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Effects of High Energy Radiation on the Mechanical Properties of Epoxy Graphite Fiber Reinforced Composites

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Report

1. A brief summary of Progress to Date*

2. Preprints of the following articles:

   a) K. W. Wolf, J. D. Memory, R. D. Gilbert and R. E. Fornes, "Effects of 0.5 MeV Electrons on the Interlaminar Shear and Flexural Strength of Properties of Graphite Fiber Composites." J. App. Phys. 54:5558-5561 (1983).

   b) G. M. Kent, J D. Memory, R. D. Gilbert and R. E. Fornes, "Variation in Radical Decay Rates in Epoxy as a Function of Crosslink Density," J. Appl. Polym. Sci. 28:3301-3307 (1983).

3. Preprints of the following articles: (All have been accepted for publication.)

   a) A. N. Netravali, R. E. Fornes, R. D. Gilbert and J. D. Memory, "Some Investigations of Water and High Energy Radiation Interactions in an Epoxy" (J. Appl. Polym. Sci.)

   b) G. M. Kent, K. Wolf, J. D. Memory, R. E. Fornes, and R. D. Gil[illegible],
   "The Effect of 0.5 MeV Electrons on the Interlaminar and Flexural Strength Properties of Carbon Fibers in Compostes" (Carbon).

   c) K. Schaffer, R. E. Fornes, R. D. Gilbert, and J. D. Memory, "ESR Study of a Cured Epoxy Resin Exposed to High Energy Radiation" (Polymer).

4. Copies of two abstracts of papers presented at the March 1983 meeting of the American Physical Society (Los Angeles, CA) entitled:**

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*The summary of Progress is included in the proposal to NASA for continuation of this work in 1984.

**Three presentations were made at the Jet Propulsion Laboratory (June, July, August 1983) and two at Lawrence Livermoor Labs (August, 1983).

a) T. Wilson, R. D. Gilbert, J. D. Memory, and R. E. Fornes, "Dynamic Mechanical Analysis of an Epoxy," Bull. Amer. Phys. Soc. 28:392 (1983).

b) K. Wolf, J. D. Memory, R. D. Gilbert and R. E. Fornes, "Interlaminar Shear Properties of Irradiated Graphite Fiber Composites," Bull. Amer. Paper. Soc. 28:549 (1983).

SUMMARY OF THE PROGRESS TO DATE

The objective of this work is to assess the effects of high energy radiation on mechanical properties and on the molecular and structural properties of graphite fiber reinforced composites so that durability in space applications can be predicted.

1. Radiation Effects on Mechanical Properties

A listing of composite systems irradiated along with the maximum radiation dose applied and type of mechanical tests performed is shown in Table 1. These samples were exposed to 1/2 MeV electrons.

In previous reports that we have submitted, we have shown that flexural strengths, as measured by a three-point bending test, tend to increase slightly with radiation dose (up to 10,000 Mrad) for T300/5208 composite samples while moduli tend to remain approximately constant. Flexural strengths of C6000/PMR15 samples show little change with radiation dose when fibers are oriented longitudinally and show a small decrease when fibers are oriented transversely while the moduli remain approximately constant in both cases.

We also reported that interlaminar shear strength (ILS) results (sample dimensions 1" by 1/2" by ≃ 0.025", notched through one-half the thickness at 0.25 cm from a line bisecting the long dimension and through one-half the thickness from the opposite side at -0.25 cm from the same line). In those tests we found first an increase with radiation dose followed by a rather significant decrease.

We concluded that these results show that (1) the interface is relatively poorly coupled to the fiber, (2) that the interface is more adversely affected by radiation than either the fiber or the matrix, and (3) that the T300/5208 system is more resistant to radiation induced change than the C6000/PMR15 system.

The ILS tests were done in a tensile mode on an Instron without any support fixtures which would prevent bending or twisting during testing. If bending or twisting does occur, then the mechanism of rupture may be strongly influenced by a peel action instead of strictly shear of the matrix or matrix fiber interface. In order to test whether peel plays a significant role, we obtained samples (3" by 1" by ca. 0.020") of T300/5208 and T300/5209 composites (5209 is a 250°F temperature cure epoxy). These samples were irradiated with 0.5 MeV electrons to dose levels of 0, 3000 Mrad, 6000 Mrad and 9000 Mrad. The fibers were oriented uniaxially in the longitudinal direction. The samples were notched similarly to those noted above but with the notches separated by 0.05 in. The cuts were made with a diamond saw. Some were notched before irradiation and some after irradiation.

A description and schematic of the support fixture used for compressive interlaminar shear tests is given in ASTM method D-695. The nut at each of the four corners was tightened to 5 in-lb of torque. Results of these tests are shown in Table 2. Both T300/5208 and T300/5209 samples show an increase in the compressive shear strengths as a function of radiation dose. The average modulus remains about the same over the radiation dose range considered. The results would suggest that without a side support, the peel mechanism plays a significant role. It is noted further that the low temperature epoxy has the higher shear strength. Also, samples notched before and after radiation show no difference in the effects of radiation.

Since each of the samples tested above was initially 3" in length and was ruptured into two segments of approximately 1-1/2 inch lengths, these were tested in a manner similar to the tests used in the earlier tensile ILS studies.

Samples from each treatment were divided into two groups. One group was tested as before in the tensile ILS studies (notch separation of 0.5 cm without a side support fixture) and one group was tested in a tensile ILS mode with a support fixture illustrated in Figure 1. The ILS strength results are shown in Figures 2-5. Both the T300/5208 and T300/5209 samples when tested with the side support fixture to prevent peeling show an increase in the ILS shear strength with radiation dose. The samples irradiated with 9000 Mrad show increases of +35% and +30% for the T300/5208 and T300/5209 samples, respectively.

The T300/5209 samples tested in the tensile mode without the support fixture show the same trend as results reported earlier. That is, first an increase in the ILS strength with radiation occurs followed by a significant decrease. The 3000 Mrad treated samples show an increase of approximately 12% compared to the control. The samples treated with 9000 Mrad show approximately 30% drop from this maximum.

However, the T300/5208 tested in this series showed a reversal in the trend which heretofore appeared to be general. The T300/5208 samples tested here had an average ILS strength of 146 kg/cm^2 for the control compared to 180 kg/cm^2 for the control samples in the previously reported study. The sets of samples were prepared at a different time but supposedly under the same conditions. The ILS strength increases to approximately 175 kg/cm^2 at 9000 Mrad, an increase of approximately 20% compared to the control.

There are at least three possible explanations why these results differ from the earlier ones. First, the samples investigated here had been previously loaded to failure in a compressive shear test--a result that could possibly affect the outcome of a subsequent mechanical test. Secondly, the possibility exists that differences in fabrication history may affect interfacial interaction energies (e.g., distribution of high stress concentrations) resulting in a different response to ionizing radiation. A third possibility is that the samples were unknowingly handled in a different manner as they were irradiated and prepared for mechanical testing.

We currently have a number of specimens prepared at exactly the same time and under the same experimental conditions as the 3" by 1" by ≈ 0.020" samples but cut to the same dimensions as those in the first study (1" by 1/2" by ≈ 0.020"). We are presently preparing large radiation dose experiments with these samples to see if we can answer which of the above possibilities is most likely.

2. <u>Surface Energy Effects:</u>

We have hypothesized that the interface is more subject to change by high energy radiation than either the matrix or the fiber. From SEM photomicrographs it is apparent that the fiber is relatively weakly coupled to the matrix since the fracture surfaces generally show clean separation between fiber and matrix. This is especially evident for the C6000/PMR15 composites although there are a few fragments that cling to the fracture surface of T300/5208 samples.

In order to test whether radiation should affect the coupling or interaction between fiber and matrix, we are investigating the effect of radiation on the surface energy of both fiber and matrix materials. The surface tensions (in force/length or energy/area) can be estimated from contact angle measurements of a liquid on the surface of the material in question as illustrated in Figure 6. From the literature we can obtain γ_{LA}, the surface tension between the liquid and air. Further, measurements of contact angles of a series of liquids on the material will permit the determination of γ_{EA} and γ_{EL}, the surface tensions between the material (e.g., epoxy) and air or liquid, respectively. Further, it can be shown that the surface tensions can be divided into a dispersion component and a polar component, and the work/area, Wa, required to separate the liquid from the material is the sum of a dispersion and a polar component ($Wa^d + Wa^p$).

Data are shown in Table 3 of contact angle as a function of radiation dose of 1/2 MeV electrons for epoxy films. In Table 4 are listed the surface tension of test liquids in air at 20°C. In Table 5 are work of adhesion of the test liquids on epoxy as a function of radiation dose. Table 6 shows the effect of radiation on the surface tension of the epoxy (using on MY720/DDS film cured at 1 hr. at 150°C, 5 hrs. at 177°C in ratio of 73/27 w/w.)

As can be seen in Tables 3-6, radiation dramatically affects the surface tension of the epoxy. The surface tensions increase significantly with radiation, particularly the polar component. Further, examination of graphite fiber bundles under magnification show that water droplets placed on the surface of the bundle are absorbed much more quickly into the irradiated bundle than into unirradiated bundles, suggesting that the surface tensions (or energies) are much higher for the irradiated fibers.

These results suggest that the increase in surface energies with radiation may indeed be the major reason that we see increases in most mechanical properties with radiation dose. At the same time, there may be covalent bonds coupling the fiber and matrix which are simultaneously destroyed with radiation. It is reasonable that the covalent bond distribution may influence the strength more than the polar forces in a peel dominated mechanism of failure by limiting the amount of material which is contributing to the strength resulting in a poorer shear strength with radiation. When support fixtures in ILS tests prevent peel, the summation of polar forces over the entire area of shear may contribute more than the covalent bond forces.

These preliminary results which cover a range of only 0-1000 Mrad of radiation are extremely exciting and we intend to pursue this line of research vigorously. We feel that this will aid greatly in answering questions related to the behavior of epoxy/graphite fiber interfaces as a function of radiation.

3. Dynamic Mechanical Analysis

The first part of our work on dynamic mechanical analysis of radiation effects on epoxy and composites has been to establish reproducibility in sample preparation and to compare results of dynamic mechanical analysis samples with different preparation histories. These procedures have been worked out very nicely for the epoxy system but we are still attempting to develop a satisfactory technique for composites.

Epoxy samples which are unirradiated have been shown by DSC to undergo additional crosslinking when taken to temperatures above the maximum cure (e.g., 177°C for MY720/DDS). This is also seen in dynamic mechanical tests in that a drop in elastic modulus (with an increase in tan δ) occurs at a temperature above 200°C as the system becomes fluid enough to permit further reaction to take place. The elastic modulus then increases as the system becomes "fully cured" followed by a drop in modulus at the ultimate glass transition (ca. 280°C). As the system remains at this temperature, slow thermal degradation takes place and, with repeated dynamic mechanical analysis through the same temperature range, the elastic modulus drops slightly and the tan δ peak associated with the ultimate glass transition occurs at lower temperatures and this peak is much broader suggesting a wider molecular weight distribution.

With radiation, we see an effect similar to high thermal treatment. For example, at 3100 Mrad, no peak is observed that is associated with further cure. The ultimate glass transition temperature is lower and the tan δ peak is broader.

4. Differential Scanning Analysis/IR

Additional measurements of radiation effects on the "extent of cure" as measured by the exothermic energy involved in DSC scans of epoxy samples have been made. The measurements were made on samples cured at higher temperatures and have been irradiated to higher dose levels than previously reported. These results confirm our earlier measurements which show that irradiation reduces the exothermic energy evolved upon heating cured epoxy. IR measurements on thin films show a reduction with radiation in the 905-910 cm^{-1} band which is associated with the epoxide group.

5. Electron Spin Resonance Studies

Previously, we have reported that the number of long lived radicals (with a half life of ca. 1 day at room temperature) in epoxy increases with increase in crosslinking density. This work was based on measurements of a series of irradiated samples cured using the same thermal conditions but with different ratios of curing agent to epoxy. To test further this hypothesis, we have completed a study using a single ratio of components (MY720/DDS:73/27:w/w) but with a series of cure temperatures (150°C, 160°C, or 170°C for 5 hrs). The results show that concentration of long lived radicals in irradiated samples increases with increase in cure temperature. The radiation dosages in this case were low (5 Mrad or 30 Mrad) and these measurements will be repeated at much higher dose levels.

We have also shown by using a method of spectral subtraction that the line shape of the decaying species is more readily revealed. At least three distinct radical species are observed and the line widths are in approximate agreement with the work of Tsay (Jet Propulsion Lab), who reported ESR studies on the same system. This method will be used further in an attempt to find the activation energies associated with radical decay of the various species and the temperature at which the various radicals begin to disappear.

We have shown also that the ESR lineshape for electron irradiated samples which have been irradiated to high dose levels (up to 5000 Mrad) changes. There is a much higher relative intensity of a narrow component in the samples with large dosages. We will attempt to answer whether this is due to a structural change induced by the radiation which results in a change in radical species or whether it is related to difference in decay rates of the species present.

In summary, we feel that the approach we are taking to monitor effects of high energy radiation on composites is providing a fundamental empirical base for predicting the behavior of these materials to long term exposures to ionizing radiation and is providing a basic understanding on the molecular level of the interaction of ionizing radiation with graphite fibers, graphite fiber composites and matrix materials used in them.

Table 1

Summary of Mechanical Tests on Irradiated Composites

Composite	Fiber Arrangement	Maximum Radiation Dose	Test*
T300/5208	Longitudinal	8,000 Mrad	TPB
T300/5208	Longitudinal	10,000 Mrad	ILS-TU
T300/5208	0/±45/0	10,000 Mrad	TPB/ILS-TU
T300/5208	90/±45/90	10,000 Mrad	TPB/ILS-TU
T300/5208	Transverse	10,000 Mrad	TPB
C6000/PMR15	Longitudinal	8,000 Mrad	TPB
C6000/PMR15	Transverse	10,000 Mrad	TPB
C6000/PMR15	Longitudinal	10,000 Mrad	ILS-TU
T300/5208	Longitudinal	9,000 Mrad	ILS-CS
T300/5208**	Longitudinal	9,000 Mrad	ILS-TU
T300/5208**	Longitudinal	9,000 Mrad	ILS-TS
T300/5209	Longitudinal	9,000 Mrad	ILS-CS
T300/5209**	Longitudinal	9,000 Mrad	ILS-TU
T300/5209**	Longitudinal	9,000 Mrad	ILS-TS

*TPB - Three Point Bending
**First tested in ILS-CS mode

ILS = Interlaminar shear
TU = Tensile, unsupported
TS = Tensile, supported
CS = Compressive, supported

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Table 2. Interlaminar Shear Stress by Compressive Force with ℄ Side Support

Sample	Radiation Dose	No. of Specimen	Shear Stress (kg/cm^2)	Standard Deviation	%CV	% Change to Control
T300/5208	0	3	581	87.8	15.1	0
	3000	5	654	48.3	7.3	+12.6
	6000	5	667	94.5	14.1	+14.8
	9000	5	784	51.6	6.5	+34.9
T300/5209 (notched	0	3	701	68.8	9.8	+ 0
after irradiation)	3000	5	765	158.3	20.7	+ 9.1
	6000	5	843	92.0	10.9	+20.3
	9000	5	909	148.9	16.4	+29.7
T300/5209 (checked	6000	2	881	29.0	3.3	+25.7
before irradiation)	9000	3	667	67,7	8.7	+11.0

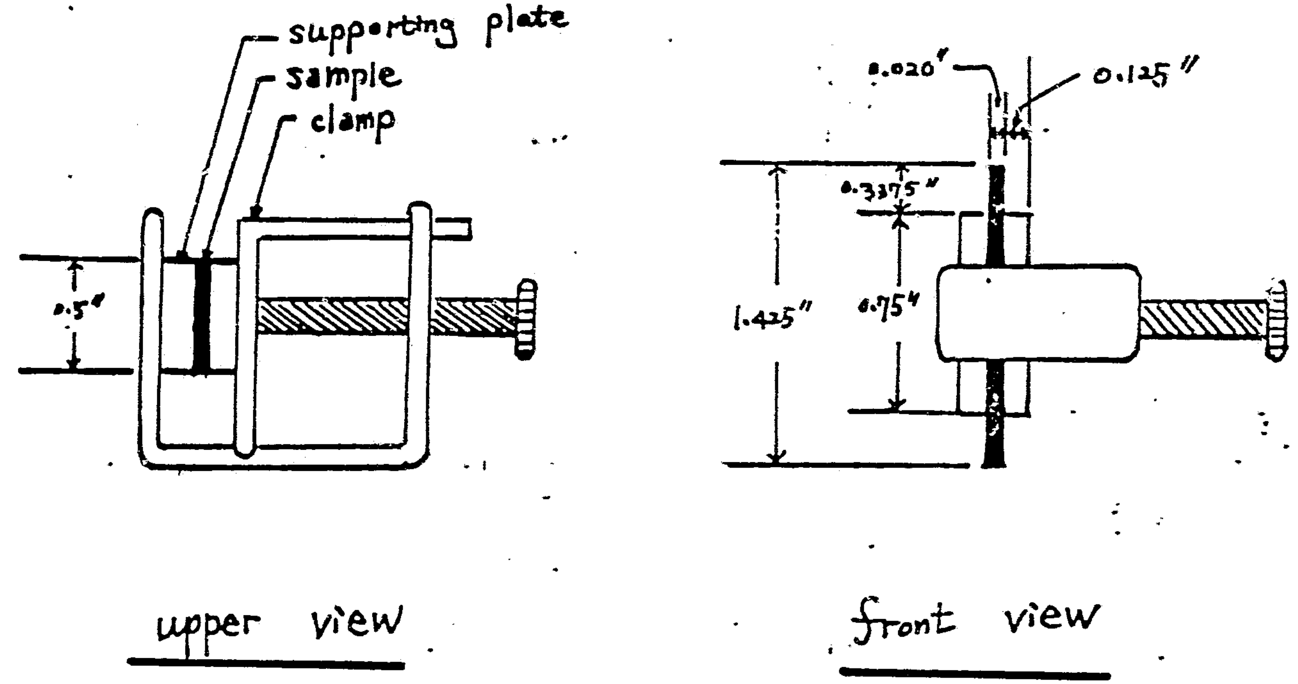


FIG.1 Description of side-supporting plate and clamp for interlaminar shear test in tensile mode.

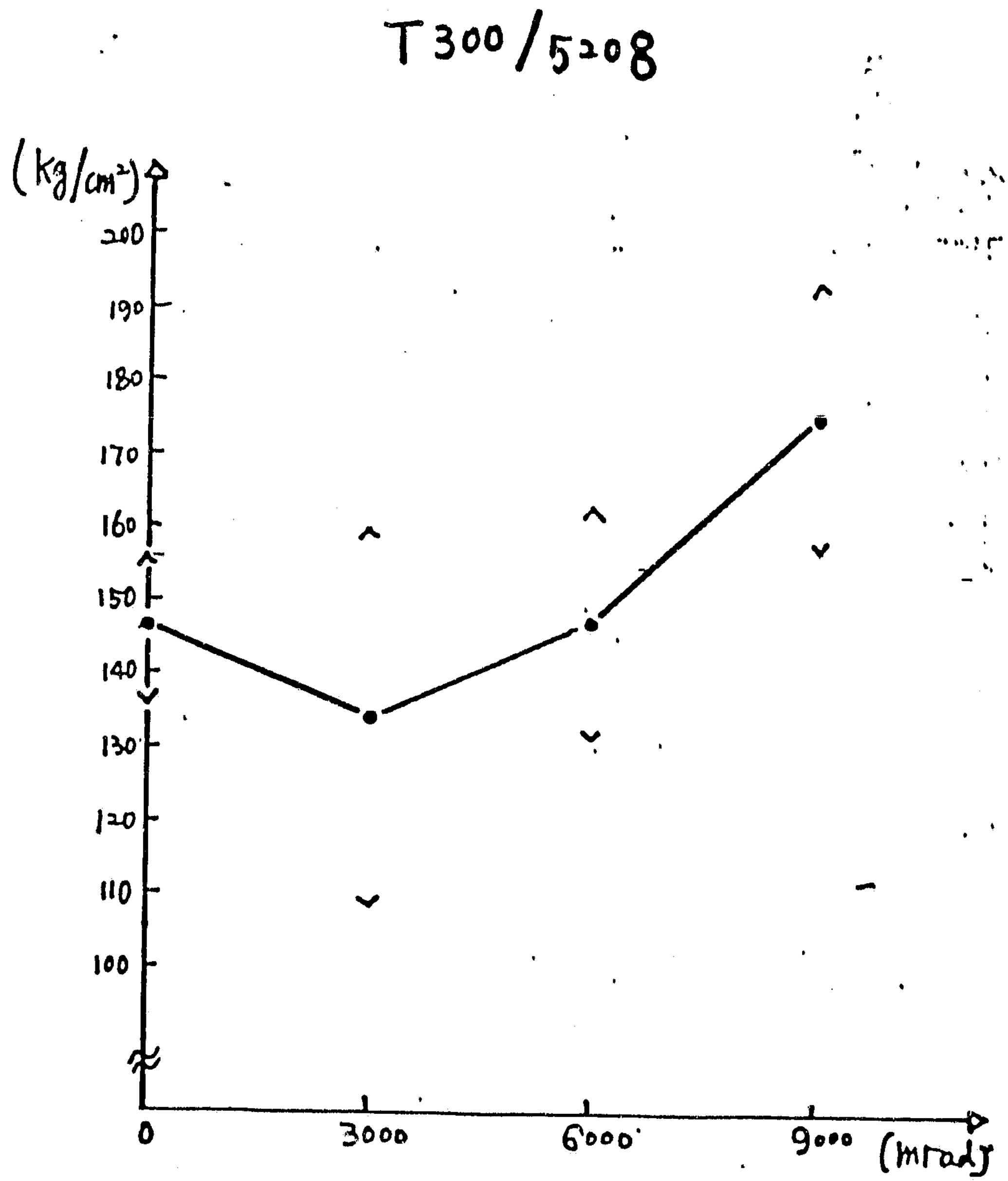


FIG. 2 Interlaminar Shear Stress versus radiation dose in tension mode without using supporting plate.

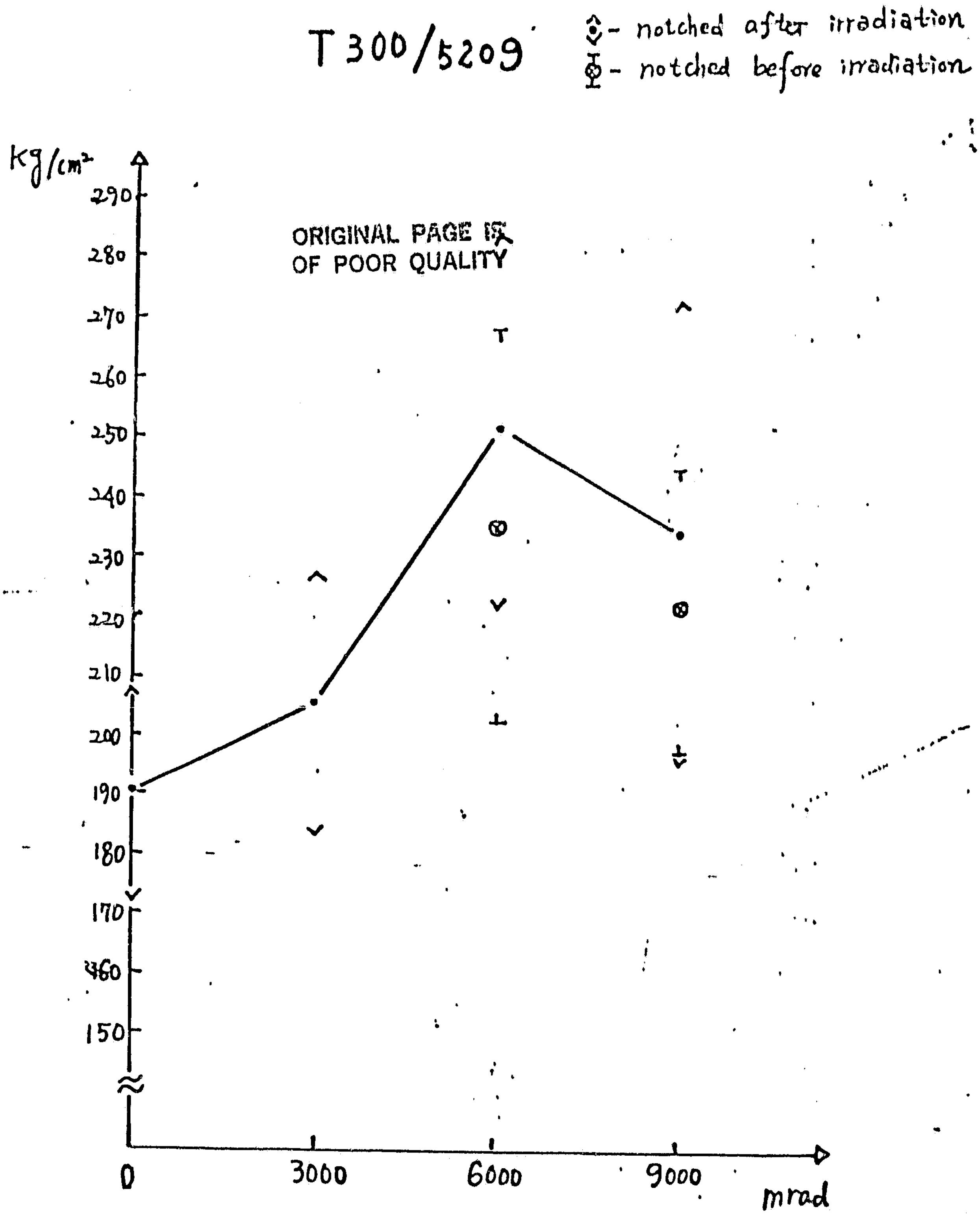


FIG. 3 Interlaminar Shear Stress versus Radiation dose in tension mode using supporting plate.

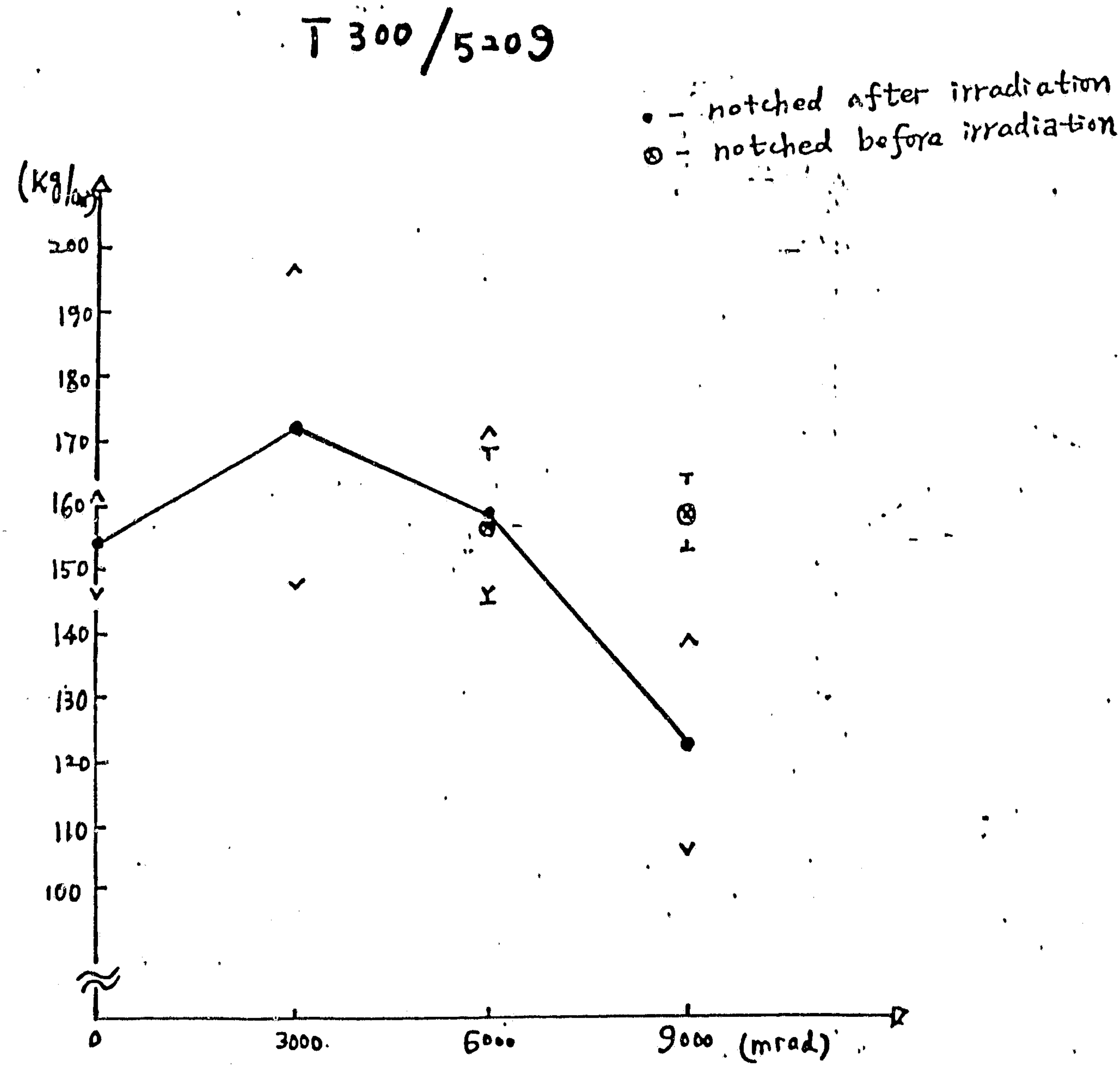


FIG. 4. Shear Stress versus radiation dose in tension mode without using supporting plate.

T300/5208

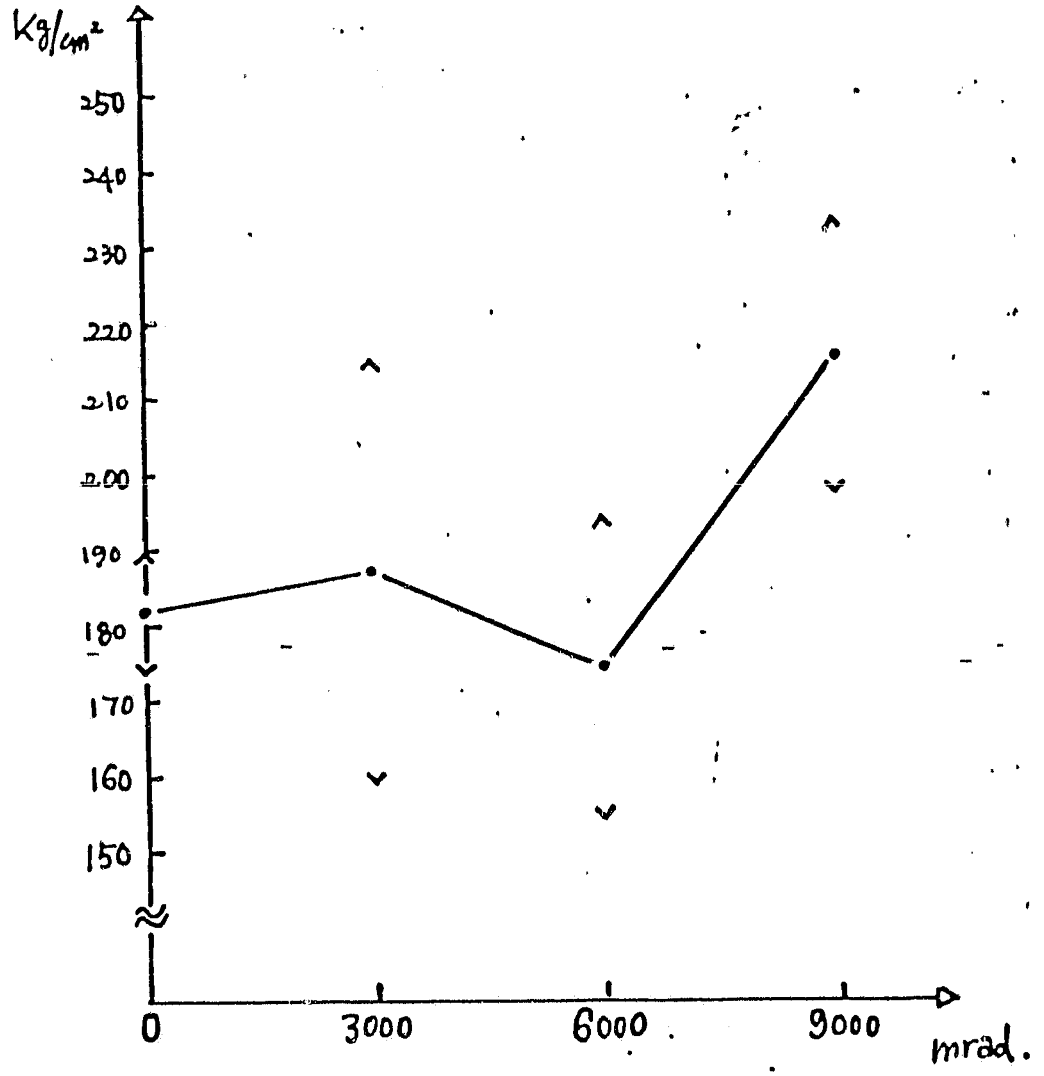
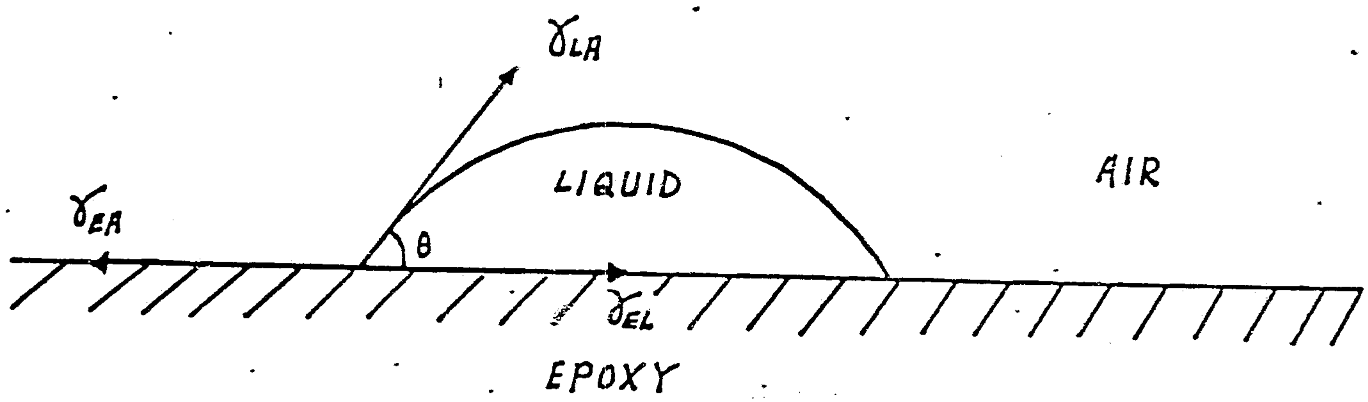


Fig. 5 Interlaminar shear stress versus Radiation dose in tension mode using supporting plate.



$$\gamma_{EA} = \gamma_{EL} + \gamma_{LA} \cos\theta$$

FIG.6 FORCES ACTING ON A LIQUID DROP RESTING ON THE EPOXY FILM.

TABLE 3

CONTACT ANGLE OF TEST LIQUIDS ON THE EPOXY FILM WITH VARIOUS IRRADIATION DOSES, AT 20°C

TEST LIQUID	DOSE (Mrad.)	CONTACT ANGLE, θ (DEGREE)	COSθ
WATER	0	100.6	-0.1851
	400	72.0	0.3090
	1000	25.0	0.9063
ETHYLENE-GLYCOL	0	70.9	0.3272
	400	53.3	0.5976
	1,000	28.3	0.8805
HEXADECANE	0	38.8	0.7793
	400	23.3	0.9184
	1,000	13.3	0.9732

TABLE 4

SURFACE TENSION ~~PROPERTIES~~ OF TEST LIQUIDS AT 20°C

TEST LIQUID	α_L (dyne/cm)$^{1/2}$	β_L	γ^d_{LA} dyne/cm	γ^p_{LA}	γ_{LA}
WATER	4.67	7.14	21.8	51.0	72.8
ETHYLENE-GLYCOL	5.41	4.35	29.3	19.0	48.3
HEXADECANE	5.25	0.00	27.6	0.00	27.6

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TABLE 5

WORK OF ADHESION OF LIQUID-EPOXY INTERFACE

LIQUID	DOSE (Mrad.)	Wa (dyne/cm)	β_L/α_L	$Wa/2\alpha_L$
WATER	0	59.3	1.53	6.35
	400	95.2		10.20
	1,000	138.8		14.90
ETHYLENE-GLYCOL	0	64.1	0.81	5.92
	400	77.2		7.13
	1,000	90.8		8.38
HEXADECANE	0	49.1	0.00	4.67
	400	52.9		5.03
	1,000	54.5		5.19

TABLE 6

SURFACE TENSION OF THE IRRADIATED EPOXY FILMS

DOSE (Mrad.)	γ^{d}_{EA}	γ^{p}_{EA} (dyne/cm)	γ_{EA}	$\gamma^{p}_{EA}/\gamma_{EA}$
0	22.09	4.92	27.01	0.18
400	25.00	39.69	64.69	0.61
1,000	27.00	133.40	160.40	0.83