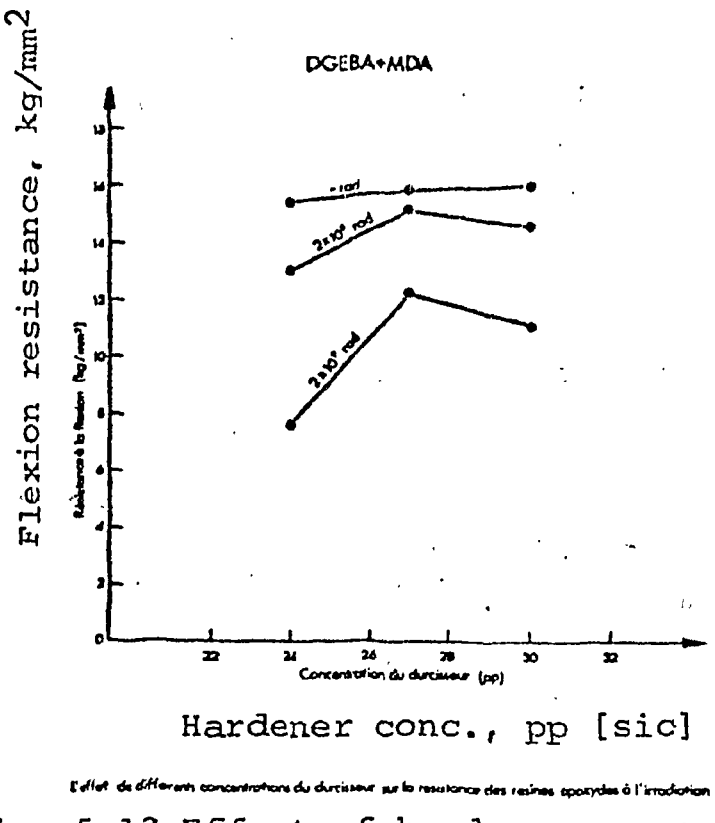
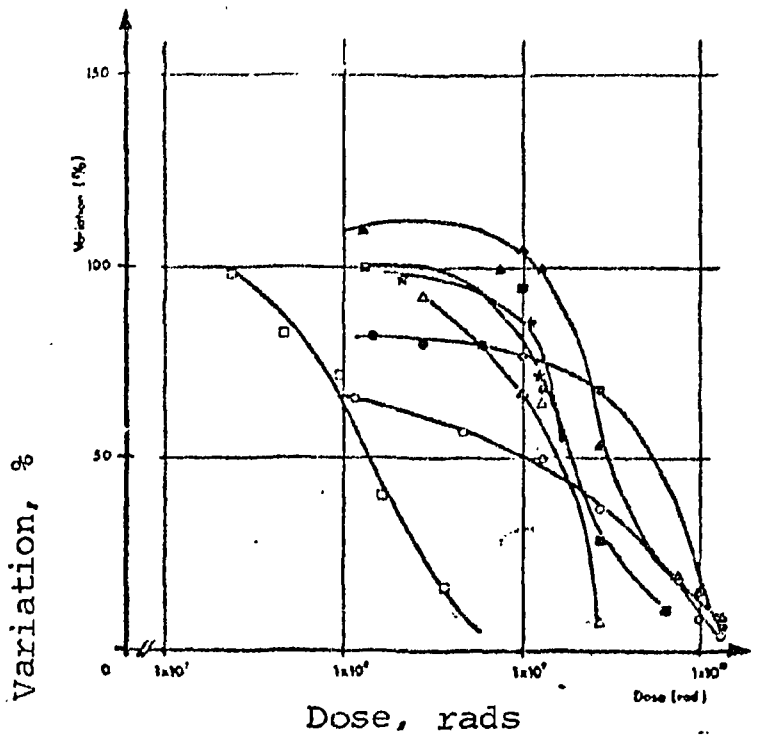


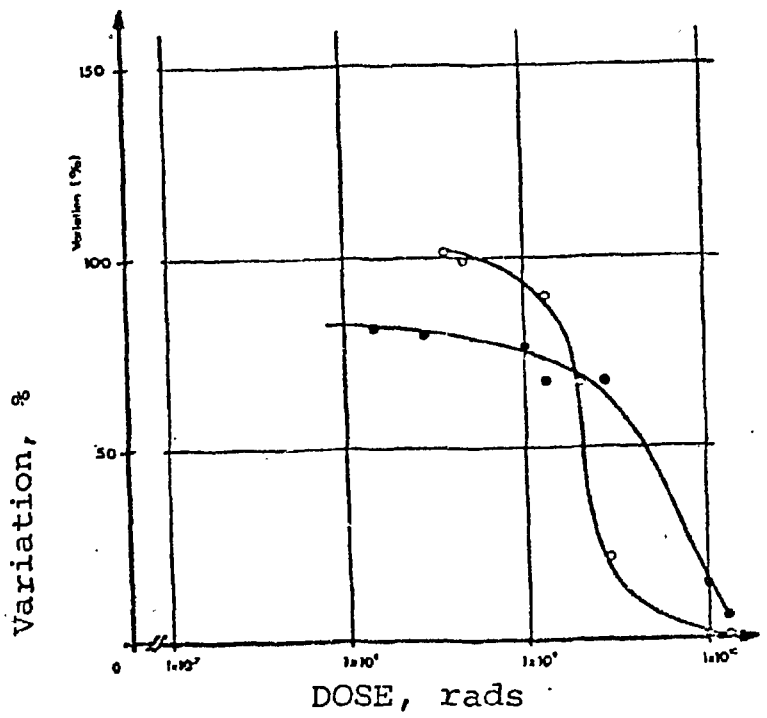

Fig. 5.13 Effect of hardener concentration on charged epoxy resin resistance to radiation.




Flexion resistance kg/mm2

- ● DGEBA+MDA+alumina (100-27-220) 11.4
- o DGEBA+MDA+silica (100-27-200) 10.5
- DGEBA+MDA+graphite (100-27-60) 6.3
- DGEBA+MDA+aerosil+$BaSO_4$ (100-27-2-150 5.8
- DGEBA+MDA+magnesia (100-27-120) 8.7
- DGEBA+MDA+paper(100-27-200 10.2
- * DGEBA+MDA (100-27) 16

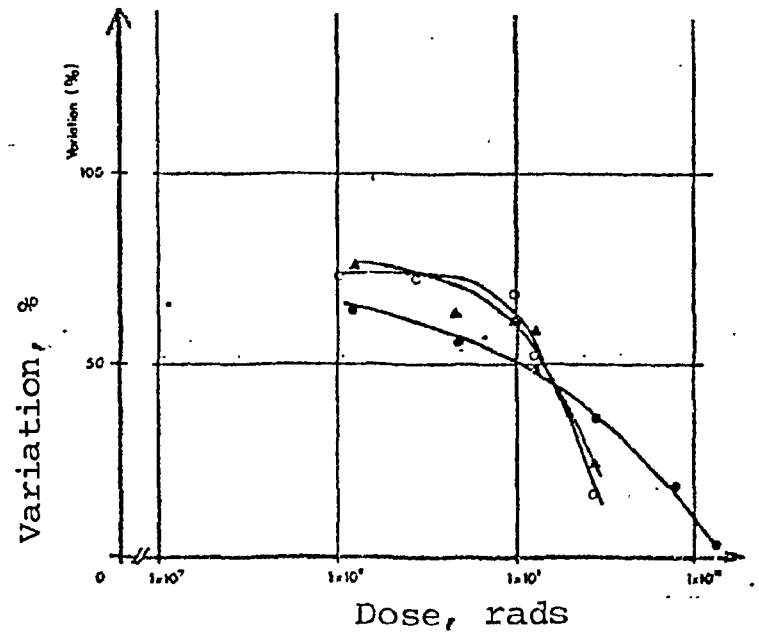
Fig. 5.14 Effect of different loadings on resistance of epoxy resins to radiation.




Flexion resistance kg/mm2

- ● DGEBA+MDA+alumina (100-27-220) 11.4
- o DGEBA+MDA+alumina (100-27-100) 12

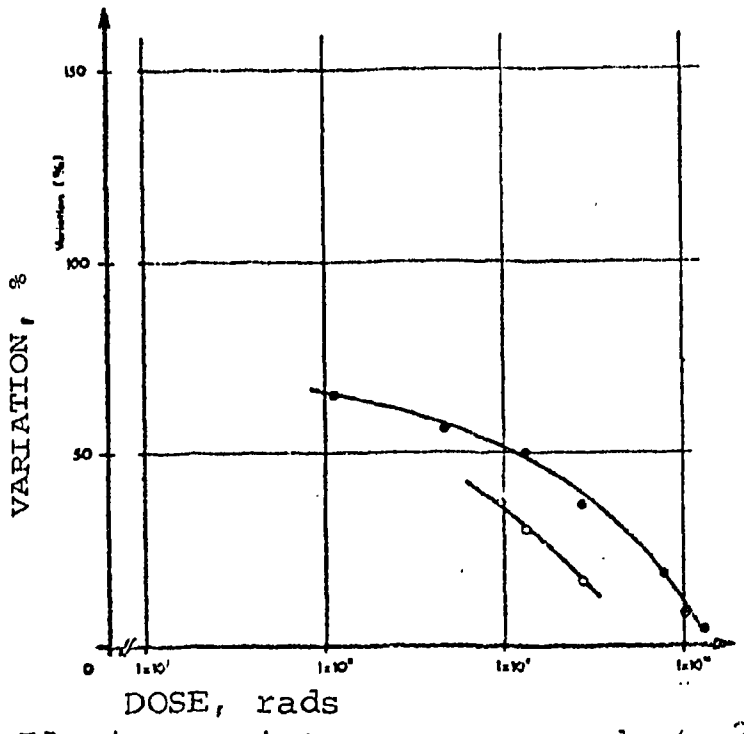
Fig. 5.15 Effect of loading concentration on rhe resistance of epoxy resins to radiation.




Flexion resistance kg/mm2

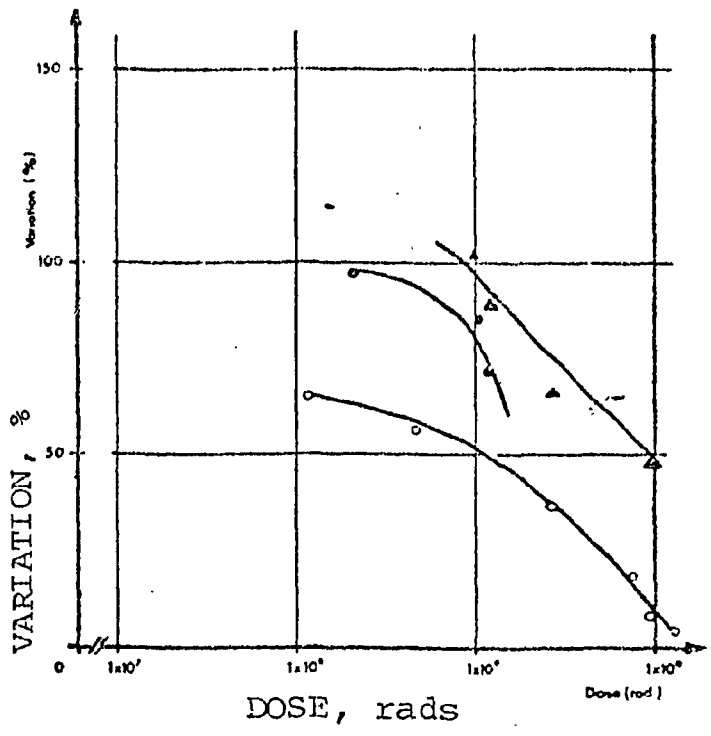
- ● DGEBA+MDA+silica (40u) (100-27-20) 10.5
- o DGEBA+MDA+silica (20u) (100-27-20) 9.3
- DGEBA+MDA+silica (5u) (100-27-20) 9.5

Fig. 5.16 Effect of grain size of charge on resistance of epoxy resins to radiation.



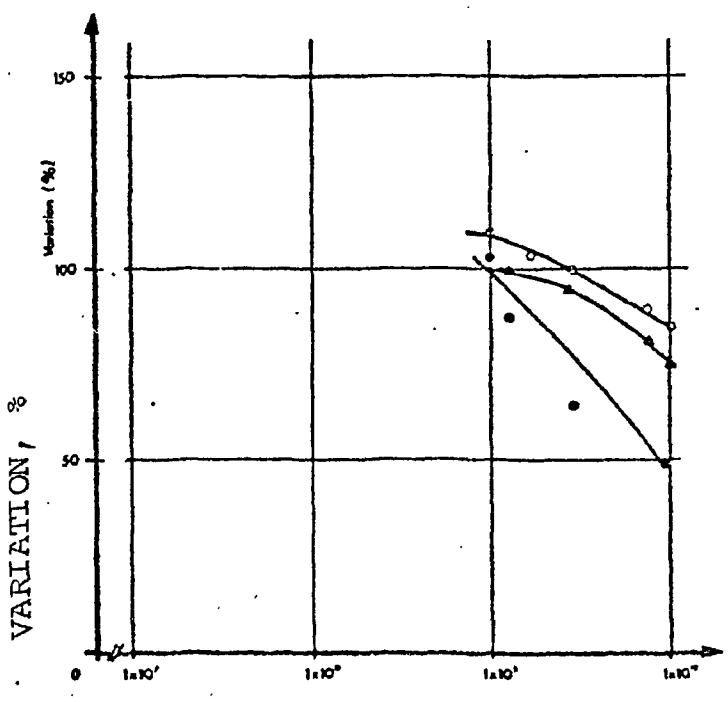

| Flexion resistance | kg/mm$^2$ |
|---|---|
| ● DGEBA+MDA+silica (40μ) (100-27-200 | 10.5 |
| o DGEBA+HPA+BDMA+silica (40μ) (100-80-2-200) | 9.4 |

Fig. 5.17 Effect of different hardeners on resistance of loaded eopxy resins to radiation



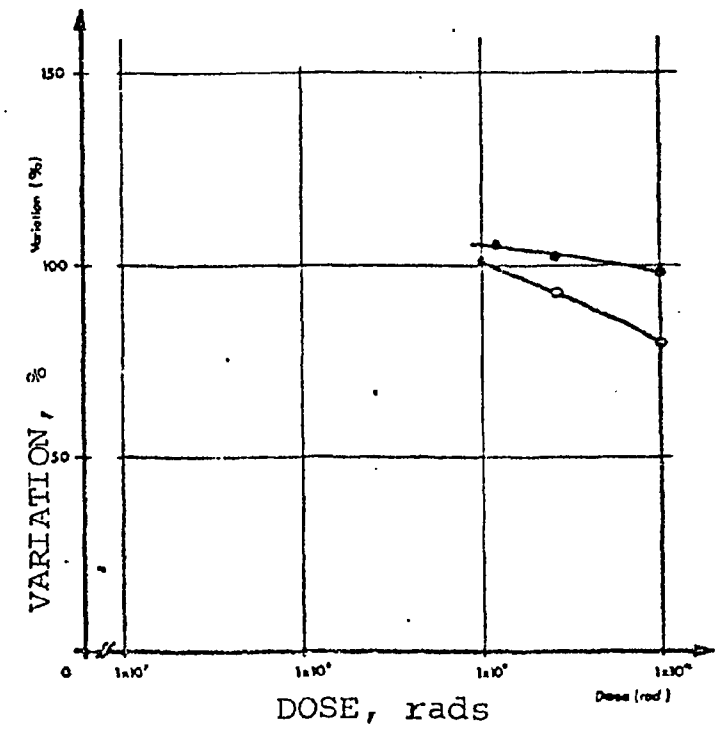

| Flexion resistance | kg/mm$^2$ |
|---|---|
| ◎ DGEBA+MDA+silica (100-27) | 17 |
| o DGEBA+MDA+silica (100-27-200) | 10.5 |
| ▲ DGEBA+MDA+flass fibers (100-27-60) | 39.1 |

Fig. 5.18 Effect of different loadings on the resistance of epoxy resins to radiation.



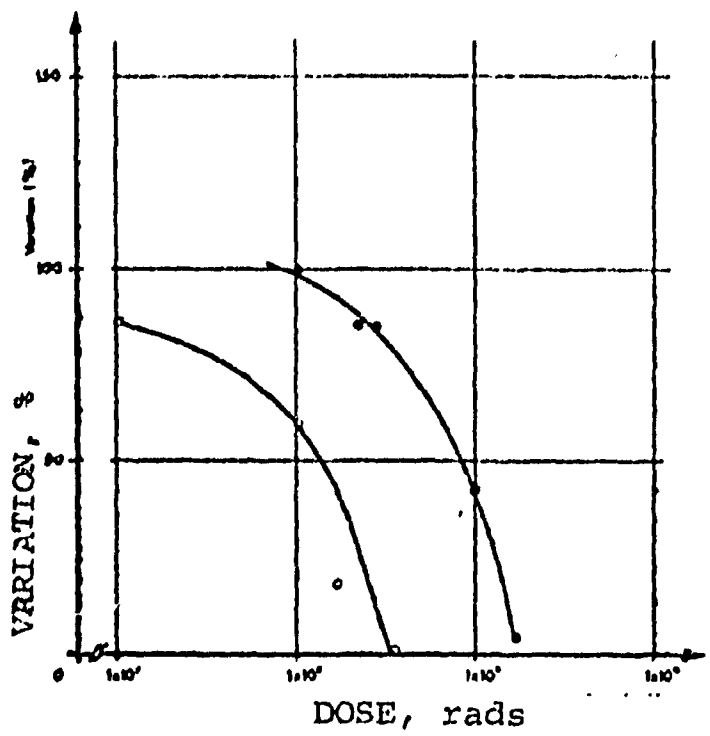

| Flexion resistance | kg/mm$^2$ |
|---|---|
| ◉ DGEBA+MDA+glass fiber | 39.1 |
| o TGMD+MDA+glass fiber | 39.4 |
| ▲ EPN+MDA+glass fiber | 36.4 |

Fig. 5.19 Effect of a given hardener on different types of layered epoxy resins as a function of absorbed dose.



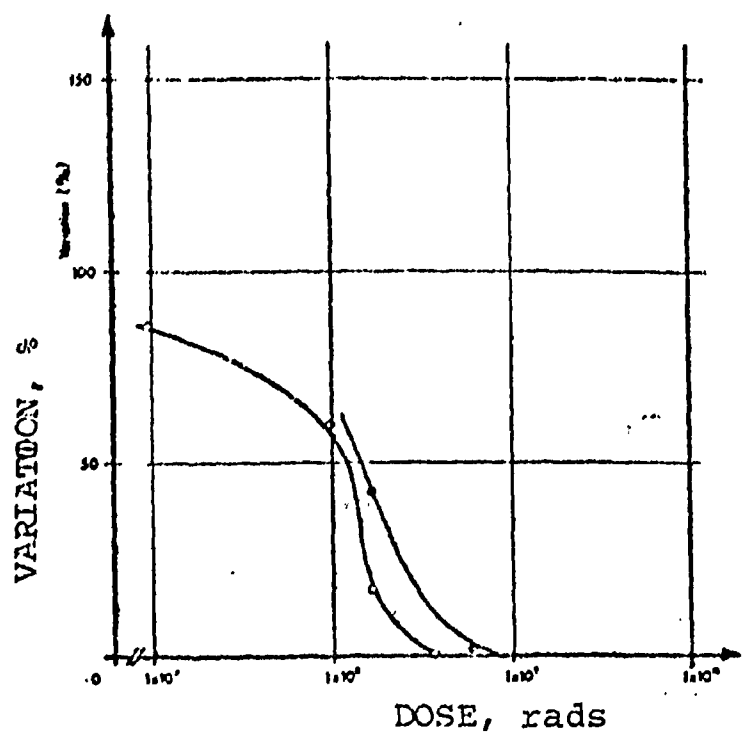

| Flexion resistance | kg/mm$^2$ |
|---|---|
| ◎ TGMD+MDA+silica fiber | 59.5 |
| o TGMD+DADPS+silica fiber | 52.8 |

Fig. 5.20 Effect of different hardeners on resistance of layered epoxy resins to radiation.



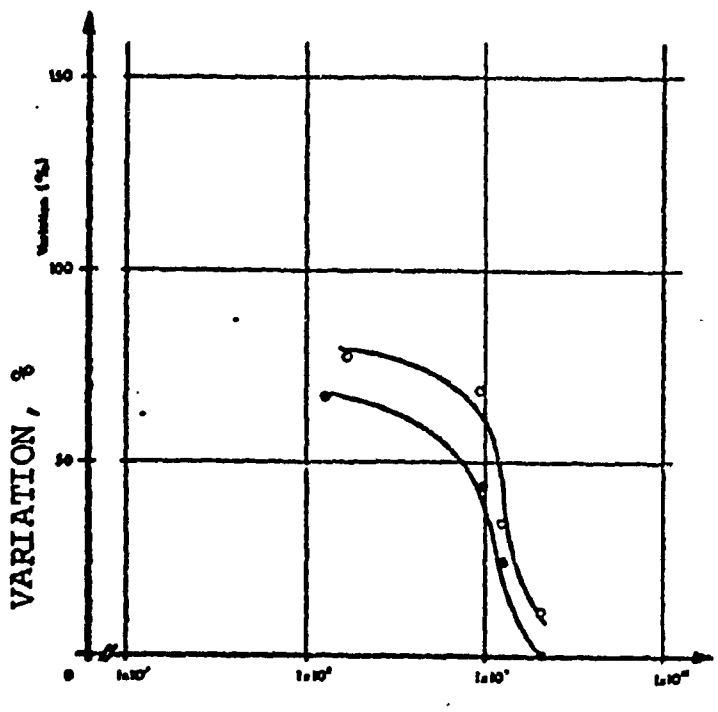

● DGEBA+EDGDP+MDA (100-20-30) 10.2 kg/mm²
o DGEBA+EDGP+TETA (100-20-12) 12.2

Fig. 5.21 Effect of different hardeners on radiation resistance of diluted epoxy resins.



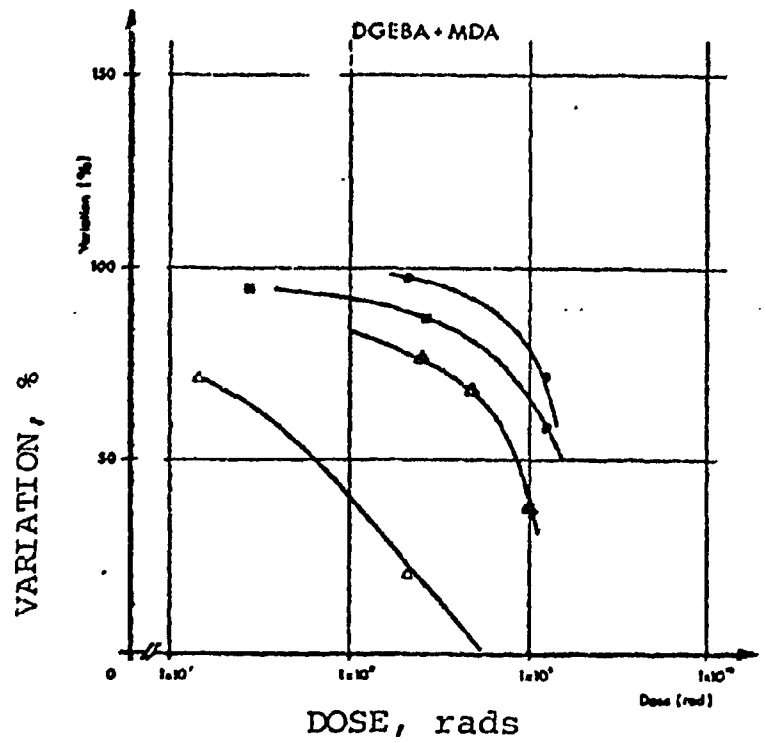

● DGEBA+EDGDP+TETA (100-20-12) 12.2 kg/mm²
o DGEBA+DBP+TETA (83-17-9) 8.9

Fig. 5.22 Effect of diluents on the radiation resistance of epoxy resins.




● DGEBA+MA (100-100) 13.9 kg/mm²
o DGEBA+MA+BDMA+PoGl 12.3

Fig. 5.23 Effect of an accelerator and a flexibilizer on the radiation resistance of an epoxy resin.




■ air, 25°C
o air, 40°C
▲ air, 80°C
△ air, 120°C

Fig. 5.24 Effect of temperature on radiation resistance of an epoxy resin (in air).

This structure shows that each particle of carbon black is able to reticulate different radical chains. This structure also has a rigid character and breakage in one of the bound chains is not critical since its resistance is still conditioned by bonds of other chains [108].

### 5.2.4 Auxiliary products

The use of auxiliary products (accelerator, diluent, flexibilizer, etc.) during the hardening of epoxy resins gives products less resistant to irradiation. These products are often of the aliphatic type, whence the low resistance (Figs. 5.21-5.23).

## 5.3 Irradiation conditions

### 5.3.1 Atmosphere

The nature of the medium has practically no effect on the mechanism of deterioration of irradiated epoxy resins. Irradiation of an epoxy resin in an inert gas such as helium or nitrogen or in a normal atmosphere does not seem to cause any difference relative to irradiation in a vacuum (i.e., physical difference). These studies were made on 6-mm-thick samples and an irradiation rate of about $10^7$ rads/hr. Similar observations on the mechanical properties of polyethylene were made in France by Chapiro [109].

The mechanical properties are a little more marked for resins highly irradiated in water (maximum 30% more deterioration at $2\times10^9$ rads). Water diffused into the testtube, physically degraded, can be transformed to hydrogen and oxygen during the irradiation [110]. These liberated gases cause internal tensions in the substance, which are the causes of the differences observed in the mechanical properties.

### 5.3.2 Temperature

It is well known that temperature accelerates all chemical processes, especially the phenomena of oxidation and radio-oxidation [111]. Thus we would expect the temperature to accelerate the deterioration of irradiated materials, which is what is observed in epoxy resins. Figure 5.24 shows that the damage increases as a function of the irradiation temperature. Under irradiation at ambient temperature, small differences have been noted below 80°C. Very important differencts were recorded starting at 120°C. Photograph 5.1 shows the physical appearance of epoxy resins irradiated at 120°C.

### 5.3.3 Effect of the nature and rate of the irradiation

Similar tests made with a nuclear reactor (neutrons plus gamma rays) and ~~used~~ spent fuel elements (gamma rays) have shown that the different radiations used, as well as the irradiation rate, give similar effects for the same absorbed energies (Figs. 5.25,5.26).

# 6. CONCLUSIONS

The stability of epoxy resins under irradiation depends principally on their molecular structure and the force of the chemical bonds. This

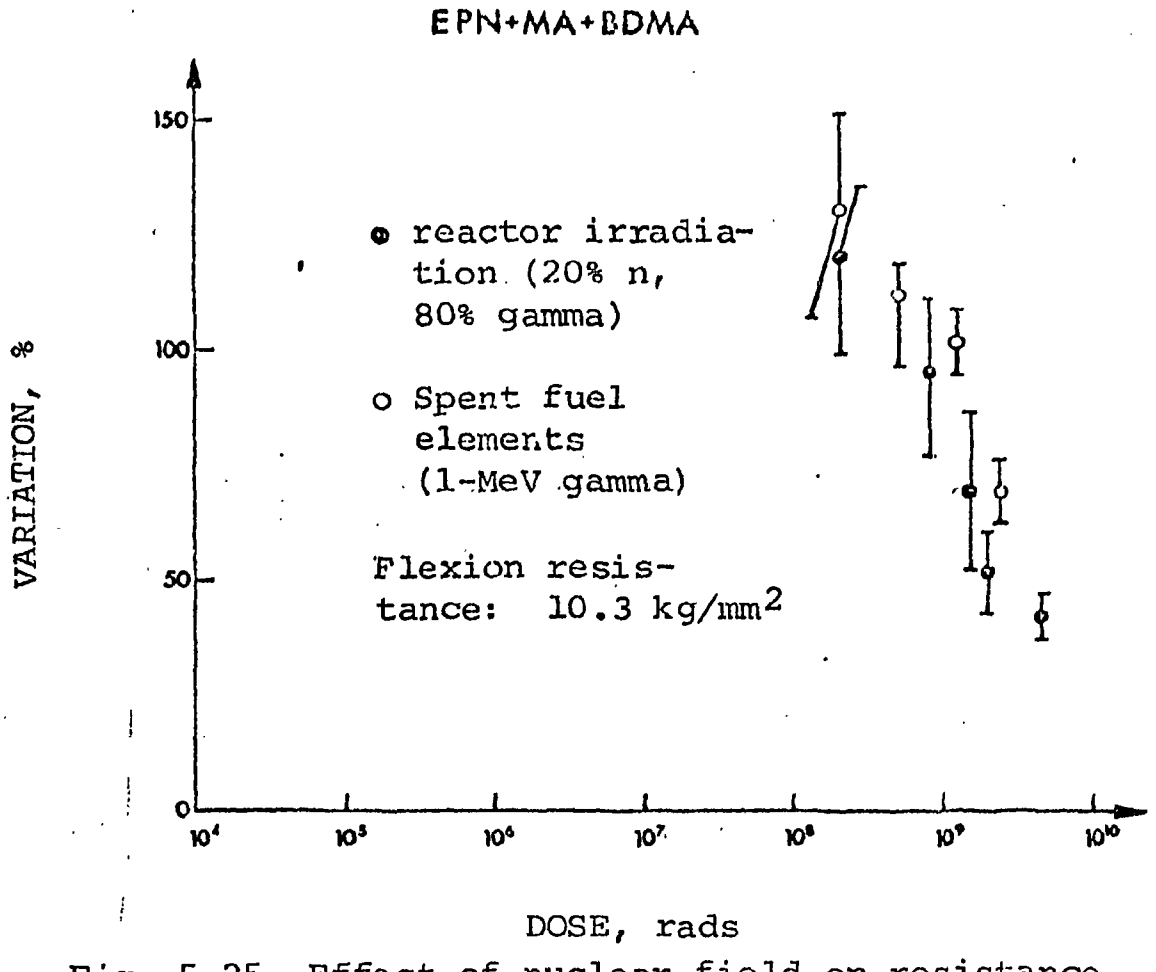



Fig. 5.25 Effect of nuclear field on resistance of epoxy resins to radiation.

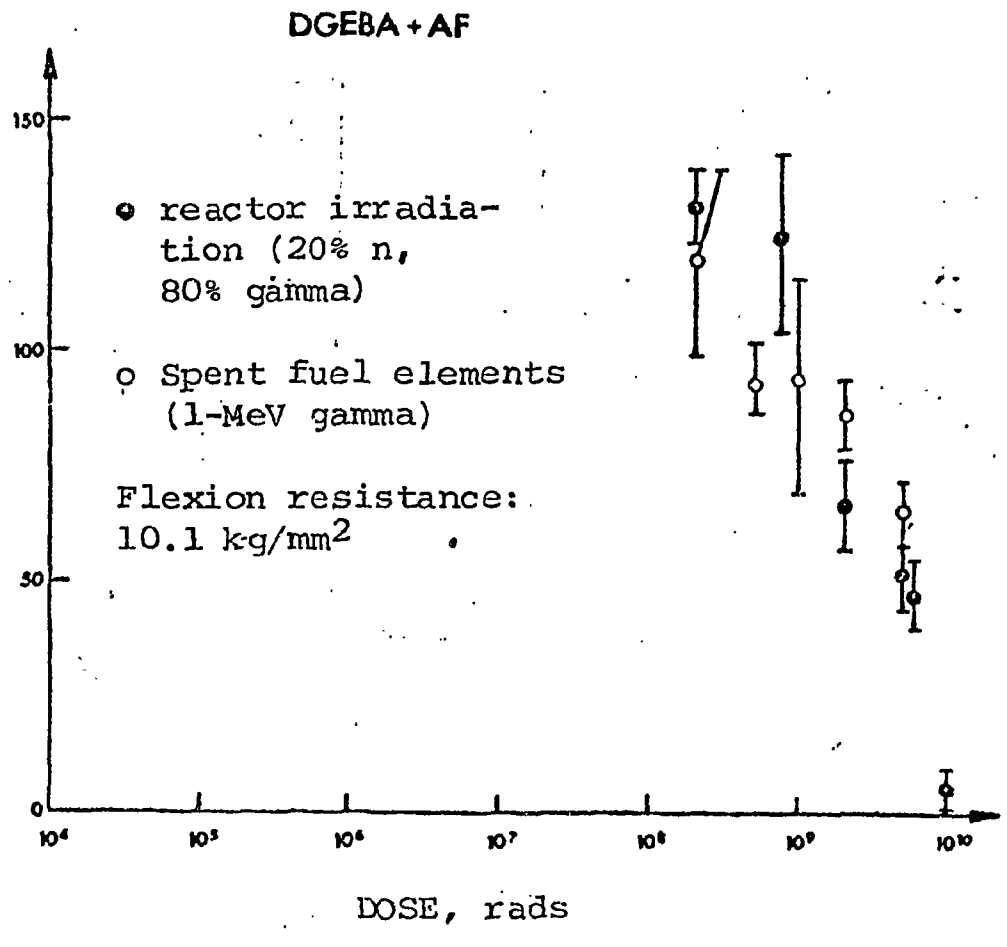


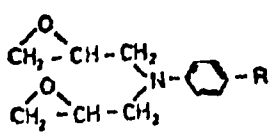

Fig. 5.26 Effect of nuclear field on resistance of epoxy resins to radiation.

effect results from the fact that the radiation energy is absorbed and decreased in the whole of a given volume.

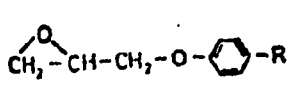
This study permitted arranging, in order of decreasing resistance, the epoxy structures.

## 6.1 Epoxy resins

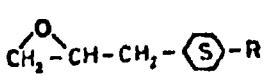
6.1.1



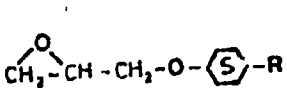
[6.1]



[6.2]

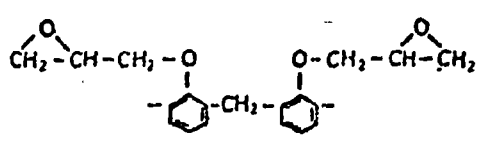


[6.3]

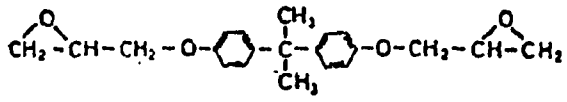


[6.4]

6.1.2

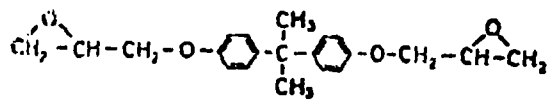


[6.5]

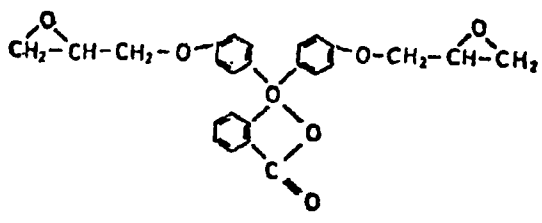


[6.6]

6.1.3

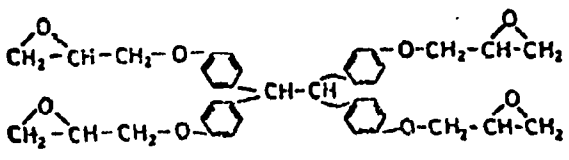


[6.6]

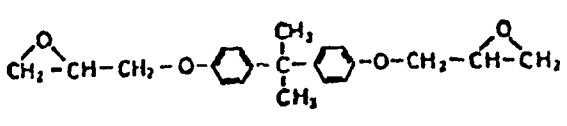


[6.7]

6.1.4

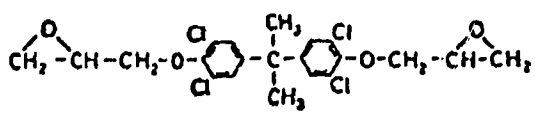


[6.8]



[6.6]

6.1.5



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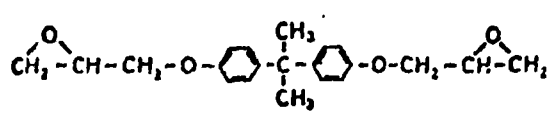
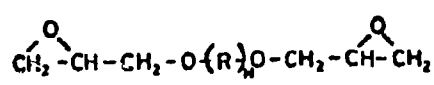
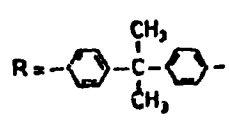


[6.6]

6.1.6





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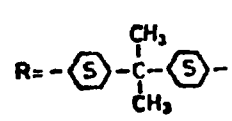

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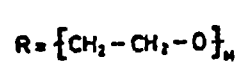
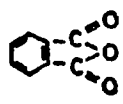


[6.11]

## 6.2 Hardeners

6.2.1



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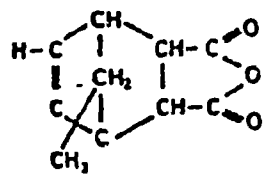

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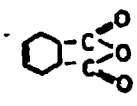

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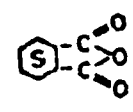
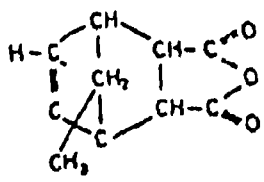
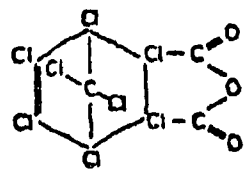


[6.15]

6.2.2



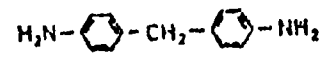
[6.13]



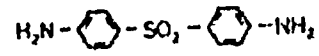
[6.16]

6.2.3

[6.17]

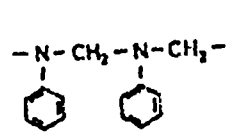


[6.18]

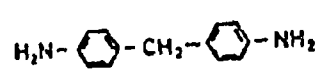


[6.19]

6.2.4



[6.20]

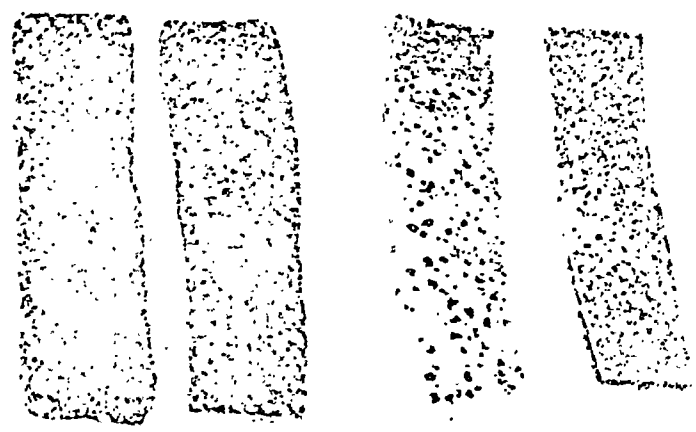


[6.18]

3 x 10⁵ rad

3 x 10⁶ rad

5 x 10⁶ rad



Air

$H_2O$

Photograph 5.1 DGEBA + MDA - 120° C.

6.3.

There are compositions which start to deteriorate between $10^7$ and $10^8$ rads and there are others which are as radiation resistant as the ceramics. The resistance to radiation can vary by a factor of 100.

Resins of the amine glycidic and novolac types, mixtures with an aromatic hardener, show a considerable improvement in radiation-resistance properties compared to other systems. The resin novolac reinforced by silica fibers and hardened with MDA is considered the most radiation-resistant organic composition.

In general, hardeners of the aromatic series show a superiority over the non-aromatic hardeners.

6.4.

From the results obtained, it appears that complete chemical hardening cannot be attained because a post-polymerization due to irradiation has often been found.

For applications in the nuclear field, this post-polymerization is all to the good because it increases, at the same time, all the physical properties of these resins during the process.

6.5.

Epoxy resins hardened in the cold are generally much less radiation resistant than those hardened at a higher temperature.

6.6.

The electrical properties of irradiated epoxy resins are only little affected by nuclear radiation, while the mechanical properties are very much affected. In general, it may be said that the change in electrical properties in a nuclear field is due to decrease in the mechanical resistance. The same result has been found for other polymers [112, 113].

6.7.

Irradiation of epoxy resins is accompanied by formation of gaseous products. From Table 6.1, it may be seen that the amount of gaseous products liberated is small compared to other polymers.

From this it may be deduced that the most radiation-resistant compositions liberate the smallest amount of gas.

6.9. [No 6.8 in original]

One is tempted to compare the resistance of the epoxy resins to radiation with their resistance to temperature. Irradiated samples are physically degraded, with results similar to those of aging in heat: change in color, fissures, blisters, etc. It has been shown that resins with a high resis-

tance to temperature are also very radiation resistant.

Exposure of a specimen in a high-energy field may be considered a priori as equivalent to its exposure in any other medium that results in absorption of energy. The radiation exposure is in a certain sense analogous to pyrolysis at low temperature.

Acknowledgment : not translated.

TABLE 6.1.

| Résine | G value |
|---|---|
| EPN + DADPS | $1 \times 10^{-2}$ |
| TGMD + DADPS | $1,5 \times 10^{-2}$ |
| DGEBA + DADPS | $3 \times 10^{-2}$ |
| DGEBA/B + A.P. | $6 \times 10^{-2}$ |
| DGEBA + DBP + TETA | $1 \times 10^{-1}$ |
| Polystyrène | $8 \times 10^{-2}$ (114) (115) |
| Polyamide (nylon) | 1,1 (114) (115) |
| Polyéthylène | 3,1 (114) (115) |
| Polyméthyl méthacrylate (plexiglas) | 1,5 (114) (115) |
| Caoutchouc naturel | $3 \times 10^{-1}$ (114) (115) |

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