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Rutherford Laboratory Report

Post Irradiation Mechanical Properties of Epoxy Resin Glass Composites

D Evans J T Morgan R Sheldon G B Stapleton

Science Research Council

Chemical Technology Group
Rutherford High Energy Laboratory
Chilton Didcot Berkshire
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POST IRRADIATION MECHANICAL PROPERTIES OF EPOXY RESIN/GLASS COMPOSITES

D Evans J T Morgan R Sheldon G B Stapleton

ABSTRACT

The effect of irradiation on the mechanical properties of epoxy resin/glass composites has been determined for 14 epoxy resin systems. The resins include glycidyl ethers and glycidyl amines with anhydride and aromatic amine curing agents.

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1. INTRODUCTION

The use of epoxy resin composites as electrical insulating materials in high energy physics applications continues to be of interest, particularly in environments where intense radiation fields are a problem. This paper describes some further work[1,2] on the radiation stability of a number of epoxy resin systems, and gives data on the radiation stability of these materials up to a total integrated dose of 2×10^{10} rads.

Data is also given concerning the effect of the post-cure temperature on the radiation stability of an epoxy resin/glass composite.

2. SPECIMEN PREPARATION AND MATERIALS EXAMINED

2.1 The epoxy resins selected for test were:-

Diglycidyl ether of Bisphenol A	- DGEBA
Epoxy Novolak	- EN
Diglycidyl Aniline	- DGA
Triglycidyl p-Amino phenol	- TGPAP
Tetraglycidyl Diamino Diphenyl Methane	- TGDM

The curing agents selected for use in conjunction with each of the above resins were:-

Methyl "Nadic" Anhydride	- MNA
Diamino Diphenyl Methane	- DDM
Diamino Diphenyl Sulphone	- DDS

All of these materials are available commercially and full details are given in the Appendix together with details of resin/hardener proportions and curing cycles.

2.2 The materials were prepared in the form of glass fabric laminates of ⅛" thickness using conventional wet lay-up techniques, as detailed in section 2.3. Laminates prepared in this manner show little variance in their physical properties and closely resemble the electrical insulating systems used in the construction of magnets for high energy physics applications. Data generated using a vacuum impregnated composite are given in Table 1, no significant difference in mechanical properties being observed between this and the type of composite prepared for this experiment.

2.3 Sufficient glass fabric to complete the experiment was cut into 9" squares, equal and at 45° to the warp. Each laminate was constructed from 20 layers of the glass fabric such that the warp direction of each subsequent layer was rotated clockwise through 45°. This technique ensures that the finished laminate will show no directionality of properties due to differences between the warp and weft direction of the fabric. After complete wetting-out of the final fabric layer, the laminate was pressed between stops, to give a nominal glass/resin ratio of 60/40, and cured in the press at the appropriate temperature. The actual glass/resin ratio was determined for each laminate and these results are included in the Appendix.

2.4 Flexural test specimens 3" x ½" were cut from the laminates using a diamond tipped cutting disc.

3. TEST PROCEDURE

3.1 The mechanical properties of the specimens in flexure were determined using three point loading by means of a commercial testing machine.* The test details are given in the following table.

Specimen size	7.5 x 1.25 x 0.32 cm approx
Span	5.08 cm
Rate of crosshead movement	1.0 cm/min
Chart speed	30 cm/min
Number of replicates	5

3.2 This procedure differs from the method recommended in ASTM D790/66 in that the specimen width is reduced and a faster rate of crosshead travel is adopted in order to reduce the time required for testing.

These modifications result in only slight differences to the determined values of flexural strength and modulus for materials of this type. (See Table 2).

4. IRRADIATION

4.1 All specimens were irradiated using the spent reactor fuel element irradiation unit at UKAEA Harwell, Berks. This facility provides gamma radiation with a mean energy of 1.0 MeV at dose rates up to a maximum of 6 megarads per hour. Calibration is by ion chamber and ferrous sulphate dosimetry and is reported to be accurate to ± 5%.

*Instron model TTCM

4.2 The specimens were irradiated in air to the following dose levels:-

$$0,\ 3 \times 10^9,\ 7 \times 10^9,\ 10^{10},\ 2 \times 10^{10} \text{ rads}$$

The temperature of the specimens during irradiation would not be expected to rise significantly above the temperature of the shielding water (19°C).

5. RESULTS

5.1 Flexural strength and modulus values were derived from the load versus deflection curves; the mean values for the 5 replicates being given in Tables 3 and 4 together with their standard deviations. The results are also presented graphically in Figures 1 to 5.

5.2 Figure 6 shows the effect of post-cure on the radiation stability of a DGEBA/MNA composite.

6. DISCUSSION OF RESULTS

6.1 From changes in flexural strength with radiation, it may be observed that diglycidyl aniline resin has relatively poor resistance to ionising radiation; this is somewhat surprising in view of the high radiation stability of the other glycidyl amine resins.

6.2 The order of radiation stability of the resins with each hardener is:-

$$\text{TGPAP} > \text{TGDM} > \text{EN} > \text{DGEBA} > \text{DGA}$$

Although the two more stable glycidyl amines prove to be considerably more stable than the glycidyl ethers.

6.3 The aromatic amine hardeners give resins which are more stable towards radiation than the MNA cured systems, DDM being marginally better than DDS. The aromatic amine systems however, would probably not be technically feasible to use in large scale commercial potting, impregnating, or encapsulating operations due to their short room temperature pot-life.

6.4 No significant differences could be detected in the radiation stability of DGEBA/MNA laminates given different post-cures.

7. CONCLUSIONS

The data shows that a significant advantage can be gained in the radiation stability of epoxy composites by the use of tri or tetra functional glycidyl amines. These materials are shown to be able to withstand doses of 10^{10} r without change in their physical properties.

It should be stressed that these resins in combination with the liquid anhydride MNA have a low viscosity and a long room temperature pot-life and therefore are extremely useful impregnating materials for use in magnet coil fabrication.

8. ACKNOWLEDGEMENTS

Acknowledgement is made to the Director of the Rutherford High Energy Laboratory, to Mr P Bowles, Chief Engineer and Mr G E Simmonds in whose division the work was performed. Thanks are also due to Mr H Parr who prepared the laminates from which the specimens were taken.

9. REFERENCES

1. Price, M J. Sheldon, R. The Influence of Structure on the Post-Irradiation Physical Properties of Epoxy Resins. RHEL/R 105.

2. Sheldon, R. Stapleton, G B. The Effect of High Energy Radiation on the Mechanical Properties of Epoxy Resin Systems used for Particle Accelerator Construction. RHEL/R 152.

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TABLE 1

Comparison of mechanical properties of laminates prepared by wet lay-up and vacuum impregnation

	Flexural strength (Kg/sq cm)	Flexural modulus (Kg/sq cm x 10^{-5})
Wet lay-up	4018 (Std dev 43)	1.85 (Std dev 0.03)
Vacuum impregnation	3846 (Std dev 276)	1.79 (Std dev 0.06)

Values from 5 replicates

TABLE 2

Effect of straining rate and specimen width on the determined values of flexural strength and modulus of epoxy/glass fabric laminate

Test Number	Specimen Width inch	Crosshead Speed cm 1 min	Flexural Strength Kg/cm^2	Flexural Modulus Kg/cm^2 x 10^{-5}
1*	1.0	0.1	4199 (2.0%)	1.84 (1.9%)
2	0.5	0.1	4249 (4.3%)	1.93 (4.1%)
3**	0.5	1.0	4500 (1.4%)	1.98 (3.0%)

Mean values of 5 replicates together with standard deviations

* Procedure recommended: ASTM D790/66

** Procedure adopted for this report

TABLE 3

FLEXURAL STRENGTH OF IRRADIATED EPOXY RESINS

Mean of five replicates with standard deviation - Kg cm^{-2}

RESIN	HARDENER	RADIATION DOSE - rads				
		0	3×10^9	7×10^9	10^{10}	2×10^{10}
DGEBA (MY 740)	MNA	3654 6.7%	3229 1.7%	2643 4.9%	1798 5.2%	1073 6.4%
	DDM	3631 6.9%	3764 6.2%	3071 4.0%	1725 7.4%	1247 6.6%
	DDS	3632 7.0%	3476 3.0%	1721 9.4%	1002 7.1%	693 5.7%
EN (LY 558)	MNA	3776 6.2%	3536 2.4%	2436 2.5%	2149 3.7%	1607 3.7%
	DDM	3596 5.3%	3899 5.9%	3574 2.5%	3302 3.7%	2798 8.4%
	DDS	3878 5.5%	4142 2.7%	3623 5.6%	2715 4.8%	1734 12.5%
DGA	MNA	4113 3.2%	3632 5.4%	1501 5.8%	983 2.8%	777 9.0%
	DDM	4459 5.1%	4279 0.7%	2360 5.4%	1708 1.5%	884 6.7%
TGPAP (ERL 0510)	MNA	3863 4.8%	3967 1.8%	3513 2.4%	2909 1.7%	1548 6.4%
	DDM	4004 2.9%	4312 5.5%	4205 2.8%	4124 2.8%	3044 5.2%
	DDS	4093 5.0%	4460 3.6%	4084 4.4%	3619 2.3%	1728 3.7%
TGDM (X33/1020) (MY 720)	MNA	3643 5.9%	3810 6.0%	3362 3.4%	2875 1.5%	1942 11.6%
	DDM	3227 20.1%	3829 4.5%	3270 19.0%	3637 8.1%	2917 10.8%
	DDS	4760 5.2%	4779 1.6%	4450 3.9%	3847 2.8%	2531 13.2%

TABLE 4

FLEXURAL MODULUS OF IRRADIATED EPOXY RESINS

Mean of five replicates with standard deviation - Kg $cm^{-2} x 10^{-5}$

RESIN	HARDENER	RADIATION DOSE - rads 0	3×10^9	7×10^9	10^{10}	2×10^{10}
DGEBA (MY 740)	MNA	1.64 7.7%	1.57 2.9%	1.43 8.8%	1.23 7.0%	1.38 4.8%
	DDM	1.68 4.4%	1.79 2.4%	1.88 7.0%	1.55 1.7%	1.62 6.8%
	DDS	1.67 2.7%	1.58 2.8%	1.42 8.2%	1.18 6.8%	1.27 11.9%
EN (LY 558)	MNA	1.84 2.7%	1.82 2.2%	1.45 3.9%	1.40 4.4%	1.29 6.7%
	DDM	1.67 3.5%	1.85 3.8%	1.83 1.9%	1.69 5.6%	1.72 12.7%
	DDS	1.75 2.9%	1.85 1.3%	1.66 1.6%	1.61 1.7%	1.47 5.2%
DGA	MNA	1.75 3.3%	1.80 7.7%	1.45 5.5%	1.41 7.2%	1.40 5.8%
	DDM	1.93 3.0%	1.93 2.2%	1.82 4.2%	1.79 4.3%	1.50 7.6%
TGPAP (ERL 0510)	MNA	1.77 3.9%	1.89 2.9%	1.82 5.1%	1.73 1.7%	1.36 11.3%
	DDM	1.81 2.3%	1.86 4.7%	1.90 2.6%	1.90 1.8%	1.85 5.7%
	DDS	1.89 6.9%	2.03 3.6%	2.02 6.4%	1.99 2.0%	1.60 13.4%
TGDM (X33/1020)	MNA	1.84 3.5%	1.90 17.9%	1.64 11.6%	1.56 2.4%	1.42 10.0%
	DDM	1.52 10.8%	1.64 7.7%	1.62 6.9%	1.67 3.8%	1.59 6.7%
	DDS	2.14 7.3%	2.07 4.8%	2.12 4.0%	2.03 3.3%	1.85 7.2%

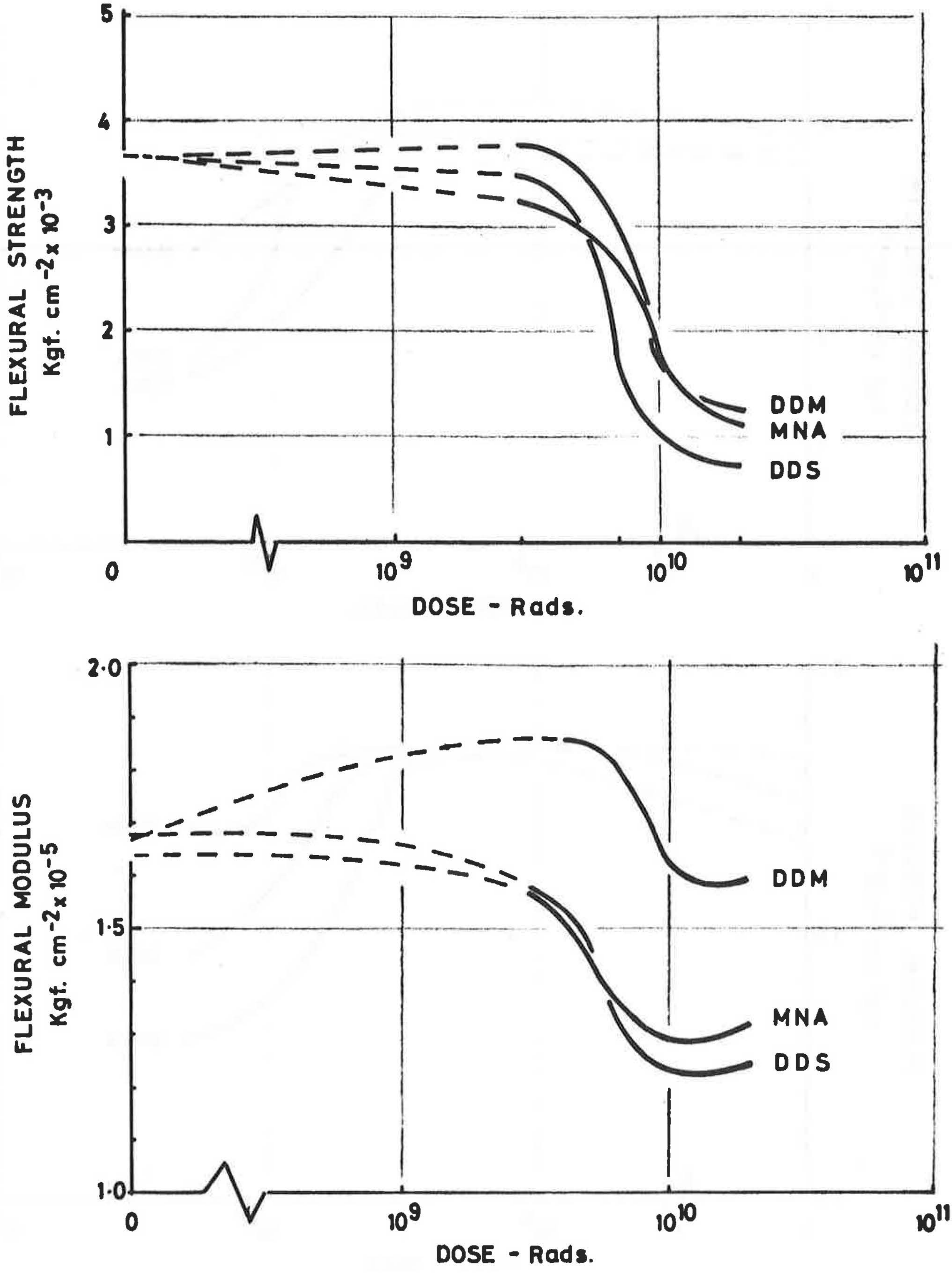


FIG. 1 CURED DGEBA RESINS. (MY 740).

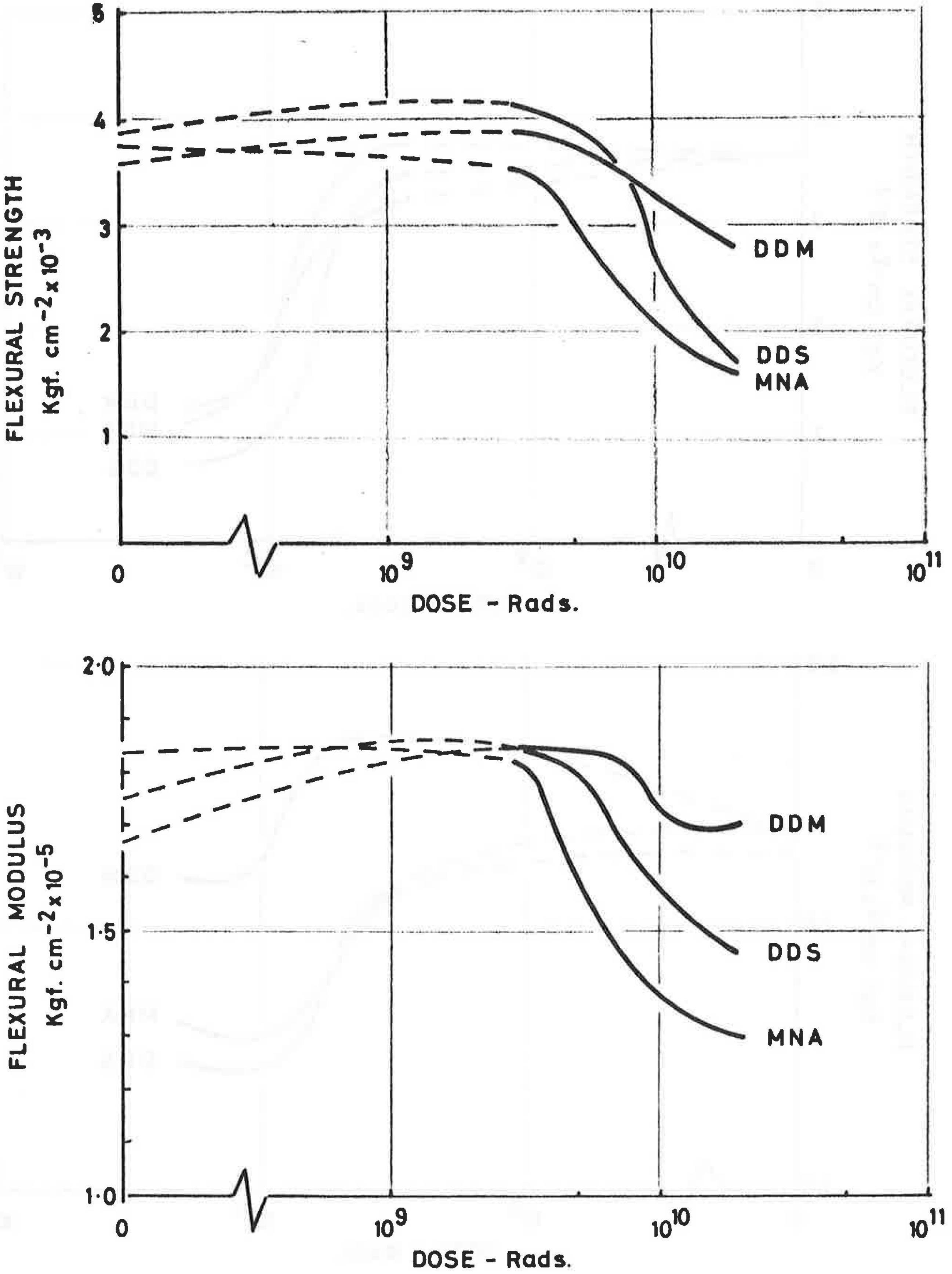


FIG. 2 CURED EN RESINS. (LY 558).

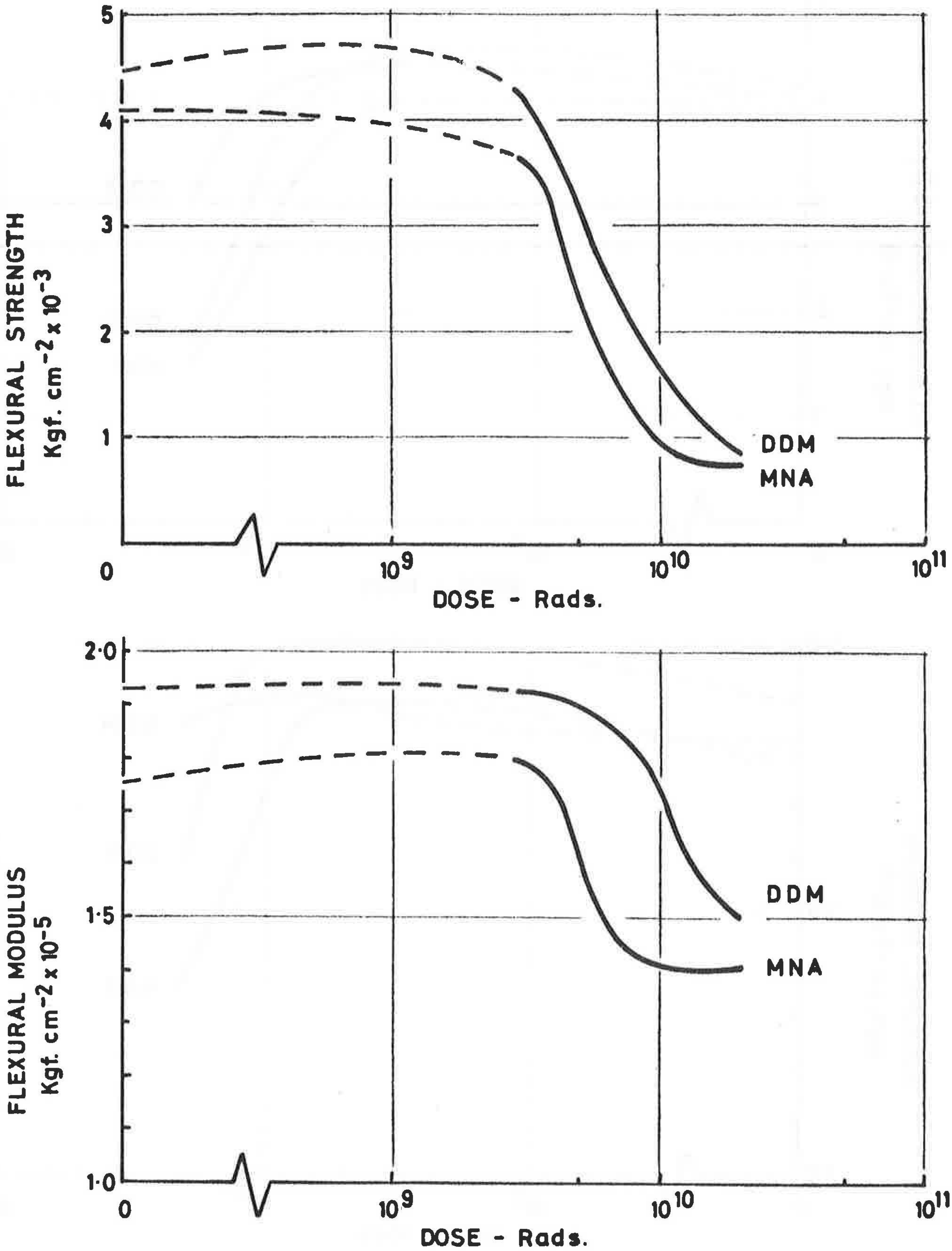
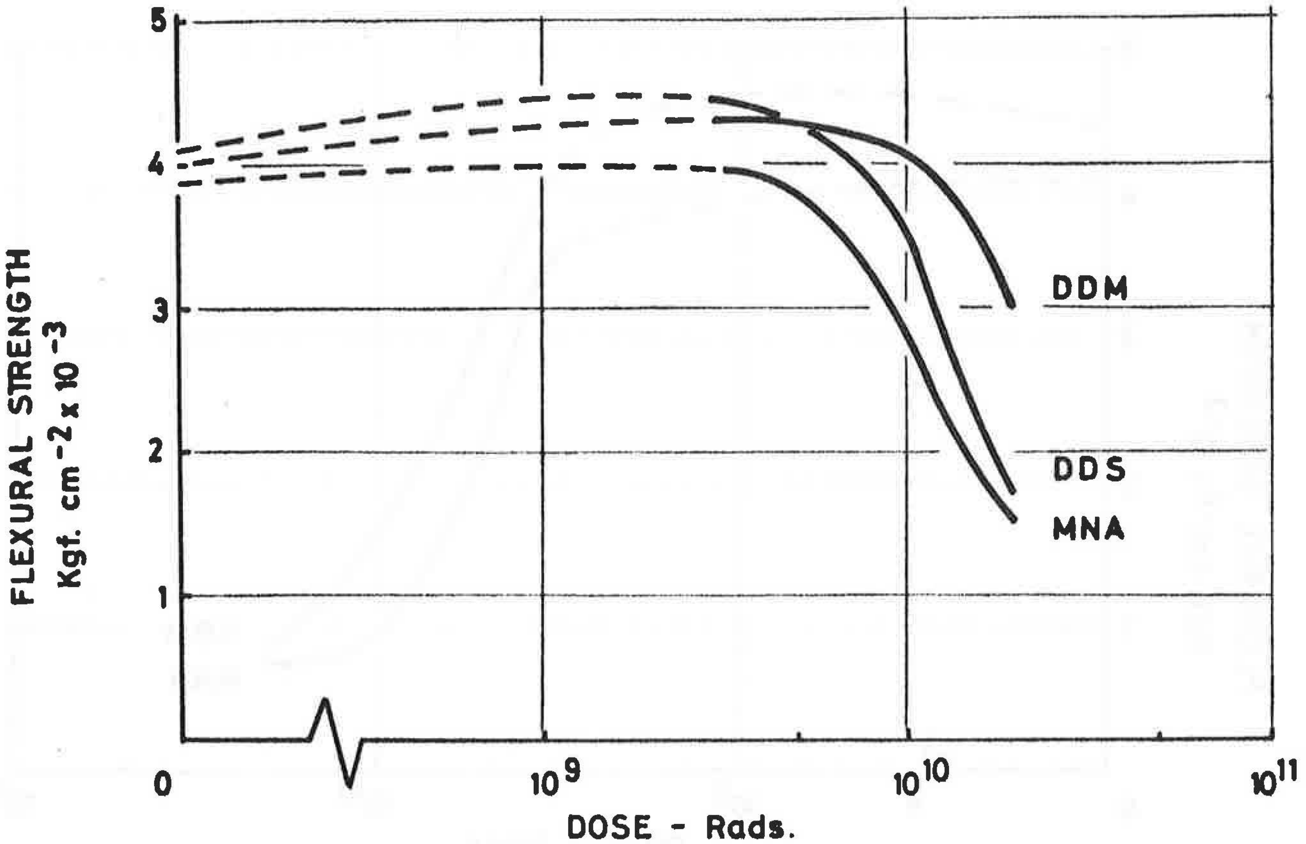


FIG. 3 CURED DGA RESINS.



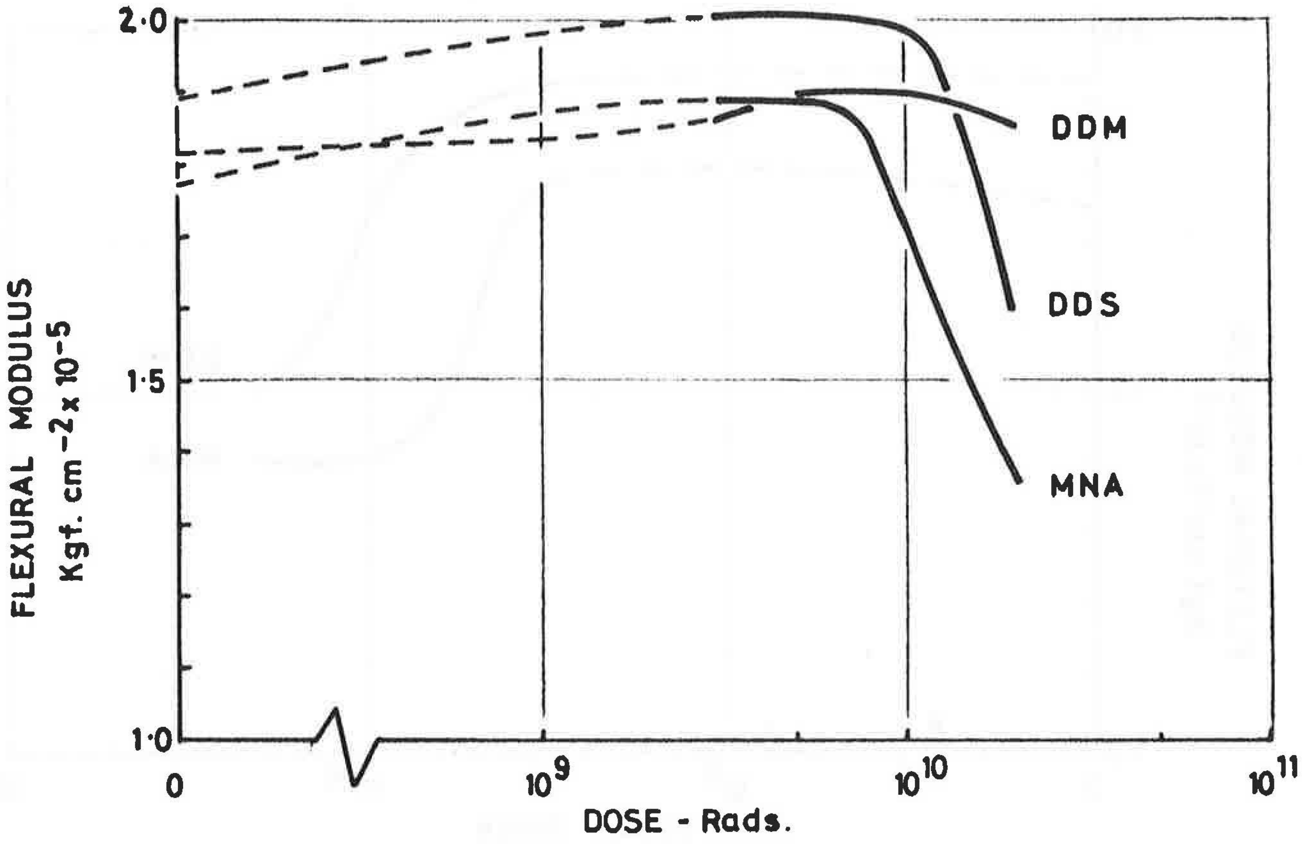


FIG. 4 CURED TGPAP RESINS. (ERL 0510).

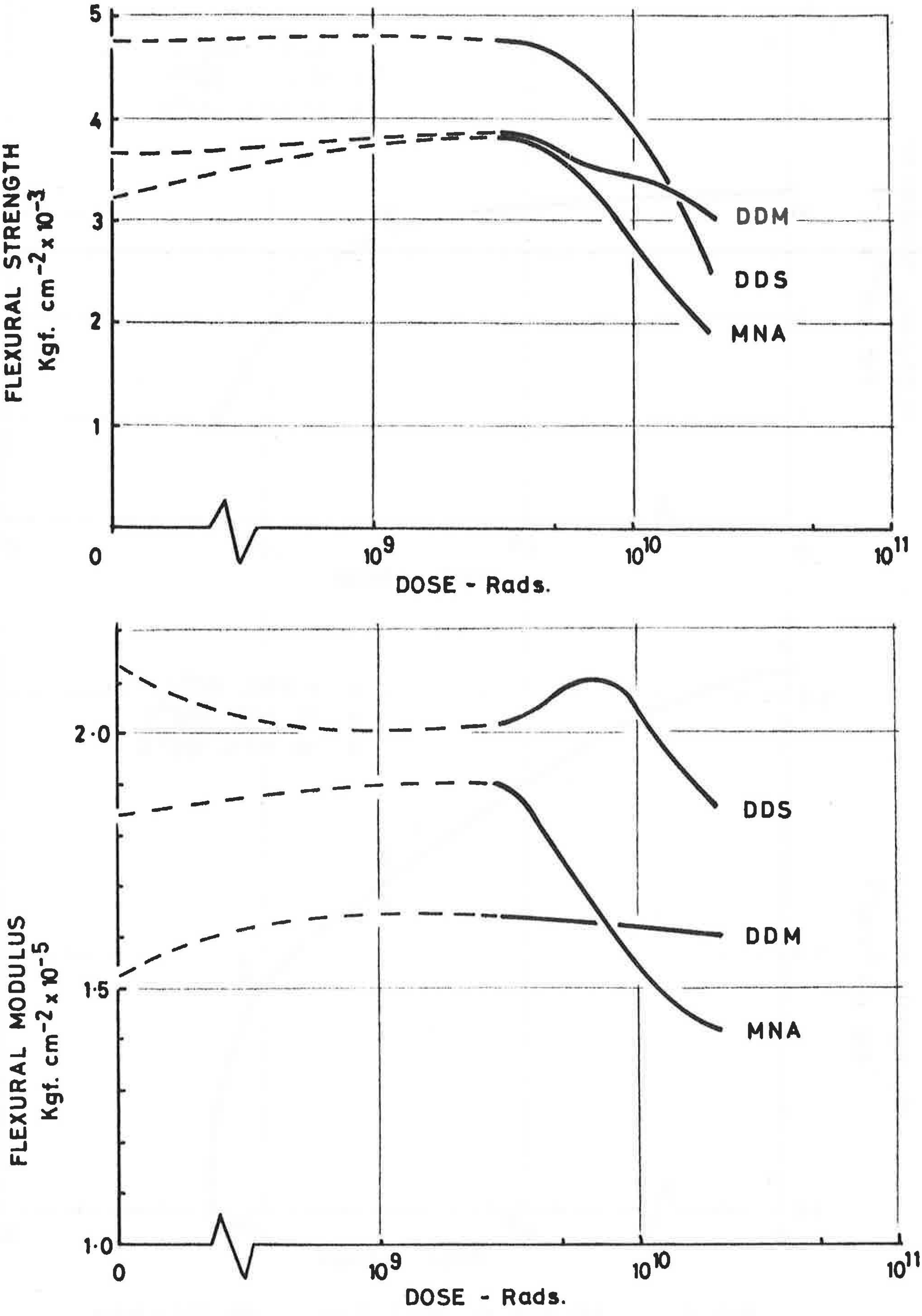
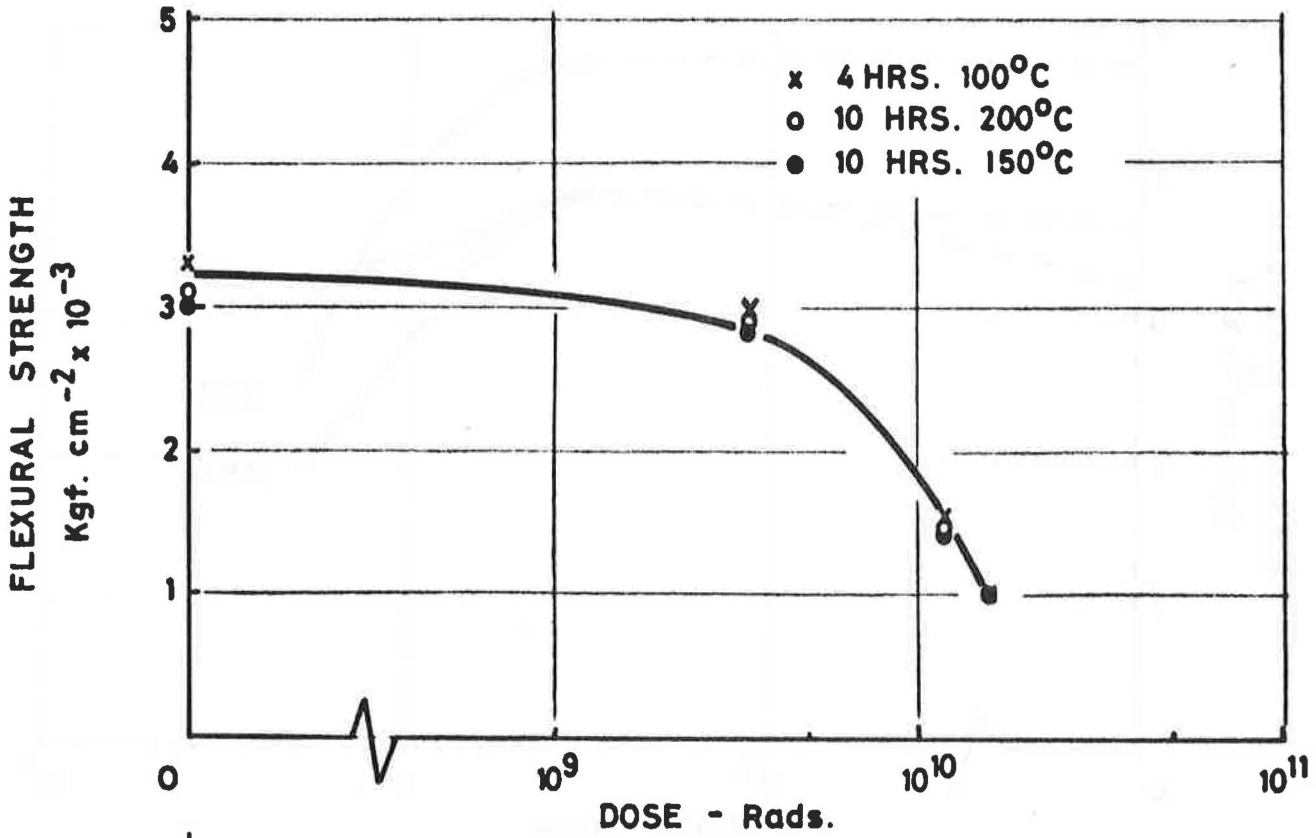


FIG. 5 CURED TGDM RESINS. (X33/1020).



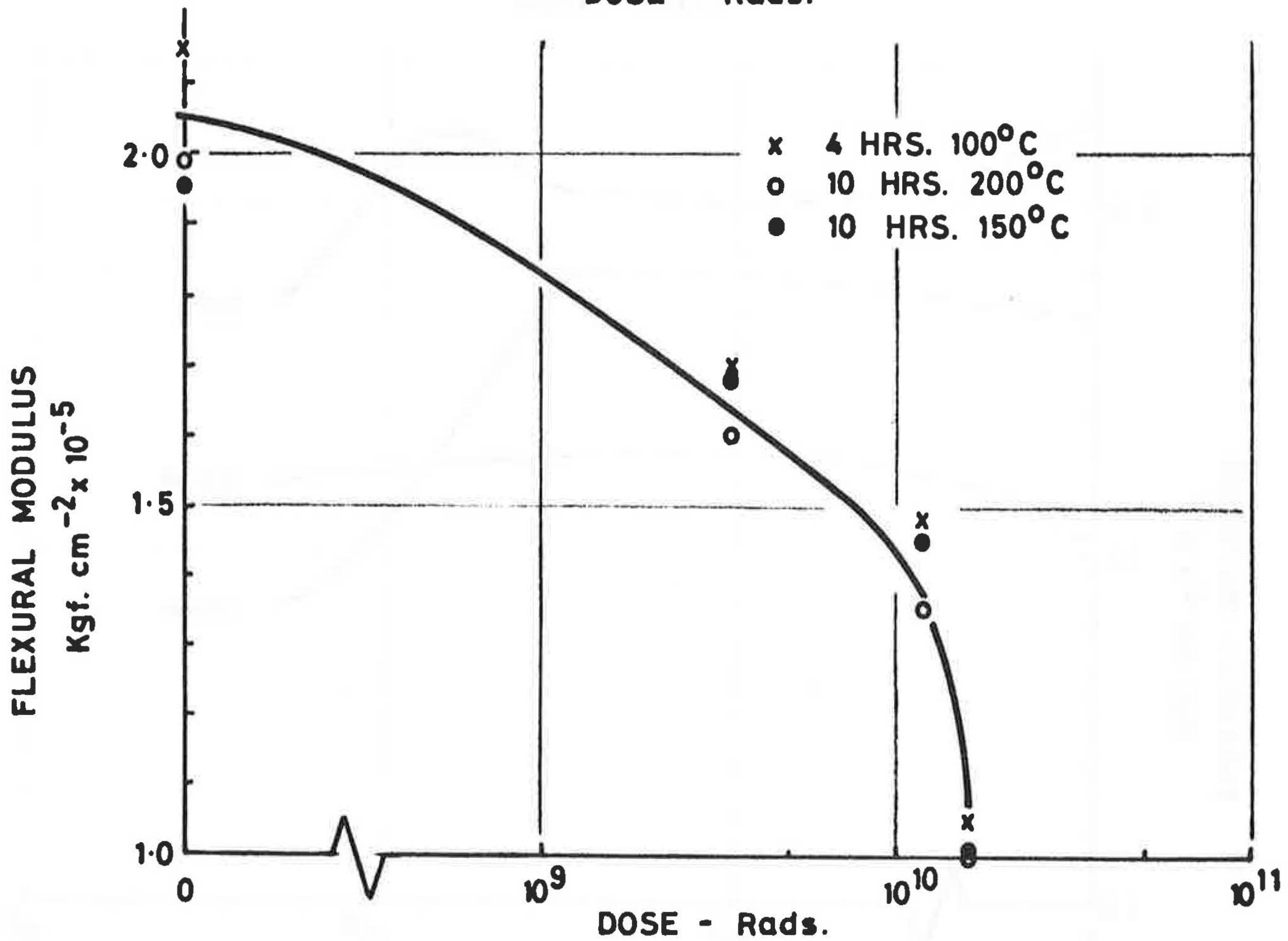


FIG. 6 EFFECT OF POST CURE. - MY 740 / MNA

APPENDIX

1. Epoxy Resins

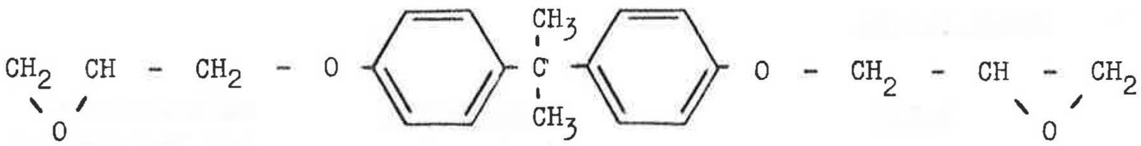
Resin	Abbreviation	Manufacturer and Designation	
Diglycidyl ether of Bisphenol A	DGEBA	CIBA	MY 740
Epoxy Novolak	EN	CIBA	LY 558
Diglycidyl aniline	DGA		
Triglycidyl amines phenol	TGPAP	BXL	ERL 0510
Tetraglycidyl diamines diphenyl methane	TGDM	CIBA	X33/1020

2. Hardeners

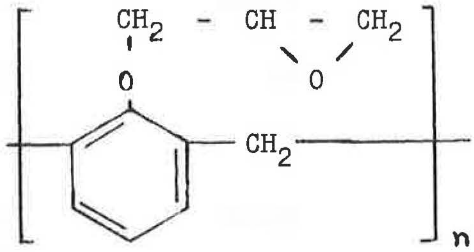
Chemical Name	Abbreviation	Manufacturer and Designation	
Methyl "Nadic" anhydride	MNA	CIBA	HT 906
Diamino diphenyl methane	DDM	CIBA	HT 972
Diamino diphenyl sulphone	DDS	F W Berk & Co Ltd	

3. IDEALISED MOLECULAR STRUCTURES OF THE RESINS AND HARDENERS

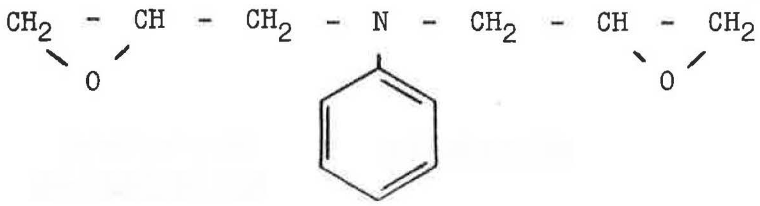
Diglycidyl ether of Bisphenol A (MY 740)



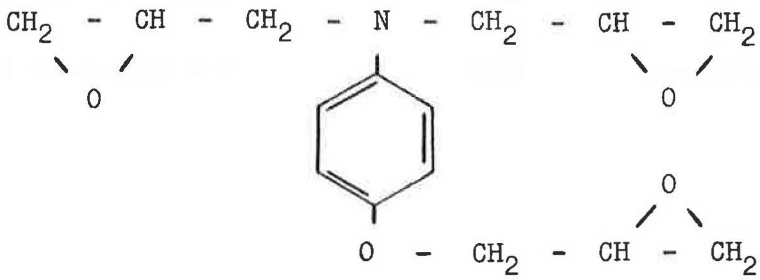
Epoxy Novolak (LY 558)



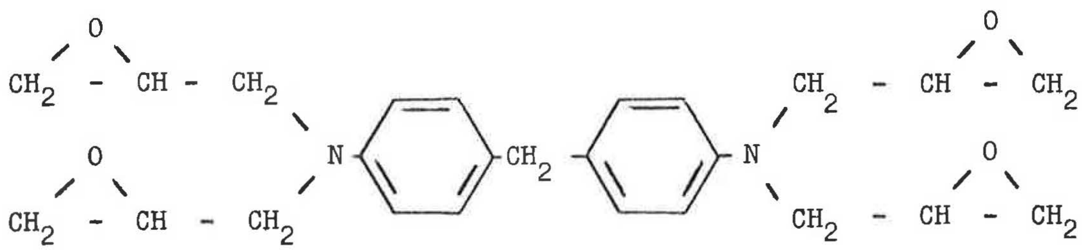
Diglycidyl aniline



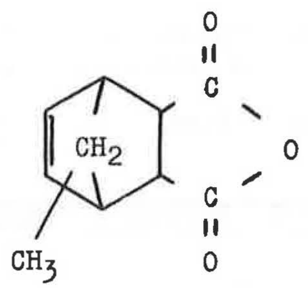
Triglycidyl p aminophenol (ERL 0510)



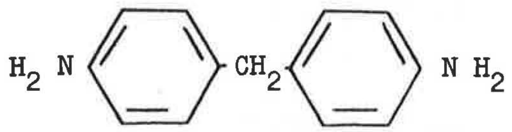
Tetraglycidyl Diaminodiphenyl methane (X33/1020)



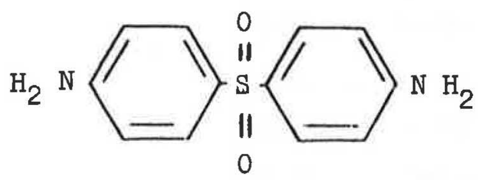
Methyl Nadic anhydride



Diamino diphenyl methane



Diamino diphenyl sulphone



4. **Glass fabric**

Manufacturer	Code No	Weave	Thickness in (approx.)	Threads per inch warp	weft	Weight oz/sq yd
Marglass Ltd	127S	Plain	0.006	36	32	5.5

5. **Determined glass/resin ratios for the laminates** (Mean of five)

DGEBA	MNA	59.95	:	40.05
	DDM	62.19	:	37.81
	DDS	60.86	:	39.14
EN	MNA	61.57	:	38.43
	DDM	59.73	:	4027
	DDS	60.10	:	39.90
DGA	MNA	60.23	:	39.77
	DDM	60.69	:	39.31
TGPAP	MNA	62.69	:	37.31
	DDM	60.35	:	60.69
	DDS	60.48	:	39.52
TGDM	MNA	59.51	:	40.49
	DDM	58.91	:	41.09
	DDS	63.20	:	36.80

6. Curing Cycles and Resin/Hardener Proportions

Resin	Hardener	Lay-up Temperature °C	Parts of Hardener Per 100 Parts Resin	Curing Cycle
DGEBA	MNA	35*	80**	2 hrs up to 150°C 2 hrs @ 150°C
	DDM	60	27	2 hrs up to 120°C 2 hrs @ 150°C
	DDS	100	36	2 hrs @ 130°C 20 hrs @ 200°C
EN	MNA	50	100*	2 hrs up to 100°C 3 hrs @ 150°C 6 hrs @ 215°C
	DDM	75	30	2 hrs @ 100°C 6 hrs @ 150°C
	DDS	100	40	2 hrs @ 120°C 6 hrs @ 200°C
DGA	MNA	35	115	2 hrs up to 100°C 4 hrs @ 150°C 2 hrs @ 180°C
	DDM	50	37	2 hrs up to 100°C 4 hrs @ 150°C 2 hrs @ 180°C
TGPAP	MNA	35	137	2 hrs up to 110°C 3 hrs @ 150°C 3 hrs @ 200°C
	DDM	50	50	2 hrs up to 150°C 6 hrs @ 150°C
	DDS	135	66	2 hrs @ 130°C 20 hrs @ 200°C
TGDM	MNA	40	110	3 hrs up to 120°C 5 hrs @ 150°C
	DDM	60	40	3 hrs up to 120°C 5 hrs @ 150°C
	DDS	135 cooled to 100	53	2 hrs @ 130°C 20 hrs @ 200°C

* Degrees Centigrade

** Plus 1 part benzyl dimethylamine

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