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THE EFFECT OF NUCLEAR RADIATION ON THE ELECTRICAL PROPERTIES OF EPOXY RESINS

by
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CONTENTS

- 1. Introduction
- 2. Effect of nuclear radiation on electrical properties of polymers
- 3. Experimental procedure
 - a) Materials
 - b) Electrical measurements
 - c) Irradiation conditions
- 4. Results
- 5. Conclusions

ACKNOWLEDGMENTS

REFERENCES

LIST OF FIGURES

LIST OF TABLES

TABLES

1. <u>Introduction</u>

The aim of this report is twofold, firstly to select on the basis of their electrical properties radiation resistant epoxy resin compositions and secondly, to recommend new epoxy resins, which will minimize future troubles from radiation induced damage for electrical insulation in nuclear environments.

Epoxy resins are used as insulating materials in nuclear applications because of :

- a) their excellent insulating properties (1) and
- b) their good radiation resistance (mechanical-physical) in irradiation fields (2), (3), (4).

As it is generally accepted that the main causes of failure of electrical insulation in nuclear radiation environments are due to the loss of mechanical strength or the evolution of gases rather than the gross changes in their dielectric properties (5), it was decided to study only the changes in electrical properties in the area where mechanical or physical deterioration were noted. Further, this study programme was mostly restricted to radiation resistant (mechanical-physical) epoxy systems.

2. The effect of nuclear radiation on the electrical properties of polymers

The electrical properties which determine an insulator's behaviour and which are studied in this paper include:

- a) The dielectric strength, which determines the maximum electric field which can be supported without failure;
- b) the electrical conductivity, which indicates the ease of charge transport;
- c) the dielectric constant, which shows the degree of polarization;
- d) the <u>loss tangent</u>, which indicates the rate of energy lost to energy stored in the dielectrics.

All these properties depend on :

- 1) the chemical structure, crystallinity, crosslinks density;
- 2) the number of free charge carriers, their mobility and their ability to transfer energy to the surrounding molecules;

- 3) the polarizable species i.e. molecules with a permanent dipole moment and the orientational movement of the polar groups;
- 4) the number and energy distribution of electron-trapping sites.

Obviously, several of these factors will be sensitive to irradiation. Ionizing radiation produces charge carriers, and the subsequent reaction may produce molecules with increased dipole moments. Also, changes in crystallinity, the formation of crosslinks, and chain scission can influence the rate at which energy transfers through the polymer and can change the location and depth of trapping sites.

The arguments above are only qualitative, indicating that radiation could affect the electrical properties. More information about the interactions of nuclear radiation with organic materials and dose units can be found in the literature (6), (7).

It must be mentioned that the effects of nuclear radiation on insulating materials are both transient and permanent in nature.

Transient phenomena can materially alter the electrical properties of a polymer during irradiation. One of the most striking transient changes is the enhancement of the electrical conductivity of the polymer. The conductivity of epoxy resins, for example, increases as much as four orders of magnitude in a strong nuclear field.

Permanent changes can be defined as the difference between the electrical properties measured before and after irradiation. These changes result from the permanent mechanical and chemical alterations in the material. The latter will be studied in detail in this paper since they determine the useful life of the insulator.

3. Experimental procedure

a) Materials

The chemical composition and the cure conditions of the epoxy resins studied, are given in Table I.

Araldites * F, B, and D are diglycidylethers of bisphenol A, X33-1.020 is a liquid polyfunctional epoxy resin and EPN 1.138 a polyfunctional epoxy novolac resin.

^{*} Commercial designation of epoxy resins. Araldite F - CY205 (CIBA) is equivalent to Epon 828 (SHELL), D.E.R. 331. (The Dow Chemical Co.) E.R.L. - 2774 (Bakelite Co.). Araldite EPN 1.138-LY558 (CIBA) is equivalent to Epikote 154 (SHELL), D.E.N. 438. (The Dow Chemical Co.)

The hardeners HY905, HY906 and HT901 are anhydrides, HT972 and HT976 aromatic amines and HY951 an aliphatic amine.

Systems a), b), c) d) and f) are classical epoxy resins and are already well known by the manufacturers. Systems e), g), h) i) and k) are recently developed systems and it is not certain that their optimum chemical compositions and cure conditions have already been obtained.

b) Electrical measurements

The tests were performed according to VDE (Verband Deutsche Elektrotechniker) 0303.

- Dielectric strength

The measurements were carried out at room temperature (22 to $26^{\circ}C$) under atmospheric pressure (\sim 740 mm Hg) and with main frequency (50 Hz). Samples under test were immersed in transformer oil to prevent breakdown over the surface.

The method used is a stepwise increase of the voltage at 2 kV/min. until break-down occurs and an electrostatic voltmeter is used as reading instrument.

The steel electrodes are spheres of 50 mm diameter. One electrode is stationary and the other electrode can be adjusted by spring loading to the required pressure.

These tests were performed on specimens in the form of sheets with dimensions $150 \times 150 \times 2 \text{ mm}^3$. The thickness was measured precisely (1/100 mm) since this value is very important for calculating the dielectric strength from the measured breakdown voltage. No special attention was given to the sample preparation and four samples were measured at each radiation level.

The spread in the measurements is within 8%.

- Volume and surface resistivity

The measurements were made under atmospheric conditions: relative humidity \sim 45% . atmospheric pressure \sim 740 mm Hg.

A megohm bridge is used for measuring the resistivity with a D.C. voltage of 1,000 V.

Dielectric specimens for studying the volume resistivity were in the form of sheets 150 x 150 x 2 mm 3 with an effective surface of 80 cm 2 while sheets of 100 x 10 x 2 mm 3 were used for the surface resistivity. The thickness is always measured precisely (1/100 mm). The samples were cleaned mechanically and chemically before testing and four samples were taken at each radiation level.

The volume resistivity is determined in function of the temperature. The method used is a stepwise rise in temperature (10 to 15°C in 30 minutes) until the point of breakdown. The surface resistivity is only measured at room temperature. Since the results were not well reproducible, this property has not been studied for all epoxy resin systems.

As the volume resistivity of an epoxy resin increases with time in an applied electric field, the measurements were performed after 1 minute of electrification time. The spread in the measurements of volume resistivity is of the order of 10%.

- Dielectric constant and dissipation factor

The measurements were made under analogue atmospheric conditions as those of the volume resistivity.

These properties were studied in function of the temperature and frequency. A Schering bridge, type 2.801 was used for the measurements at 50 Hz, a low frequency Dekameter, type DK 05 for 10^2 to 10^5 Hz and a Q-meter, type 260 for the high frequency range (up to 10^7 Hz).

The dimensions of the samples were the same for the measurements at 50 Hz as those used for measuring the volume resistivity. The dielectric specimens for frequencies between 10^2 to 10^7 Hz were in the form of discs, 2 mm thick and 40 mm in diameter. Four samples were taken at each radiation level.

A 10% spread is typical of the dielectric constant and dissipation factor test points.

c) <u>Irradiation conditions</u>

The irradiations were performed in the water reflector of the ASTRA-reactor at Seibersdorf (Austria). This radiation facility produces mainly gammas. The dose rate corresponds to $\sim 10^7$ rad/hr with a reactor power of 5 M. Watt and an ionization chamber is used as dosimeter.

In all cases, test samples were irradiated in demineralized water at $\sim 30^{\circ}\text{C}$. The absorption of water during irradiation is between 0,5 and 2,5 per cent for samples with dimensions 150 x 150 x 2 mm³. Before measuring the electrical properties the unirradiated and irradiated samples were dried under vacuum (10^{-2} torr) at 40° C during 20 hrs.

4. Results

The test data are summarized for each material in the annex and a list of figures and tables is added to the results.

The data are to a great extent self-explanatory, however, some remarks concerning the different figures and tables may be added.

- Only absolute values are plotted in the graphs, whilst these and the percentage changes of the irradiated values are given in the tables.
- Experimental points are directly connected in some of the figures, to facilitate the identification of points since several curves are plotted on one figure.
- The spread in the results is not plotted in the graphs. As mentioned in paragraph 3b) it is of the order of 10%.
- The dosage values given in the graphs and in the table are expressed in rad (1 rad = 100 erg/g).

5. <u>Conclusions</u>

Dielectric strength:

- 1) In general, a decrease of the dielectric strength as a function of the absorbed dose is noted. The increase in dielectric strength observed with analdite X33-1.020 + HT972 is consistent with the observation that the particular analdite used, showed additional polymerization under irradiation. The larger molecules which result from this process may be capable of withstanding larger voltages than the smaller molecules which are obtained by ordinary curing procedures.
- 2) All the new epoxy resin systems (from g) to k)) still give 90% of their initial value at 1 x 10^9 rad.
- 3) Araldite D cured with HY951 retains only 84% of its initial value at 6.8×10^8 rad. At 1×10^9 rad it was completely damaged mechanically and the electrical strength could not be measured.

Surface resistivity

- 1) The surface resistivity of the epoxy resins studied is $\sim 1 \times 10^{13}$ ohm for the hot cured and $\sim 1 \times 10^{12}$ ohm for the system cured at room temperature.
 - 2) Small changes are noted up to 1 \times 10 9 rad for the four studied systems.
- 3) The surface resistivity of analdite B cured with hardener HT901 decreases rapidly above 1 x 10^9 rad.

Volume resistivity (Q_v)

- l) For both irradiated and non-irradiated epoxy resins, a pronounced dependence of volume resistivity on temperature can be noted over the whole temperature scale. Also at any temperature ϱ_v for irradiated specimens is less than ϱ_v for non-irradiated ones.
- 2) The volume resistivity at room temperature of unirradiated epoxy resins is of the order of 10^{16} ohm cm.
 - 3) The most radiation resistant systems are:

 araldite X33-1.020 + HY972

 araldite B (CT200) + HY906 + X157/2.426

 araldite EPN 1.138 + HT972

 araldite EPN 1.138 + HY905 + DY062.

Practically no changes are noted at 1×10^9 rad and room temperature (Figs. 5, 7, 8, 9).

- 4) Araldite F cured with aromatic amines or anhydrides gives approximately the same results. Amines give somewhat better results at higher temperatures (Fig. 12).
- 5) The very often used CERN system for electrical applications, Araldite D + HY951, is the least radiation resistant. Under atmospheric conditions, it has only 10^{13} ohm cm at 6.8×10^8 rad (Fig. 6).
- 6) Araldite B cured with HY906 is more radiation resistant than when cured with HT901 (Fig. 14).

Dielectric constant ϵ and dissipation factor (tg δ)

- 1) For both irradiated and non-irradiated epoxies, the dielectric constant decreases while the dissipation factor increases with increasing frequency.
- 2) The dielectric constant and dissipation factor are almost always higher for the irradiated epoxies than for the non-irradiated ones. The differences, however, are mostly not large. When large differences do occur in dissipation factor at the lower frequencies in some systems (Figs. 25, 26, 28, 29, 30), these are probably caused by radiation induced degradation, leading to mobile dipoles which could follow the field at $10^2 10^3$ Hz but not at higher frequencies.
- 3) The dielectric constant and dissipation factor measured at room temperature and at 50 Hz are relatively insensitive to radiation over a wide range of doses for most of the systems studied.

- 4) The dissipation factor at high frequencies is mostly higher in araldites cured with amines than in those cured with anhydrides (compare Figs. 24 and 25).
- 5) The dielectric constant and dissipation factor for all resins increase with temperature. For temperatures higher than the glass transition temperature (loss of Van de Waals forces), the dependence of the dielectric constant and dissipation factor was quite different from that at temperatures below the glass transition.
- 6) The irradiated samples are more temperature sensistive than the unirradiated ones. The sensitivity increases with the absorbed dose.
- 7) The large changes in araldite D + HY951 are certainly due to mechanical damage of the specimen. An infinite dissipation factor is noted at a dose of 5 x 10^8 rad and 35°C .
 - 8) Radiation resistant systems are:

araldite EPN 1.138 + HY905 + DY062 araldite EPN 1.138 + HT972 araldite X33-1.020 + HT972 araldite F (CY205) + HT972

General conclusions

- 1) Significant changes are measured in the electric properties of organic insulating materials as a function of nuclear radiation and temperature or frequency.
- 2) Results of the tests performed in this study have indicated that both crosslinking and degradation are probably occurring in all of the systems studied, and the latter appears to predominate in all systems at the highest doses investigated for each composition.

Degradation first occurs in those parts of the polymer structure which are the most mobile (free to move). Thus pendent groups, ends of long chains etc. will break first. It should be noted that it is these "loose ends" which to a great extent are responsible for the changes in electrical properties, (e.g. araldite D + HY951).

3) Polyepoxides can be degraded at room temperature by nuclear radiation doses of 2 x 10^8 rad e.g. araldite D + HY951 but recently developed epoxy resins e.g. araldite EPN 1.138 + HT972 are absolutely undamaged at 1 x 10^9 rad.

The same conclusion has already been reached by studying the mechanical behaviour of epoxy resins in an irradiation field (2).

4) All resins, containing a high aromatic content and cured with an aromatic amine or anhydride gave good radiation resistant materials.

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LIST OF FIGURES

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Figs. 1 - 14: Volume resistivity vs. temperature for irradiated epoxy resins.
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Fig. 1: Araldite F (CY205) + HT972
Fig. 2: Araldite F (CY205) + HT976
Fig. 3: Araldite F (CY205) + HY905
Fig. 4: Araldite B (CT200) + HT901
Fig. 5: Araldite B (CT200) + HY906 + (X157/2.426)
Fig. 6: Araldite D (CY230) + HY951
Fig. 7: Araldite EPN 1.138 + HT972
Fig. 8: Araldite EPN 1.138 + HY905 + (DY062)
Fig. 9: Araldite X33-1.020 + HT972
Fig. 10: Araldite F (CY205) + HT972
         Araldite EPN 1.138 + HT972
         Araldite X33-1.020 + HT972
Fig. 11: Araldite F (CY205) + HY905
         Araldite EPN 1.138 + HY905
Fig. 12: Araldite F (CY205) + HT972, HT976, HY905
Fig. 13: Araldite EPN 1.138 + HY905 + (DY062), HT972
Fig. 14: Araldite B (CT200) + HT901, HY906 + (X157/2.426).
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Figs. 15 - 23: Dissipation factor and dielectric constant vs. temperature for irradiated epoxy resins.

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Fig. 15: Araldite F (CY205) + HT972

Fig. 16: Araldite F (CY205) + HT976

Fig. 17: Araldite F (CY205) + HY905

Fig. 18: Araldite B (CT200) + HT901

Fig. 19: Araldite B (CT200) + HY906 + (X157/2.426)

Fig. 20: Araldite D (CY230) + HY951

Fig. 21: Araldite EPN 1.138 + HT972

Fig. 22: Araldite EPN 1.138 + HY905 + (DY062)

Fig. 23: Araldite X33-1.020 + HT972
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Figs. 24 - 30 : Dissipation factor and dielectric constant vs. frequency for irradiated epoxy resins.

```
Fig. 24: Araldite F (CY205) + HT972

Fig. 25: Araldite F (CY205) + HY905

Fig. 26: Araldite B (CT200) + HT901

Fig. 27: Araldite B (CT200) + HY906 + X157/2.426

Fig. 28: Araldite D (CY230) + HY951

Fig. 29: Araldite EPN 1.138 + HT972

Fig. 30: Araldite X33-1.020 + HY905 + DY062
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LIST OF TABLES

Table I : Chemical composition of the epoxy resin systems.

Table II : Dielectric strength vs. radiation dose for different epoxy resins.

The values in brackets give the percent of the initial value.

Table III : Surface resistivity vs.radiation dose for different epoxy resin systems.

TABLE I

EPOXY RESIN SYSTEMS*

	Chemical composition of epoxy resins	Cure Cycle
a)	Araldite F (CY2O5) + HT972 (100 - 27 phr)	2h/100°C
b)	Araldite F (CY205) + HT976 (100 - 35 phr)	3h/130°C + 8h/160°C
c)	Araldite F (CY205) + HY905 (100 - 100 phr)	5h/160 [°] C
d)	Araldite B (CT200) + HT901 (100 - 30 phr)	14h/140°C
e)	Araldite B (CT200) + HY906 + X157/2426 (100 - 35 - 3 phr)	4h/80°C + 24h/140°C
f)	Araldite D (CY230) + HY951 (100 - 10 phr)	cured at room temperature + 12h/50°C.
g)	EPN 1.138 + HY905 + DY062 (100 - 105 - 0,5 phr)	4h/80°C + 16h/140°C
h)	EPN 1.138 + HT972 (100 - 34 phr)	4h/80°C + 10h/140°C
i)	X33-1.020 + HY905 + DY062 (100 - 136 - 0,5 phr)	4h/80°C + 16h/140°C
k)	X33-1.020 + HT972 (100 - 40 phr)	4h/80°C + 10h/140°C

^{*} Manufactured by CIBA A.G. - BASEL - SWITZERLAND

DIELECTRIC STRENGTH TABLE II

MO THE POSTERO SEE DEFE		IO	ELECTRIC STRE	NGTH (kV/mm)	DIELECTRIC STRENGTH (KV/mm) vs RADIATION DOSE (RAD)	DOSE (RAD)	
REDIN COMPOSITION	ı	2.31 x 10 ⁸	2.31 x 10 ⁸ 5.61 x 10 ⁸	6.82 × 10 ⁸ 1.21 × 10 ⁹	1.21 × 10 ⁹	1.24 x 10 ⁹ 2.75 x 10 ⁹	2.75 x 10 ⁹
a) Araldite F (CY205) + HT972	21.2				17.7 (83.5)*		16.1 (76)
b) Araldite F (CY205) + HT976	21.4				18.5 (86.5)		17.5 (82)
c) Araldite F (CY205) + HY905	19.0				18.2 (96)		17.8 (93.5)
d) Araldite B (CT200) + HT901	18.1	,			17•4 (96)		14.5 (80)
e) Araldite B (CT200) + HY906 + X157/2.246	18.8				15.7 (83.5)		
f) Araldite D (CY230) + HY951	19.6	19.5 (100)		16.5 (84)	0		
g) Araldite EPN 1.138 + HY905 + DY062	22.5		21.0 (93.5)			20.0 (89)	
h) Araldite EPN 1.138 + HT972	19.1		20.0 (105)			18.5 (97)	
i) Araldite X35-1.020 + HY905 + DY062	20.1		18.7 (93.5)			18.0 (90)	
k) Araldite X35-1.020 + HT972	23.4		23.3 (100)			25.2 (108)	

The values in brackets give the percentage of the initial value.

TABLE III

SURFACE RESISTIVITY

Resin Composition		1.21 x 10 ⁹ rad	2.75 x 10 ⁹ rad
a) Araldite F (CY205) + HT972	$^{\circ}$ 2.5 x $10^{13}\Omega$	4.5 x 10 ¹² Ω	1 x 10 ¹³ Ω
b) Araldite F (CY205) + HT976	1 x 10 ¹³ Ω	-	-
c) Araldite F (CY205) + HY905	1.1 x 10 ¹³ Ω	1 x 10 ¹² Ω	6 x 10 ¹¹ Ω
d) Araldite B (CT200) + HT901	1.7 x 10 ¹³ Ω	1 x 10 ¹² Ω	5 x 10 ⁸ Ω
e) Araldite B (CT200) + HY906 + X157/2.426	$7 \times 10^{12} \Omega$	7•5 x 10 ¹² Ω	-
f) Araldite D (CY230) + HY951	1.1 x 10 ¹² Ω	-	-
g) Araldite EPN 1.138 + HY905 + DY062	$9 \times 10^{12} \Omega$	-	-
h) Araldite EPN 1.138 + HT972	1.1 x 10 ¹³ Ω	-	-
i) Araldite X33-1.020 + HY905 + DY062	1.6 x 10 ¹³ Ω	-	-
k) Araldite X33-1.020 + HT972	8 x 10 ¹² Ω	-	-

























































