
**Gas Evolution from Epoxy Resins
by High Energy Radiation**

J T Morgan G Scott R Sheldon G B Stapleton



Science Research Council

Chemical Technology Group
Rutherford High Energy Laboratory
Chilton Didcot Berkshire
1970

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GAS EVOLUTION FROM EPOXY RESINS BY HIGH ENERGY RADIATION

J T Morgan

G Scott *

R Sheldon

G B Stapleton

ABSTRACT

The changes in mechanical properties and the rate of gas evolution during irradiation have been determined for a number of cast epoxy resin systems.

The gas evolution rate is approximately constant up to 3000 Mrad and mass spectrometric analysis shows that the gases evolved consist chiefly of hydrogen, carbon monoxide and carbon dioxide together with small quantities of lower hydrocarbons. G values for the evolution of the various gases are given and these results together with IR absorption studies have indicated the types of reaction likely to be involved in the radiolysis of epoxy resins.

Flexural tests have been used to assess the changes in mechanical properties and these were determined after irradiation up to 4000 Mrad in air and 3000 Mrad in vacuum.

Chemical Technology Group
Rutherford High Energy Laboratory
Chilton Didcot Berkshire

* Professor of Polymer Chemistry
The University of Aston
in Birmingham

August 1970

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1. INTRODUCTION

The use of epoxy resin/glass fabric composites in the manufacture of nuclear physics equipment is well established.^(1,2) One important application in this field is in the construction of large magnet coils, where mechanical and electrical integrity need to be maintained in an environment of:-

- a. mechanical and electrical stresses often occurring cyclically,
- b. high energy radiation,
- c. fluctuating temperature.

Of these, radiation is the most damaging, causing a loss in the mechanical properties of the epoxy resin. The subsequent cracking, crazing or loss of adhesion may cause mechanical failure of the magnet or may permit the ingress of moisture which would impair its electrical performance.⁽³⁾

A further effect of radiation on organic materials is the evolution of gaseous by-products and this becomes important when the rate of formation of gas exceeds the rate at which it can diffuse through the material.⁽⁴⁾ This could result in cracking, or expansion of the insulation with subsequent displacement of the tightly packed conductors.

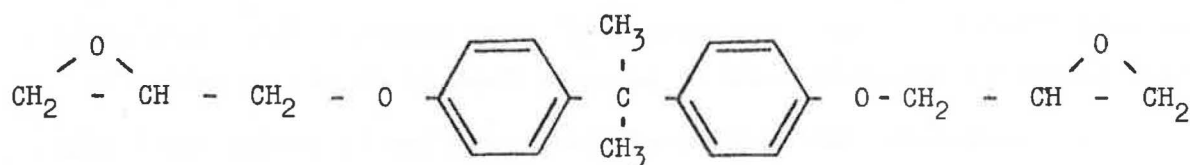
The purpose of this work is to examine the quantity and composition of gases evolved during irradiation and to determine the radiation stability of a number of cast epoxy resin systems. These results may give an indication of the chemical reactions involved during radiolysis and help to establish whether a correlation exists between gas evolution and changes in mechanical properties.

2. EPOXY RESINS

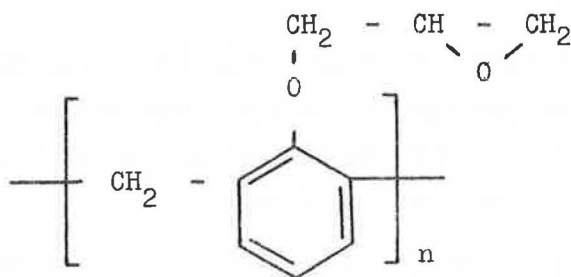
Epoxy resins are suited to the manufacturing techniques used in magnet coil impregnation because they harden without the evolution of volatile reaction products and exhibit small shrinkage effects. Crosslinking may be produced by the use of amines, acid anhydrides or catalytic agents and the kinetics are such that normally, aliphatic amines are room temperature curing agents whereas aromatic amines and anhydrides require the use of elevated temperatures. The curing temperatures used in this report are selected so as to be representative of the temperatures which would be used in magnet coil manufacture. This may involve the use of rather lower temperatures than those recommended by the resin manufacturer but this minimises the problems of magnet coil impregnation particularly in regard to resin rich cracking.⁽³⁾

Epoxy resins representative of three basically different molecular structures were selected for test:-

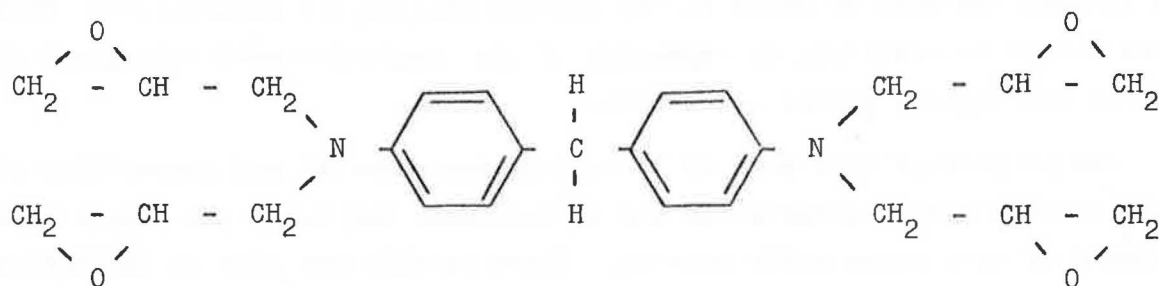
Pure Bisphenol A diglycidyl ether (DGEBA)



Epoxy Novolak



Glycidyl amine



An aromatic amine (diamino diphenyl methane - DDM) and an acid anhydride (methyl Nadic anhydride - MNA) were chosen as curing agents for each of the above resins. Additionally, an aliphatic amine (triethylene tetramine - TETA), which would not normally be of interest since it gives resins of inferior radiation resistance, was included in the programme because it was considered that this might aid analysis of the data.

3. SAMPLE PREPARATION

Details of the resins and hardeners, of the proportions used and the curing cycles, are given in Appendix I.

3.1 Mixing

The resin and hardener were weighed into a suitable vessel and thoroughly mixed and degassed using a vacuum mixer; slightly elevated temperatures were required in some cases in order to achieve a suitable

viscosity for mixing and pouring. (See Appendix I)

3.2 Specimens for gas evolution tests

The mixed resins were cast into small blocks. "Drillings" from these were then collected and crushed with a pestle and mortar in order to obtain the material in a finely divided form.

3.3 Mechanical test specimens

Experience had shown that specimens machined from cast sheet gave rather poor replication of mechanical test results, due to the presence of notches. A mould was therefore constructed so that parallel sided specimens suitable for flexural testing could be moulded directly. (Figure 1).

Sixty specimens of each of seven resin systems were prepared; it was not possible to mould suitable specimens from the glycidyl amine and epoxy Novolak resins with TETA hardener because of the exothermic reaction at elevated mixing temperatures.

3.4 Thin films for infra-red studies

The mixed resin was poured onto a flat polished steel plate which had previously been treated with a release agent*, a similar plate was placed on top and the whole assembly heated to the appropriate curing temperature in an oven. The films were removed after cooling and were approximately 0.002 cm in thickness.

4. TEST PROCEDURES

4.1 Gas evolution experiments

The powdered resin was weighed into 12 x 75 mm Pyrex test tubes, these were then necked and finally sealed under vacuum (approximately 10^{-3} mm Hg). After irradiation, the quantity of gas evolved was determined in the following manner. The capsule was placed inside a chamber of known volume, which was then closed and evacuated to approximately 10^{-3} mm Hg. The chamber was then isolated from the vacuum pump and the capsule cracked open by means of a hand operated screwed plunger. The resultant pressure rise was determined using a diaphragm pressure transducer connected to a digital read-out.** This test was carried out in duplicate at each radiation dose level. For control purposes, tubes which had not been

* Releasil 14 - Midland Silicones Ltd Barry Glamorgan

** PACE Wiancko Model DM1 - Whittaker Corporation of America

exposed to radiation were also included in order to establish the extent to which residual gases were released from the resin after sealing.

For mass spectrometric analysis of the composition of the evolved gas, samples of the powdered resin were weighed into breaker seal tubes. These were then sealed after leaving under high vacuum (approximately 10^{-4} mm Hg) for at least 16 hours.

This test was carried out in duplicate at one radiation dose level. This technique has previously been used to study gases evolved during irradiation.⁽⁵⁾

4.2 Change in mechanical properties with radiation

This was determined by measuring the flexural strength and modulus of the cast resin specimens after various doses of high energy radiation. The test was carried out in accordance with ASTM D790/59T using a commercial testing machine.*

The flexural test specimens were irradiated in the presence of air; additional specimens were irradiated in glass tubes sealed under vacuum in order to establish whether the presence of oxygen significantly affects the rate of degradation.

4.3 Infra-red spectra

Strips of film approximately 1 x 3 cm were cut to fit the specimen holder of the spectrometer.** Films prepared from DGEBA with each of the three hardeners were irradiated in glass tubes sealed under vacuum and their infra-red spectra compared with unirradiated specimens stored under vacuum. The infra-red spectra were determined within approximately 2 hours of opening the tubes in order to minimise oxidative reactions of trapped free radicals.⁽⁶⁾

The infra-red spectra of glycidyl amine/MNA films prepared at the two different curing temperatures were also determined in order to show the effects of a higher temperature cure.

5. IRRADIATION

All specimens were irradiated using the spent fuel gamma irradiation unit at UKAEA Harwell Berks. The mean energy of the gamma radiation is 1.0 MeV and dose rates up to a maximum of 6 megarad per hour are possible.

* Model TTCM - Instron Ltd High Wycombe Bucks

** Infrascan H 900 - Hilger & Watts, London NW1

Calibration is by ion chamber and ferrous sulphate dosimetry, and is reported⁽⁷⁾ to be accurate within 5%.

5.1 Radiation dose levels

The radiation dose levels used for the various specimens are as follows:-

Specimen	Radiation dose level - Mrad
Breaker seal tubes	200
Capsules for gas evolution rates	300, 600, 900, 1500, 2000, 3000
Flexural test specimens irradiated in air	300, 600, 900, 1500, 4000
Flexural test specimens irradiated in sealed tubes	300, 900, 3000
Films for infra-red irradiated in sealed tubes	200

6. EXPERIMENTAL RESULTS

The results of these experiments are given in the form of graphs and tables as follows.

6.1 Gas evolution rate

The volume of gas evolved at each radiation dose level was calculated from the pressure reading, due allowance being made for the volume of the glass capsule and the epoxy resin sample.

$$\text{Gas evolved (NTP cm}^3/\text{gm)} = 273 \text{ p (40-g/2.2-r/1.3)}/760\text{Tr}$$

where p = pressure reading (mm Hg)
 T = temperature (K)
 g = wt of glass capsule (g)
 r = wt of epoxy resin (g)

These values are given in table 1 and the mean values are shown plotted against radiation dose in figures 2-4.

These plots are approximately linear, the slopes giving the gas evolution rates in NTP cm³/Mrad gm.

6.2 Composition of evolved gas

This was determined using a commercial mass spectrometer.* The results of the analysis are given in volume per cent of each gas, in table 4.

* Varian MAT CH4

The mass spectrometer could not discriminate between carbon monoxide and nitrogen at mass number 28. A GLC analysis of the gases evolved from a DGEBA/TETA sample showed the absence of nitrogen and it was assumed that nitrogen would not be present in any of the other gas samples.

The results of the mass spectrometer analysis, together with the results of the gas evolution experiments have been used to compute the G value for the evolution of each gas, these values being given in table 3.

6.3 Change in mechanical properties with radiation

Flexural strength and modulus values were derived from the load versus deflection curves and the mean values of five replicates at each radiation dose level are given in tables 4-9, together with their standard deviations. Figures 5-11 show the mean flexural strength values plotted against radiation dose.

6.4 Changes in infra-red spectra with radiation

Infra-red spectra of the epoxy resins before and after irradiation showed only small differences.

The anhydride cured resin showed a reduction in height of the absorption peaks at 1850 and 1770 cm^{-1} , corresponding to a loss in concentration of anhydride and carboxylic acid groups by irradiation.

The amine cured resins showed the formation of small peaks at 1710 cm^{-1} and this probably corresponds to the formation of carbonyl groups, during irradiation.

6.5 Changes in infra-red spectra with cure temperature : (glycidyl amine/MNA)

The infra-red absorption spectrum of the specimen of glycidyl amine/MNA cured at 160°C showed the following differences to the specimen cured at 100°C :-

- a. A greater absorption at 3500 cm^{-1} - hydroxyl
- b. A lesser absorption at 1850 cm^{-1} - anhydride
- c. A lesser absorption at 900 cm^{-1} - epoxy

7. DISCUSSION OF RESULTS

The gases evolved from cured epoxy resins on irradiation consist chiefly of hydrogen, carbon monoxide and carbon dioxide, together with small quantities of lower hydrocarbons. No larger fragments were detected in the gaseous by-products and this is in agreement with the "cage effect."⁽⁸⁾ Large molecules are restricted from leaving the "cage" formed by the surrounding molecules,

Product is carbon monoxide⁽¹¹⁾, whereas for benzoic acid it is carbon dioxide. Reactions I and II involve chain scission but in reaction I it is possible that the two free radicals so formed may recombine. Reaction III does not involve scission of the polymer network.

By analogy with its action as a chromophore in the absorption of UV energy, the carbonyl group may be described as acting as a 'radiophore.'

For amine cured resins, the amount of carbon monoxide evolved during radiolysis is less than for the anhydride cured resins; more carbon monoxide being evolved in the case of the aliphatic amine than for the aromatic amine curing agent.

By comparison with the effect of radiation on simple alcohols⁽¹²⁾ it would appear that a likely reaction⁽¹³⁾ is:-

IV.



This would tend to be confirmed by the infra-red spectra, which show the appearance of a small absorption at 1710 cm^{-1} after irradiation. The carbonyl group so formed would then act as a radiophore to further degradation.



Most of the epoxy resin systems show an increase in flexural strength and modulus with irradiation and this indicates an increase in crosslink density of the polymer.

The crosslinking is probably initiated by the release of hydrogen atoms from the polymer chains by radiation, with the creation of free radicals. A hydrogen atom may abstract a further hydrogen atom from an adjacent polymer chain, thus leaving two free radicals in close proximity for combination.⁽¹⁴⁾

There appears to be no simple relationship between gas evolution and changes in mechanical properties and this is due to one or more of the following reasons:-

- degradation reactions do not necessarily result in the release of gases
- gas evolution has been shown to be due in part to the degradation of unreacted groups
- both chain scission and crosslinking occur simultaneously.

Water was not detected in the gases evolved from any of the resins and it is likely that radiation degradation follows a different mechanism to that occurring during pyrolysis, where water is one of the main degradation products. (15)

From the mechanical tests it may be observed that the radiation stability of epoxy resins cured with DDM and MNA are superior to those cured with TETA, DDM being marginally better than MNA. The epoxy Novolak and glycidyl amine resins are superior to DGEBA and when cured with DDM show no loss in mechanical properties after 4000 Mrad.

8. CONCLUSIONS

One of the main effects of high energy radiation on epoxy resins is the removal of hydrogen atoms, those in the aliphatic parts of the molecule being more readily removed than those attached to aromatic systems. The hydrogen atoms may combine or abstract further hydrogen atoms and form gaseous hydrogen. The fate of the free radicals so formed will in part determine the radiation stability of the material. They may combine to form crosslinks or dissociate, resulting in chain scission. In the presence of oxygen, peroxide radicals will be formed and this accounts for the faster breakdown of specimens irradiated in the presence of air. The epoxy Novolak systems appear to be less sensitive to the presence of oxygen and this may be because the substituted phenolic groups in the resin act as an inbuilt antioxidant and so inhibit the oxidative reaction.

Main chain scission probably occurs, the bonds adjacent to a carbonyl group being particularly vulnerable.

The mechanical test data shows that there is no simple relationship between gas evolution and changes in mechanical properties and materials which are relatively stable towards radiation may have high rates of gas evolution.

Translation of gas evolution and mechanical test data into the effects of radiation on a composite structure such as a magnet coil is difficult. The ability of gases evolved during irradiation to diffuse out of the resin is important and this will be determined to some extent by the dose rate. Irradiation tests using model coil sections or composite specimens may be necessary to enable the importance of gas evolution to be fully evaluated.

9. ACKNOWLEDGEMENT

Acknowledgement is made to the Director of the Rutherford High Energy Laboratory for permission to publish this paper and to Mr G E Simmonds in whose department the work was performed.

10. REFERENCES

1. Cross - System design and the choice of materials for the Nimrod vacuum system. Vacuum, Feb-April (1960).
2. Hadden, Sheldon - The reinforced vacuum envelope for the 7 GeV Proton Synchrotron. Second International Reinforced Plastics Conference BPF (London 1960).
3. Sheldon, Stapleton - Resin encapsulation of magnet coils. Second International Conference on Magnet Technology. (Oxford 1967).
4. Morgan, Sheldon, Stapleton - Effect of radiation on Nimrod end conductor - unpublished.
5. Williams - Analysis of irradiated materials for satellite applications using a mass spectrometer. RAE (Farnborough) Technical Report No. 68038 (1968).
6. Parkinson, Binder - Post-irradiation oxidation and molecular weight changes in polystyrene and polymethylmethacrylate. ASTM Special Technical Publication No. 276 (1959).
7. AERE, Harwell Technical Leaflet No. HL 64/5562.
8. Franck, Rabinowitch - Trans. Faraday Soc. 30, 120 (1934).
9. Charlesby - Atomic Radiation and Polymers. Pergamon (1960).
10. Prevost-Bernas, et al - Discussions of Faraday Soc. 12, 98 (1952).
11. Spinks, Woods - An Introduction to Radiation Chemistry. Wiley (1964).
12. Bolt, Carroll - Radiation Effects on Organic Materials. Academic Press (1963).
13. Pluym, Van de Voorde - Radiation damage of epoxy resins used in Magnet coil insulation. Second International Conference on Magnet Technology (Oxford 1967).
14. Sisman, Bopp - Nucleonics, 13, 10 (1955).
15. Lieng-Huang Lee - J. Polymer Sci. 3, 859 (1965).

TABLES

- Table 1. Gas evolution - NTP cm³/gm.
2. Composition of gas evolved during irradiation (200 Mr) volume %.
 3. G values for gases evolved from epoxy resins by high energy radiation.
 4. Flexural strength of irradiated DGEBA resins.
 5. Flexural strength of irradiated epoxy Novolak resins.
 6. Flexural strength of irradiated glycidyl amine resins.
 7. Flexural modulus of irradiated DGEBA resins.
 8. Flexural modulus of irradiated epoxy Novolak resins.
 9. Flexural modulus of irradiated glycidyl amine resins.

TABLE 1
Gas Evolution - NTP cm³/gm

Resin	Hardener	Radiation Dose - Mrad					
		300	600	900	1500	2000	3000
DGEBA	TETA	1.70	2.64	3.67	6.6	7.63	-
		1.87	2.76	3.91	6.3	7.59	-
	DDM	0.90	1.44	2.13	3.8	4.53	7.95
		0.91	1.56	2.22	3.7	5.14	9.21
	MNA	3.37	4.32	6.21	10.5	14.0	19.0
		3.63	7.5	5.98	11.0	12.4	16.6
Epoxy Novolak	TETA	1.61	3.24	3.47	6.3	7.42	10.91
		1.53	3.48	3.55	6.2	7.68	10.77
	DDM	0.75	1.32	1.71	3.4	4.16	10.3
		0.79	1.38	1.80	3.2	4.11	6.4
	MNA	3.97	6.3	7.97	10.4	13.1	20.2
		3.94	5.8	7.06	10.4	13.7	19.01
Glycidyl amine	TETA	1.79	-	4.14	-	9.54	15.6
		1.78	3.24	4.35	7.8	9.41	14.6
	DDM	1.11	2.04	2.86	5.2	6.54	9.28
		1.15	2.46	2.82	5.1	6.56	9.49
	MNA (100°C)	4.5	7.44	7.01	13.5	19.46	36.2
		3.92	7.03	9.71	17.2	20.5	33.3
	MNA (160°C)	2.46	3.42	6.58	8.9	12.6	16.8
		2.17	3.12	5.77	9.3	12.7	16.4

TABLE 2

Composition of gas evolved during irradiation (200 Mr) Volume %

Resin	DGEBA			EPOXY NOVOLAK			GLYCIDYL AMINE			
Hardener Cure Temperature	TETA	DDM	MNA	TETA	DDM	MNA	TETA	DDM	MNA 100°C	MNA 160°C
Hydrogen	88.4	77.1	B R O K E N	92.0	89.6	18.0	91.9	89.8	22.3	45.4
Carbon Dioxide		0.8		0.7		55.3			60.7	32.4
Nitrogen and/or Carbon Monoxide	10.0	20.9		5.9	10.2	26.7	7.2	8.7	17.0	22.0
Ethane	0.3	0.3		0.2				0.1		
Methane	1.3	0.9		1.2	0.2		0.9	1.4		0.2
Hydrogen	78.5	75.2	19.9	89.5	66.5	16.5	75.5	84.2	24.0	37.1
Carbon Dioxide	0.6	1.4	56.9		1.5	59.7			63.4	47.4
Nitrogen and/or Carbon Monoxide	18.8	21.8	23.2	8.9	29.2	23.8	19.0	13.7	10.5	15.2
Oxygen	0.08	0.2			0.4				2.0	
Argon									0.1	
Ethane	0.4	0.2		0.4				0.2		
Methane	1.6	1.2		1.1	2.1		4.8	1.9		0.26
C ₃ and C ₄ Hydrocarbons	0.02				0.3		0.7			

TABLE 3

G values for gases evolved from epoxy resins by high energy radiation

Resin	DGEBA			EPOXY NOVOLAK			GLYCIDYL AMINE			
Hardener Cure Temperature	TETA	DDM	MNA	TETA	DDM	MNA	TETA	DDM	MNA 100°C	MNA 160°C
Hydrogen	0.21	0.10	0.10	0.21	0.10	0.10	0.23	0.15	0.14	0.14
Carbon Dioxide	0.001	0.0014	0.35	0.001		0.33			0.38	0.14
Carbon Monoxide	0.037	0.028	0.14	0.017	0.011	0.15	0.019	0.018	0.082	0.062
Ethane	0.001	0.0015		0.0007				0.0003		
Methane	0.0037	0.0015		0.0026	0.0002		0.0022	0.0026		0.0008
C ₃ and C ₄ Hydrocarbons	0.00003									

TABLE 4

Flexural Strength of irradiated DGEBA resins

IN VACUUM

Hardener	Dose - Mrad	0	300	900	3000
TETA	Mean Kg/cm ²	1126	982	389	138
	Standard Deviation %	19.8	15.9	19.5	7.2
DDM	Mean Kg/cm ²	1382	1208	1165	1169
	Standard Deviation %	3.4	7.2	17.6	12.4
MNA	Mean Kg/cm ²	1171	1269	1287	1420
	Standard Deviation %	18.8	3.9	1.5	3.8

IN AIR

Hardener	Dose - Mrad	0	300	600	900	1500	4000
TETA	Mean Kg/cm ²	1126	638	658		114	
	Standard Deviation %	19.8	12.1	7.6		15.3	
DDM	Mean Kg/cm ²	1382	1223	1212	1068	1000	755
	Standard Deviation %	3.4	8.5	8.8	10.9	3.3	10.2
MNA	Mean Kg/cm ²	1171	1242	1303	1231	1398	526
	Standard Deviation %	18.8	3.6	2.0	3.6	1.6	9.8

TABLE 5

Flexural Strength of irradiated epoxy Novolak resins

IN VACUUM

Hardener	Dose - Mrad	0	300	900	3000
DDM	Mean Kg/cm ²	1213	1344	1326	1511
	Standard Deviation %	7.6	8.6	12.8	2.4
MNA	Mean Kg/cm ²	914	1123	925	1155
	Standard Deviation %	18.6	16.3	15.4	16.5

IN AIR

Hardener	Dose - Mrad	0	300	600	900	1500	4000
DDM	Mean Kg/cm ²	1213	1288	1397	1303	1443	1451
	Standard Deviation %	7.6	12.9	3.4	9.6	3.3	4.5
MNA	Mean Kg/cm ²	914	1071	1103	1174	1282	960
	Standard Deviation %	18.6	12.0	19.5	5.9	8.8	19.3

TABLE 6

Flexural Strength of irradiated glycidyl amine resins

IN VACUUM

Hardener	Dose - Mrad	0	300	900	3000
DDM	Mean Kg/cm ²	1414	1452	1555	1507
	Standard Deviation %	5.9	12.6	6.7	3.8
MNA	Mean Kg/cm ²	1080	1278	1316	1270
	Standard Deviation %	7.3	19.2	15.6	14.3

IN AIR

Hardener	Dose - Mrad	0	300	600	900	1500	4000
DDM	Mean Kg/cm ²	1414	1440	1567	1474	1524	1487
	Standard Deviation %	5.9	3.9	7.9	14.0	5.7	3.1
MNA	Mean Kg/cm ²	1080	870	1198	910	1355	796
	Standard Deviation %	7.3	13.0	16.2	9.3	8.3	22.3

TABLE 7

Flexural Modulus of irradiated DGEBA resins

IN VACUUM

Hardener	Dose - Mrad	0	300	900	3000
TETA	Mean Kg/cm ²	39640	41800	40380	
	Standard Deviation %	1.8	3.7	5.3	
DDM	Mean Kg/cm ²	29780	33650	34450	37860
	Standard Deviation %	5.2	1.4	3.7	1.9
MNA	Mean Kg/cm ²	37550	40250	36090	38810
	Standard Deviation %	5.3	3.2	0.7	0.8

IN AIR

Hardener	Dose - Mrad	0	300	600	900	1500	4000
TETA	Mean Kg/cm ²	39640	37980	40870			
	Standard Deviation %	1.8	1.7	4.3			
DDM	Mean Kg/cm ²	29780	33000	33920	35130	35910	38090
	Standard Deviation %	5.2	1.1	1.1	1.6	5.3	4.2
MNA	Mean Kg/cm ²	37550	34950	35920	35800	37890	38580
	Standard Deviation %	5.3	1.9	1.8	2.2	1.8	2.3

TABLE 8

Flexural modulus of irradiated epoxy Novolak resins

IN VACUUM

Hardener	Dose - Mrad	0	300	900	3000
DDM	Mean Kg/cm ²	31310	33010	37060	39690
	Standard Deviation %	1.3	4.1	2.7	1.2
MNA	Mean Kg/cm ²	39740	41600	38710	40750
	Standard Deviation %	3.6	5.4	5.1	2.1

IN AIR

Hardener	Dose - Mrad	0	300	600	900	1500	4000
DDM	Mean Kg/cm ²	31310	35760	37060	36270	38040	37910
	Standard Deviation %	1.3	2.2	6.4	7.5	3.8	2.3
MNA	Mean Kg/cm ²	39740	38980	39950	39090	40860	39150
	Standard Deviation %	3.6	2.3	1.3	1.4	1.0	1.6

TABLE 9

Flexural Modulus of irradiated glycidyl amine resins

IN VACUUM

Hardener	Dose - Mrad	0	300	900	3000
DDM	Mean Kg/cm ²	35610	38450	38560	39200
	Standard Deviation %	2.7	3.1	0.9	2.4
MNA	Mean Kg/cm ²	39340	41220	40780	41490
	Standard Deviation %	3.2	1.3	1.4	2.1

IN AIR

Hardener	Dose - Mrad	0	300	600	900	1500	4000
DDM	Mean Kg/cm ²	35610	36000	37860	37540	38170	38150
	Standard Deviation %	2.7	1.9	5.7	3.2	3.2	1.6
MNA	Mean Kg/cm ²	39340	41270	40380	41540	41400	41340
	Standard Deviation %	3.2	2.1	1.9	2.4	2.5	0.6

FIGURES

Figure 1. Mould for flexural test specimens.

2. DGEBA resins.
3. Epoxy Novolak resins.
4. Glycidyl amine resins.
5. DGEBA/DDM.
6. DGEBA/MNA.
7. DGEBA/TETA.
8. Epoxy Novolak/DDM.
9. Epoxy Novolak/MNA.
10. Glycidyl amine/DDM.
11. Glycidyl amine/MNA.

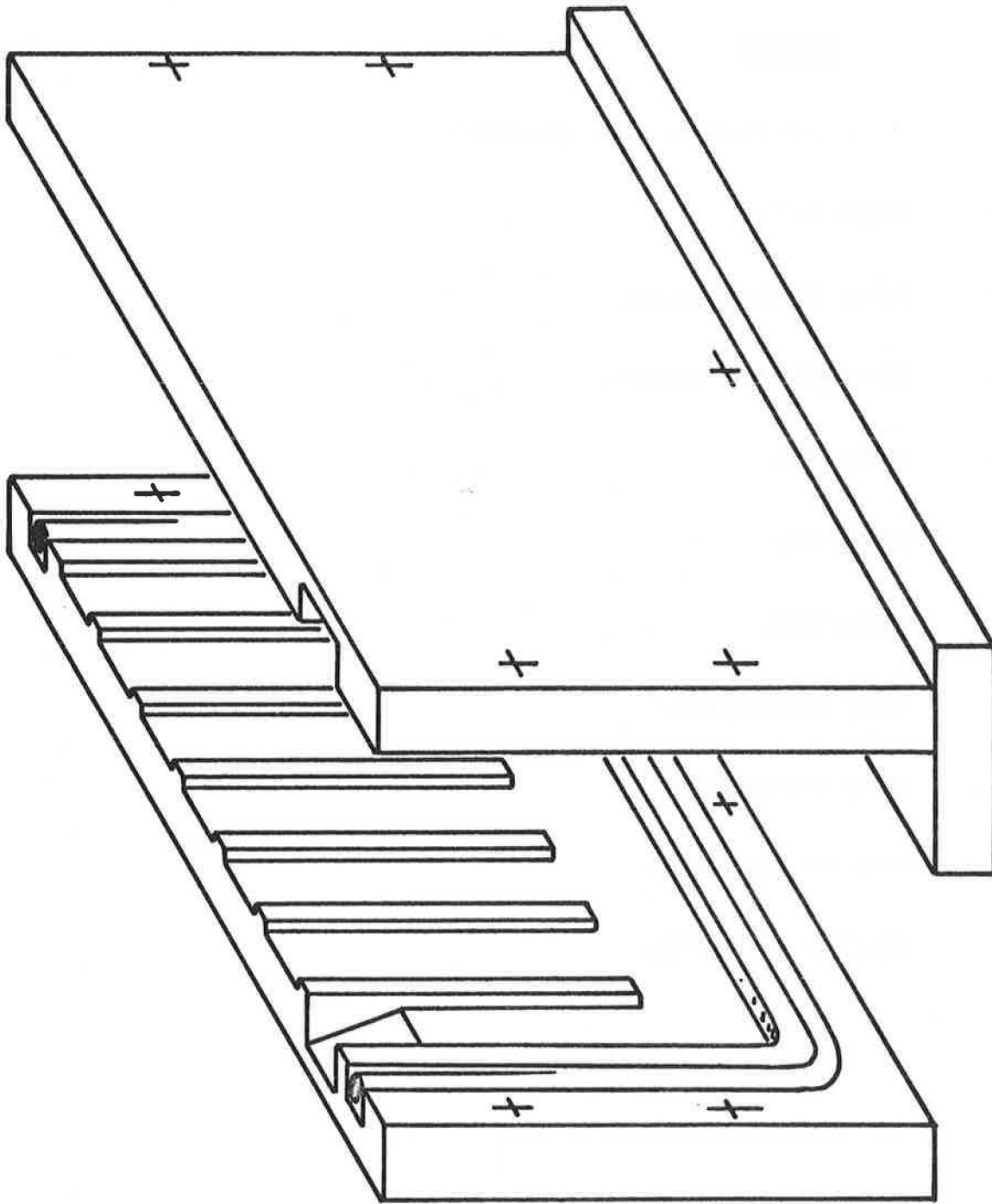
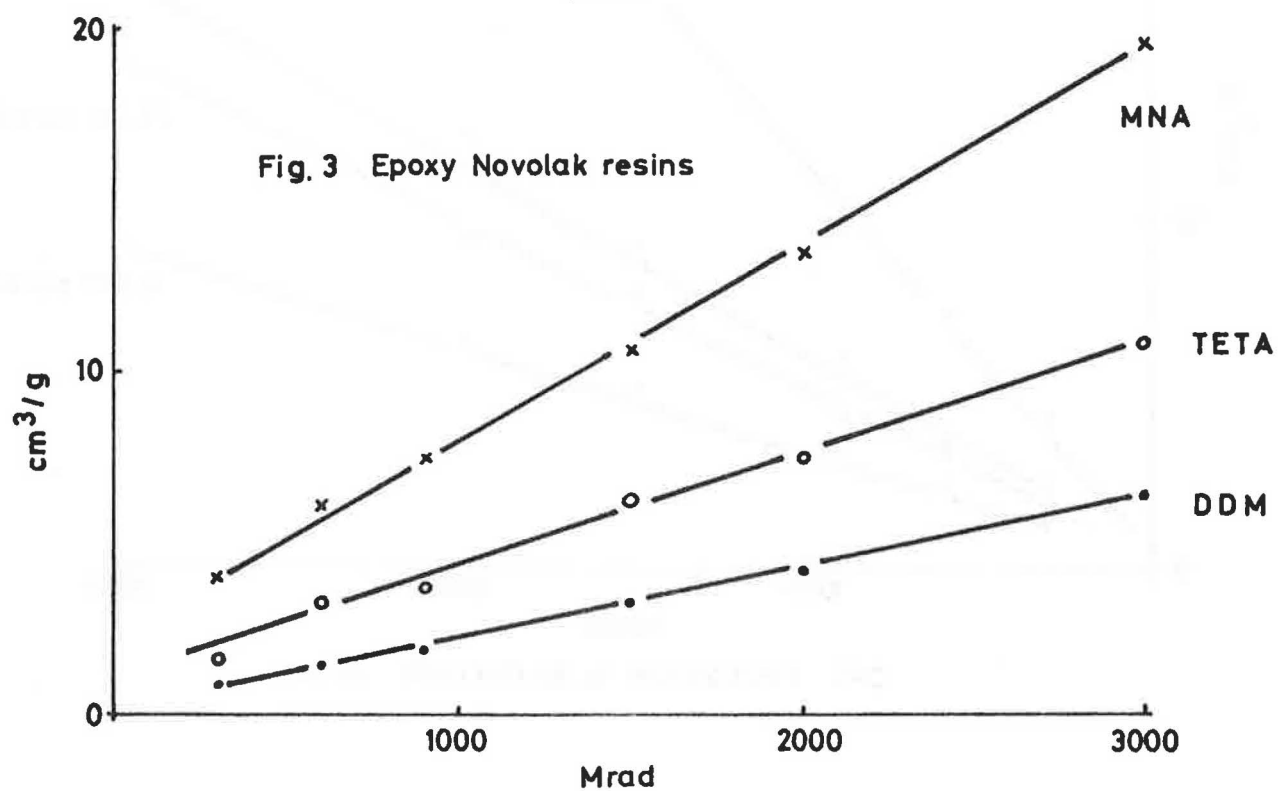
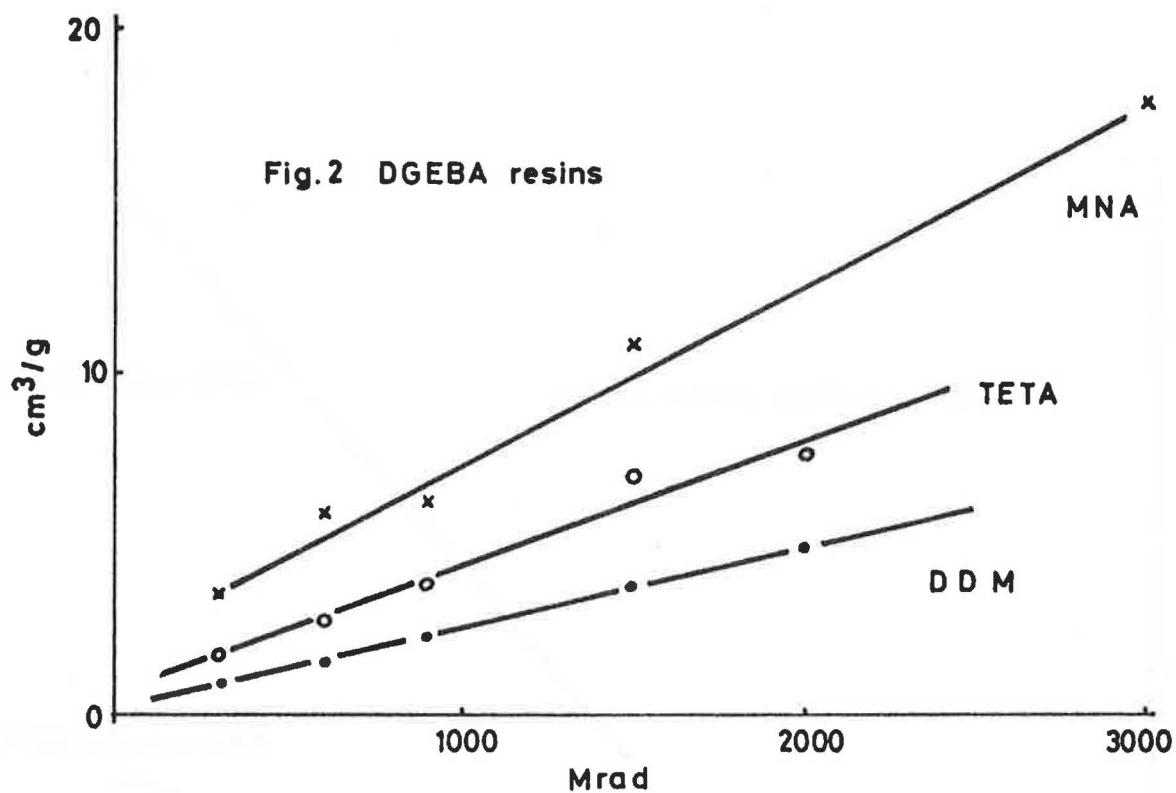


FIG.1 MOLD FOR FLEXURAL TEST SPECIMENS.



GAS EVOLUTION Vs RADIATION DOSE.

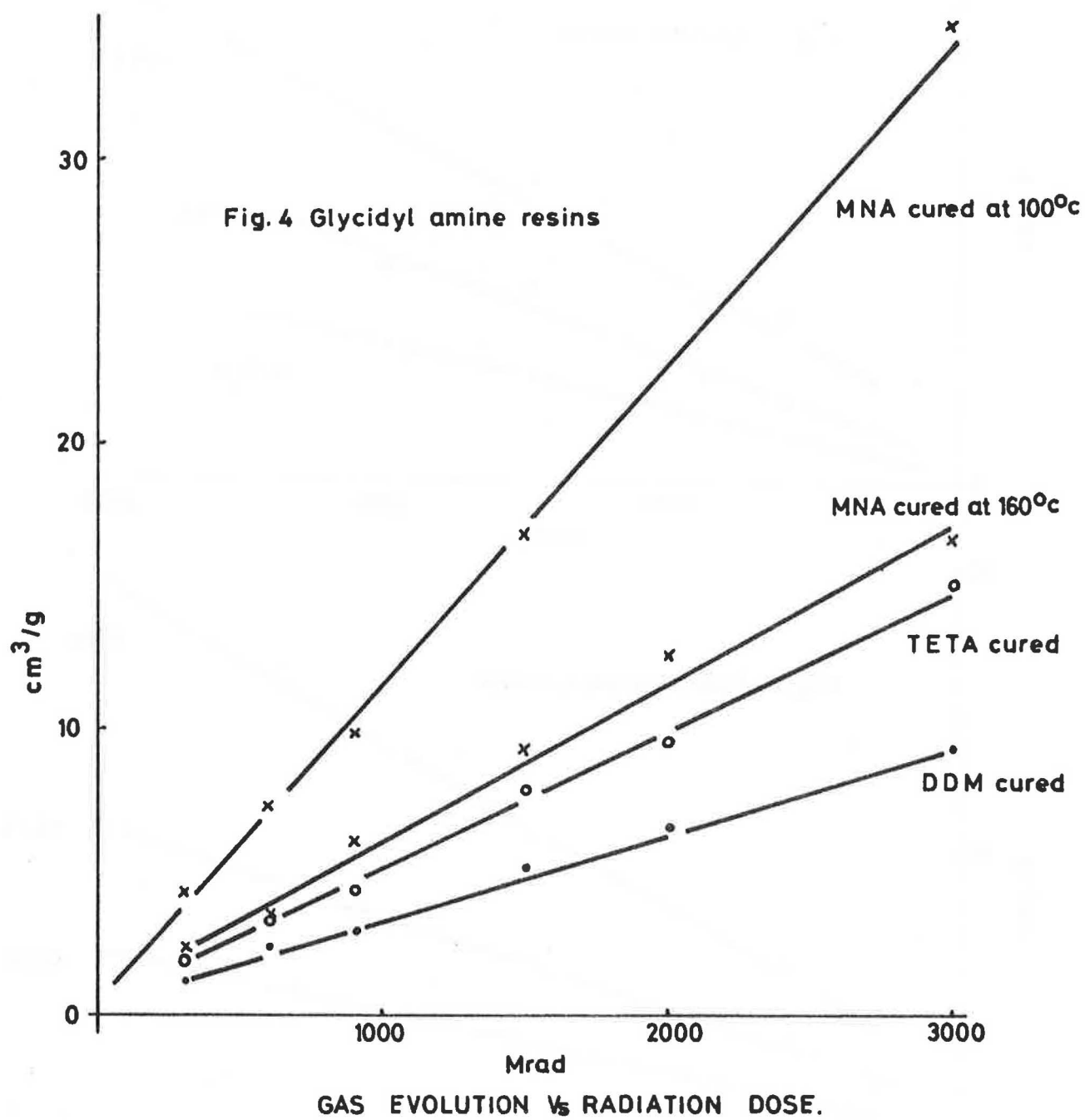


Fig. 5 DGEBA / DDM

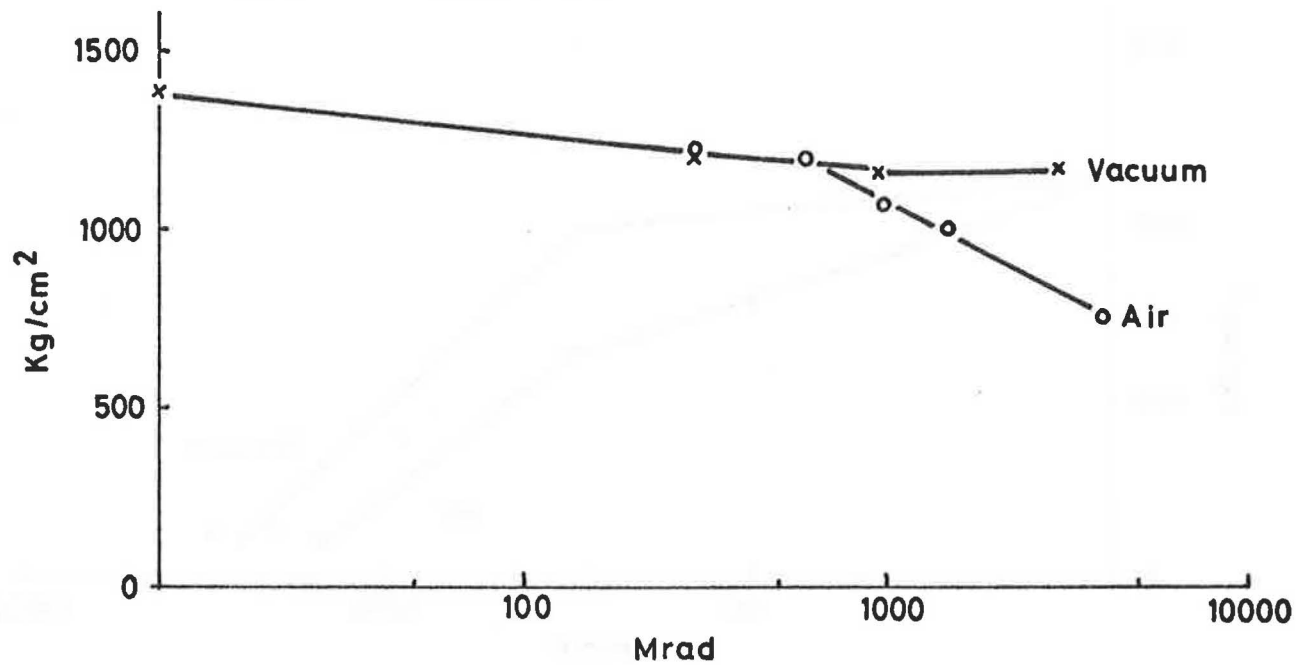
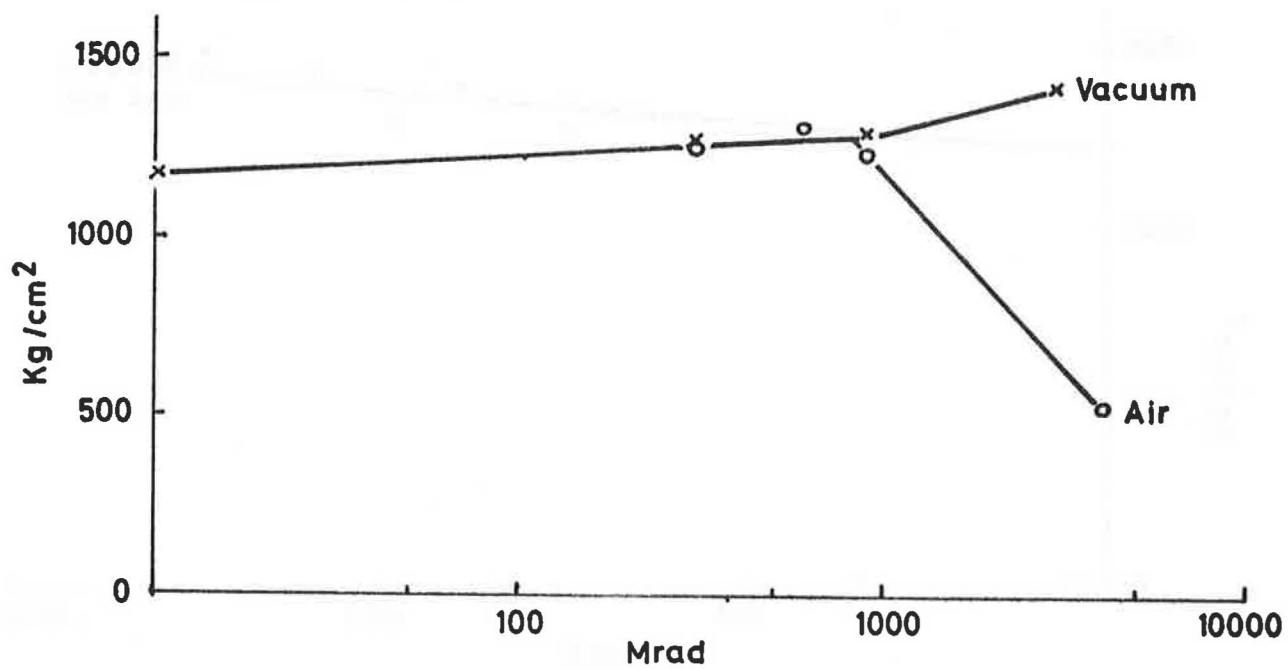


Fig. 6 DGEBA / MNA



FLEXURAL STRENGTH Vs RADIATION DOSE.

Fig.7 DGEBA / TETA

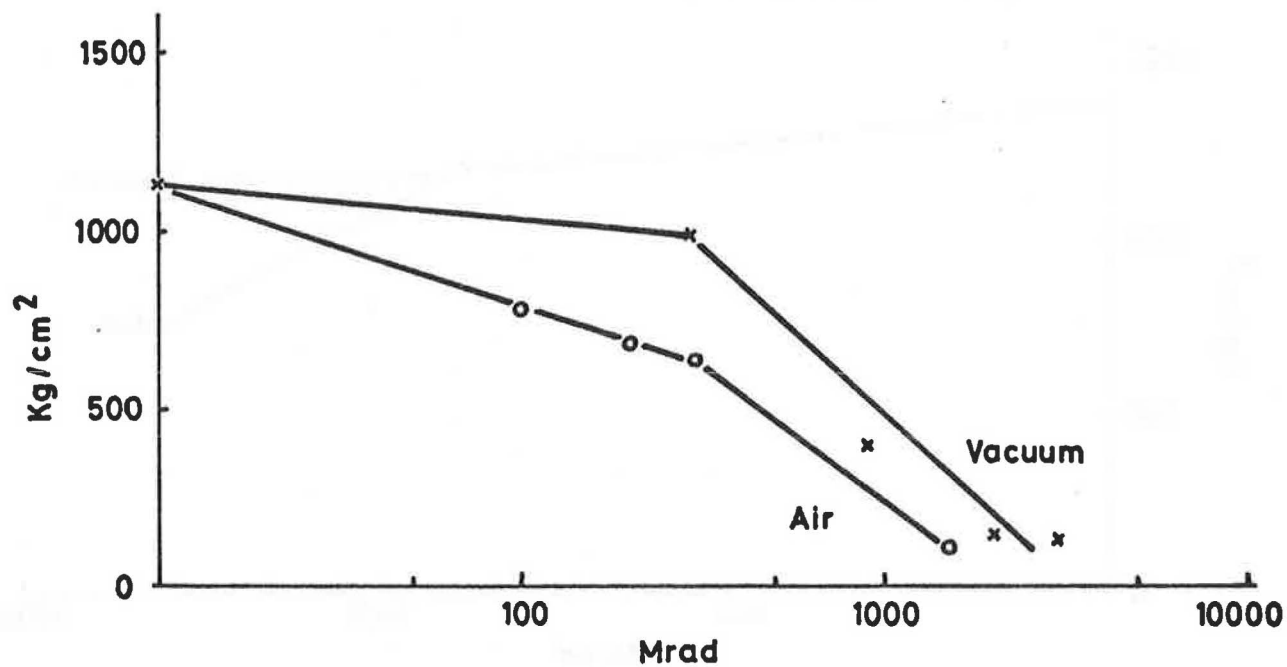
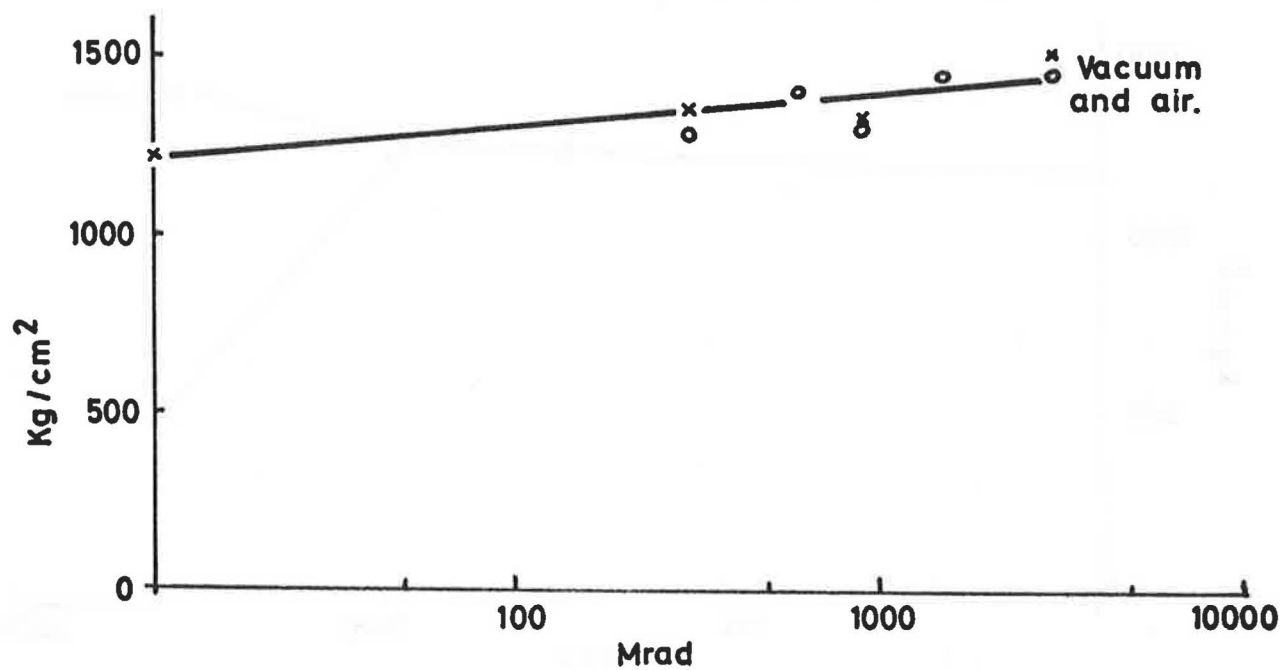


Fig. 8 Epoxy Novolak / D D M



FLEXURAL STRENGTH Vs RADIATION DOSE.

Fig. 9 Epoxy Novolak / M N A

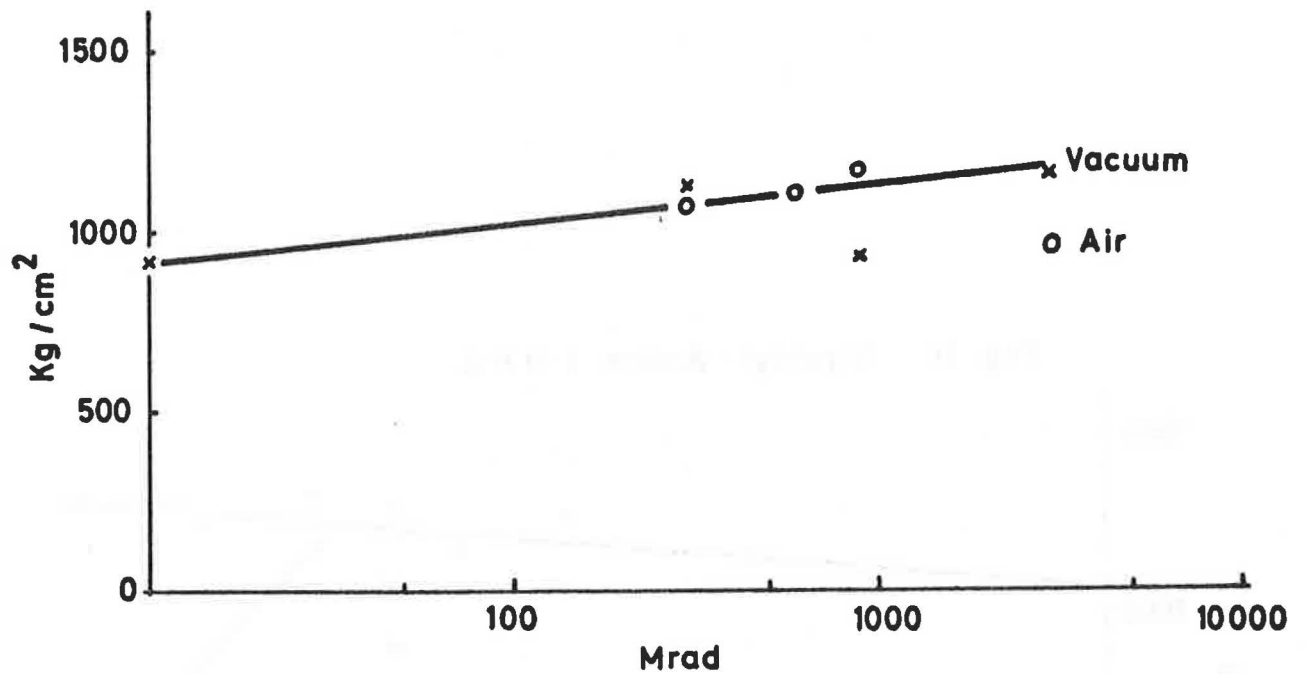
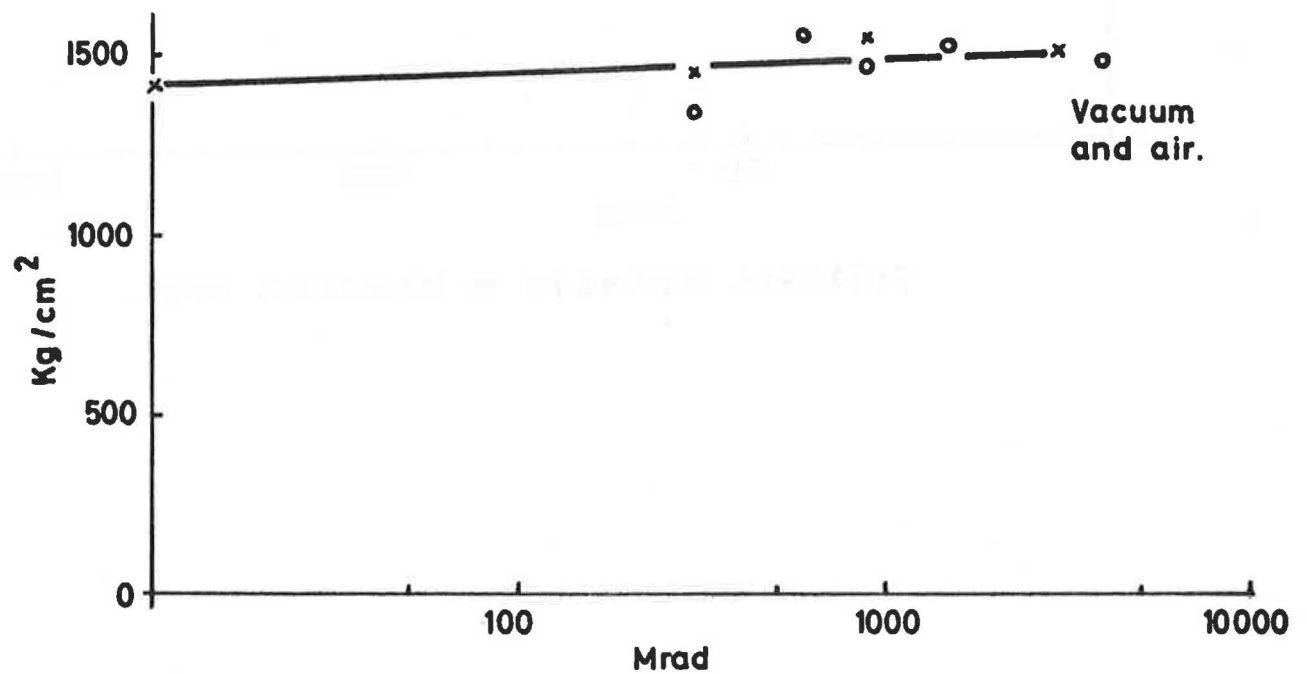
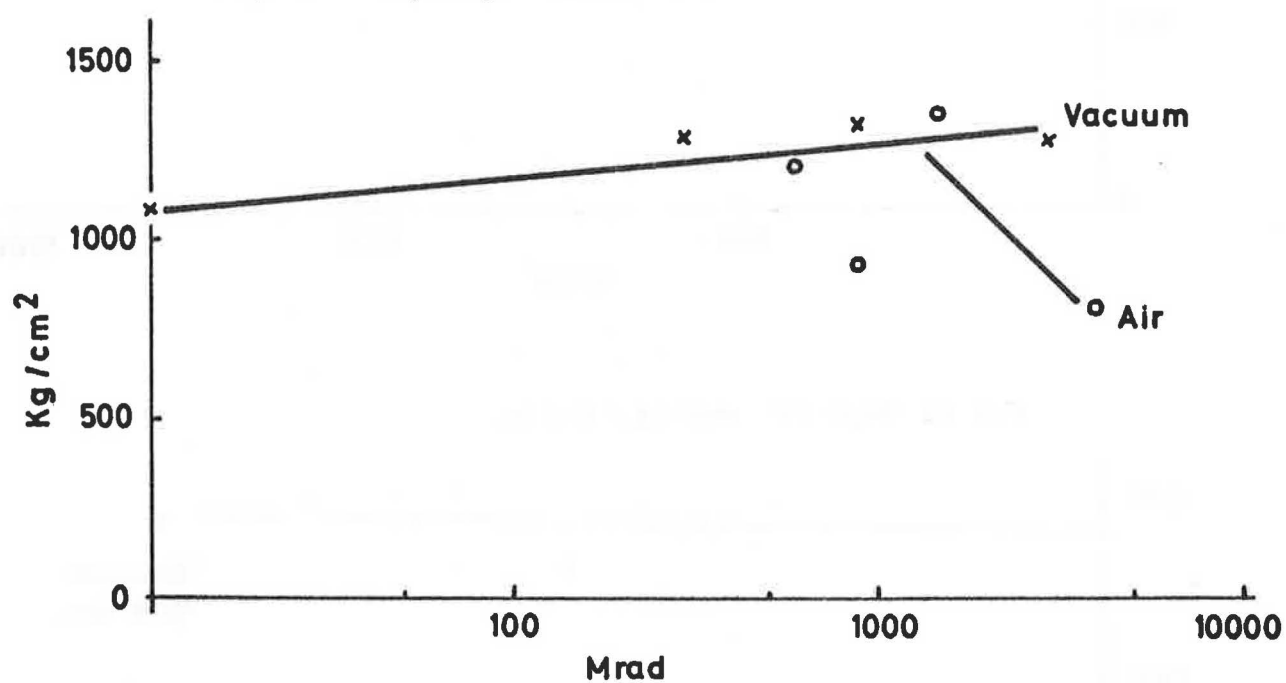


Fig. 10 Glycidyl Amine / D D M.



FLEXURAL STRENGTH Vs RADIATION DOSE.

Fig. 11 Glycidyl Amine / MNA



FLEXURAL STRENGTH Vs RADIATION DOSE.

APPENDIX

1. EPOXY RESINS

Resin	Abbreviation	Manufacturer & Designation	
Diglycidyl ether of Bisphenol A	DGEBA	Ciba	MY 790
Epoxy Novolak	-	Ciba	LY 558
Glycidyl amine	-	Ciba	X33/1020

2. HARDENERS

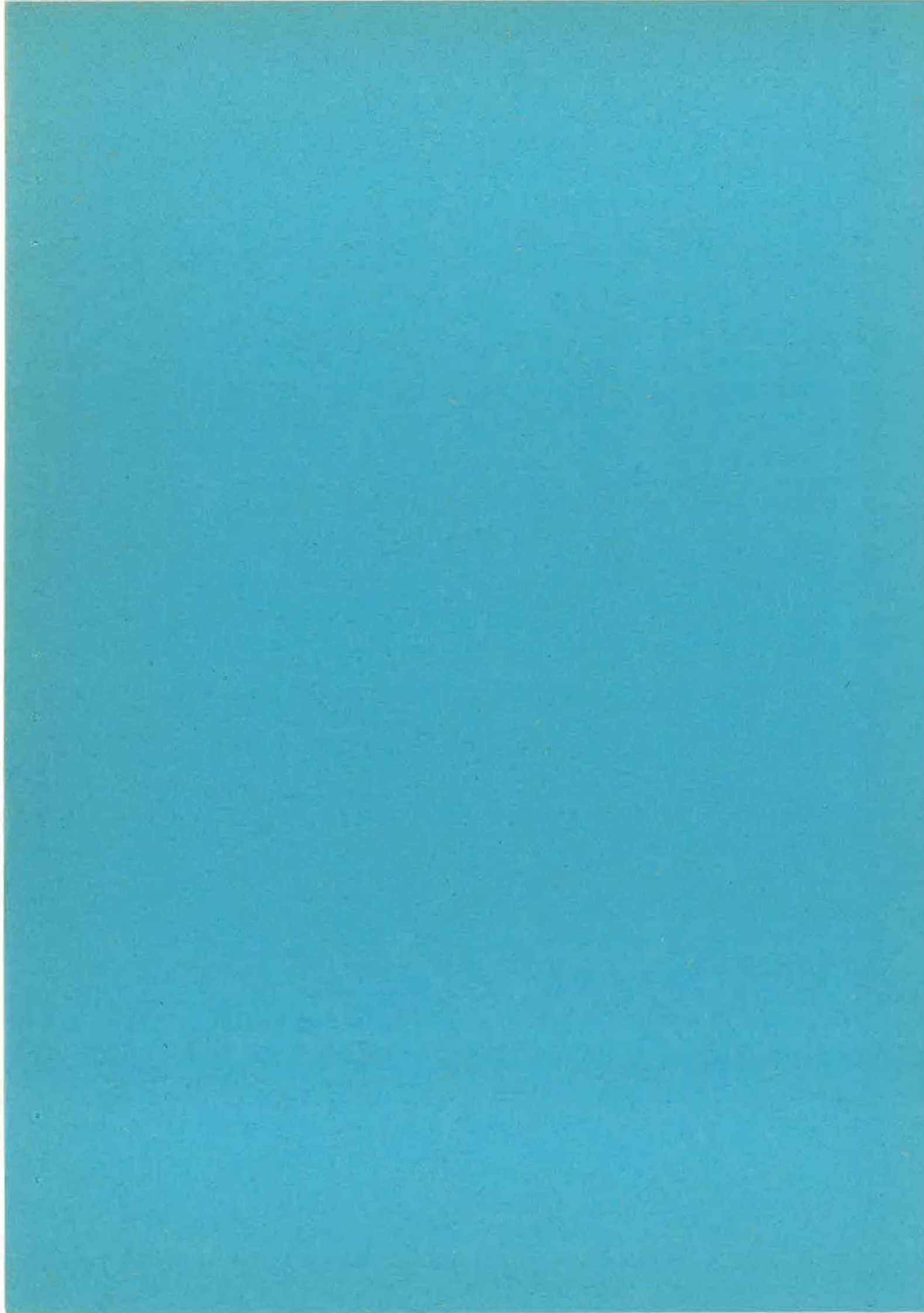
Type	Chemical Name	Abbreviation	Manufacturer & Designation	
Aliphatic Amine	Triethylene tetramine	TETA	Ciba	HY 951
Aromatic Amine	Diamino diphenyl methane	DDM	Ciba	HT 972
Acid anhydride	5 methylenedimethylene 1234 tetrahydrophthalic anhydride	MNA	Ciba	HT 906

3. CURING CYCLES AND RESIN/HARDENER PROPORTIONS

RESIN	HARDENER	MIXING TEMP.	PARTS OF HARDENER PER 100 PARTS RESIN	CURE CYCLE
DGEBA (1)	TETA	resin RT hardener RT	10	16 hrs. @ RT 2 hrs. @ 50°C
	DDM	resin RT hardener 95°C	28	10 hrs. @ 100°C
	MNA	resin RT hardener 35°C	80 (2)	10 hrs. @ 100°C
EPOXY NOVOLAK	TETA	resin 55°C hardener RT	10	20 hrs. @ RT 2 hrs. @ 50°C
	DDM	resin 60°C hardener 95°C	30	2 hrs. @ 100°C 10 hrs. @ 160°C
	MNA	resin 60°C hardener 35°C	90 (2)	2 hrs. @ 100°C 10 hrs. @ 160°C
GLYCIDYL AMINE	TETA	resin 55°C hardener RT	14	10 hrs. @ RT 2 hrs. @ 50°C
	DDM	resin 55°C hardener 95°C	40	10 hrs. @ 50°C 10 hrs. @ 100°C
	MNA	resin 55°C hardener 35°C	110 (3)	10 hrs. @ 100°C
	MNA	resin 55°C hardener 35°C	110 (3)(4)	10 hrs. @ 100°C 2 hrs. @ 160°C

NOTES:

- (1) The DGEBA resin tended to crystallise on standing and it was necessary to warm slightly and then cool to room temperature before use.
- (2) Plus 1 part Benzyl dimethylamine accelerator.
- (3) " 2 " " " "
- (4) For gas evolution tests only.



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