Conf-821049--2

Note: This is a preprint of a paper to be presented at the "Symposium on Radiation Damage Analysis for Fusion Reactors" at the St. Louis meeting of TMS-AIME, October 24-28, 1982, and is to be included in the Proceedings to be published in the Journal of Nuclear Materials. Contents of this paper should not be quoted nor referred to without permission of the authors.

CONF-821049--2

DE83 001898

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DEBONDING OF EPOXY FROM GLASS IN IRRADIATED LAMINATES

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Operated by
UNION CARBIDE CORPORATION
for
U. S. DEPARTMENT OF ENERGY

October 18, 1982

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ABSTRACT

Glass-fabric-filled epoxies irradiated at 4.7 K and examined at room temperature by 20x stereomicroscopy showed an internal flaw structure which increasingly filled the sample as the γ-dose was increased. These flaws were determined to be areas where the plastic had debonded from the glass fibers. The extent of this process correlated well with the dose-dependent loss of mechanical strength. Evidence is reported for a similar mechanism in polyimides although visible flaws have not yet been produced. Possible mechanisms for debonding are suggested. New experiments are also suggested to clarify further the failure mechanism.

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*Research sponsored by the Division of Materials Science, U. S. Department of Energy under contract W-7405-eng-26 with the Union Carbide Corporation.

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1. INTRODUCTION

Glass fabric filled organic laminates are important as electrically insulating structural members in the construction of large superconducting magnets. Designers of practical power-producing magnetic confinment fusion energy machines hope to be able to use such laminates, especially epoxies, as has been done in experimental test machines. However, the radiation-induced loss of strength in these materials imposes design restrictions to keep degradation within acceptable limits in the lifetime of a machine.

To initiate the development of a body of engineering data needed by designers, several studies under identical conditions have been done at ORNL on the electrical and mechanical properties of filled epoxies and polyimides after low temperature irradiation doses from 3 - 100 MGy. The materials and experimental details have been described [1, 2, 3]. After completion of the last epoxy study [3] we had accumulated an array of flexure test samples whose remarkable appearance changes with dose called for closer examination. Especially noteworthy was the apparent reversal, in the intermediate dose range, of the trend to darker and darker coloration with increasing dose. These optical findings are reported here.

2. RESULTS AND DISCUSSION FOR EPOXIES

2.1 Optical Observations

The chronological sequence of experimental treatment of the samples prior to the optical studies is summarized in Table I. The entire array of flexure specimens is displayed in Fig. 1 (at step 5 in the sequence).

Detailed microscopic examination of these samples was done to probe the nature of the appearance changes visible to the naked eye, both at the flexure

break and in the undisturbed regions near either end of the specimens. (The 1/4-length at each end of a specimen received no bending stress during the test.) The "white spots" seen by the naked eye as accentuating the weave pattern in most intermediate-dose cases were the most interesting feature. With a 20x - 40x stereomicroscope using various illuminations (vertical from below or variable oblique from above) it was possible to see that the white spots had all the characteristics of internal void or gas-film surfaces. At such a surface light arriving obliquely from the more dense optical medium (the plastic) is reflected at the interface.* Thus such an interface area appears bright or light colored, especially by contrast with areas where light is absorbed in thicker portions of the irradiation-darkened plastic layer.

Figure 2 shows some details of these bright areas, but without stereo depth and the dynamic highlights of a moving light source, it cannot convey much of the impact of the microscope observations. With these observational advantages it was easy to see that the bright areas had exactly the form and texture of the uppermost surface of the glass cloth, proving that they were areas of separation or debonding of the plastic from the glass.

2.2 Optical and Mechanical Data Correlation

Table II summarizes the microscope observations of debonding in the two G-10CR materials, along with measured flexure strength loss percentages taken from the curves of reference [3]. As noted in the caption of Fig. 1, the surface texture of the G-11CR samples interfered somewhat in the optical observations, so that qualitative descriptors for the degree of debonding

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* Total internal reflection occurs in a high-refractive-index medium (epoxy: $n' = 1.58$ or glass: $n' = 1.52$) when light strikes the interface with low-index medium (air or vacuum: $n = 1$) at incidence angle more oblique than Θ_c given by: $\sin \Theta_c = n'/n$. A fully-bonded epoxy/glass interface is invisible ($n'/n \approx 1$), but with a layer of void or gas between them $n'/n = 0.63$ and $\Theta_c = 39°$, so the interface becomes visible under a wide variety of illumination.

could not be determined as accurately as for G-10CR. We estimate, however, that the response to dose would be about the same as for G-10CR(BF) while the corresponding strength losses are slightly lower.

In general the flexure strength in these experiments had decreased about 50% before debonding areas became clearly discernable. At doses below that point the material may be considerably weakened as evidenced by response to externally applied stress, but not be so weak as to develop visible flaws from the action of internal stresses alone. These internal stresses are discussed in 2.3.

2.3 When and How Does Debonding Occur

It is no surprise that the delamination commonly seen in mechanical fracture of irradiated epoxy laminates is largely a separation of the plastic from the surface of the glass. But is was not expected that this debonding would occur extensively in moderately irradiated material that has not been mechanically stressed.

At present it is not known at what stage in the experimental sequence of treatments the debonding occured. It is known that aside from the fracture region there were no gross changes in appearance between the earliest observations (Table I, step 3a.) prior to mechanical testing and the later detailed observations. In fact, the variability of white-spot coverage at one end vs the other end (visible in Fig. 1 especially in the G-10CR at 5.5 MGy) was seen at step 3a.

We believe it is unlikely that visible debonding developed spontaneously during the 5 K irradiation. More likely possibilities are that separation of the irradiation-weakened plastic from the glass required assistance from some internal stress such as: 1) the thermal expansion differential between glass and plastic during warmup, 2) internal pressure from the formation of gas

bubbles at the interface due to preferential accumulation there of the hydrogen freed by the irradiation and mobilized during the warmup.

2.4 Influence of Boron Plus Thermal Neutrons

The thermal neutron flux present in the irradiations yielded a ^{10}B (n,α) ^{7}Li reaction in the boron-containing glasses. Some of the resulting energetic α-particles escaped from the glass before being brought to rest within a total range of 5 microns (which was also the radius of the glass fibers). The total energy deposition rate by these particles*, without concern for any distinction between the various mechanisms involved, was calculated as a function of position in the plastic outside the glass fibers and was compared with the γ energy deposition rate. At the glass surface it added about 76% of the γ value; in the first micron of plastic outside the glass it averaged about a 56% addition. This should be the important region for enhancement of debonding by the energy deposition from the ^{10}B reaction.

Both visible debonding and measured percent strength loss agreed fairly well that there was a 50-100% enhancement of either effect by the ^{10}B (n,α) process in the flux mixture used in these experiments. The degree of debonding matched most closely in the two kinds of G-10 materials when boron-free samples at one γ dose were compared with boron-containing samples at the next lower dose step as listed in Table II. These steps (3, 5.5, 10, 24 MGy) increased about a factor of two from one to the next. The percentage loss in flexure strength (within the 30-70% loss range), as read from the curves of strength vs γ dose [3], was the same in both G-10 materials when the boron-free G-10CR(BF) was at 1.5x the γ dose of the boron-containing G-10CR.

All of this suggests that property degradation as a function of gross energy deposition is fairly independent of the particular mode of energy

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*Particles include both 1.77 MeV α and 1.02 MeV Li. The Li range is about 2μ.

deposition. However, only two modes were involved in this experiment and the data are so coarse as to put at least a ± 25% uncertainty on that relation.

3. DEBONDING IN POLYIMIDES

Mechanical properties of two different brands of glass fabric filled polyimide laminates, as well as an unfilled polyimide have been studied in identically the same way as the epoxies reported here [4]. Debonded areas were not observed. However, three important differences must be noted between the epoxy and polyimide data:

1) At the highest dose (100 MGy) the filled polyimides lost only about 35% of their flexure strength, which by comparison with the epoxies, is below the threshold for expected visibility of debonding.

2) The polyimide plastics were fairly dark colored initially, and although they darkened only a little more by 100 MGy, observation of internal details was difficult. Also, the refractive index of polyimide is about 1.78, which is quite a bit higher than that of the glass, so the fibers inside were initially fairly visible, unlike in the epoxies. This may hinder observation of separation interfaces.

3) While the filled polyimides lost 35% of their strength at 100 MGy, the unfilled variety, although naturally much weaker to begin with, was virtually unchanged at that dose. (It should be noted that the unfilled variety was a somewhat different type of polyimide resin/catalyst system from that used in the filled varieties, which may cloud the comparison.) This observation suggests that it may not be the plastic but rather the plastic/glass bonding which is weakening in the filled polyimides. Furthermore, the fractured region of a filled sample delaminates, breaking plastic from glass quite cleanly in the 100 MGy case.

We conclude that a debonding process is probably important in glass filled polyimides as in epoxies, but further study is needed. According to

laminate manufacturers this should be no surprise, as the glass-plastic bond is quite different from that in the epoxies and it is not considered to be as strong in the unirradiated material [5].

4. CONCLUSIONS AND IMPLICATIONS

Glass-fabric-filled epoxy laminates irradiated at < 5 K to γ doses of 6 - 25 MGy not only lose 40-90% of their initial flexure strength (as tested at 77 K after warmup to 307 K), but they also develop visible areas of separation or debonding between the glass and plastic at some stage prior to the application of mechanical stress. Low-power stereomicroscopy is adequate to discern the nature of these debonded areas which to the naked eye simply look like lighter-colored regions in the otherwise radiation-darkened plastic. Between the minimum dose at which they become visible and the maximum dose at which the plastic is still transparent enough for internal details to be seen, the extent of debonded areas increases with dose in a manner semiquantitatively similar to the decrease in mechanical strength. Both debonding and strength loss are enhanced in a predictable manner by the addition of α-particle damage near the glass-plastic interface when boron present in the glass captures thermal neutrons from the radiation environment. Although visible debonding has not yet been found in polyimide laminates (probably because doses studied up to now were too small) the same basic weakening of the glass-plastic bond apparently prevails in determining the amount of mechanical strength degradation.

Because the glass-plastic bond proves to be the most radiation-sensitive part of these laminates any development which improves that feature should directly reduce the loss of mechanical strength with dose. Whenever the weakest link is the intermaterial bonding then delamination is the major mechanical failure mode, and the greatest loss of strength occurs in interlaminar shear

or interlaminar tension loading modes. Although most applications for these materials in fusion device magnets envision designs limiting loads primarily to interlaminar compression it may be impossible to eliminate small components of the radiation-sensitive loading modes which could easily become the critical determinant of the failure point.

In order to understand better the debonding mechanism, experiments are planned to look for visible debonding before or during the warmup from 5 K. Ultrasonic techniques are under consideration as an additional and quantitative method of detecting debonding. The possible role of gas migration in debonding should be better understood when mechanical testing is done at 4 K with and without prior warmup in tests identical in all other respects.

REFERENCES

[1] R. H. Kernohan, R. R. Coltman, Jr., and C. J. Long, "Radiation Effects on Insulators for Superconducting Magnets," Annual Progress Report, ORNL-TM-6193, Oak Ridge National Laboratory, January 1978.

[2] R. R. Coltman, Jr., C. E. Klabunde, R. H. Kernohan, and C. J. Long, "Radiation Effects on Organic Insulators for Superconducting Magnets," Annual Progress Report, ORNL-TM-7077, Oak Ridge National Laboratory, November 1979.

[3] R. R. Coltman, Jr. and C. E. Klabunde, "The Strength of G-10CR and G-11CR Epoxies After Irradiation at 5 K by Gamma Rays," accepted for publication in J. Nucl. Mater.

[4] R. R. Coltman, Jr. and C. E. Klabunde, J. Nucl. Mater., 103 & 104, 717, (1981).

[5] J. R. Benzinger, Spaulding Fibre Co.; and J. V. Gauchel, Owens-Corning Fiberglass, private communications, September 1982.

Table I. Chronological Sequence of Sample Treatment

1. Irradiate in liquid He at < 5 K to specified γ-dose.

   (with small fluxes of fast and thermal neutrons present)

2. Warm to 307 K gradually; collect evolved gases.

   a. Hold in He gas at 307 K up to 1 week.

3. Remove from irradiation cryostat to room.

   a. Make casual visual observations.

   b. Store in desiccator atmosphere at room temperature, up to a few weeks.

4. Insert individual samples in mechanical testing rig.*

   a. Immerse in liquid N_2 bath; test load to sample fracture.

   b. Remove; store fractured samples in plastic pouches (for weeks or years).

5. Detailed microscopic examination and photographs.

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* Main basis for present report are Flexure-test Specimens: (1.6 x 3.2 x 50 mm, cut from 1.6 mm manufactured sheet, axis parallel to weave warp). Tested in 3-point bending jig, 25 mm between the two base points.

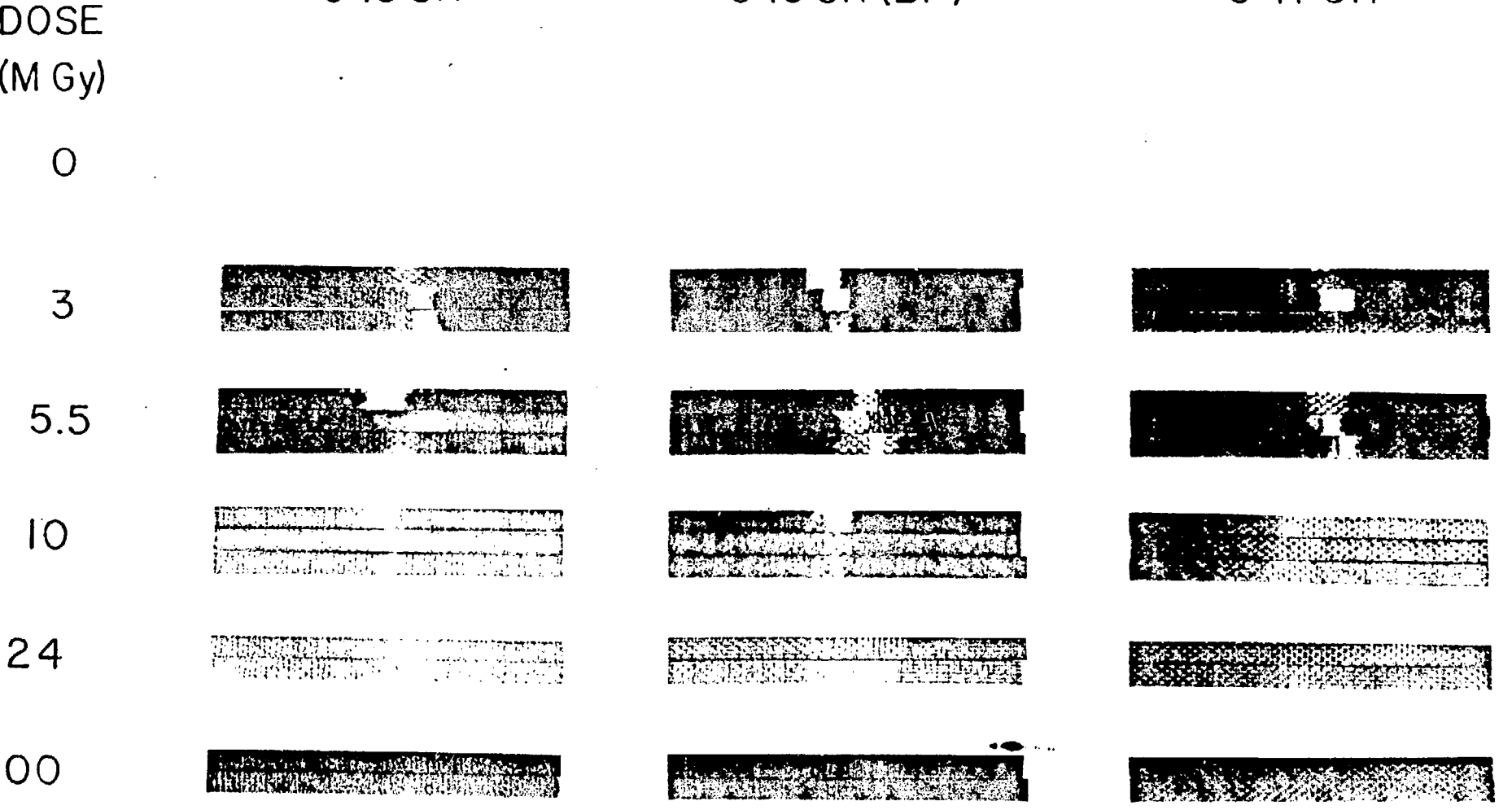
Table II. Summary of Observations on G-10CR

γ Dose	Optical Microscope Observations			Mechanical Measurements
	Visible Debonding Areas		Coloration of Plastic	Strength Loss (%)
	G-10CR (with boron)	G-10CR(BF) (boron-free)		(with boron) (boron-free)
(MGy)				
3	Little	None	Brown	42 27
5.5	Some	Little	Darker Brown	67 50
10	Extensive	Some	Darker Brown	81 73
24	Complete Coverage	Nearly Complete	Very Dark Brown	90 85
100	-Little light reaches 1st glass layer- (fracture is almost invisible)		Nearly Black	93 91

FIGURE CAPTIONS

Fig. 1. Flexure samples after irradiation and mechanical testing. Two, three, or four samples of each material/dose combination are shown lying together, side by side. Bright area near the center of most 50 mm-long samples is the flexure-test break. To illustrate all aspects of their appearance some samples are shown compression face up and others show the tension face. Sample outer surface texture varies according to material: G-10CR = random "orange peel" rough; G-10CR(BF) = very smooth (best for optical studies); G-11CR = texture of the weave at its high points, but smooth across valleys of weave. Besides light reflections from surface texture there are internal reflections from debonded areas. The epoxy is progressively darkened with increasing dose, but samples at intermediate doses, 5 - 24 MGy, appear lighter as the bright reflecting debonded areas fill the sample. At 100 MGy the epoxy is so dark that no light penetrates to the first glass layer so even the broken area is not visible. This picture, taken with light incident obliquely from left and right above, cannot show the translucent-to-opaque transition that occurs as the samples fill with debonded areas. Note how the degree of debonding in the (BF) samples with boron-free glass lags behind that of the G-10CR (containing boron) at 5.5 and 10 MGy.

Fig. 2. G-10CR(BF) sample irradiated to 10 MGy at 4.9 K and observed at 300 K. Oblique illumination; 21x magnification (edges of 3.2 mm-wide sample are visible at two corners). The glass-cloth fill pattern is highlighted in areas where epoxy has separated from the glass creating internally-reflecting interfaces (void-space or gas-bubble films). Low points in the outer weave surface, where the outer layer of epoxy is thickest, appear dark as light is absorbed in the depths of the irradiation-darkened plastic. The area pictured is mid-way in the right half of the top sample (in the group of three at this dose) shown in Fig. 1, and is only partially filled with debonded areas.


G-10 CR
G-10 CR (BF)
G-11 CR
DOSE
(M Gy)
0
3
5.5
10
24
00