

Effects of Electron Bombardment on Properties of Various Glasses

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Soda-lime, borosilicate, and lead glass specimens were exposed to various dosages of 2 m.e.v. electrons. The effects of the irradiation on flexural strength, density, chemical durability, heat of solution, and electrical resistivity were investigated. The results showed that for dosages up to 300 megareps several small effects were noted but were considered to be of minor significance as far as bottle serviceability is concerned.

I. Introduction

THE purpose of this investigation was to make a preliminary study of the effects of cathode-ray bombardment on physical and chemical properties of various glasses. The results indicate the effect of irradiation on bottle serviceability and have practical significance in view of the potential use of glass containers for products that can be sterilized in the package by high energy radiations.

The several properties that were investigated as a function of radiation dosage and glass type were flexural strength, density, chemical durability, heat of solution, and electrical resistivity.

The Quartermaster Research and Engineering Command performed the irradiations and the testing was done by Owens-Illinois. This report describes the procedures used and results obtained from tests of irradiated glass rod specimens.

II. General Discussion

Theories on the effects of radiation on materials have been discussed by many authors and no attempt will be made here to give a full description of the various processes involved. The main concern of this report is to describe the effects observed after high-energy electron bombardment of glass. Irradiation of solids can produce many types of defects, such as lattice vacancies, interstitials, color-centers, thermal spikes, and electron excitation. In the case of glass, the principal effects of electron bombardment are color-center formation and lattice defects from the displacement of atoms. Electrons that possess enough energy to produce displacements are in the relativistic range (about 1 m.e.v.). The probability that an electron will produce a displacement is small. In addition, the energy transfer is usually small and the displaced atoms do not have enough energy to

Table I. Chemical Analysis of Glasses

	Boro-silicate (%)	Soda-lime (%)	Lead (%)
SiO ₂	80.80	67.88	34.98
B ₂ O ₃	12.96	1.30	
BaO		2.16	
R ₂ O ₃	2.17	2.84	0.23
CaO		5.48	
MgO	0.04		0.07
Na ₂ O	4.16	3.90	0.05
K ₂ O	0.02	15.70	5.96
PbO		0.47	57.80
Sb ₂ O ₃			0.80
Total	100.15	99.73	99.89

cause further damage. Therefore, a simple type of defect can be expected, namely, isolated pairs of vacancies and interstitials.

In most solids, the short range of penetration of electrons causes inhomogeneity with depth in a specimen of significant size. This makes it difficult to accurately interpret the results of properties measurements of irradiated materials. The range of the 2 m.e.v. electrons used in this investigation is on the order of 1150 mg. per sq. cm. The maximum range presented by the rod specimens used in this investigation was 1250 mg. per sq. cm. It is believed that for purposes of bottle serviceability the radiation effects can be considered uniform throughout the specimens.¹

III. Experimental Procedure

(1) Glass Specimens

Glass rods of three commercial types were obtained: borosilicate, soda-lime, and lead glass. The borosilicate and soda-lime rods were 5 mm. in diameter and the lead glass was 3 mm. A smaller diameter was used for the heavier lead glass to obtain an equally uniform variation of dosage with depth. Chemical analyses of the glasses are shown in Table I.

The rods as received were cut into specimens 5³/₈ in. in length. Each specimen was then abraded, in a band about 1 in. long, at the center of its length. The strength of glass is closely associated with the condition of its surface. Uniform abrading serves a two-fold purpose in the present case: (1) by controlled abuse before irradiation it is possible to minimize the effects of variations in surface damage due to radiation alone, and (2) abrasion causes all specimens to break at about the same location in strength tests and thus narrows the data distribution, increasing the significance of the results.

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¹ J. G. Trump and R. J. Van de Graaff, "Irradiation of Biological Materials by High-Energy Röntgen Rays and Cathode Rays," *J. Appl. Phys.*, 19, 599-604 (1948); p. 603.

Two hundred rods each of borosilicate and soda-lime glass and 160 of lead glass were prepared. None of the three groups of rods was completed in one work period. The rods were placed in a desiccator as they were prepared in order to minimize the effects of varying atmospheric conditions. A holder was made to prevent the rods from contacting each other in the desiccator, thereby reducing further abuse of the surface.

Specimens were packaged for storage and shipment as follows: A wooden rack was made having twenty $5\frac{1}{2}$ by $\frac{1}{4}$ in. grooves. A $6\frac{1}{2}$ in. wide strip of 0.002 in. polyethylene film was laid over the rack and the rods were pressed into the grooves. A small amount of silica gel was sprinkled into the grooves and a second piece of film laid over. The package was sealed around the edges and between the rods by placing a sheet of aluminum foil over the top layer of film and running a Teflon-coated iron at about 250°F. over it. This sealing process served to protect the rods from inadvertent damage in handling and also from changes in humidity conditions. One hundred and twenty rods of each glass were sent out for irradiation and the remainder were used for control specimens.

(2) Irradiation of Specimens

The specimens were sent to the Quartermaster Research and Engineering Command at Natick, Massachusetts, for irradiation. The irradiation was performed with 2 m.e.v. electrons from a Van de Graaff generator. Groups of rods were exposed to dosages of 1, 3, 10, 30, 100, and 300 megareps. The rods passed under the scanned electron beam carried on a conveyer mechanism but the rods were not rotated. Scanning the beam permitted the entire rod to be exposed to the radiation. Repeated passes under the beam at preset conditions were used to achieve the higher doses. Initial dose rates were determined by chemical methods. After exposure, a two-year delay ensued owing to circumstances beyond the authors' control. The specimens were therefore stored in darkness and at a temperature which did not exceed 25°C. Tests were made at the end of this period. The results are reported even though the authors are aware that some "recovery" effects could have occurred.

(3) Flexural Strength Tests

The rods, still in their plastic envelopes, were tested to destruction on a Tinius-Olsen Lo-Cap Tester using four-point loading.

(4) Chemical Durability Tests

The Owens-Illinois water and acid crushed-sample tests were run on a portion of the irradiated specimens after they had been broken. These tests are similar to the United States Pharmacopoeia XV Type I test and also can be correlated to the A.S.T.M. P-W test by use of a graph. Variations in the normality of the acid used in the tests and the units in which the results are reported account for the major differences in the various tests.

Because of the small amounts of sample available and the poor resistance of the lead glass to acid attack, it was necessary to modify the normal procedure used for testing bottle glasses. About 50 gm. of each specimen was crushed and sieved until slightly more than 10 gm. of glass that passed a No. 40 sieve but was retained on a No. 50 sieve was obtained. This glass was washed in water and ethyl alcohol and then dried in the usual manner. Five grams of the crushed glass was used for the water attack test and 5 gm. for the acid attack test. The samples were covered with 25 ml. of purified water or dilute sulfuric acid in an Erlenmeyer flask and held at a temperature of 90°C. for 4 hours. At the end of this period, the alkali leached from the crushed glass was determined by suitable titration. As is customary 0.001 *N* H₂SO₄ was used for the soda-lime glasses. It was found that the alkali leached from the lead glasses neutralized practically all

Table II. Results of Flexural Strength Tests*

Glass	Irradiation (megareps)	Average stress (lb./sq. in.)	
		Control	Irradiated
Borosilicate	300	7,100	7,300
Soda-lime	300	10,000	10,400

* Specimens irradiated at lower dosages showed comparable results.

of the 0.02 *N* H₂SO₄, so the test was repeated using 0.05 *N* H₂SO₄.

(5) Density

Density measurements were made by the sink-float method for the soda-lime and borosilicate specimens; the Archimedes method was used for the heavier lead specimens.

(6) Electrical Resistivity

Electrical resistivity measurements were performed on a d.-c. Wheatstone bridge circuit. Room temperature resistivity measurements were made since heating the specimens would anneal out any effect produced by the irradiation. Measurements are usually made in the temperature region 240° to 450°C. Because of the extremely high resistance of lead and borosilicate glasses, only the soda-lime resistivity was measured.

(7) Heat of Solution

The heat of solution apparatus consisted of a thermos bottle, stirrer, and Beckman thermometer. The thermos bottle was given a plastic coating to protect the glass from hydrofluoric acid used in the test. One-gram samples were used for the borosilicate, 4 gm. for lead, and 1.5 gm. for the soda-lime glass.

IV. Results

(1) Flexural Strength

The results of the flexural strength tests on the 300 megareps soda-lime and borosilicate specimens (Table II) showed that irradiation had no effect on the strength of these glasses. The irradiated soda-lime rods showed an average stress of 10,400 lb. per sq. in. as compared with 10,000 for the control specimens. The irradiated borosilicate specimens gave values of 7300 lb. per sq. in. as compared with 7100 for the controls. The specimens irradiated at lower dosages showed comparable results.

Large deviations were found in the strength of lead glass specimens. The average values are not considered of sufficient reliability to report here. The deviations are attributed to dimensional and other irregularities resulting from the hand-drawing process. The borosilicate and soda-lime rods were machine drawn and their strength deviations were much lower.

(2) Chemical Durability

Table III shows the test results obtained on the control, 100-megarep, and 300-megarep specimens of the three types of glass. It is evident that irradiation dosages of 100 to 300 megareps did not change the resistance of the glasses to water and dilute acid attack to any significant degree.

The specimens exposed to doses of less than 100 megareps were not tested since it is considered unlikely the results obtained would be any different.

Table III. Crushed Sample Chemical Durability Test Results on Irradiated Glasses

Glass	Irradiation (megareps)	Per cent Na ₂ O dissolved in			
		H ₂ O	H ₂ SO ₄		
			0.001 N	0.02 N	0.05 N
Borosilicate	None*	0.0006	0.004		
	100	.0006	.004		
	300	.0006	.004		
Soda-lime	None*	.039		0.049	
	100	.039		.049	
	300	.039		.049	
Lead	None*	.001		.31†	0.69
	100	.001			.78
	300	.001		.31†	.77

* Control.

† Attacking acid nearly neutralized at end of test.

Table IV. Density of Glass Specimens

Irradiation (megareps)	Lead (gm./cc.)	Soda-lime (temp., °C.)*	Boro-silicate (temp., °C.)*
None†	4.2462	30.70	30.9
3	4.2470	30.80	30.9
10	4.2459	30.80	30.9
30	4.2449	30.80	30.9
100	4.2424	30.85	30.9
300		30.85	30.9

* Temperatures of the liquid used in the sink-float method of density determination.

† Control.

(3) Density

Results of the density measurements are shown in Table IV. No changes in density existed between the control and irradiated specimens of the soda-lime or borosilicate glasses. Since density changes were being sought rather than specific values, the actual densities of the soda-lime and borosilicate glasses were not determined. Instead, the temperature of the flotation liquid is reported in Table IV. A temperature change of 0.1°C. represents a density change of 0.0002 gm. per cc. The actual densities of the lead glass specimens are shown in the table. A slight decrease in density of the lead glass was observed as the dosage increased. The maximum dosage of 100 megareps caused a decrease in density of approximately 0.1%. The decrease in density may be expected because of the formation of lattice vacancies and interstitials by the radiation. However, it is not evident why this occurred only in the lead glass and not in the soda-lime or borosilicate glasses.

(4) Electrical Resistivity

Data obtained from the room temperature electrical resistivity measurements on the soda-lime glass specimens are shown in Table V. The high resistance of lead and borosilicate glasses made room temperature measurements impossible and heating the specimen would tend to anneal out any effect of the irradiation. The results showed that there was no commercially significant effect on the resistivity of the soda-lime glass.

Table V. Electrical Resistivity of Soda-Lime Glass

Irradiation (megareps)	Log electrical resistivity
None*	11.4 ± 0.5
1	11.8 ± 0.5
3	11.8 ± 0.5
10	10.9 ± 0.5
30	11.6 ± 0.5
100	11.0 ± 0.5
300	11.1 ± 0.5

* Control.

Table VI. Heat of Solution Measurements

Glass	Irradiation (megareps)	Calories per gram of glass
Soda-lime	None*	571.6
	1	566.0
	3	566.7
	10	570.4
	30	572.3
	100	566.2
	300	574.2
Borosilicate	None*	564.0
	1	558.7
	3	560.7
	10	562.8
	30	569.2
	100	576.0
	300	593.0
Lead	None*	273.8
	3	274.6
	10	274.8
	30	274.2
	100	274.9
	300	275.3

* Control.

(5) Heat of Solution

The results of the heat of solution measurements are shown in Table VI. There was no significant change in the heat of solution of the soda-lime and lead glass specimens due to the irradiation. The borosilicate glass showed a noticeable increase in the heat of solution when exposed to a dose of 300 megareps. This gave a value of 593.0 calories per gram as compared with 564.0 calories per gram for the control specimens.

V. Summary

The results showed that irradiation with 2 m.e.v. electrons produced only small effects on the flexural strength, chemical durability, density, electrical resistivity, or heat of solution of several commercial glasses. These results were for irradiation dosages up to 300 megareps. The only visible effect was an olive-brown discoloration of the glass, an effect which is well known and has been widely discussed in the literature. Ways to avoid this discoloration are known, such as by the addition of cerium, but this is a costly method at present.