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(Supplement to ORNL-928)

C. D. Bopp
O. Sisman

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RADIATION STABILITY OF PLASTICS AND ELASTOMERS

(Supplement to ORNL-928)

C. D. Bopp
O. Sisman

Experimental Measurements by

W. K. Kirkland
R. L. Towns

July 23, 1953

DATE ISSUED

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RADIATION STABILITY OF PLASTICS AND ELASTOMERS

C. D. Bopp O. Sisman

ABSTRACT

Radiation-induced changes in the physical properties of several plastics that were not included in ORNL-928 and the radiation-induced changes in the commercial elastomers are reported. In addition, a number of fabrics and some specially prepared materials are examined.

For the most part, reactor radiation was used, but other types of radiation are compared with reactor radiation in producing changes in the properties of the materials studied. The effect of the presence of oxygen during irradiation and the effect of time of aging subsequent to irradiation are also studied. The rate of gas evolution and the rate of change in volume are given for many of the materials studied, and a correlation is drawn with the chemical structure. Also, changes in the mechanical properties of the polymers are correlated with their chemical structure.

INTRODUCTION

This report is a supplement to a previous study (*1*)* of the radiation stability of a number of commercial plastics. The radiation stability of commercial elastomers is described in Chapter 1; the stability of a number of additional plastics is described in Chapter 3.

All soft, flexible plastics and elastomers which are not extensively degraded by radiation are hardened by cross-linking. Attempts made to increase resistance to hardening are described in Chapter 2. Mixtures of natural rubber and butyl rubber were tried, and the effect of increasing the filler material and the antioxidant in elastomer formulations was determined, but none of these measures were successful.

Most of the radiation exposures were made in the maximum flux region of the ORNL Graphite Reactor. Exposures made with other types of radiation are described in Chapter 4. To increase the intensity of ionizing radiation, some irradiations were conducted in which the materials were wrapped in cadmium during the exposure. Even then, some of the hard plastics showed but small change after an exposure of six months. Irradiations are planned at higher intensities in high-flux facilities which have recently become available.

Comparison of the damage from fast-neutron and gamma radiation was made from the increase in damage for cadmium-wrapped specimens. [Since damage by thermal neutrons is small for materials with low absorption cross sections, the effect of the cadmium is to produce additional gamma-radiation damage by converting thermal-neutron to gamma radiation by the (n,γ) reaction.] Comparative irradiations were also made with neutron-free gamma radiation from Au^{198} and Co^{60} sources. A study of the effect of intensity was made with the Co^{60} source by varying the distance from the source and increasing the exposure for the irradiations made further from the source so that approximately equal energy absorption for all irradiations would be produced. The energy absorption required to produce similar changes in most of the physical properties of the materials studied was the same within a factor of about 2 for the various sources of ionizing radiation employed.

Listed in Chapters 6 and 7 are the change in volume and the evolution of gas which accompany the radiation-induced cross-linking of many of the polymers. Certain other polymers show no uniform decrease in volume. It is thought that the decrease which would otherwise be produced by cross-linking is masked by chain cleavage. Gassing occurs even for polymers which are degraded extensively by chain cleavage. More than likely, most of the gassing results from cross-linking, since the hydrogen produced by cross-linking can diffuse more readily through the polymer than can the hydrocarbons produced from chain cleavage.

Listed in "Discussion of Results" is a correlation of the radiation stability with the chemical structure of the materials tested. This correlation

*See bibliography.

permits prediction of the behavior of materials which have not been tested.

The present study has been confined to room-temperature conditions. While certain hard materials have good stability and show little change, all soft materials (which are not degraded) are hardened. For this reason, it is not expected that changes in temperature will greatly affect the stability of hard, resistant materials until the point is reached at which the material becomes soft and elastic. It is therefore planned to study the stability of these materials at their softening points.

In certain instances, good stability is shown by mixtures of certain polymers and mineral fillers, although the polymers alone show poor stability. This applies only for hard materials and not to soft, flexible materials. It is planned to study this effect more fully.

Chapter 1

RADIATION STABILITY OF COMMERCIAL ELASTOMERS

GROUP 1 FORMULATIONS

Commercial elastomer formulations, for the most part, are based on eight polymers, although a large number of formulations exist that suit various applications. Owing to poor mechanical properties for uncompounded polymers, vulcanized formulations were chosen for testing. Gasket formulations were chosen over electrical insulation formulations since mechanical properties were to be studied more intensively than electrical properties. The recipes of the first group of elastomers tested (Group 1) were chosen so that each material would have durometer hardness in the range from 60 to 70. The recipes are listed in Table 1.1.

During irradiation, the materials were sealed in air (see Chapter 5) in aluminum cans. Exposures were conducted in hole 19 of the ORNL Graphite Reactor. This irradiation facility is more fully described in a report (2) in which the fast-neutron flux (above 1 Mev) is estimated as 4% of the thermal flux, the epithermal flux above the cadmium cut-off is estimated as 60% of the thermal flux, and the gamma flux (if the energy of the gammas is taken as 1 Mev) is estimated as 50% of thermal flux. The radiation exposure is listed as nvt, the product of the thermal-neutron flux in neutrons/cm^2·sec and the exposure time in seconds.

Descriptions of the testing procedures are given in the Appendix. Most of the tests are modifications of ASTM standard procedures. The testing laboratory was kept at 50 ± 2% relative humidity and 77 ± 2°F. Test results are given in Figs. 1.1 through 1.9. The chemical structural formulas are given in Table 1.2. Stress-strain curves are given for several radiation exposures, and other physical and mechanical properties are plotted as a function of exposure.

Natural rubber, Neoprene W, GR-S, Hycar OR, Hycar PA, and Silastic 7-170 all harden with irradiation. Butyl rubber and Thiokol soften with irradiation. Both butyl rubber and Thiokol eventually become fluid; however, about 20 times the exposure is required to produce softening in Thiokol as is required for softening butyl rubber to the same extent. A comparison of the change in durometer hardness for the polymers is shown in Fig. 1.10.

Although the tensile strength of Hycar OR and Silastic is initially increased, long exposure causes the strength to be decreased. The tensile strength of the other elastomers is decreased, with no initial increase. The materials which are hardened regain tensile strength after long exposure, but only after severe embrittlement has reduced the elongation to less than 1% of the initial value. Since the materials are hard and brittle at this time, they have none of their original elastomeric characteristics.

Irradiation increases the specific gravity of the elastomers which are hardened and decreases the specific gravity of the elastomers which are softened.

A marked loss in weight occurs only for Thiokol and Hycar PA.

The volume resistivity deteriorates only for Neoprene W and Hycar PA. It is believed that the change in electrical properties of these two plastics is associated with their hygroscopicity, which develops after long exposure and is due to HCl formation. Neoprene W contains chlorine, as is shown by its structural formula in Table 1.2; Hycar PA contains a very small amount of chlorine-containing material, although this is not shown in its structural formula.

TABLE 1.1 COMPOSITION OF GROUP 1 ELASTOMERS

COMPONENTS	PARTS BY WEIGHT						
	Natural Rubber (32A43)[a]	Neoprene W (32A44A)[b]	Hycar OR-15 (32A45A)[c]	GR-I 50 (32A46A)[d]	GR-S 50 (32A47)[e]	Hycar PA-21 (32A48)[f]	Thiokol ST (3000 ST)
Natural rubber	100						
Neoprene W		100					
Hycar OR-15			100				
GR-I 50				100			
GR-S 50					100		
Hycar PA-21						100	
Thiokol ST							100
Zinc oxide	5	5	5	5	5		0.5
SRF black	70	45	55	75	70		60
Stearic acid	1	0.5		2		1	3
Phenyl-β-naphthylamine	1	2					
Sulfur	3		1.5	1.5	1.75	0.5	
Captax	0.6			0.5			
Magnesium oxide		2					
Permalux		0.5					
Altax			1				
Tetramethyl thiuram disulfide				1			
Santocure					1.5		
HMF (Philblack O)						40	
Trimene base						3	
GMF (p-quinone dioxime)							1.5
Ca-10							2

[a]Cured 25 min at 292°F.
[b]Cured 20 min at 307°F.
[c]Cured 30 min at 307°F.
[d]Cured 60 min at 307°F.
[e]Cured 40 min at 307°F.
[f]Cured 60 min at 310°F.

Compression set Test A (see Appendix) shows that butyl rubber and Thiokol have a high sensitivity to radiation, since the compression-set value increases by several hundred per cent as these materials soften and lose resilience. The other polymers, which are hardened, show decreased compressibility and therefore decreased compression set. For the latter materials, a better indication of the radiation damage is given by compression set Test B (Table 1.3), since, in this test, materials are compressed before irradiation and are irradiated in the compressed condition. Radiation-induced hardening increases the compression-set value as determined by this test.

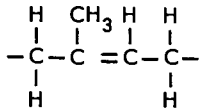
Vulcollan is a new elastomer which is not yet produced commercially. Unlike many other elastomers, it shows good mechanical properties without a filler or other compounding materials. The radiation stability of Vulcollan is similar to that of Hycar PA, and a comparison of radiation-produced changes is given in Table 1.4.

Of the eight formulations tested, the one based on butyl rubber is much less resistant than those based on the other seven commercial polymers. The other polymers all show about the same rate of hardening, with the exception of Thiokol which softens. Thiokol retains its strength no better than the materials which harden.

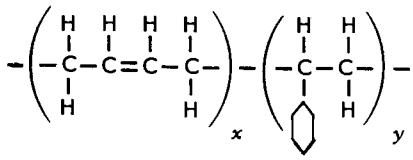
Specimens were not stressed during irradiation, except in the case of compression set Test B. It is known that ozone attacks stretched specimens of some elastomers and that ozone is formed by the irradiation of air (5). To investigate ozone attack, natural rubber was irradiated while stretched; preliminary results are shown in Fig. 1.11. It is presumed that the degree of ozone-induced cracking

TABLE 1.2. STRUCTURAL FORMULAS OF ELASTOMERS

Natural rubber

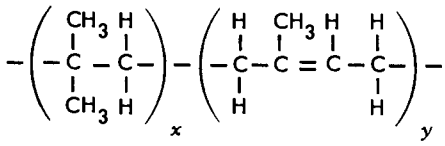


GR-S



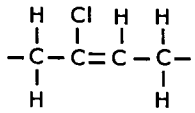
($x/y = 6$)

Butyl rubber GR-I

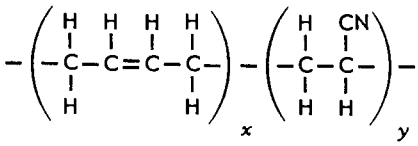


($x/y = 50$)

Neoprene

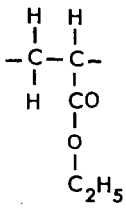


Hycar OR

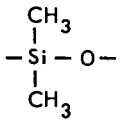


($x/y = 2$)

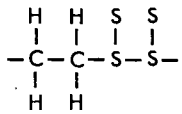
Hycar PA



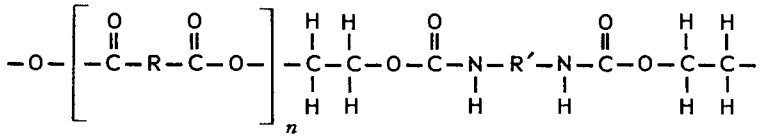
Silastic



Thiokol



Vulcollan



(also $C_{98}H_{128}O_{44}N_4$)

is affected by the amount of elongation, the circulation of air, the radiation intensity, and the exposure period. (The importance of the circulation of air is shown by the fact that the side of the specimen which was partially shielded by the stretching jig showed no attack.) It is planned to investigate more fully the effect of these conditions of exposure. Owing to the merging of cracks, the depth of cracks rather than the width or number will be used as a measure of the severity of attack (6).

TABLE 1.3. RECOVERY OF ELASTOMERS COMPRESSED 25% DURING IRRADIATION

Compression Set Test B

ELASTOMER	RECOVERY (%)			
	In Jig 190 hr		In Jig 840 hr	
	Unirradiated	Irradiated, 0.03×10^{18} nvt (7.5 hr in reactor)	Unirradiated	Irradiated, 0.16×10^{18} nvt (40 hr in reactor)
Natural rubber (32A43)	93	52	90	25
GR-S 50 (32A47)	90	53	88	22
Butyl rubber, GR-I (32A46)	91	23	88	Tarry fluid
Neoprene W (32A44)	62	20	42	12
Hycar OR-15 (32A45)	92	62	90	24
Hycar PA-21 (32A48)	92	58	91	14
Silastic 7-170	97	27	95	0
Thiokol ST (3000 ST)	90	2	82	0

TABLE 1.4. RADIATION-PRODUCED CHANGES IN VULCOLLAN COMPARED WITH THOSE IN HYCAR PA-21

	IRRADIATION EXPOSURE (10^{18} nvt)	TENSILE STRENGTH (psi)	ELONGATION (%)	SHORE DUROMETER HARDNESS	SHORE ELASTICITY	SPECIFIC GRAVITY, 25/4°C	CHANGE IN WEIGHT (%)	VOLUME RESISTIVITY (ohm-cm)	DIELECTRIC STRENGTH (volts/mil)
Hycar PA-21	0	2000	330	62	70	1.269		10^{10}	115
	0.12	1400	115	70	50	1.270	−0.1		115
	1.6	400	20	88	25	1.276	−1.7		115
	5.4	1500	2	99		1.290	−7.0	10^{6}	115
Vulcollan	0	5400	600	74	100	1.237		3×10^{8}	>210
	0.12	1900	250	72	80	1.242	0.05	3×10^{8}	>210
	1.6	600	50	74	30	1.245	−0.19	3×10^{8}	>210
	5.4	240	10	90	25	1.256	−5.8	3×10^{8}	200

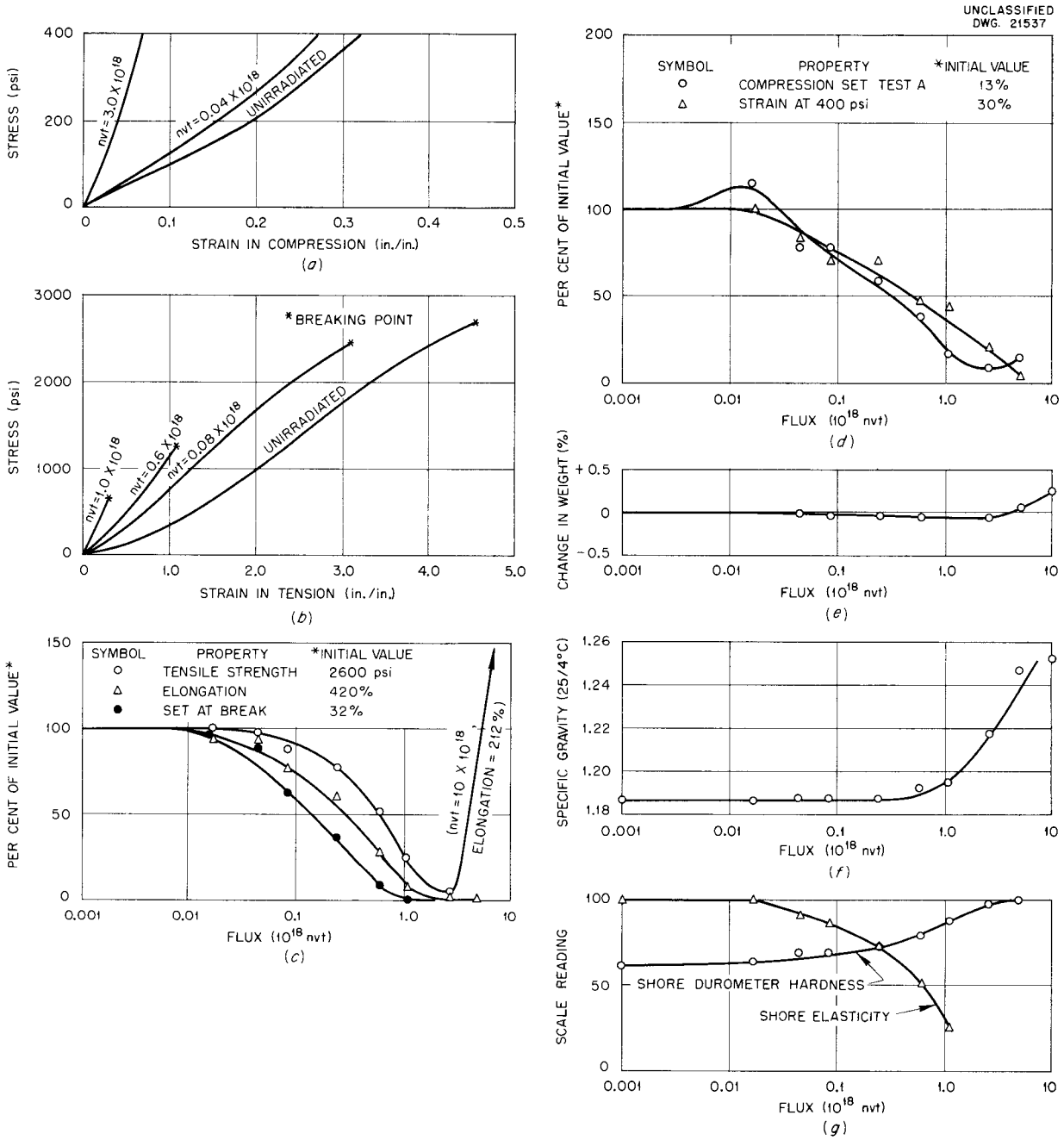


Fig. 1.1. Physical and Mechanical Properties of Irradiated Natural Rubber (32A43).

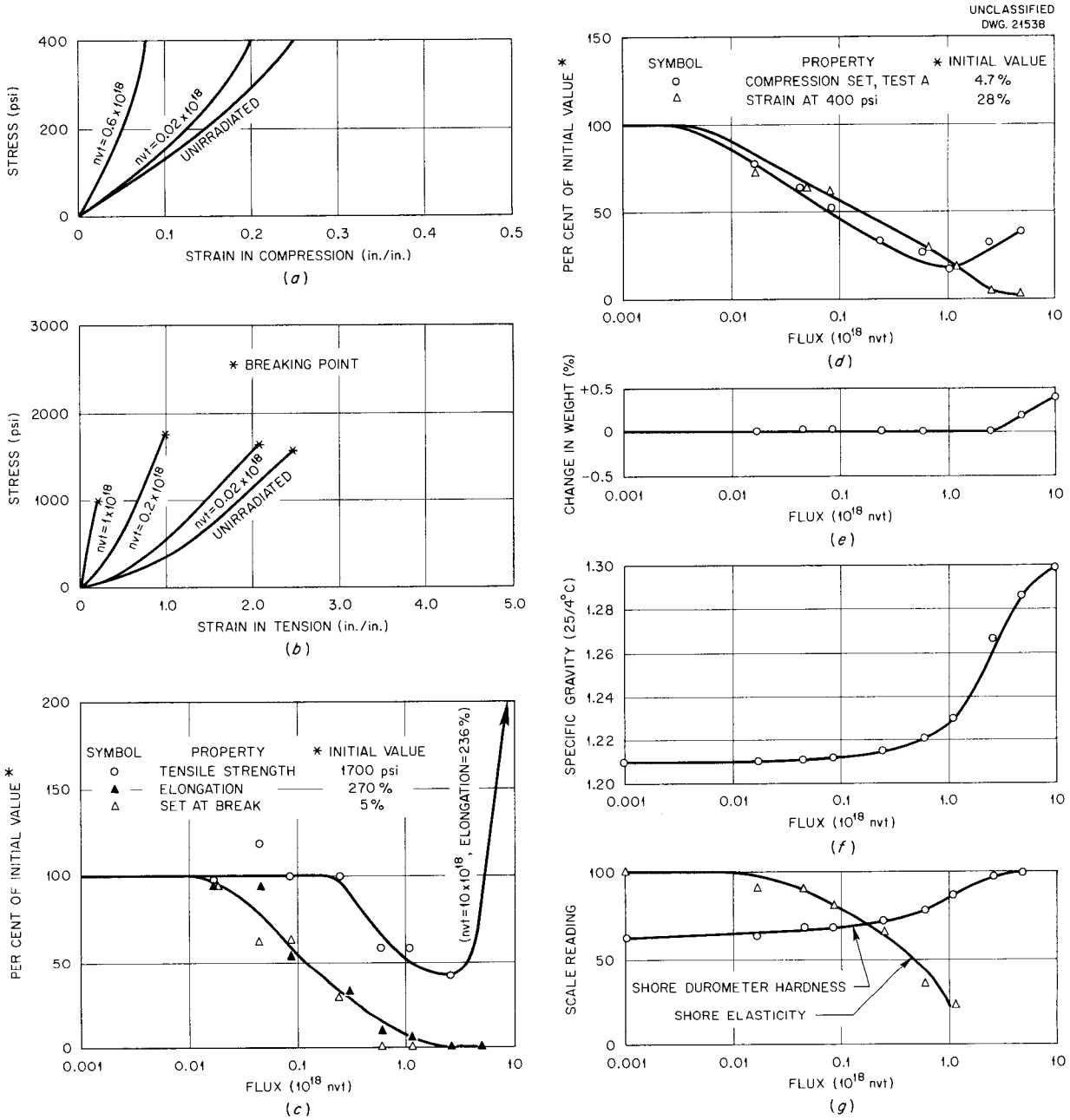


Fig. 1.2. Physical and Mechanical Properties of Irradiated GR-S 50 (32A47).

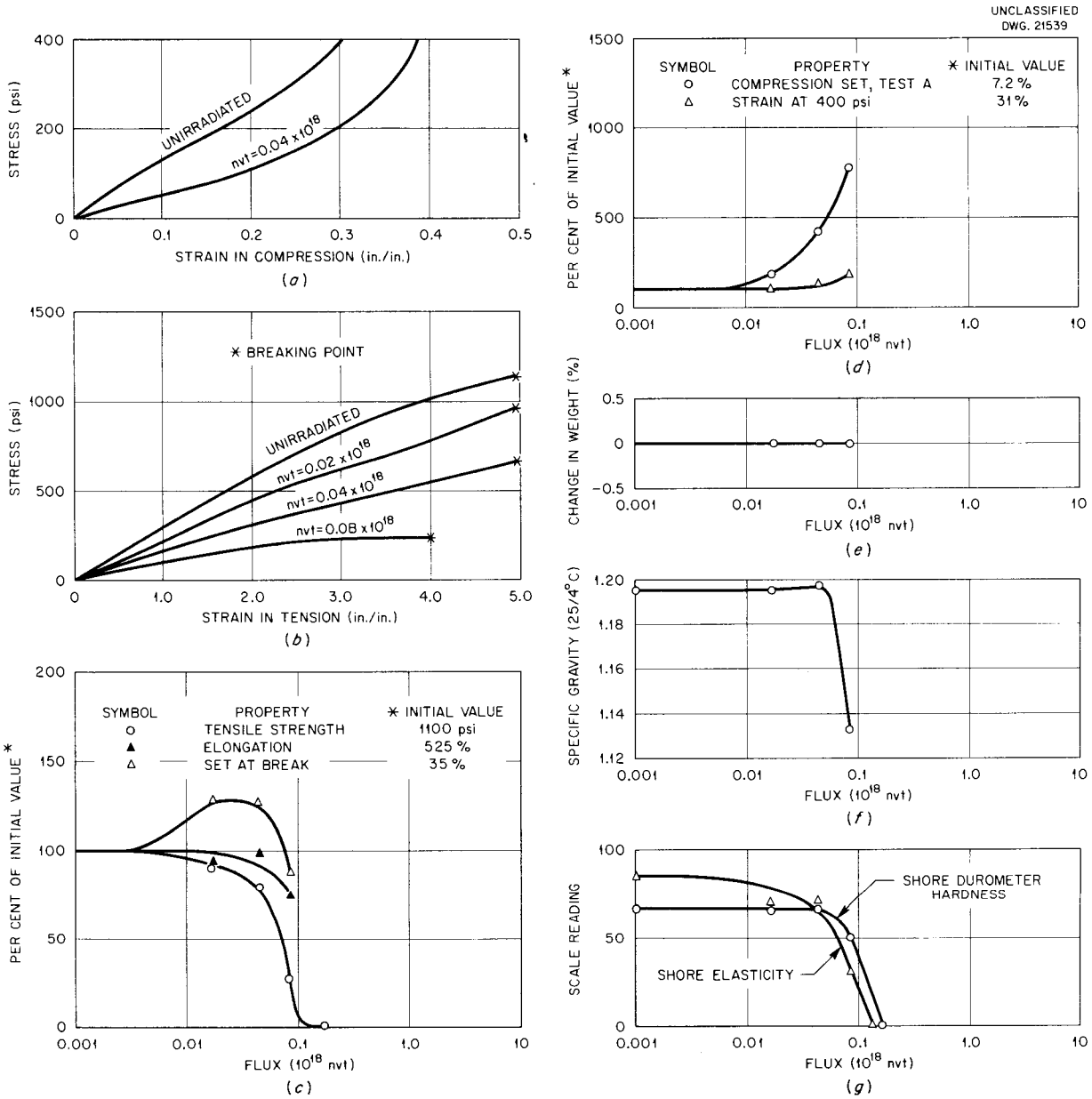


Fig. 1.3. Physical and Mechanical Properties of Irradiated Butyl Rubber, GR-I 50 (32A46).

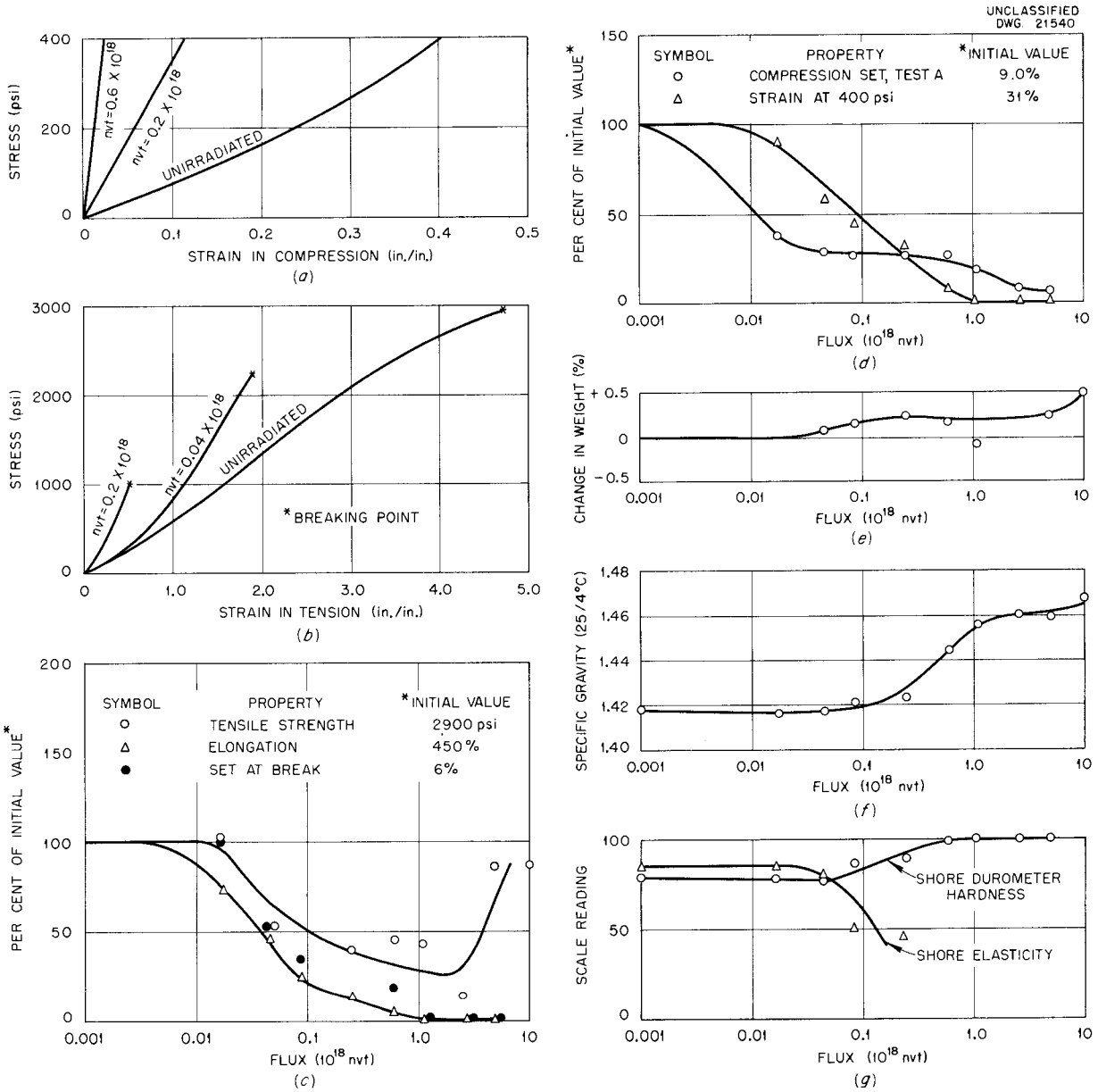


Fig. 1.4. Physical and Mechanical Properties of Irradiated Neoprene W (32A44).

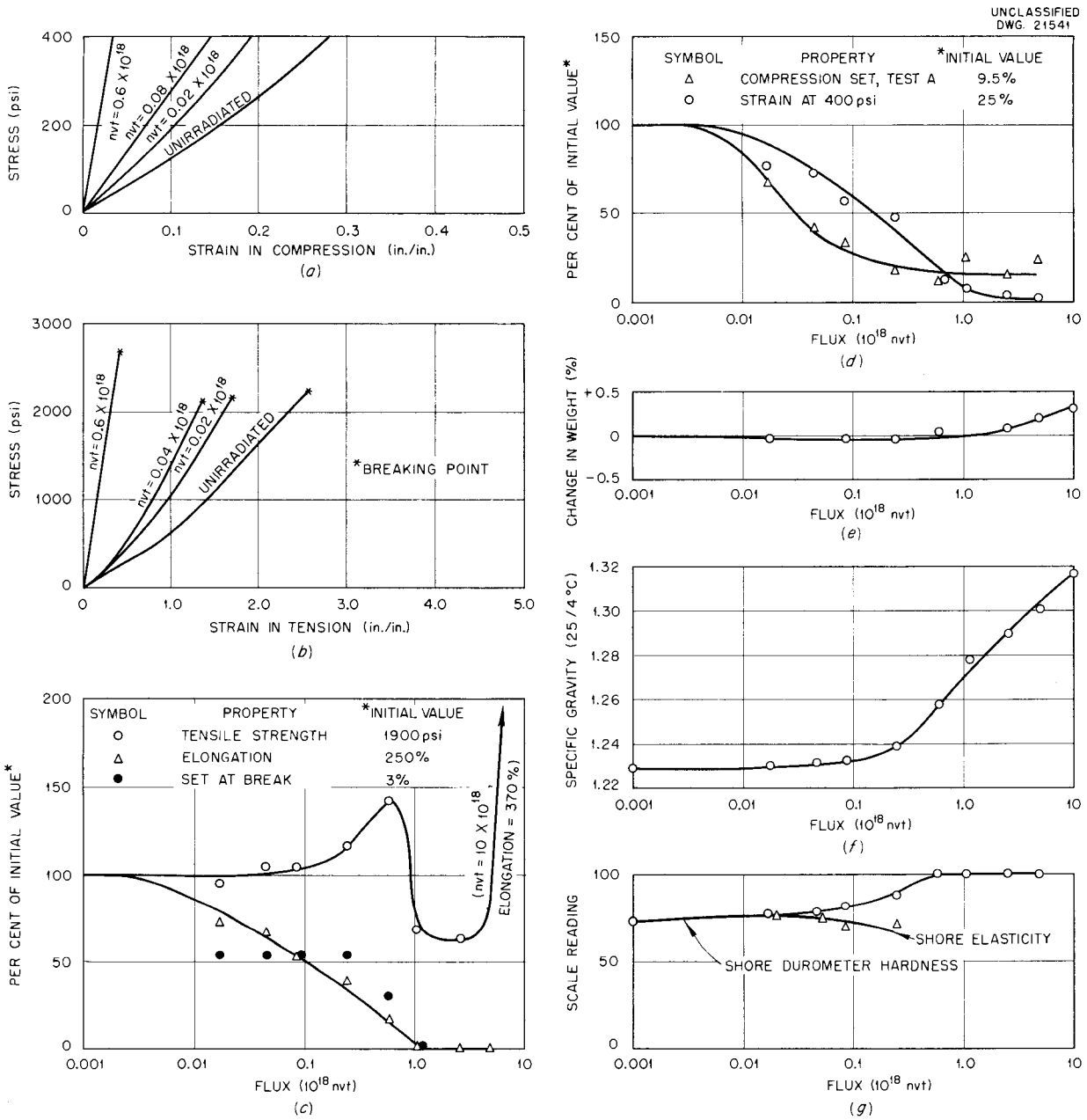


Fig. 1.5. Physical and Mechanical Properties of Irradiated Hycar OR-15 (32A45).

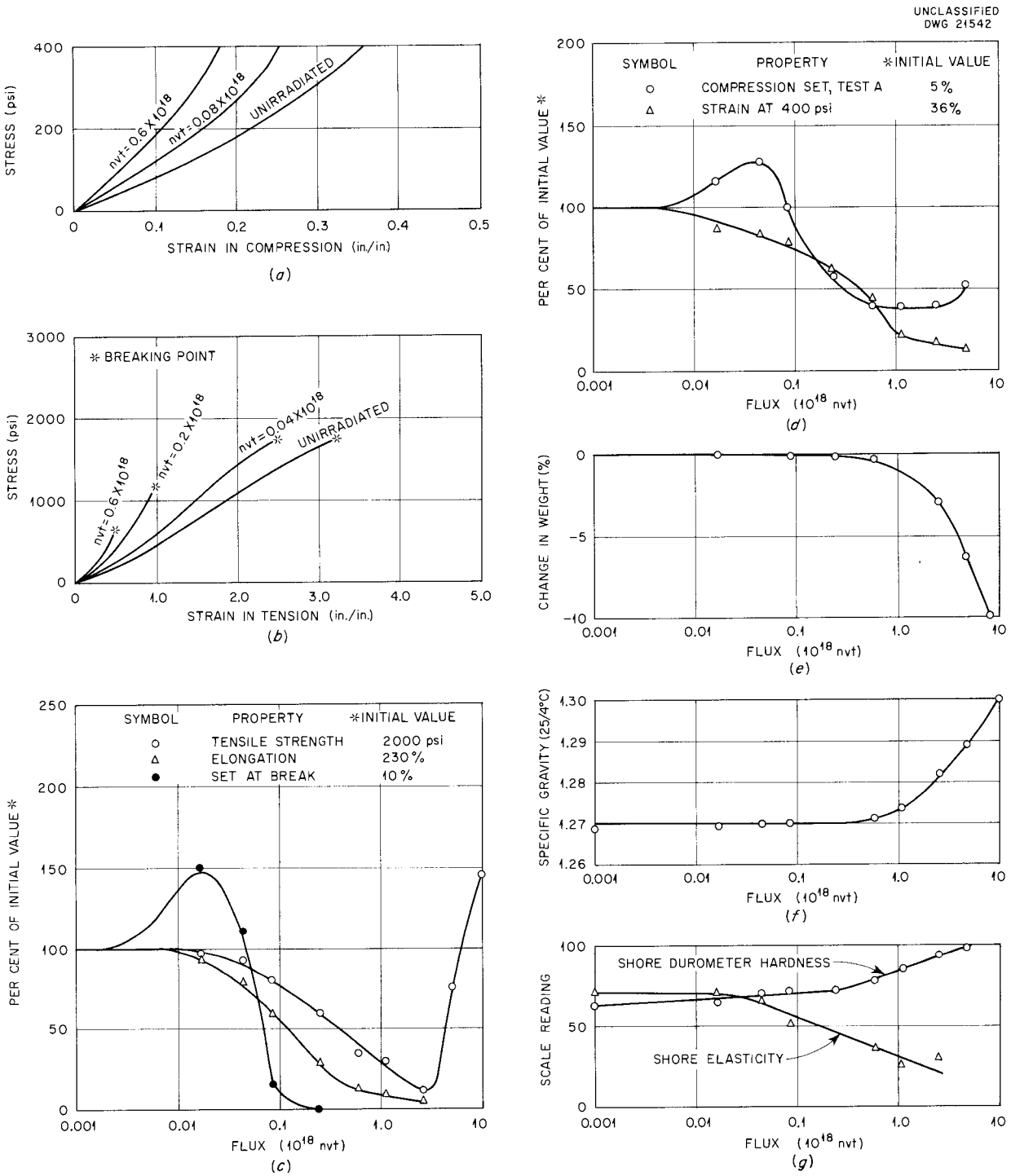


Fig. 1.6. Physical and Mechanical Properties of Irradiated Hycar PA-21 (32A48).

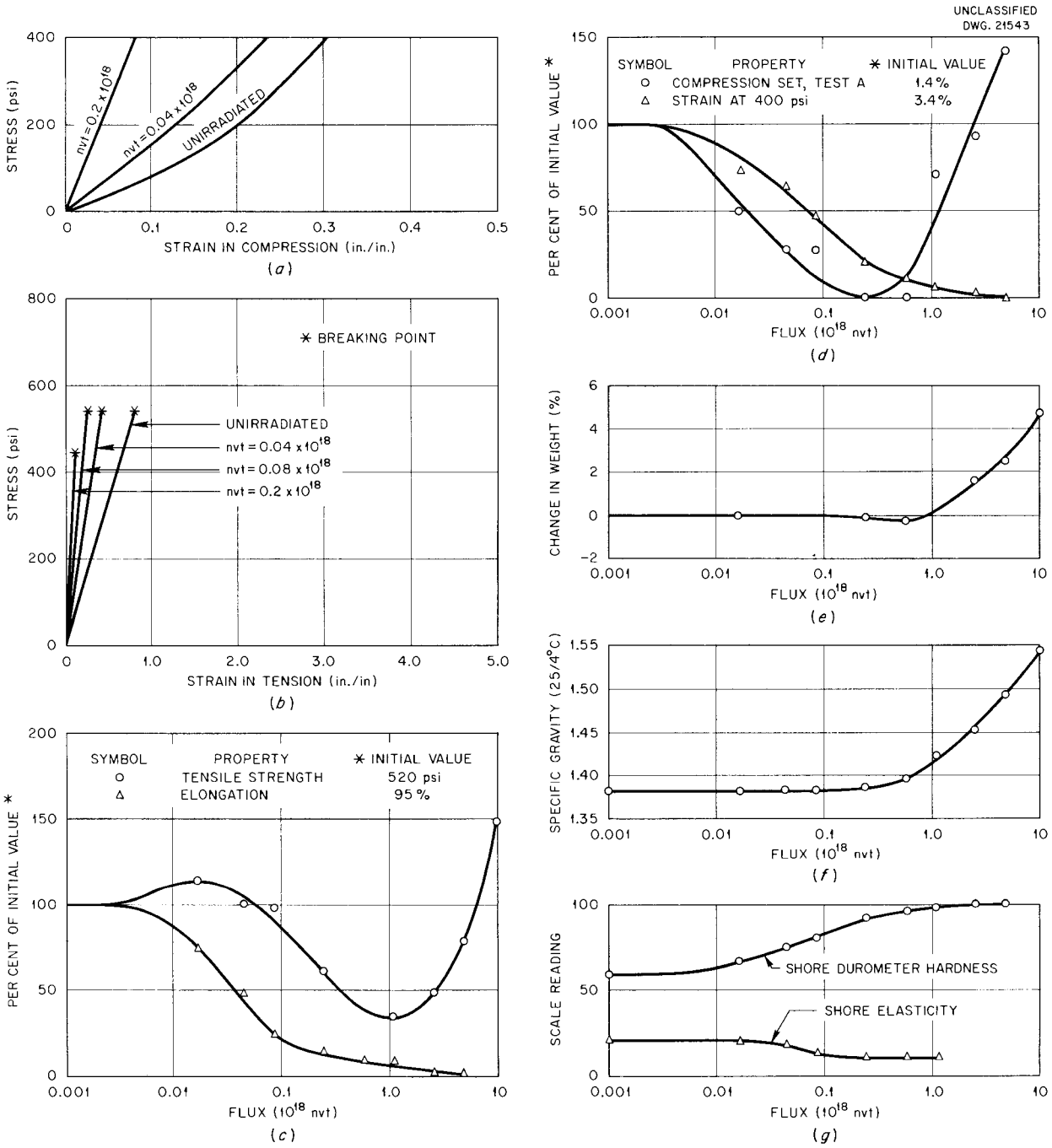


Fig. 1.7. Physical and Mechanical Properties of Irradiated Silastic 7-170.

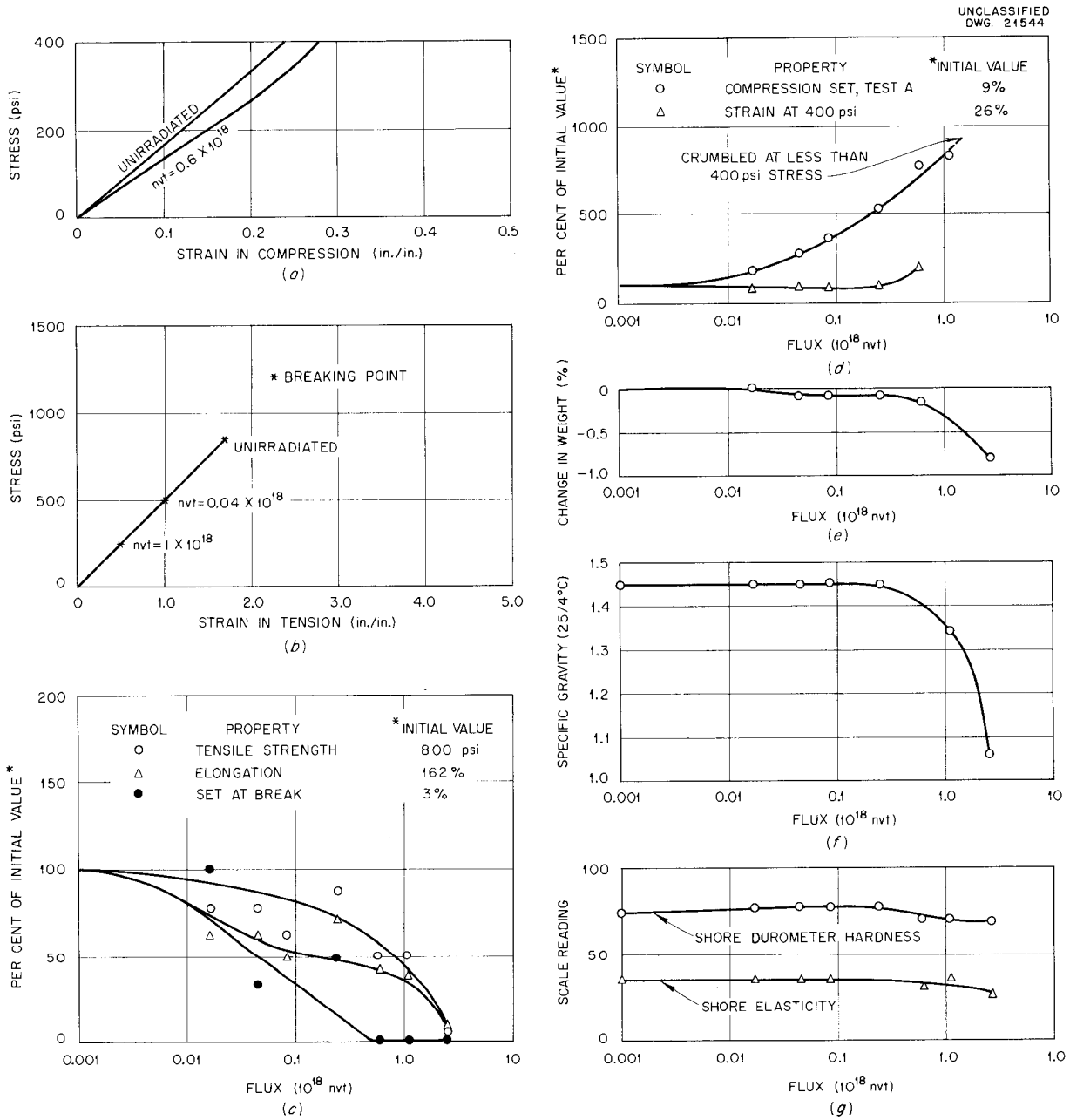


Fig. 1.8. Physical and Mechanical Properties of Irradiated Thiokol ST (3000ST).

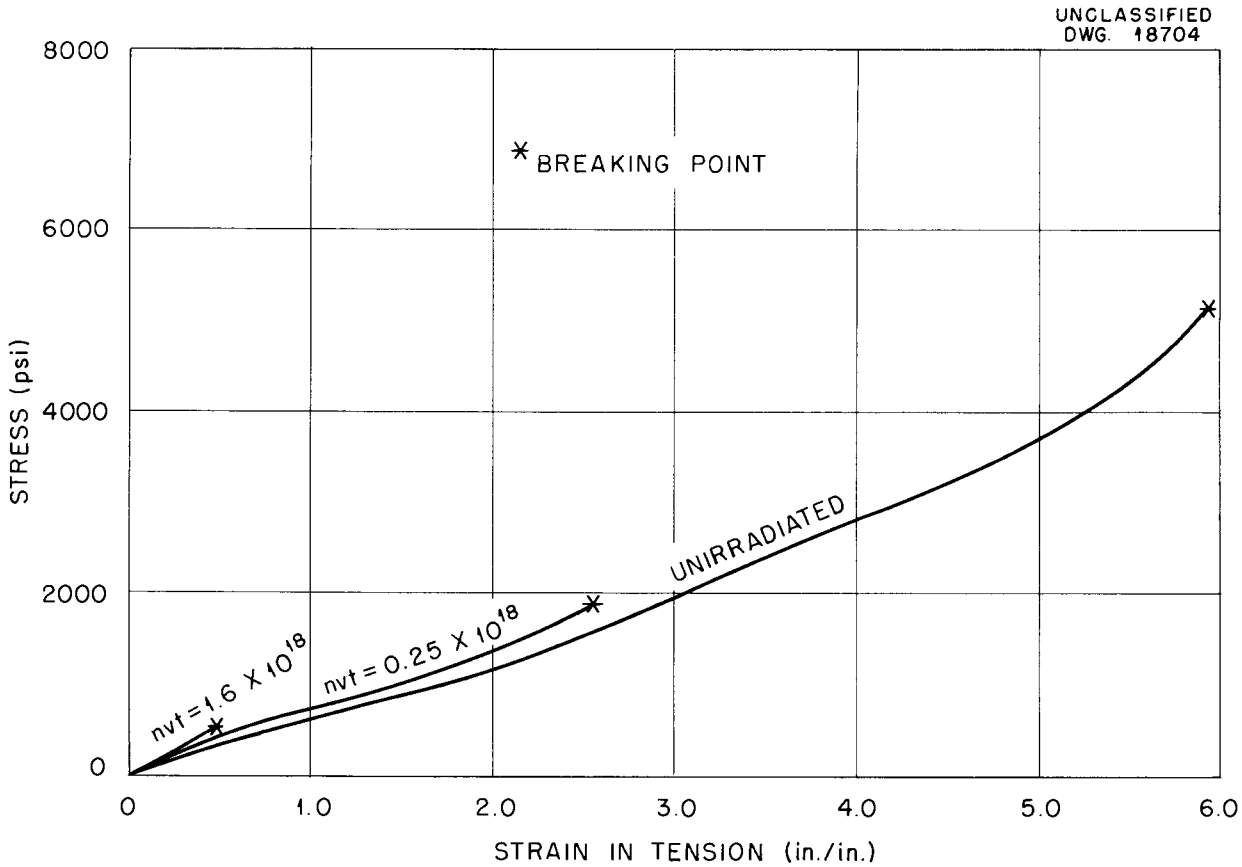


Fig. 1.9. Stress-Strain Curves for Irradiated Vulcollan.

Since frictional heating is an important consideration in the design of synthetic rubber tires, it is planned to investigate the effect of radiation on dynamic losses. A vibrating-reed type of measurement (7) will be employed.

GROUP 2 FORMULATIONS

The contention that the polymer portion of the material determines, for the most part, the radiation stability of elastomer formulations is supported by studies made on a second group of formulations (Tables 1.5 and 1.6). These materials were provided by the Materials Laboratory of the Wright Air Development Center. Not so many radiation exposures were made in this instance, since it was expected that results would be very similar to those obtained for Group 1. The results obtained on the Group 2 formulations are shown in Tables 1.7 and 1.8.

Each formulation of Group 2 shows similar stability to the formulation of Group 1 that includes the same polymer (Hycar OS is similar to GR-S). Three additional polymers are included in Group 2: Neoprene GN, Hypalon, and FBA. The elastomers based on these three polymers are hardened like most other elastomers.

The natural rubber formulations which include various plasticizers all show similar stability and are hardened at about the same rate as the natural rubber formulation without a plasticizer.

The experimental procedure used for Group 2 was similar to that employed for Group 1, except that Group 1 elastomers were irradiated in cans which contained air, while the air was replaced by helium for Group 2 irradiations. The effect of the oxygen in the air is discussed in Chapter 5.

TABLE 1.5. COMPOSITION OF GROUP 2 ELASTOMERS CURED 20 min AT 310°F

COMPONENTS	PARTS BY WEIGHT											
	Polybutadiene (P1S1C1)	Hycar OR-15 (P1S1C2)	Hycar OS-10 (P1S1C3)	Neoprene GN (P1S1C4)	Neoprene W (P1S1C5)	Butyl Rubber (P1S1C6)	Thiokol ST (P1S1C7)	Silastic 250 (P1S1C8)	Natural Rubber (P1S1C9)	Hycar PA-21 (P1S1C10)	Hypalon S2 (P1S1C11)	FBA (P1S1C12)
Polybutadiene X453	100											
Hycar OR-15		100										
Hycar OS-10			100									
Neoprene GN				100								
Neoprene W					100							
Butyl rubber, GR-I						100						
Thiokol ST							100					
Silastic 250*								100				
Natural rubber**									100			
Hycar PA-21										100		
Hypalon S2											100	
FBA***												100
Zinc oxide	5	5	5	5	5	5	0.5		5			
Stearic acid	1	1.5	1	1	0.5	2	1		3	1		
Sulfur	2	2	3			2			3	0.5		
Methyl Tuads	0.3											
SRF black	20	20	20	20	20	20	40		20	20	20	
Altax		1.75										
Captax			1						1		3	
Neozone "A"				2	2							
ELC magnesium oxide				4	2	3						
Permalux				0.5								
NA22					0.5							
Triuram M						1						
Polyac						1						5
GMF							1.5					
Triamine base										3		
Litharge											40	
Staybelite resin											2.5	
Lead peroxide												20

*Cured 15 min at 300°F.

**Standard smoked sheet.

***Poly-1,1-dihydroperfluorobutyl acrylate.

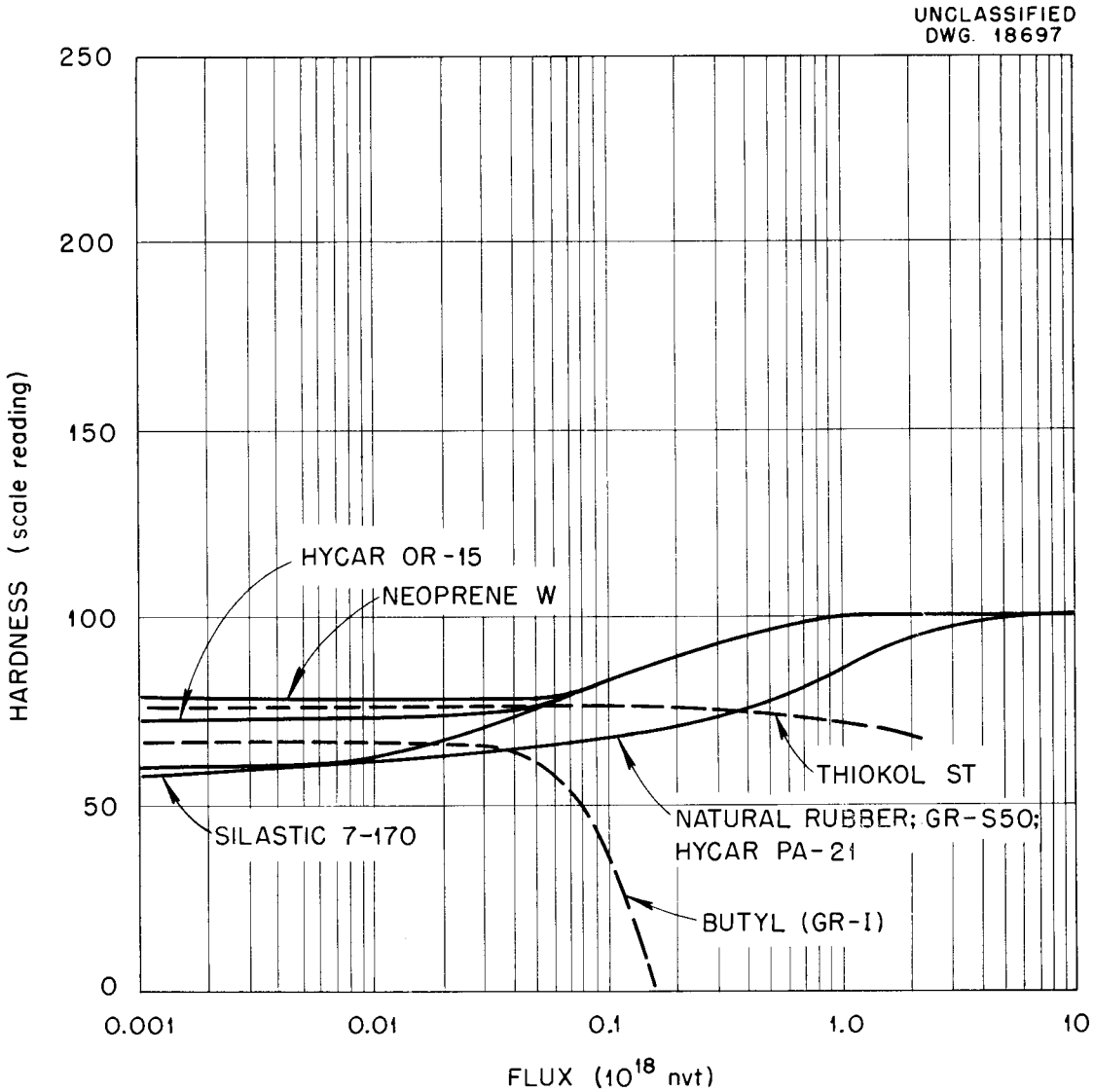


Fig. 1.10. Shore Durometer Hardness of Irradiated Elastomers.

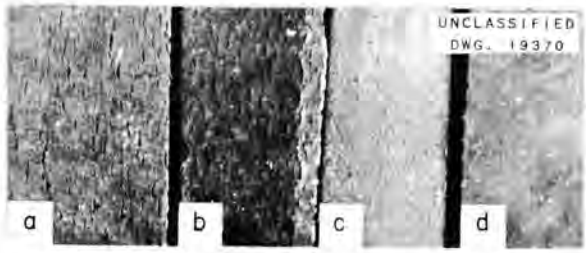


Fig. 1.11. Ozone-induced Cracking of Natural Rubber Stressed During Irradiation. 10X.

(a) Stretched 25%, irradiated in air for an exposure of 0.6×10^{18} nvt.

(b) Stretched 25%, irradiated in air for an exposure of 0.1×10^{18} nvt.

(c) Stretched 25%, not irradiated, exposed to laboratory atmosphere for same period as (a) was irradiated.

(d) Not stretched, but irradiated in air for same period as that used for (a).

TABLE 1.6. COMPOSITION OF VARIOUS PLACTICIZED NATURAL RUBBER COMPOUNDS CURED 20 min AT 310°F

COMPONENT	PARTS BY WEIGHT					
	L.P. Oil (P1S2C1)	Dioctyl Phthalate (P1S2C2)	Dioctyl Sebacate (P1S2C3)	Tributoxy Ethyl Phosphate (P1S2C4)	TP90B (P1S2C5)	Plasticizer "SC" (P1S2C6)
Smoked sheet	100	100	100	100	100	100
Stearic acid	1	1	1	1	1	1
Zinc oxide	5	5	5	5	5	5
Sulfur	3	3	3	3	3	3
Captax	1.5	1.5	1.5	1.5	1.5	1.5
SRF black	30	30	30	30	30	30
L.P. oil	30					
Dioctyl phthalate		30				
Dioctyl sebacate			30			
Tributoxy ethyl phosphate				30		
TP90B					30	
Plasticizer "SC"						30

TABLE 1.7. RADIATION-PRODUCED CHANGES IN THE PHYSICAL PROPERTIES OF GROUP 2 ELASTOMERS

ELASTOMER	IRRADIATION EXPOSURE (10^{18} nvt)	TENSILE STRENGTH (psi)	ELONGATION (%)	SHORE DUROMETER HARDNESS	SPECIFIC GRAVITY, 25/4°C	VOLUME RESISTIVITY (ohm-cm)
Polybutadiene (P1S1C1)	0	670	360	49	1.040	10^{14}
	0	590	355	49	1.040	10^{14}
	0.25	460		67	1.045	10^{14}
	0.54	280	20	79	1.055	10^{10}
	1.3	1200	< 2	98	1.087	10^{9}
Hycar OR-15 (P1S1C2)	0	1270	310	59	1.122	10^{11}
	0	1540	360	59	1.122	10^{11}
	0.25	1600	110	76	1.131	10^{11}
	0.54	2600	45	97	1.146	10^{11}
	1.3	7800	< 2	100	1.177	10^{13}
Hycar OS-10 (P1S1C3)	0	1240	375	52	1.119	$> 10^{14}$
	0	1360	390	52	1.119	$> 10^{14}$
	0.25	1600	180	67	1.121	6×10^{13}
	0.54	800	70	77	1.128	2×10^{12}
	1.3	3600	25	100	1.144	5×10^{12}
Neoprene GN (P1S1C4)	0	2520	475	62	1.363	2×10^{11}
	0	2460	475	62	1.363	2×10^{11}
	0.25	990	45	85	1.372	4×10^{9}
	0.54	1900	20	99	1.386	10^{8}
	1.3	3300	< 2	100	1.390	10^{8}
Neoprene W (P1S1C5)	0	3330	700	53	1.346	2×10^{11}
	0	2800	650	53	1.346	2×10^{11}
	0.25	Sample lost				
	0.54*	Sample broken		98	1.360	2×10^{10}
	1.3	7200	< 2	100	1.384	10^{10}
Thiokol (P1S1C7)	0	1100	195	70	1.464	10^{8} to 10^{10}
	0	1000	175	70	1.464	10^{8} to 10^{10}
	0.25	630	90	75	1.464	10^{10}
	0.54*	400	60	72	1.462	10^{9}
	1.3	450	70	73	1.469	10^{7}
Silastic 250 (P1S1C8)	0	160	330	19	1.205	10^{14}
	0	150	320	19	1.205	10^{14}
	0.25	160	7	81	1.214	10^{14}
	0.54*	Sample broken		93	1.204	10^{12}
	1.3	230	< 2	97	1.253	10^{14}
Natural rubber (P1S1C9)	0	2250	460	47	1.045	$> 10^{14}$
	0	2210	450	47	1.045	$> 10^{14}$
	0.25	430	65	67	1.049	10^{14}
	0.54*	400	30	80	1.053	10^{14}
	1.3	110	< 2	92	1.072	10^{12}

TABLE 1.7. (continued)

ELASTOMER	IRRADIATION EXPOSURE (10^{18} nvt)	TENSILE STRENGTH (psi)	ELONGATION (%)	SHORE DUROMETER HARDNESS	SPECIFIC GRAVITY, 25/4°C	VOLUME RESISTIVITY (ohm-cm)
Hycar PA-21	0	610	235	45	1.217	6×10^{11}
(P1S1C10)	0	720	275	45	1.217	6×10^{11}
	0.25	340	60	55	1.222	10^{11}
	0.54*	300	30	70	1.226	3×10^{10}
	1.3	500	3	80	1.240	5×10^{10}
Hypalon S2	0	2410	250	78	1.488	6×10^{13}
(P1S1C11)	0	2550	250	78	1.488	6×10^{13}
	0.25	1800	38	90	1.495	4×10^{12}
	0.54*	1500	6	96	1.500	2×10^{13}
	1.3	3000	< 2	100	1.504	2×10^{13}
FBA**	0			58	1.793	
(P1S1C12)	0			58	1.793	
	0.25			94	1.806	
	0.54*			99	1.745	

*Exposed to moisture during irradiation as a result of water leaking into the sample can.

**Poly-1, 1-dihydroperfluorobutyl acrylate.

TABLE 1.8. RADIATION-PRODUCED CHANGES IN THE PHYSICAL PROPERTIES OF PLASTICIZED NATURAL RUBBER

PLASTICIZER	IRRADIATION EXPOSURE (10^{18} nvt)	TENSILE STRENGTH (psi)	ELONGATION (%)	SHORE DUROMETER HARDNESS	SPECIFIC GRAVITY, 25/4° C	VOLUME RESISTIVITY (ohm-cm)
L.P. oil	0	1310	560	30	1.038	$> 10^{14}$
(P1S2C1)	0	1330	560	30	1.038	$> 10^{14}$
	0.25	440	97	55	1.039	10^{14}
	0.54	160	20	67	1.044	10^{14}
	1.3	Sample broken		83	1.059	10^{10}
Dioctyl	0	715	420	30	1.048	10^{14}
phthalate	0	890	460	30	1.048	10^{14}
(P 1S2C2)	0.25	330	90	52	1.054	10^{14}
	0.54	200	30	65	1.059	10^{14}
	1.3	130	10	80	1.072	10^{14}
Dioctyl	0	915	510	28	1.046	10^{14}
sebacate	0	930	540	28	1.046	10^{14}
(P 1S2C3)	0.25	260	60	57	1.049	10^{14}
	0.54	Sample broken		70	1.055	10^{14}
	1.3	140	7	86	1.067	10^{14}
Tributoxy ethyl	0	1150	440	31	1.094	10^{9}
phosphate	0	Sample slipped out of grips		31	1.094	10^{9}
(P1S2C4)	0.25	280	55	59	1.108	10^{9}
	0.54	320	27	76	1.115	10^{10}
	1.3	300	5	92	1.130	10^{10}
TP90B	0	1360	370	54	1.180	10^{5}
(P1S2C5)	0	1260	340	54	1.180	10^{5}
	0.25	700	50	78	1.181	10^{5}
	0.54	300	10	87	1.186	10^{5}
	1.3	410	3	95	1.203	10^{5}
Plasticizer	0	1220	390	40	1.110	10^{11}
"SC"	0	1240	390	40	1.110	10^{12}
(P1S2C6)	0.25	510	57	68	1.113	10^{11}
	0.54	260	22	80	1.121	10^{12}
	1.3	110	3	91	1.130	10^{10}

Chapter 2
RADIATION STABILITY OF SPECIALLY COMPOUNDED ELASTOMERS

The effect of radiation on the physical properties of a number of elastomer formulations is described in Chapter 1. In order to study the effect of variations in the recipe, special formulations of natural rubber and Neoprene W were made in an attempt to improve their radiation stability.

Almost all rubber formulations contain small amounts of compounds called "stabilizers" or "antioxidants" which protect the rubber by absorbing energy which would otherwise damage the polymer. Special formulations were made for testing the possibility that relatively large amounts of antioxidants might afford protection against ionizing radiation. Also, an attempt was made to improve the radiation stability of natural rubber by including large amounts of mineral filler in the recipe, since it had been determined (1) that certain mineral-filled plastics are much less damaged by radiation than are unfilled polymers.

The recipes containing large amounts of antioxidant and mineral filler are listed in Table 2.1. In Table 2.2, the radiation stability of the materials is compared with that of corresponding compounds which do not contain these additives. Although a slight improvement can be seen for a few properties, no over-all improvement is realized for either the recipes with large amounts of antioxidant or the recipe with a large amount of mineral filler. For some properties, the percentage change is less because of the lower initial values for the compounds with additives; however, the percentage decrease in elongation (a particularly radiation-sensitive property) is greater for all the compounds with additives.

Natural rubber is hardened by radiation, while butyl rubber is softened. It was thought that compounding the two materials would result in a mixture which would be more radiation resistant than either. Four mixtures were tried. The recipes are given in Table 2.1, and a comparison of the properties of the irradiated mixtures is made in Table 2.3. The mixtures all decrease more rapidly in tensile strength and elongation than does natural rubber (which is more stable than butyl rubber). The change in durometer hardness is less for both the 50-50 mixtures and the 25-75 mixtures than for natural rubber. This constancy in durometer hardness is believed to result from the combined effects of degradation, which softens butyl rubber, and cross-linking, which hardens natural rubber. For most applications, the constancy in hardness will not compensate for the loss in tensile strength and elongation; therefore no net improvement over natural rubber is achieved by the mixtures.

TABLE 2.1. COMPOSITION OF SPECIALLY COMPOUNDED ELASTOMERS

COMPONENTS	PARTS BY WEIGHT							
	Formula 17FBB194	Formula 17FBB196	Formula 17FBB197	Formula 17FBB198	Formula 17FBB199	Formula 17FBB200	Formula 17FBB201	Formula 16RCB1
Natural rubber	100		100	50	25	10	100	100
Neoprene W		100						
Butyl rubber				50	75	90		
Zinc oxide	5	5	5	5	5	5	5	5
Stearic acid	1	0.5	1	2	2	2	2	1
SRF black		40	70	70	70	70	70	70
ϕBNA*	1	2	1	1	1	1	1	1
Captax	0.6		0.6	0.75	0.75	0.75	0.7	
Sulfur	3		3	2.5	2	1.5	2.5	
Asbestos fiber	250							
Magnesium oxide		2						
DDM**		10						10
Accelerator		0.5						
Dibutyltin dilaurate			10					
DPG***				0.2	0.3	0.5	0.2	
Calcium silicate				10	10	10		
Butyl reclaim							60	
Lead peroxide								10
Chloranil								5
TOTAL PARTS BY WEIGHT	360.6	160.0	190.6	191.45	191.05	190.75	241.4	202

*Phenyl-β-naphthylamine.
**Dodecyl mercaptan.
***Diphenyl guanidine.

TABLE 2.2. RADIATION-PRODUCED CHANGES IN THE PHYSICAL PROPERTIES OF ELASTOMERS CONTAINING LARGE AMOUNTS OF ANTIOXIDANT AND MINERAL FILLERS

ELASTOMER	IRRADIATION EXPOSURE (10^{18} nvt)	TENSILE STRENGTH (psi)	ELONGATION (%)	SHORE DUROMETER HARDNESS	SHORE ELASTICITY	COMPRESSION SET		SPECIFIC GRAVITY, 25/4°C	CHANGE IN WEIGHT (%)	VOLUME RESISTIVITY (ohm-cm)	DIELECTRIC STRENGTH (volts/mil)
						Strain Immediately After Application of Load (%)	Final Deformation (%)				
Neoprene W	0	2900	450	78	85	31	9	1.418		10^{11}	300
(32A44)	0.25	1200	50	90	45	8	2	1.423		10^{8}	300
	0.60	900	20	98		3	2	1.444	0.10	10^{8}	200
Neoprene W with	0	1500	440	79	72	26	60	1.356		10^{11}	300
dodecyl mercaptan	0.25	800	40	84	40			1.363			360
(17FBB196)	0.60	800	10	92	25	3	3.4	1.379	0.28	10^{12}	380
Natural rubber	0	2600	420	61	100	30	13.0	1.186		10^{10}	200
(32A43)	0.25	2000	250	72	70	18	7.1	1.187		10^{10}	200
	0.60	1300	110	80	50	14	4.5	1.192	−0.03	10^{11}	150
Natural rubber with	0	2100	280	65	83	25	6	1.22		10^{11}	120
dodecyl mercaptan	0.25	1400	100	75	60			1.22			120
(16RCB1)	0.60	350	10	86	20	12	1.6	1.23	0.03	10^{11}	
Natural rubber with	0	2900	220	68	75	22	11	1.19		10^{12}	115
dibutyltin	0.25	1300	110	76	40			1.19			115
dilaurate	0.60	750	40	82	30	6	3	1.19	−0.16	10^{12}	115
(17FBB197)											
Natural rubber with	0	1100	90	83	30	15	10	1.72		10^{11}	>400
asbestos filler	0.25	1000	40	94	25			1.72			>400
(17FBB194)	0.60	1200	10	97		4	1.1	1.73	0.02	$>10^{12}$	>400

TABLE 2.3. RADIATION-PRODUCED CHANGES IN THE PHYSICAL PROPERTIES OF ELASTOMERS COMPOUNDED WITH MIXTURES OF NATURAL RUBBER AND BUTYL RUBBER

ELASTOMER	IRRADIATION EXPOSURE (10^{18} nvt)	TENSILE STRENGTH (psi)	ELONGATION (%)	SHORE DUROMETER HARDNESS	SHORE ELASTICITY	COMPRESSION SET		SPECIFIC GRAVITY, 25/4°C	CHANGE IN WEIGHT (%)	VOLUME RESISTIVITY (ohm-cm)	DIELECTRIC STRENGTH (volts/mil)
						Strain Immediately After Application of Load (%)	Final Deformation (%)				
Natural rubber–butyl	0	2100	315	69	77	30	10	1.223		10^{10}	130
rubber, 50:50	0.25	800	65	72	50			1.218		10^{10}	190
(17FBB198)	0.60	400	40	74	35	20	19	1.208	–0.14	10^{10}	280
Natural rubber–butyl	0	1700	230	69	83	28	6	1.232		10^{10}	140
rubber, 25:75	0.25	400	70	64	30			1.223		10^{10}	120
(17FBB199)	0.60	170	30	60	25	Too tarry to test		1.121	0.18	10^{10}	120
Natural rubber–butyl	0	1600	205	70	80	25	5	1.235		10^{12}	140
rubber, 10:90	0.25	200	110	52	30			1.235		10^{13}	110
(17FBB200)	0.60	Tarry				Too tarry to test		1.10	0.05		
Natural rubber-butyl	0	2000	375	63	90	25	8	1.175		10^{8}	150
reclaim, 100:60	0.25	900	115	71	60			1.175		10^{9}	180
(17FBB201)	0.60	500	30	79	35	14	3.8	1.175	0.03	10^{9}	220

Chapter 3
RADIATION STABILITY OF COMMERCIAL PLASTICS

The section on Radiation Stability of Commercial Plastics covers the work which has been done on plastics since ORNL-928 (*1*) was published. Radiation-produced changes in some of the physical properties of the new materials are shown in Figs. 3.1 to 3.10 (see also, Charts 1 to 14). The procedures employed in making irradiations and in making physical-properties tests are the same as those described previously.

Polystyrene has excellent radiation stability, since it shows no change in hardness or other physical properties until after long exposure; however, polystyrene is a relatively hard and brittle material and is unsuited for many applications. Soft materials like polyethylene (which is useful for many applications for which polystyrene is too hard) are hardened by radiation. Royalite and Pliotuf (Figs. 3.5 and 3.3), plastics which are mixtures or alloys of polystyrene and styrene-butadiene copolymer, are softer and more flexible than is unmodified polystyrene. The radiation stability of Royalite and Pliotuf was studied in order to see whether these materials would show better resistance to hardening, due to their polystyrene content, than does polyethylene.

Like polyethylene, Royalite and Pliotuf were found to harden with irradiation. For no irradiation time is either Royalite or Pliotuf softer than polyethylene. In this instance, soft, polystyrene-containing materials show no better resistance to hardening than does polyethylene.

The hardening of polyethylene is believed to result from cross-linking (*4*). Another process competitive with cross-linking is cleavage of C – C bonds. That both butyl rubber (Fig. 1.3) and methyl methacrylate (*1*) show a lower order of radiation stability than does polyethylene is believed to be due to the low resistance to chain cleavage at quaternary carbon atoms which are present in these materials. Polyalphamethyl styrene (Fig. 3.4) has a structure similar to that of polystyrene except that methyl groups are substituted for part of the hydrogen atoms in polystyrene to give quaternary carbon atoms. The result is greatly decreased radiation stability (compared with polystyrene) for the methyl-substituted polystyrene, and this is strong evidence for poor radiation stability of the quaternary carbon atom.

Chain cleavage is believed to occur in polyvinyl butyral and in polyvinyl formal (Figs. 3.8 and 3.9) to a greater extent than in polyethylene. The predominant changes in these materials are an initial softening that is followed by embrittlement. The decreased resistance to chain cleavage as compared with the resistance of polyethylene is accounted for by the C – O linkages. Apparently the presence of the C – O linkages in a group which bridges the main polymer chain (as in polyvinyl butyral and polyvinyl formal) is as effective in decreasing resistance to chain cleavage as are the C – O linkages that occur in the main chain [as in polyallyl diglycol carbonate (*1*) and Vulcollan elastomer, Table 1.5]. Polyallyl diglycol carbonate softens at first and then becomes embrittled in a manner similar to that of polyvinyl butyral and polyvinyl formal. Vulcollan does not contain so high a proportion of C – O linkages, and initially it hardens like most other elastomers; however, after a long exposure it becomes brittle and crumbles. Selectron polyester also contains a relatively small number of C – O linkages. In this material, cross-linking is the predominant process, as is shown by hardening.

Mylar polyester film (Fig. 3.1) contains C–O linkages and, in addition, phenyl groups are connected directly as part of the main chain as in the case of phenol formaldehyde polymer (*1*). The embrittlement of Mylar indicates low stability against chain cleavage.

Triallyl cyanurate polymer (Chart 2) has a three-dimensional type of structure rather than the linear-type structure of most of the polymers studied. Some specimens of this material showed very good stability; others showed cracking. It is thought that internal strains were present in the sheets from which the faulty specimens were cut. Further study is indicated.

The hardening of the silicone-glass laminate (Fig. 3.2) indicates that cross-linking is the predominant radiation-produced process. Like most other elastomers, Silastic (Fig. 1.7) also shows hardening. Si–O linkages would be expected to be relatively stable to chain cleavage, since the bonding energy is greater than that for C–C linkages (*8*).

Chlorine-containing materials were observed previously to blister and soften, and the blisters were filled with HCl. Pliovic (Fig. 3.7) and Geon (Fig. 3.6), which are polyvinyl chloride-type plastics, also show blistering. After initial softening, these polymers harden (probably because of cross-linking).

Orlon, Dacron, and Nylon polymers were irradiated in the form of filter cloth (Fig. 3.10). Dacron cloth is embrittled much like Mylar film (Fig. 3.1), which has a similar chemical structure. The Orlon cloth and the Nylon cloth were hardened and shrunken, and the Orlon cloth was shrunken considerably more than the Nylon cloth. The hardening of Nylon sheet plastic was studied previously (*1*).

It was recently discovered (*9*) that Orlon fabric, when heated to 225°C and held there for approximately 3 hr, is transformed into a new material which shows very good heat resistance. This material resembles charred cloth but, unlike other types of charred cloth, shows considerable strength. (One type of weave has a breaking load of about 40 lb for a 1-in.-wide strip of fabric.) The chemical structure of this material has not yet been determined. After an irradiation dose of 10^{19} nvt, the heat-treated Orlon fabric showed little change in breaking load. A preliminary test shows that the dynamic elastic modulus is increased, although the material still retains much flexibility.

Large exposures are necessary for measuring the radiation stability of the more resistant plastics. Although high-flux facilities for making such exposures have only recently become available, some increase in exposure was obtained in the ORNL Graphite Reactor by wrapping the samples in cadmium (see Chapter 4). The results of these exposures – from three- to eightfold greater than exposures previously reported (*1*) – are given in Table 3.1. Some of the more radiation-resistant plastics show only slight damage at 3×10^{10} rep. Greater exposures are planned in a higher flux reactor.

TABLE 3.1. CHANGES IN PLASTICS[a] PRODUCED BY REACTOR IRRADIATION FOR 1.3×10^{19} nvt IN CADMIUM

(About 3×10^{10} rep)

PROPERTY	POLYSTYRENE	POLYVINYL CARBAZOLE	ANILINE FORMALDEHYDE	KARBATE (Phenolic-Bonded Graphite)	FABRIC-ASBESTOS PHENOLIC
Tensile strength, lb/in.^{2}					
b	6000	2000			
c	6000	2000			
Impact strength, ft-lb/in. of notch					
b			0.27	0.27	3.9
c			0.27	0.27	3.6
Elongation, %					
b	1.4	0.3			
c	1.4	0.3			
Elastic modulus					
b	4.8×10^5	6×10^5			
c	4.8×10^5	6×10^5			
Specific gravity, 25/4°C					
b	1.046	1.19	1.205	1.70	1.70
c	1.076	1.19	1.205	1.70	1.64
Change in weight, %					
b	0		0	0	0
c	1.7		0.50	0.25	−3.3
Rockwell hardness					
α scale					
b	105	113	107	90 to 110	121
c	96 to 102	113	106	90 to 110	106
R scale					
b	122	125	128	90 to 110	120
c	116 to 120	125	124	90 to 110	112

[a] Formulas and compositions listed (*1*).
[b] Not irradiated.
[c] Irradiated for 1.3×10^{19} nvt.

CHART 1. MINERAL-FILLED MELAMINE

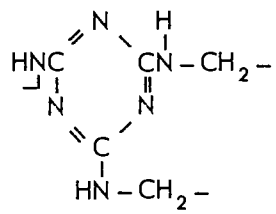
Classification: Amino resin

Trade Name: Melmac 592

Company: Americal Cyanamid Co., Plastics & Resins Division, New York, New York

Resin: Melamine formaldehyde

Chemical Formula:



Filler: Mineral

Description: Opaque, brown; darkens upon irradiation

Thickness: 0.11 to 0.13 in.

PROPERTIES OF IRRADIATED MATERIAL

EXPOSURE (10^{18} nvt)	SHEAR STRENGTH (psi)	ROCKWELL HARDNESS		SPECIFIC GRAVITY, 25/4°C	VOLUME RESISTIVITY (ohm-cm)
		R Scale	α Scale		
0	7000	123	125	1.73	10^{12}
15	4000	120	121	1.69	10^{12}

CHART 2. TRIALLYL CYANURATE POLYMER

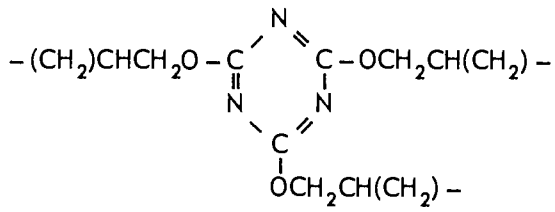
Classification: Allyl polymer

Trade Name: PDL-7-669

Company: American Cyanamid Co., New York, New York

Resin: Triallyl cyanurate

Chemical Formula:



Description: Transparent

Thickness: $\frac{1}{4}$ in.

PROPERTIES OF IRRADIATED MATERIAL

EXPOSURE (10^{18} nvt)	SHEAR STRENGTH (psi)	ROCKWELL HARDNESS		VOLUME RESISTIVITY (ohm-cm)
		R Scale	α Scale	
0	2000	125	111	10^{11}
10	2000	125	111 to 113	10^{11}

CHART 3. ARALDITE, TYPE B

Classification: Epoxy resin

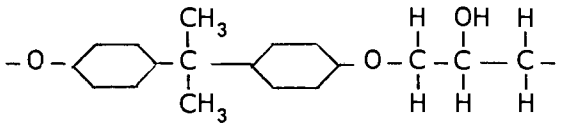
Trade Name: Araldite casting resin, type B

Company: Ciba Company, Inc.

Resin: Polymer of bisphenol A (2, 2-parahydroxyphenylpropane) and epichlorohydrin

Filler: None

Chemical Formula:



Description: Opaque

Thickness: 0.14 to 0.18 in.

PROPERTIES OF IRRADIATED MATERIAL

EXPOSURE (10^{18} nvt)	SHEAR STRENGTH (psi)	ROCKWELL HARDNESS	
		R Scale	α Scale
0	8000	125	109
3.6	6000	125	111

CHART 4. STYRON 637 AND STYRON 671

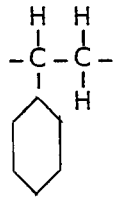
Classification: Styrene polymers

Trade Names: Styron 637, Styron 671

Company: The Dow Chemical Co., Midland, Michigan

Resin: Polystyrene

Chemical Formula:



Description: Transparent, colorless; Styron 637 is a special grade of polystyrene designed to have improved light stability; Styron 671 has high heat resistance

Thickness: 0.074 to 0.083 in.

PROPERTIES OF IRRADIATED MATERIAL

EXPOSURE (10^{18} nvt)	SHEAR STRENGTH (psi)	ROCKWELL HARDNESS		SPECIFIC GRAVITY, 25/4°C	INCREASE IN WEIGHT (%)	VOLUME RESISTIVITY (ohm-cm)
		R Scale	α Scale			
0	6000	122	105	1.050		6×10^{14}
15	6000	122	105	1.074	0.91	6×10^{14}

CHART 5. MYLAR FILM

Classification: Polyester

Trade Name: Mylar film

Company: E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Delaware

Resin: Polyethylene terephthalate

Chemical Formula:

Description: Transparent, colorless; darkens upon irradiation

Thickness: 0.002 in.

Speed of Tensile Testing: Mean rate of stressing, 200 lb/in.^{2}·sec

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{15}
0.7	10^{15}
1.2	10^{12}

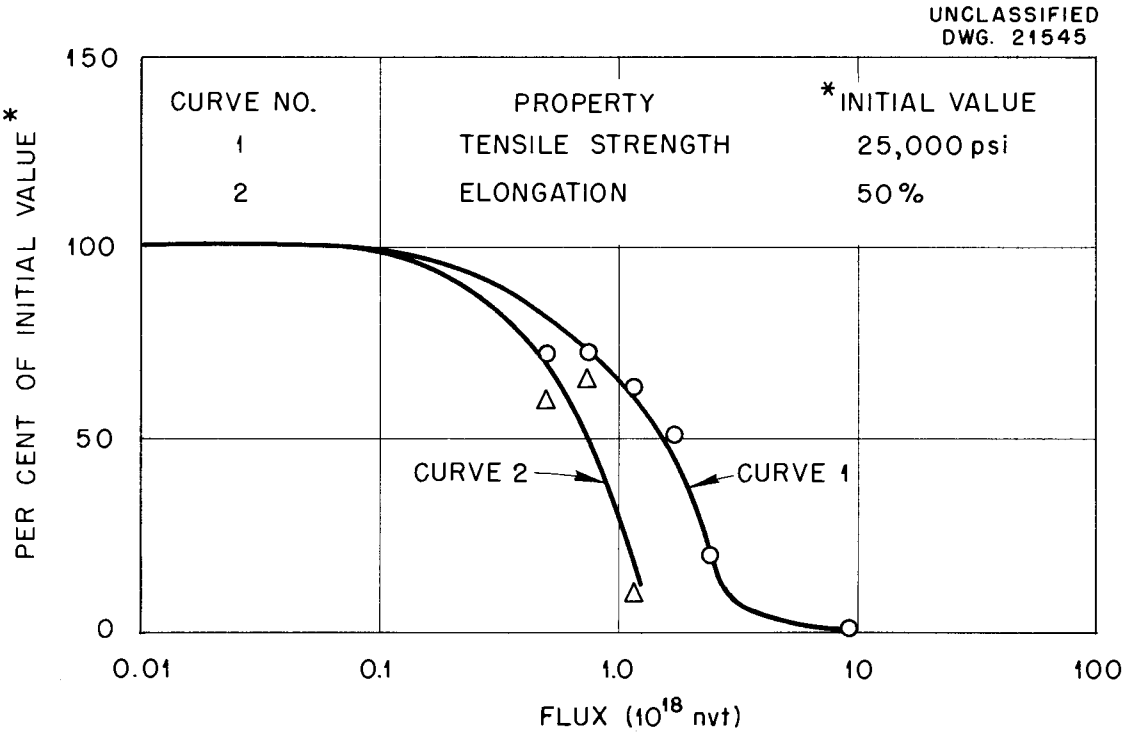


Fig. 3.1. Physical Properties of Irradiated Mylar Film.

CHART 6. SILICONE-VARNISHED GLASS LAMINATE AND SILICONE GLASS TAPE

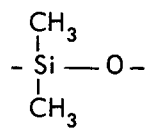
Classification: Silicone

Trade Name: Dow Corning silicone-varnished glass, Dow Corning silicone glass tape

Company: Dow Corning Corp., Midland, Michigan

Resin: Silicone

Chemical Formula:



Filler: Glass cloth

Description: Translucent, light brown; darkens upon irradiation

Thickness: Laminate, 0.063 to 0.066 in.
Tape, 0.016 to 0.017 in.

Speed of Tensile Testing of Tape: Mean rate of stressing, 100 lb/in.^{2}·sec

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{14}
1	10^{7}

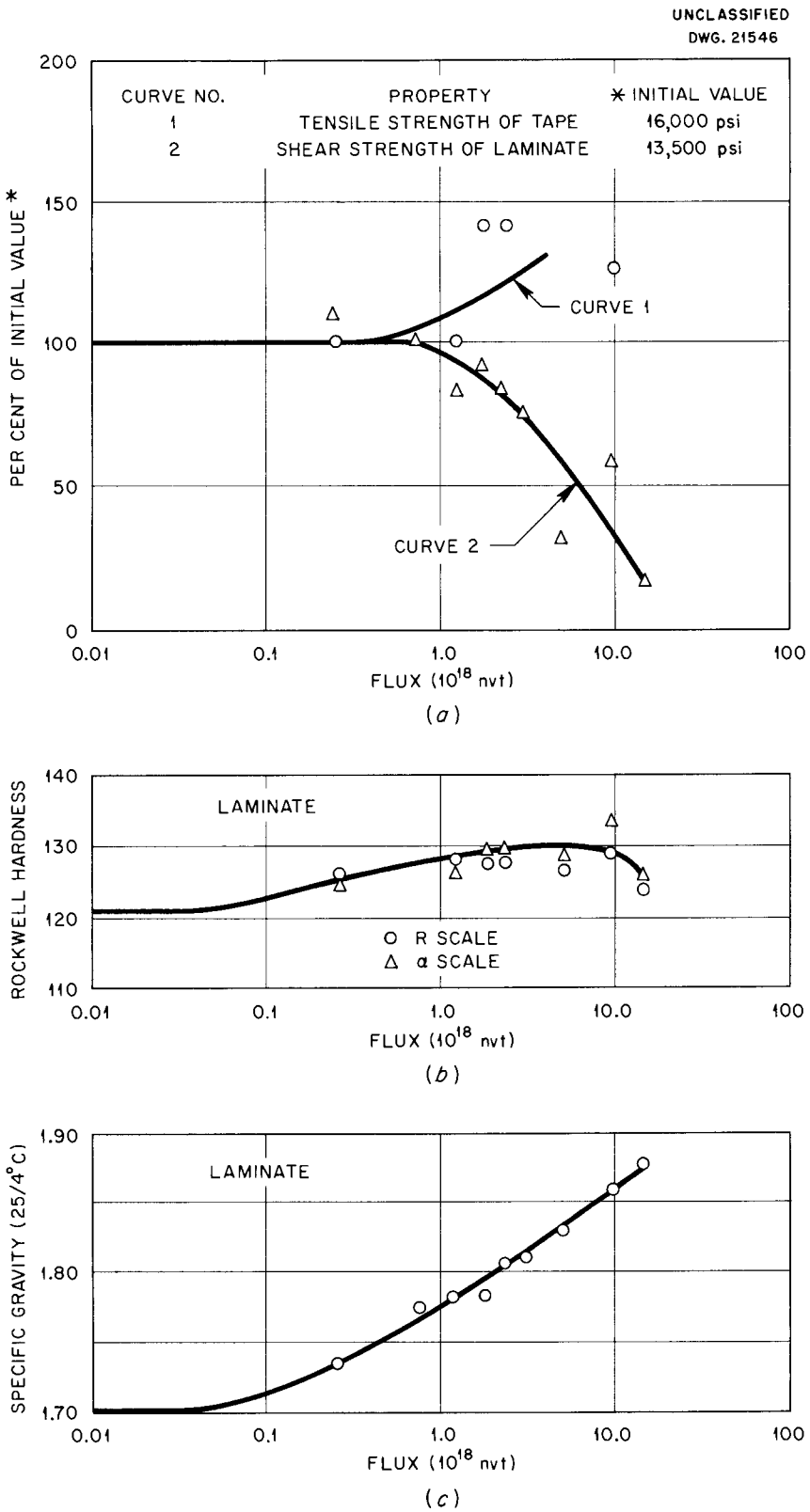


Fig. 3.2. Physical Properties of Irradiated Silicone-Varnished Glass Laminate and Silicone Glass Tape.

CHART 7. PLIOTUF

Classification: Styrene copolymer

Trade Name: Pliotuf

Company: Goodyear Tire & Rubber Co., Akron, Ohio

Resin: Blend of high-styrene–butadiene copolymer with rubber

Description: Opaque, white

Thickness: 0.075 to 0.082 in.

Speed of Tensile Testing: Mean rate of straining, (1.1 to 2) $\times 10^{-4}$ units/sec
Mean rate of stressing, 30 to 60 lb/in.^{2}·sec

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{14}
0.5	10^{8}

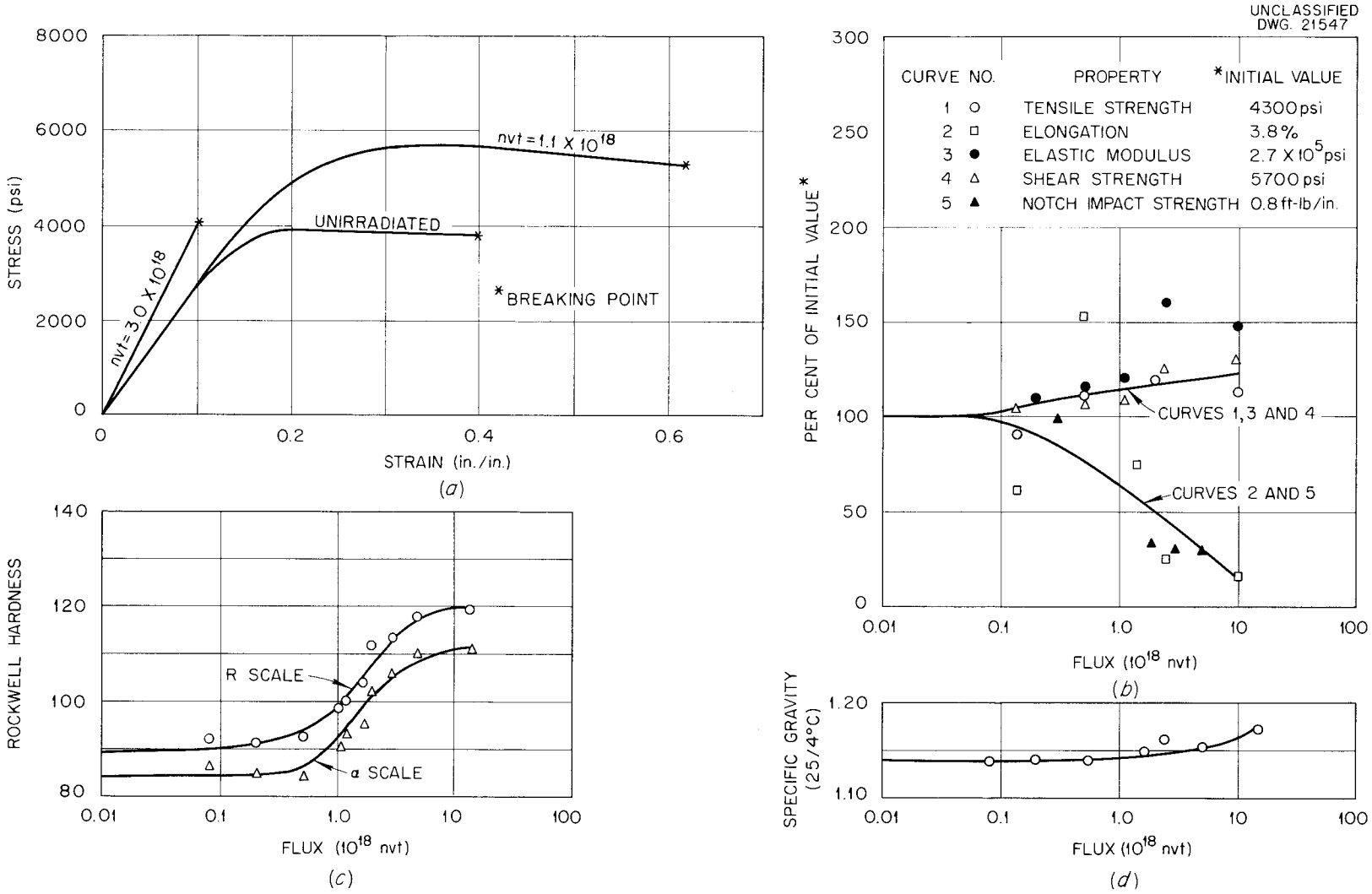


Fig. 3.3. Physical Properties of Irradiated Pliotuf.

CHART 8. POLYALPHAMETHYL STYRENE

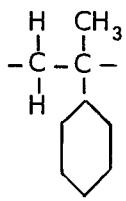
Classification: Styrene polymer

Trade Name: Experimental plastic Q-817

Company: The Dow Chemical Co., Midland, Michigan

Resin: Polyalphamethyl styrene

Chemical Formula:



Filler: None

Description: Transparent, colorless; darkens upon irradiation

Thickness: 0.165 to 0.170 in.

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{15}
1	5×10^{9}

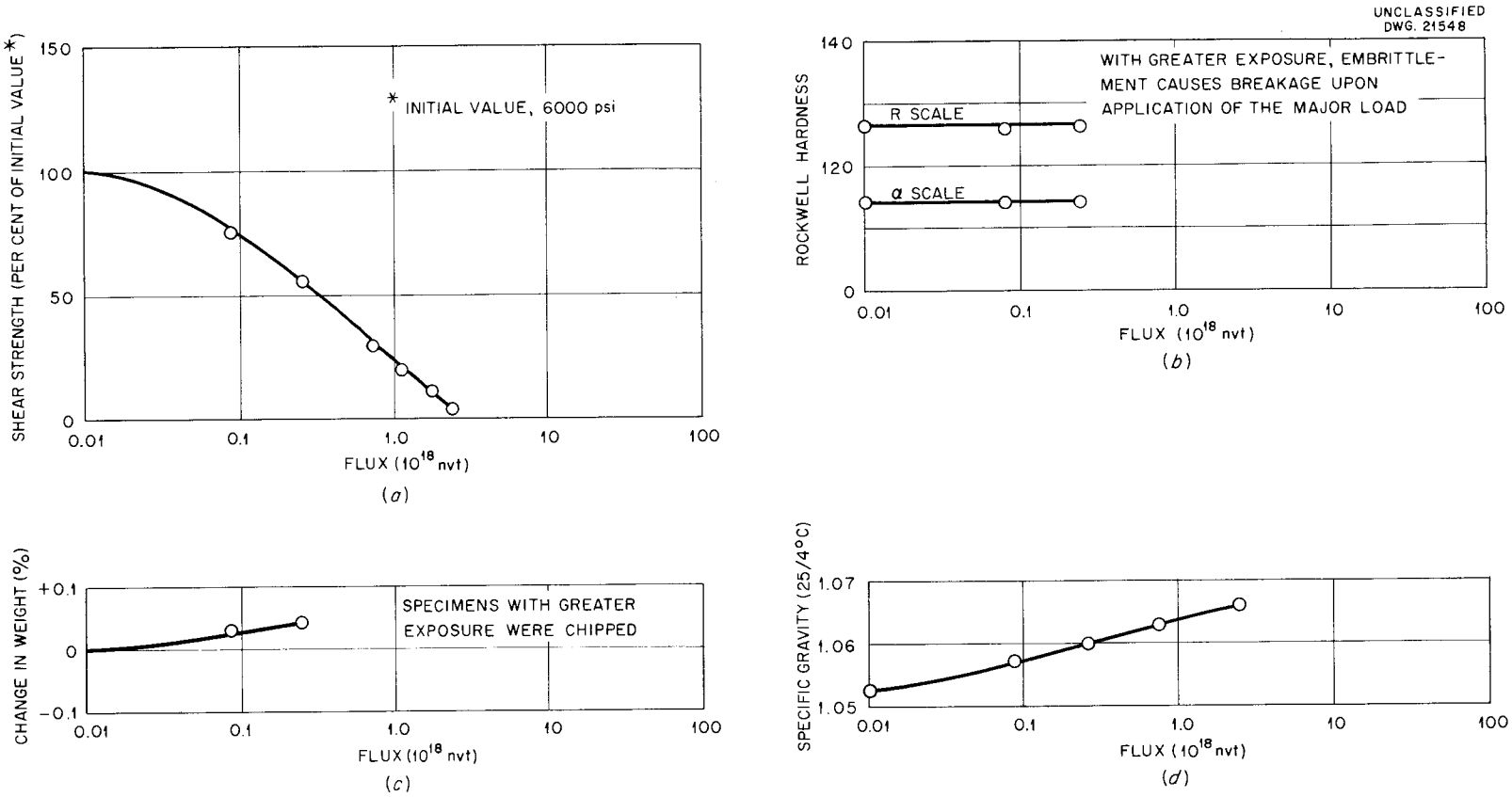


Fig. 3.4. Physical Properties of Irradiated Polyalphamethyl Styrene.

CHART 9. ROYALITE

Classification: Styrene copolymer

Trade Name: Royalite

Company: U.S. Rubber Co., Chicago, Illinois

Resin: Styrene-acrylonitrile copolymer combined with butadiene-1,3-acrylonitrile copolymer

Filler: None

Description: Opaque, a blue-colored sheet laminated to a grey-colored sheet

Thickness: 0.060 to 0.062 in.

Speed of Tensile Testing: Mean rate of straining, (1.5 to 2.5) $\times 10^{-4}$ units/sec
Mean rate of stressing, 30 to 70 lb/in.^{2}·sec

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{12}
10	10^{10}

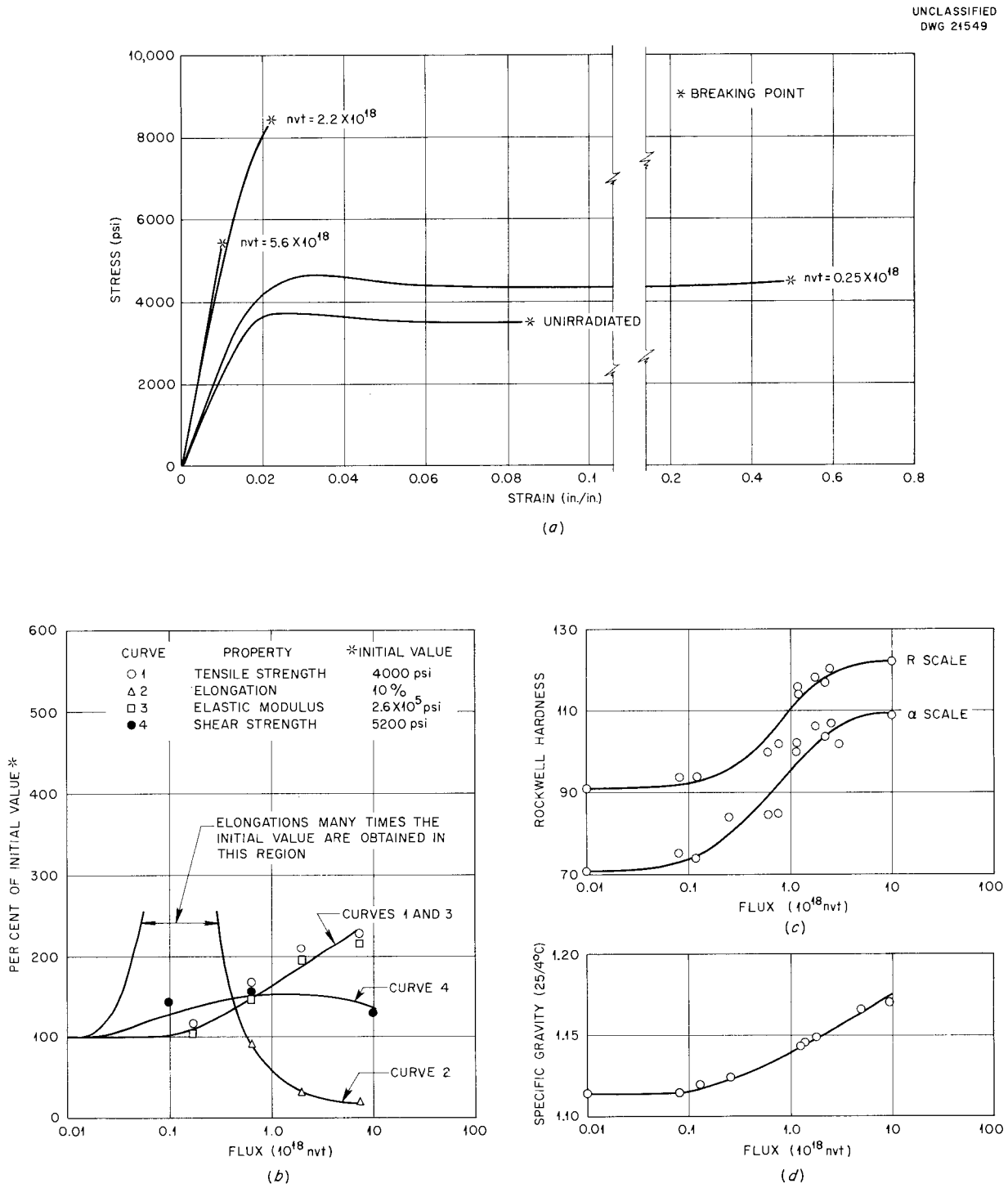


Fig. 3.5. Physical Properties of Irradiated Royalite.

CHART 10. GEON

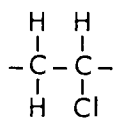
Classification: Vinyl polymer

Trade Name: Geon 2046

Company: B. F. Goodrich Chemical Co., Cleveland, Ohio

Resin: Polyvinyl chloride

Chemical Formula:



Description: Opaque

Thickness: 0.08 in.

Speed of Tensile Testing: 6 in./min

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{13}
3	10^{6}

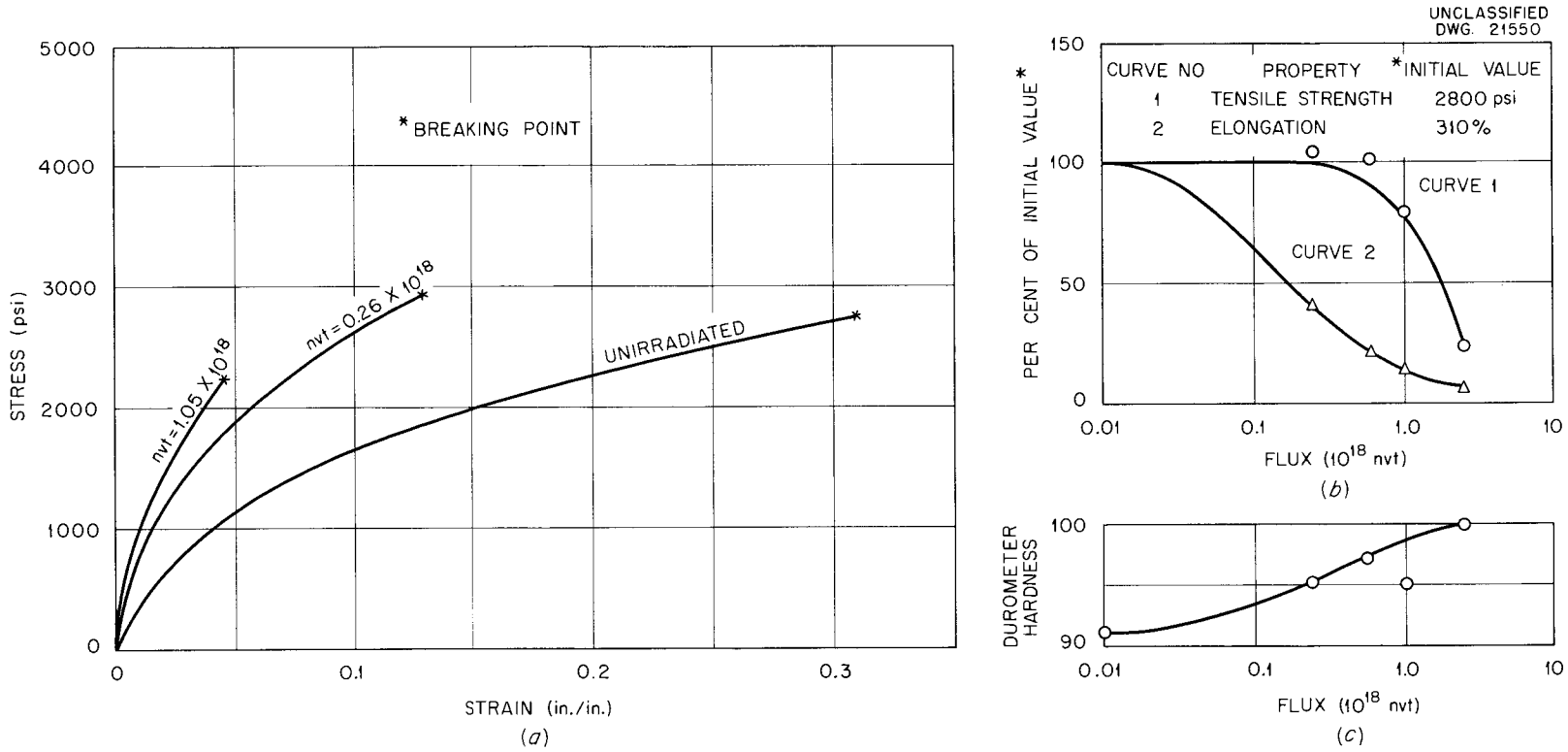


Fig. 3.6. Physical Properties of Irradiated Geon 2046.

CHART 11. PLIOVIC

Classification: Vinyl copolymer

Trade Name: Pliovic

Company: Goodyear Tire & Rubber Co., Akron, Ohio

Resin: Internally plasticized vinyl chloride copolymer

Filler: None

Description: Translucent, amber colored; darkens upon irradiation

Thickness: 0.08 to 0.10 in.

Speed of Tensile Testing: Mean rate of straining, $(1.2 \text{ to } 2.5) \times 10^{-4}$ units/sec
Mean rate of stressing, 40 to 60 lb/in.^{2}·sec

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{14}
0.5	10^{7}

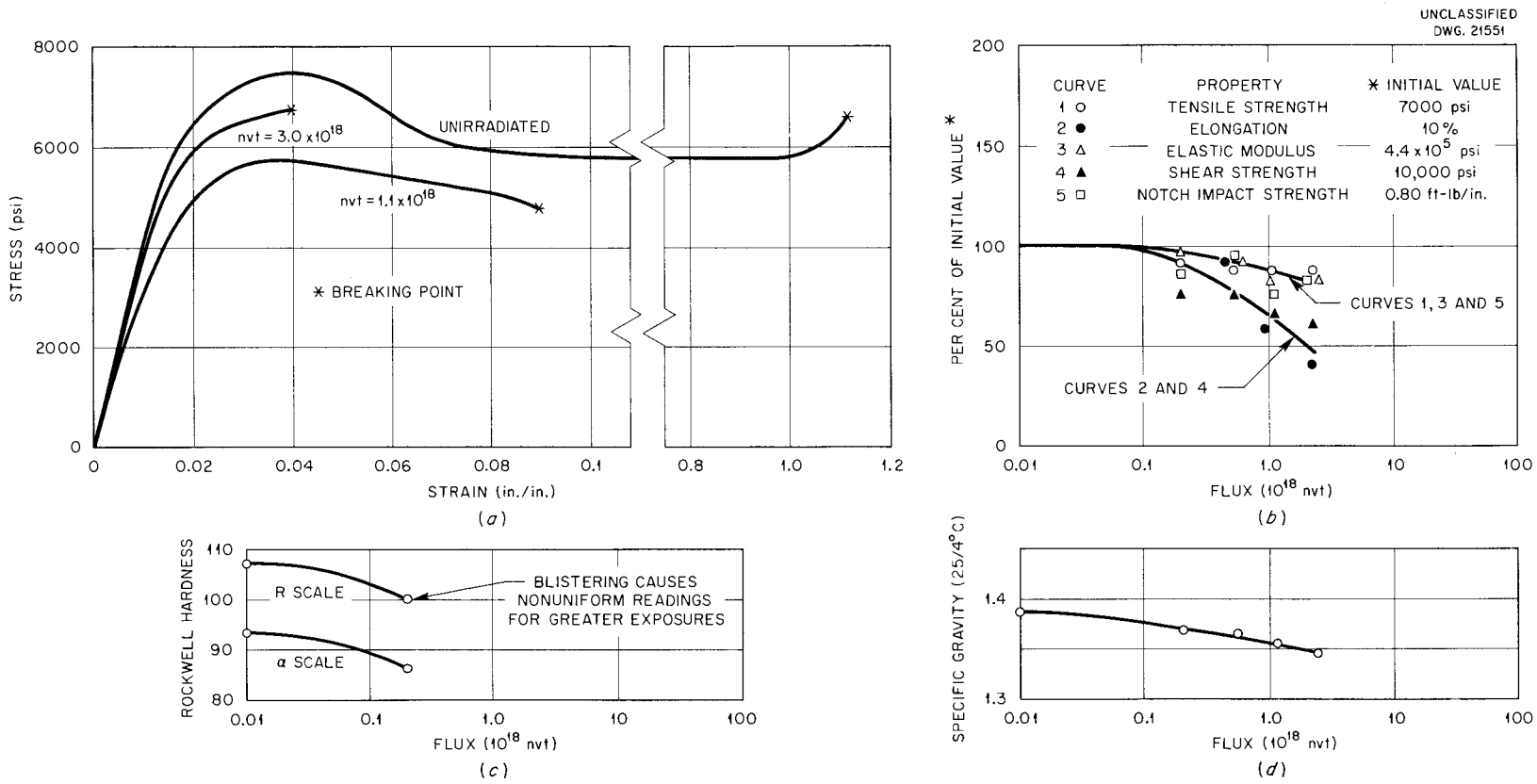


Fig. 3.7. Physical Properties of Irradiated Pliovic.

CHART 12. POLYVINYL BUTYRAL

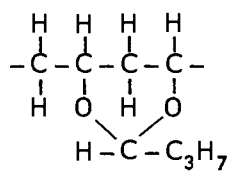
Classification: Vinyl polymer

Trade Name: Butacite film

Company: E. I. du Pont de Nemours & Co. (Inc.), Wilmington, Delaware

Resin: Polyvinyl butyral

Chemical Formula:



Description: Translucent, white; darkens upon irradiation

Thickness: 0.016 to 0.017 in.

Speed of Tensile Testing: 5 in./min

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{10}
1	10^{10}

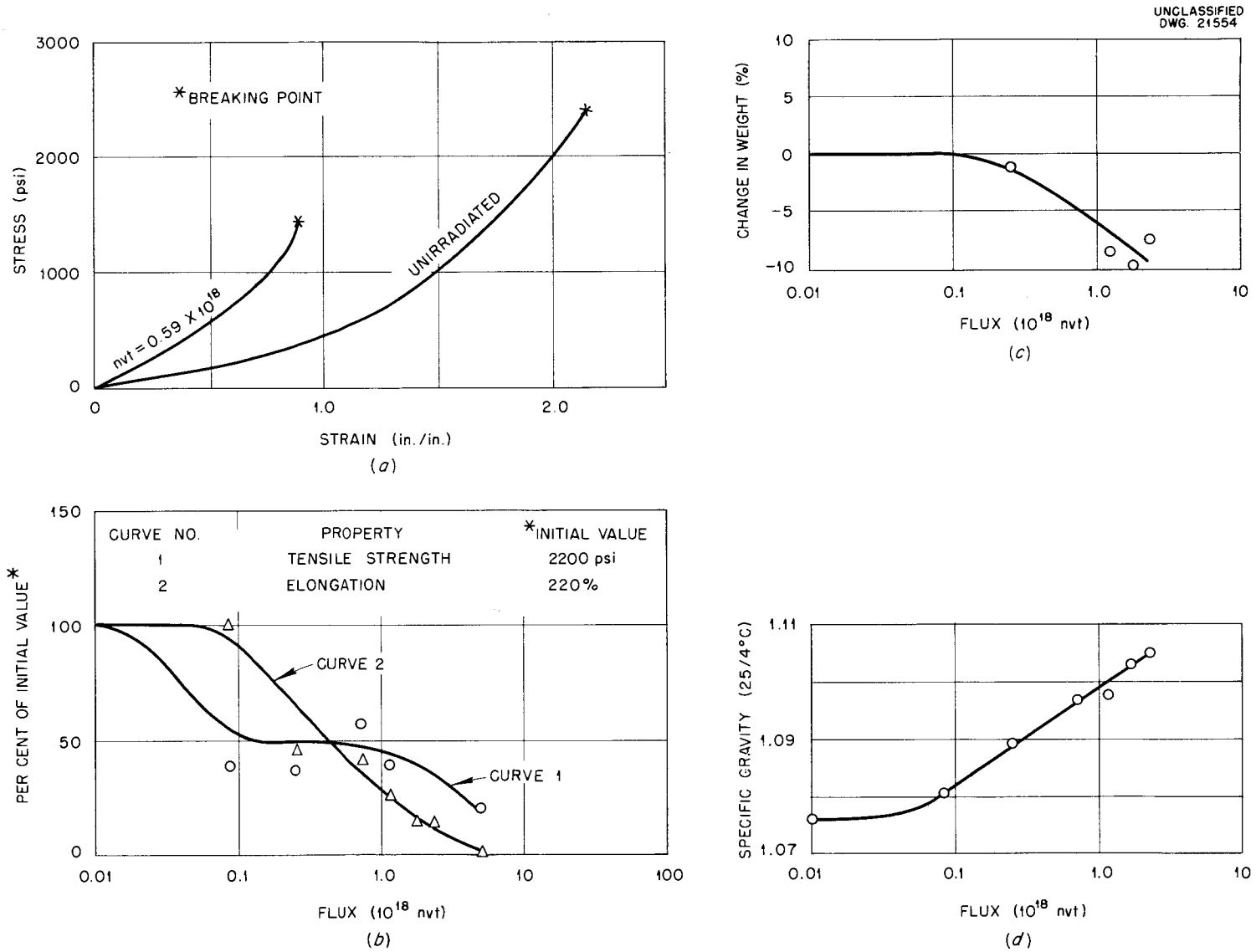


Fig. 3.8. Physical Properties of Irradiated Polyvinyl Butyral.

CHART 13. POLYVINYL FORMAL

Classification: Vinyl polymer

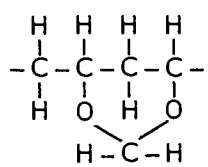
Trade Name: Formvar

Company: Shawinigan Products Corp., New York, New York

Composition: Formvar 7/90 S, 100 parts
Dioctylphthalate, 10 parts
DS207 (dibasic lead stearate), 0.5 part

Resin: Polyvinyl formal

Chemical Formula:



Description: Translucent, light brown

Thickness: 0.0045 to 0.0060 in.

Speed of Tensile Testing: Mean rate of straining, (1.5 to 3.0) $\times 10^{-4}$ units/sec
Mean rate of stressing, 20 to 60 lb/in.^{2}·sec

Exposure (10^{18} nvt)	Volume Resistivity (ohm-cm)
0	10^{14}
2	10^{14}

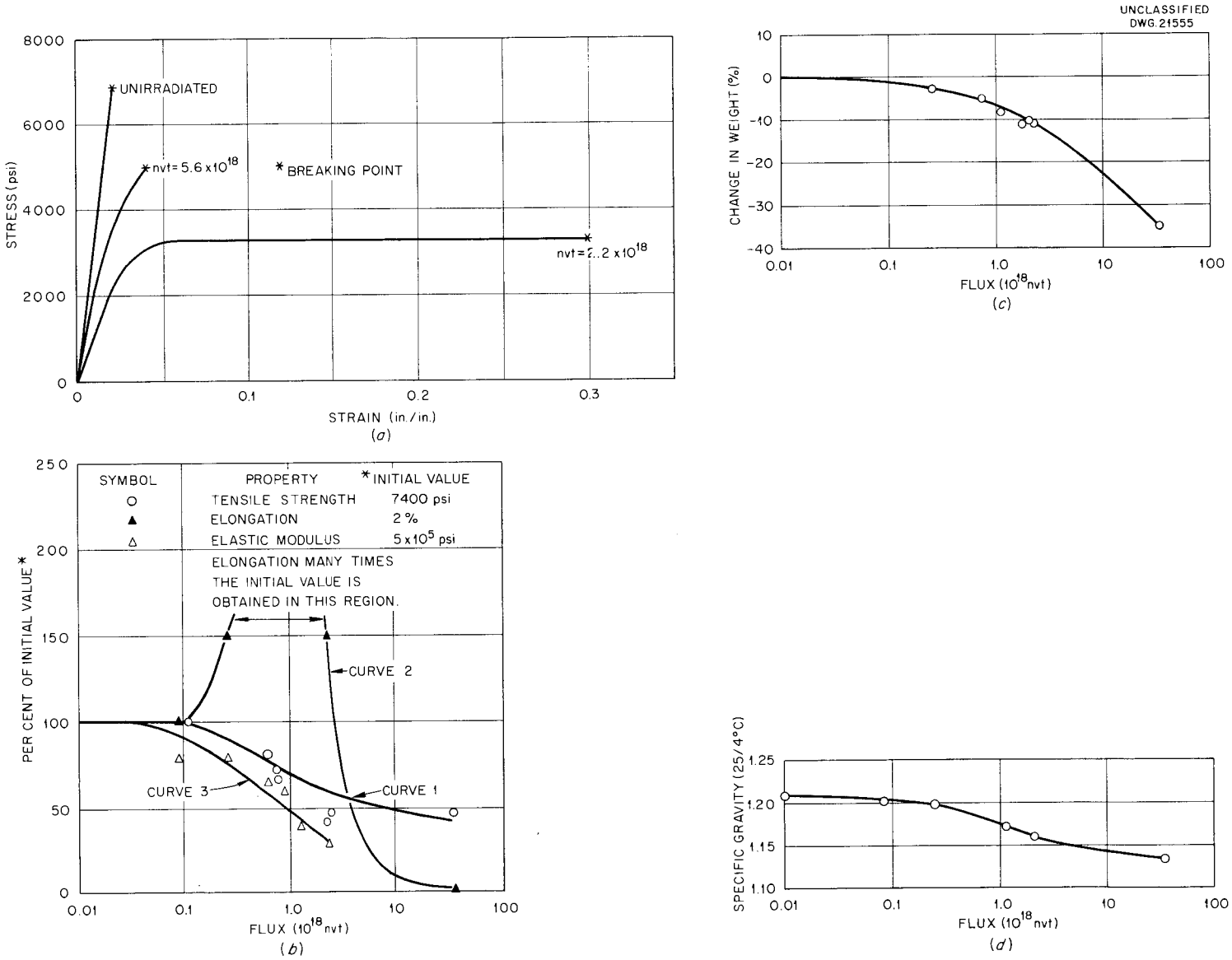
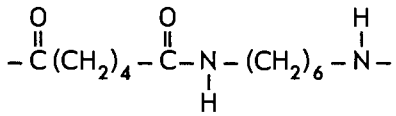
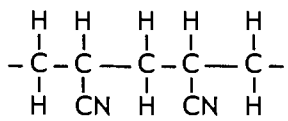


Fig. 3.9. Physical Properties of Irradiated Polyvinyl Formal.

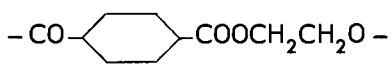
CHART 14. CHEMICAL FORMULAS OF FILTER CLOTHS



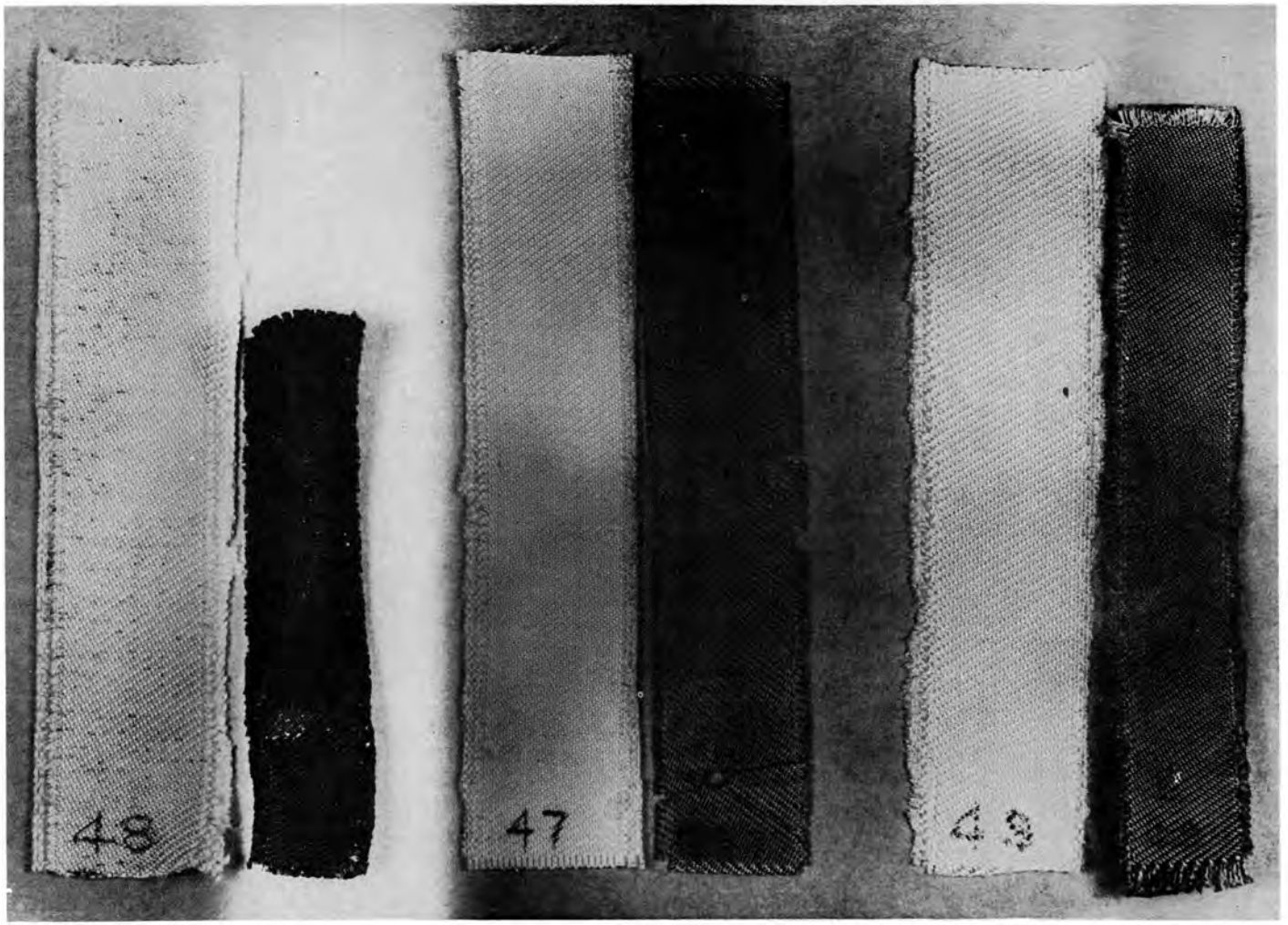
Nylon



Orlon



Dacron



UNIRRADIATED IRRADIATED UNIRRADIATED IRRADIATED UNIRRADIATED IRRADIATED

Orlon Dacron Nylon

Fig. 3.10. Filter Cloth Exposed to a Flux of 10^{19} nvt.

Chapter 4

DAMAGE BY RADIATION OTHER THAN REACTOR RADIATION

Most of the information on the radiation stability of polymers was obtained by using reactor radiation. However, it is important to know whether the data can be extrapolated to other kinds of radiation. Since radiation damage to organic solids results from ionization, it is to be expected that all types of ionizing radiation will cause similar damage and that the extent of the damage will be nearly proportional to the amount of energy absorbed.

Gamma radiation interacts to produce electrons, which are ionizing particles. Fast neutrons are slowed by scattering, and in organic materials, the energy released is transferred primarily to hydrogen nuclei (because of their large stopping power), and protons are formed which cause ionization in much the same manner as do the electrons from the gamma radiation. In organic materials which are damaged by ionizing radiation, damage due to displaced atoms is masked by damage from ionization. Ionization damages the organic compounds by breaking chemical bonds.

Thermal neutrons do appreciable damage to only materials which contain elements with high thermal neutron cross sections. The thermal neutron-produced damage is due both to ionizing radiation (to gammas and betas emitted in the absorption process) and to the recoil of the atoms which emit radiation.

In Tables 4.1 through 4.4, the changes produced by other types of radiation are compared with changes produced in hole 19 of the ORNL Graphite Reactor (at a power level of about 3600 kw, the energy absorbed from both fast-neutron and gamma radiation by polyethylene in hole 19 is 3.5×10^6 rep/hr). The other types of radiation employed were reactor radiation with the gamma component increased eightfold and the fast-neutron component unchanged (1.0×10^7 rep/hr), radiation from a Co^{60} source at 10^4, 10^5, and 10^6 rep/hr, and radiation from a Au^{198} source (log mean level of 2×10^4 rep/hr).

The method used for calculating the intensity of the reactor radiation has been described (*1*). Energy absorption from both fast neutron and gamma radiation is taken into account. The intensity of radiation from the Au^{198} and Co^{60} sources was measured with ionization chambers. The calibration of the ion chambers was checked at about 10^4 rep/hr by comparison with Victoreen roentgen meters. At the higher intensities, the ion chamber was checked for saturation by varying the voltage across the electrodes. There was no voltage dependence for the current.

REACTOR EXPOSURE WITH GAMMA INTENSITY INCREASED WITH CADMIUM

If test specimens are wrapped in cadmium during exposure in the reactor, the gamma flux is increased by the $Cd^{113}(n,\gamma)Cd^{114}$ reaction over that normally present. If it is assumed that all damage by reactor radiation results from fast-neutron and gamma radiation and that the damage by each is proportional to the energy absorbed by the sample, then the equivalent damage (or energy absorbed) is

$$(N + G_1)a = (N + G_2)b ,$$

and the ratio of the exposure (in nvt) without cadmium to the exposure within a cadmium enclosure that produces the same change is

$$\frac{a}{b} = \frac{N + CG_1}{N + G_1} ,$$

where

N = energy absorbed from fast neutrons,
G_1 = energy absorbed from gammas without cadmium,
G_2 = energy absorbed from gammas with cadmium ($G_2 = CG_1$),
a = exposure (nvt) for a given change without cadmium,
b = exposure (nvt) for the same change with cadmium,
C = G_2/G_1.

Now by letting

$$y = \frac{a}{b} = \frac{\text{nvt}_0}{\text{nvt}_{Cd}}$$

and

$$x = \frac{N}{G_1} ,$$

then

$$y = \frac{x + C}{x + 1} . \quad (1)$$

TABLE 4.1. INCREASE IN EFFECTIVENESS OF EXPOSURE OBTAINED WITH CADMIUM

MATERIAL	PROPERTY CHOSEN FOR STUDY	BEFORE IRRADIATION	AFTER IRRADIATION	EXPOSURE WITH Cd (10^{18} nvt)	EXPOSURE WITHOUT Cd TO PRODUCE EQUIVALENT CHANGE (10^{18} nvt)	EXPOSURE RATIO WITHOUT Cd / WITH Cd
Plastics						
1. Methyl methacrylate polymer	Tensile strength, psi	8,000	3000 to 5000	0.018	0.043 to 0.049	2.4 to 2.7
	Elongation, %	2 to 5	0.9 to 1.4	0.018	0.03	2
2. Monofluorotrichloroethylene	Impact strength, ft-lb/in. of notch	1.7	0.4 to 0.8	0.018	0.06 to 0.07	3 to 4
3. Teflon	Specific gravity, 25/4°C	2.17	2.20	0.018	0.07	4
4. Polyvinyl chloride (Saran B-115)	Shear strength, psi	2,900	1600	0.13	0.22	1.7
	Rockwell hardness	R 76 α 20	R 25 α −90	0.13	0.22	1.7
5. Polyvinyl chloride acetate	Tensile strength, psi	10,000	7500 to 7600	0.23	0.39	1.7
	Rockwell hardness	R 122 α 104	R 111 α 91	0.23	0.39	1.7
6. Phenol formaldehyde resin (no filler)	Impact strength, ft-lb/in. of notch	0.53	0.24 to 0.27	0.23	1.1	5
7. Phenol formaldehyde resin (paper base)	Shear strength, psi	12,000	6000 to 6500	0.13	0.6	5
8. Phenol formaldehyde resin (paper laminate)	Rockwell hardness	R 122 α 115	R 10 α −40	2.2	>8	>4
9. Urea formaldehyde resin (cellulose filler)	Shear strength, psi	10,000	3500 to 4000	0.13	0.6	5
10. Allyl diglycol carbonate polymer	Rockwell hardness	R 119 α 90	R 8 α −140	2.2	4 to 6	2 to 3
11. Polyethylene	Impact strength, ft-lb/in. of notch	11.2 11.2	6.1 3.0	0.13 0.23	0.32 0.70	2.5 3.1
Elastomers						
12. GR-S 50	Elongation, %	260 to 280	180 to 200	0.018	0.060	3.3
	Durometer hardness	67	75	0.018	0.042	2.3
13. Hycar OR-15 (32A45)	Tensile strength, psi	1,900	2500	0.13	0.4	3
	Elongation, %	220 to 230	30	0.13	0.60	4.6
	Durometer hardness	78	96	0.13	0.4	3
14. Hycar PA-21	Tensile strength, psi	2,000	700	0.13	0.6	5
	Elongation, %	330	40	0.13	0.60	4.6
	Durometer hardness	65	83	0.13	0.8	6
15. Natural rubber (32A43)	Tensile strength, psi	2,600	1700	0.13	0.35	3
	Elongation, %	400	140	0.13	0.45	3.5
	Durometer hardness	68	78	0.13	0.2	2
16. Neoprene W (32A44)	Elongation, %	400 to 500	215 to 230	0.018	0.04	2
17. Silastic 7-170	Elongation, %	60 to 100	30 to 35	0.018	0.065	4
	Durometer hardness	60	72	0.018	0.03	2
18. Thiokol ST (3000ST)	Tensile strength, psi	800 to 900	200 to 400	0.23	1.5	6.5
	Elongation, %	150	40	0.23	1.5	6.5
	Durometer hardness	75	65	0.23	>2	>8

In Table 4.1, the exposure (in nvt) required to produce a given property change is compared with and without cadmium for a number of plastics and elastomers. In Fig. 4.1, x vs. y, as defined in Eq. 1, is plotted for each of the materials listed; y is the ratio of the exposures taken from Table 4.1, and x is calculated from the calorimetric determination of the energy absorbed from fast-neutron and gamma radiation (2) by the elements. A sample calculation for polyethylene has been given (*1*). (The compositions of the elastomers are given in Table 1.1, with the exception of

TABLE 4.2. COMPARISON OF THREE LEVELS OF INTENSITY OF RADIATION FROM A Co^{60} SOURCE WITH THE ORNL GRAPHITE REACTOR IN THE DAMAGE PRODUCED IN ELASTOMERS

ELASTOMER	TENSILE STRENGTH (psi)	ELONGATION (%)	SHORE DUROMETER HARDNESS
Natural rubber (32A43)			
a	2900	430	68
b	2600	370	72
c	2300	280	72
d	2600	360	72
e	2700	380	70
Neoprene W (32A44)			
a	2800	460	87
b	1700	130	88
c	1300	50	85
d	1800	80	92
e	2200	130	90
GR-S 50 (32A47)			
a	1700	240	70
b	1500	140	77
c	1050	50	83
d	1200	80	82
e	1200	95	77
Thiokol ST (3000ST)			
a	750	130	75
b	770	105	78
c	580	95	76
d	730	105	74
e	800	100	80
Silastic 7-170			
a	430	90	60
b	490	35	76
c	510	20	83
d	550	30	81
e	600	40	80

[a] No irradiation.

[b] Exposed in the ORNL Graphite Reactor for 0.07×10^{18} nvt (for materials of about this hydrogen content the level of intensity of ionizing radiation is 2×10^6 rep/hr and the dosage is 5×10^7 rep).

[c] Exposed to a Co^{60} source at a level of intensity of 1.4×10^6 rep/hr for a dosage of 6×10^7 rep.

[d] Exposed to a Co^{60} source at 2.0×10^5 rep/hr for 8×10^7 rep.

[e] Exposed to a Co^{60} source at 2.3×10^4 rep/hr for 3.6×10^7 rep.

TABLE 4.3. COMPARISON OF DAMAGE PRODUCED BY Co^{60} GAMMA RADIATION AND REACTOR RADIATION

	TENSILE STRENGTH (psi)	ELONGATION (%)	ELASTIC MODULUS (10^5 psi)	DUROMETER HARDNESS	ROCKWELL HARDNESS		SPECIFIC GRAVITY, 25/4°C
					α Scale	R Scale	
Plastics							
Allyl diglycol carbonate polymer (CR-39)							
a	6000	3	3.3		90	112	1.318
b	6000	3	2.7		80	102	1.290
c			1.5		0.6	0.6	2.1
Linen fabric bakelite (phenolic)							
a	12000	4	10		114 to 116	123	1.340
b	6000	0.5	10		112 to 116	122	1.337
c	0.7	0.7					
Unfilled phenolic (Catalin)							
a	5500	1	6.0		109	123	1.300
b	5500	1	4.2		105	119	1.303
c			1.6		1.0	0.3	
Nylon (FM-10001)							
a	8900	40	3.2		86	103	1.135
b	8800	30	2.5		88	106	1.136
c					1.1	1.1	
Royalite							
a	4000	> 10	2.6		70	89	1.113
b	6000	9.1	3.8		78	96	1.124
c	1.2	1.2	1.2		0.7	1.4	0.6
Elastomers							
Natural rubber (32A43)							
a	2600	420		62			1.186
b	1400	100		79			1.196
c	1.2	0.8		0.6			0.8
Neoprene W (32A44)							
a	2900	450		79			1.418
b	1800	20		92			1.428
c		1.2		3			3

TABLE 4.3. (continued)

	TENSILE STRENGTH (psi)	ELONGATION (%)	ELASTIC MODULUS (10^5 psi)	DUROMETER HARDNESS	ROCKWELL HARDNESS		SPECIFIC GRAVITY, 25/4°C
					α Scale	R Scale	
Elastomers							
Hycar OR-15 (32A45)							
a	1900	250		74			1.229
b	4200	35		97			1.261
c	0.5	0.8		0.7			1.0
GR-S 50 (32A47)							
a	1700	270		69			1.210
b	1600	40		90			1.220
c	1.7	1.7		1.0			0.4
Thiokol ST (3000ST)							
a	800	160		74			1.450
b	700	80		74			1.454
c		2.5					
Silastic 7-170							
a	520	95		59			1.382
b	680	7		93			1.396
c		0.7		0.7			1.4

[a] Before irradiation.
[b] After 2.8×10^9 rep from Co^{60}.
[c] Ratio of energy absorbed from Co^{60} to the energy absorbed in the reactor for an exposure in the reactor which produces the same value of the physical property as listed in (*b*).

Silastic, for which the proportion of filler material was not known; the composition of unfilled polymers was calculated from their chemical structural formulas.) When C is taken as 8, the curve of Fig. 4.1 is given by Eq. 1. This curve gives the best fit for the experimental points. It follows then that the energy absorbed from gamma radiation has been increased eightfold.

The sensitivity of determining the y values of Fig. 4.1 depends on the rate of change of the property chosen for study. When more than one property is studied, the agreement shown in Table 4.1 indicates that the damage produced with cadmium is similar in nature to that produced without cadmium. This implies that the damage produced by gamma radiation is similar to that produced by fast neutrons.

The cadmium-produced damage increase will not be so great for materials in which appreciable damage results from thermal neutrons, since cadmium screens out the thermal neutrons. Since fluorine and chlorine have high cross sections for thermal neutrons, additional damage for materials which contain these elements comes from beta radiation and recoil atoms resulting from the absorption of thermal neutrons. For the materials which contain chlorine or fluorine (fluorothene, Teflon, Saran, Neoprene W, and vinyl chloride acetate polymer) the experimental points fall below the curve, since the thermal neutron-produced damage was not taken into account.

TABLE 4.4. COMPARISON OF CHANGES PRODUCED BY THE GAMMA RADIATION FROM Au^{198} AND REACTOR RADIATION[a]

	TENSILE STRENGTH (psi)	ELONGATION (%)	DUROMETER HARDNESS	SHEAR STRENGTH (psi)	ROCKWELL HARDNESS	
					α Scale	R Scale
Hycar PA-21 (32A48)						
b	2000	230	65			
c	200	60	52			
d	0.1	0.5				
Thiokol ST (3000ST)						
b	800	160	75			
c	350	100	69			
d	0.5	2				
Nylon FM-10001						
b				11,000	66	98
c				9,000	78	104
d				0.3	0.3	0.3
Royalite (butadiene-styrene copolymer)						
b				5,200	71	92
c				8,200	84	102
d				0.2	0.3	0.3
Butyl rubber (32A46)						
c	Tarry mass					
d	~1					

[a] 1.5×10^4 rep/hr from the Au source; 1×10^6 to 3.5×10^6 rep/hr from the reactor, depending upon the material.
[b] Nonirradiated.
[c] Au^{198}-irradiated, 8×10^7 rep.
[d] Ratio of energy absorbed from Au^{198} to the energy absorbed in the reactor which produces the same value of the physical property as listed in c.

RADIATION FROM Co^{60}

In order to study radiation-produced changes at a low level of intensity, irradiations were made at various distances from a Co^{60} source in the ORNL canal. In Table 4.2, levels of intensity of 1.4×10^6 rep/hr, 2.0×10^5 rep/hr, and 2.3×10^4 rep/hr are compared with reactor radiation (2×10^6 rep/hr for materials of about the hydrogen content of the compounded elastomers) at roughly similar exposures in rep. The changes produced in elastomers were chosen for study because they are relatively sensitive and permit study at low intensity. Elongation is a property which is particularly sensitive for short exposure.

On the basis of energy absorbed, the low level of intensity for Co^{60} is somewhat less effective in producing change than is the high level of intensity; however, the difference is small. While the results are not identical, roughly within a factor of 2, the exposure (in rep) of reactor radiation required to produce a given change is the same as the exposure (in rep) of Co^{60} radiation required to produce the same change.

Table 4.3 gives a comparison of gamma radiation and reactor radiation for a longer exposure. Within a factor of 2, there is agreement in changes produced in most properties. Thermal-neutron reactions were neglected in the calculation of the energy absorbed from reactor radiation. That this is not a good approximation for chlorine-containing materials (due to the high absorption cross section of chlorine) is shown by the high ratio of Co^{60}

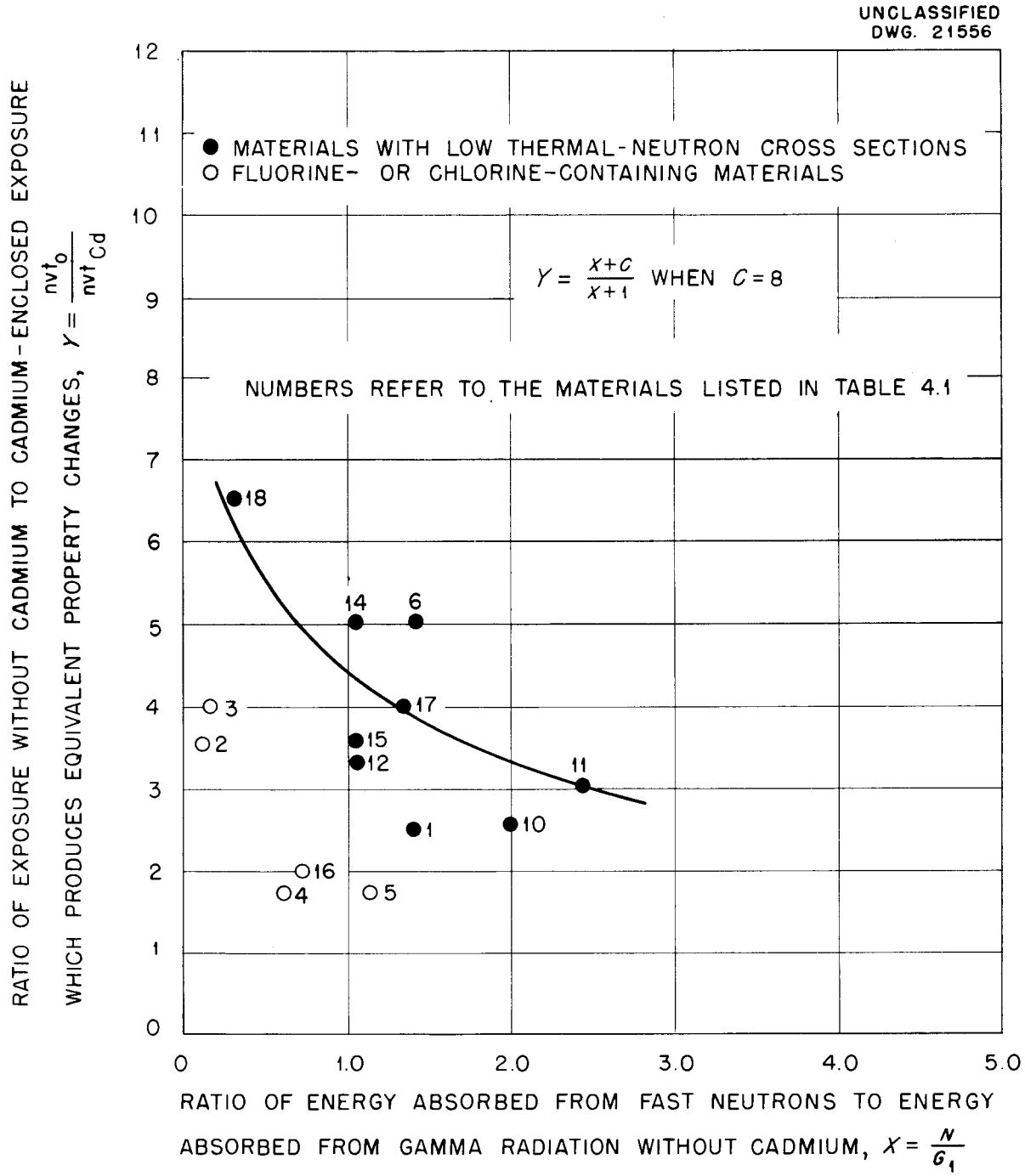


Fig. 4.1. Increase in Effectiveness of Exposure Obtained with Cadmium.

radiation to reactor radiation exposure obtained for Neoprene W. The energy absorption of the materials, relative to polyethylene in the reactor, is given in Table 7.1.

The Co^{60} source and the reactor give approximately similar results, and this indicates that Co^{60} can be used in future radiation-stability studies with organic materials. The advantages of Co^{60} over the reactor include less limitation as to the size of specimens and no problem as to induced radiation (Co^{60} irradiation space is limited at present).

RADIATION FROM Au^{198}

A Au^{198} source with a log mean level of intensity of 1.5×10^4 rep/hr was also employed in irradiations. Since the half life of the source is only 2.7 days, it was replaced with a freshly activated source once every week. In Table 4.4, changes induced by Au^{198} radiation are compared with changes induced by reactor radiation. There appears to be somewhat greater damage for Au^{198} radiation than for reactor radiation. Further study is required before the significance of this difference can be explained.

Chapter 5
EFFECT OF OXYGEN AND THE TIME OF AGING AFTER IRRADIATION

For many organic liquids, the radiation damage is greater if the material is irradiated in the presence of oxygen (*12*). As discussed in Chapter 2, no improvement in resistance was gained by the inclusion of an antioxidant in elastomer formulations. To study further the effect of oxygen, plastics and elastomers were irradiated in the absence of oxygen.

Duplicate sets of specimens were irradiated – first, in cans containing an atmosphere of pure oxygen and second, in cans containing an atmosphere of pure helium. Except for slight surface darkening in some materials which were irradiated in oxygen, no appreciable difference could be detected in radiation stability between materials irradiated in oxygen and those irradiated in helium atmospheres. The physical properties of materials irradiated in helium and in oxygen are shown in Table 5.1. Further evidence that the presence of oxygen does not greatly affect the mechanical properties of specimens of this thickness is shown by the agreement obtained (Chapter 1) between the radiation stability of Group I elastomers which were irradiated in air and Group II elastomers which were irradiated in helium.

None of the elastomers were stressed during irradiation in the above tests. Since ozone attacks only stressed elastomers, there was no ozone damage (see Chapter 1).

It is conceivable that during the irradiation of a material, decomposition products might be formed which would continue to degrade the material as it aged after irradiation. To see whether such processes occur, specimens of the elastomers and plastics were irradiated and some of their physical properties were measured at various aging times after irradiation. Since the physical properties of many of these materials change with time whether or not they have been irradiated, a nonirradiated specimen was observed along with each irradiated specimen. No aging change was detected in moderately damaged specimens. Some severely damaged specimens continued to change after removal from the radiation field, but the change was small in comparison with the initial radiation damage; neither appreciable radiation-induced aging nor postradiation healing was detected in any of these materials.

TABLE 5.1. PROPERTIES OF PLASTICS AND ELASTOMERS IRRADIATED IN OXYGEN AND IN HELIUM

MATERIAL	EXPOSURE (10^{18} nvt)	PROPERTY CHOSEN FOR STUDY	BEFORE IRRADIATION	AFTER IRRADIATION IN HELIUM	AFTER IRRADIATION IN OXYGEN
Plastics					
Methyl methacrylate polymer	0.19	Shear strength, psi	8000	2000	2200
		Impact strength, ft-lb/in. of notch	0.34	0.19	0.19
Vinyl chloride acetate polymer	0.05	Rockwell hardness	R 122 α 104	R 117 α 101	R 117 α 101
Cellulose acetate polymer	0.19	Shear strength, psi	6000 to 6500	2500	2500
		Impact strength, ft-lb/in. of notch	1.1 to 1.6	0.20	0.20
Monochlorotrifluoroethylene polymer	0.19	Shear strength, psi	5000 to 5500	2000	1700
		Impact strength, ft-lb/in. of notch	1.6 to 1.7	0.35	0.35
Nylon FM-1	2.3	Rockwell hardness	R 105 α 65	R 118 α 85	R 118 α 85
Polyethylene	2.3	Shear strength, psi	2200	1600	1600
		Rockwell hardness	R −20 α −150	R 90 α −70	R 90 α −70
Plaskon alkyd	2.3	Impact strength, ft-lb/in. of notch	0.4	0.4	0.4
Styron 475	2.3	Impact strength, ft-lb/in. of notch	0.5	0.2	0.2
Elastomers					
GR-S 50 (32A47)	0.61	Durometer hardness	69	73	73
Hycar PA-21 (32A48)	0.61	Durometer hardness	62	78	78
Hycar OR-15 (32A45)	0.61	Durometer hardness	75	100	100
Natural rubber (32A43)	0.61	Durometer hardness	60	80	80
Neoprene W (32A44)	0.61	Durometer hardness	80	98	98
Silastic 7-170	0.61	Durometer hardness	59	95	95
Thiokol ST (3000ST)	0.61	Durometer hardness	74	64	64

Chapter 6

RADIATION-INDUCED CHANGE IN THE SPECIFIC VOLUME

For most materials which are hardened by radiation, the specific volume change can be correlated with radiation exposure. Certain materials show no uniform change in either hardness or specific volume. For these materials, it is assumed that the effect of chain cleavage masks the change in specific volume and hardness which otherwise would be produced by cross-linking.

Most materials which are increased in hardness by radiation show a decrease in specific volume. There are insufficient data available for long irradiation periods to give precise values, but within the accuracy obtained, the experimentally determined values of specific volume may be fitted to the first-order rate equation

$$(1) \quad V_R - V_\infty = (V_0 - V_\infty)\,[\exp(-kR)] \ ,$$

where

V_R = the specific volume at 25°C, cm^3/g;
R = the irradiation period, 10^{18} nvt;
V_0 = the specific volume before irradiation at 25°C, cm^3/g;
V_∞ = the limiting specific volume approached for long periods of irradiation, cm^3/g (a constant for the material);
k = a constant for the material, $1/(10^{18}$ nvt).

For small values of R, the relationship between the specific volume and the irradiation period is nearly linear. This is predicted by Eq. 1 since for small values of R, $\exp(-kR)$ is approximately $(1 - kR)$ and Eq. 1 becomes

$$(2) \quad V_R = V_0 - (V_0 - V_\infty)\,kR \ .$$

In Table 6.1 the constant of Eq. 2 $(V_0 - V_\infty)k$ is listed for the materials studied which show a uniform decrease in specific volume. Some of the elastomers were irradiated for periods sufficient to estimate V_∞ in order to calculate k. For polyethylene and polystyrene, the value of V_∞ is estimated from other data (10,11).

TABLE 6.1. RADIATION-INDUCED CHANGE IN THE SPECIFIC VOLUME*

MATERIAL	SPECIFIC VOLUME AT 25°C (cm^3/g)		$(V_0 - V_\infty)k$ ($cm^3/g \cdot 10^{18}$ nvt)	k [$1/(10^{18}$ nvt)]
	Initial Value, V_0	Saturated Value, V_∞		
Natural rubber				
(32A43)	0.8480	0.7900	0.016	0.27
(P1S1C9)	0.9569		0.018	
Plasticized natural rubber				
(P1S2C1)	0.9634		0.017	
(P1S2C2)	0.9542		0.018	
(P1S2C3)	0.9560		0.015	
(P1S2C4)	0.9141		0.017	
(P1S2C5)	0.8474		0.014	
(P1S2C6)	0.9009		0.017	
Polybutadiene				
(P1S1C1)	0.9640		0.033	
Hycar OR				
(32A45)	0.8130	0.7580	0.025	0.45
(P1S1C2)	0.8912		0.032	
GR-S 50				
(32A47)	0.8280	0.7680	0.018	0.30
Hycar OS-10				
(P1S1C3)	0.8958		0.017	
Hycar PA-21				
(32A48)	0.7883	0.7565	0.0032	0.10
(P1S1C5)	0.8217		0.012	
Neoprene W				
(32A44)	0.7060	0.6810	0.018	0.72
(P1S1C5)	0.7438		0.016	
Neoprene GN				
(P1S1C4)	0.7340	0.7160	0.022	1
Silastic 7-170	0.7250	0.6400	0.014	0.16
Silastic 250				
(P1S1C8)	0.8300		0.025	
Vulcollan	0.8084		0.003	
Polyethylene	1.097	0.88	0.005	0.04
Polystyrene				
(Amphenol)	0.9523	0.82	0.001	0.01
(Styron 637)	0.9540	0.82	0.001	0.01
(Styron 671)	0.9525	0.82	0.001	0.01

*Parameters of Eqs. 1 and 2.

Chapter 7

RADIATION-INDUCED GASSING

Small pieces (0.2 to 0.5 g) of elastomers and plastics were sealed in glass capsules and irradiated. The capsules were broken open, and the volume of gas evolved was measured over mercury.

In the range from about 1 to 50 ml, the gas evolved is proportional to the exposure in nvt for the materials listed in Table 7.1, except for polyvinyl formal and materials which evolve less than 0.2 $ml/g \cdot 10^{18}$ nvt. The gas evolved by polyvinyl formal is proportional to the square root of the nvt. For the other materials, the value listed in Table 7.1 is the slope of the linear portion of the plot of the volume of gas per gram of polymer vs. nvt. In the case of polyvinyl formal, the value listed is the gas evolved at 10^{18} nvt. Only one measurement was available for materials which evolved less gas than 0.2 $ml/g \cdot 10^{18}$ nvt because of the long exposure period required to obtain measurable quantities of gas; therefore it is not certain, for these materials, whether the quantity of gas evolved is proportional to exposure.

In Table 7.1, the yields are also expressed as molecules of gas per 100 ev of energy absorbed. The amount of energy absorbed by materials irradiated in a reactor is highly dependent upon the hydrogen content, since hydrogen has a high stopping power for fast neutrons. The energy absorption was calculated from the composition of the materials by using calorimetrically determined values of the elements. The calculation for polyethylene given (*1*) illustrates the method.

In Table 7.2, certain representative polymers are listed in order of the amount of gas produced by radiation. The ranking of the solid polymers with regard to gassing is similar to the ranking which has been found for liquids with similar chemical structures (*12,13*). This is in contrast to the ranking based on change in mechanical properties (cf. "Discussion of Results," this report) which bears no direct relation to the ranking based on gas evolution.

Evolution of hydrogen gas results from the radiation-produced cross-linking of polyethylene; evolution of light hydrocarbons results from chain cleavage of polyethylene molecules. Since hydrogen diffuses with ease through the polymer, the volume of gas produced is proportional to the weight of the specimen; since hydrocarbons diffuse with difficulty, the volume of gas is approximately proportional to the area. For polyethylene specimens of about 5 to 10 cm^2/g of specific area, the composition of the gas has been reported to be about 98% hydrogen and 2% hydrocarbons (*4*).

Organic liquids with unsaturated structures evolve less gas than liquids with saturated structures (*13*). This may be attributed to the absorption of hydrogen or hydrocarbons at double bonds. Very low rates of gas evolution are given by liquids with aromatic structures. This may be attributed both to unsaturation and to high stability of the aromatic structure which permits it to dissipate radiant energy without decomposition. In these respects, the gassing of organic solids is similar to that of liquids.

The gassing rate of polyethylene plastic is of the same order as that of the paraffin oils which also have the chemical structure $(CH_2)_n$. The physical state, then, would seem to affect the gassing rate less than the chemical structure. It is likely that the low values obtained for some of the paraffin oils are due to the presence of small amounts of unsaturated compounds. Highly refined mineral oil shows nearly the same rate of gassing as does polyethylene.

Hycar PA-21 is a saturated elastomer which shows a rate of gassing similar to that of polyethylene. Its structural formula is similar to that of polyethylene except for the replacement, by a substituent group, of one of the hydrogen atoms attached to every other carbon atom. Since the rate of gassing and the rate of increase in hardness and decrease in specific volume are similar to the rate for polyethylene, the rate of radiation-induced cross-linking is evidently little affected by this substitution. Hycar PA-21 crumbles after very long exposure, unlike polyethylene and many other elastomers which break with a conchoidal fracture after long exposure. The crumbling is thought to result from decreased resistance to chain cleavage produced by the substituent group.

Butyl rubber and polymethyl methacrylate, which have both hydrogen atoms attached to every other carbon atom replaced by substituent groups to form quaternary carbon atoms, show low resistance to chain cleavage, as is evidenced by deterioration in strength for exposure periods which are too short to harden polyethylene. It is thought that most of the gassing of these polymers results (as for poly-

TABLE 7.1. YIELD OF GAS PRODUCED BY REACTOR IRRADIATION OF PLASTICS AND ELASTOMERS

MATERIAL	GAS EVOLVED ($ml/g \cdot 10^{18}$ nvt)	ENERGY ABSORPTION*	YIELD (molecules/100 ev)
Plastics			
Allyl polymer			
Triallyl cyanurate	0.5	0.7	0.04
Acrylic polymer			
Methyl methacrylate polymer	12	0.7	0.9
Amino resins			
Aniline formaldehyde polymer	0.3	0.7	0.02
Melamine formaldehyde polymer (cellulosic filler)	4.0	0.6	0.3
Urea formaldehyde polymer (cellulosic filler)	6.0	0.6	0.5
Casein plastic	2.6	1	0.1
Cellulosics			
Cellulose acetate	6.8	0.7	0.5
Cellulose acetate butyrate	11	0.7	0.8
Cellulose propionate	13	0.7	1.0
Cellulose nitrate	41	0.7	3.0
Ethyl cellulose	13	0.7	1.0
Ethylene polymer			
Polyethylene	38	1.0	2.0
Furane resin (asbestos and carbon filler)	<0.05	~0.4	<0.01
Nylon FM-3003	11	0.8	0.7
Phenolics			
No filler	1.1	0.7	0.08
Cellulosic filler			
Linen fabric	4.7	0.7	0.5
Paper base	6.0	0.7	0.5
Paper laminate	6.0	0.7	0.5
Mineral filler			
Asbestos fabric	<0.05	~0.3	<0.01
Asbestos fiber	<0.05	~0.3	<0.01
Asbestos (Haveg 41)	<0.05	~0.3	<0.01
Graphite (Karbate)	<0.01	~0.4	<0.001
Polyester resins			
Allyl diglycol carbonate polymer	21	0.9	1.2
Plaskon alkyd	1.1	0.5	~0.05
Selectron 5038	3.4	0.7	0.3
Mylar film	1.2	0.7	0.09
Silicone plastics			
Silicone tape	10		
Silicone-varnished glass laminate	7		

TABLE 7.1. (continued)

MATERIAL	GAS EVOLVED (ml/g· 10^{18} nvt)	ENERGY ABSORPTION*	YIELD (molecules/100 ev)
Plastics			
Styrene polymers			
Polystyrene (Amphenol)	0.1	0.7	0.008
Styrene-butadiene copolymer (Royalite)	0.8	0.8	0.01
Pliotuf	0.15	0.8	0.01
Vinyl polymers			
Polyvinyl formal	37	0.7	2.8
Elastomers			
Natural rubber (32A43)	2.7	0.6	0.2
Natural rubber with asbestos filler (17FBB194)	1.1	0.5	0.11
Natural rubber with dibutyltin dilaurate (17FBB197)	3.5	0.6	0.3
Natural rubber with dodecyl mercaptan (16RCB1)	2.8	0.6	0.2
Natural rubber–butyl rubber mixtures			
50:50 (17FBB198)	4.5	0.6	0.4
25:75 (17FBB199)	5.4	0.6	0.5
10:90 (17FBB200)	6.0	0.6	0.5
Natural rubber with butyl reclaim (17FBB201)	4.5	0.6	0.4
Butyl rubber, GR-I 50 (32A46)	6.6	0.7	0.5
GR-S 50 (32A47)	1.3	0.6	0.11
Hycar OR-15 (32A45)	1.7	0.6	0.14
Hycar PA-21 (32A48)	9.3	0.6	0.8
Neoprene W (32A44)	1.0	0.5	0.10
Neoprene W with dodecyl mercaptan (17FBB196)	1.1	0.5	0.11
Silastic 7-170	7.0	0.6	0.6
Thiokol ST (3000ST)	1.3	0.4	0.17
Vulcollan	8.1	0.6	0.7

*Relative to polyethylene.

ethylene) from cross-linking. The somewhat lower rate of gassing (than that for polyethylene) may result from a larger portion of the energy absorbed from radiation going into chain cleavage. (It was observed above that for polyethylene the gas evolved from cross-linking greatly outweighs the gas from chain cleavage.)

That natural rubber cross-links like polyethylene is evidenced by increased hardness and increased specific gravity. That the gassing is less than it is for polyethylene may be due to absorption of part of the hydrogen at double bonds.

Unfilled phenolic polymer, aniline formaldehyde polymer, and polystyrene have phenyl groups in their

TABLE 7.2. RELATION OF GASSING TO CHEMICAL STRUCTURE

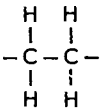
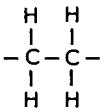
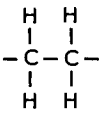
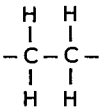
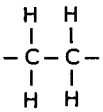
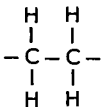
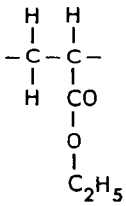
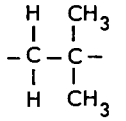
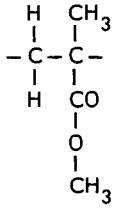
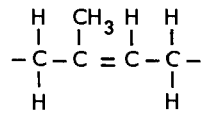
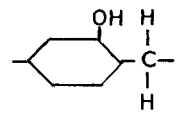
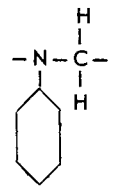
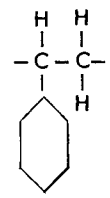
POLYMER	MOLECULES/100 ev	STRUCTURE
Polythene	2.0	
Paraffin oils		
Light mineral oil (USP)	1.8	
SAE 90 oil	1.3	
SAE 10 oil	1.3	
Light machine oil	0.8	
Vacuum pump oil, heavy grade	0.6	
Hycar PA-21	1.6	
Butyl rubber	1.0	
Polymethyl methacrylate	0.9	

TABLE 7.2. (continued)

POLYMER	MOLECULES/100 ev	STRUCTURE
Natural rubber	0.2	
Unfilled phenolic polymer	0.08	
Aniline formaldehyde polymer	0.02	
Polystyrene	0.008	

structural formulas. The gassing rate of these polymers is of the same order as the rate of evolution of hydrocarbons (due to chain cleavage) from polyethylene and is much less than the rate of evolution of hydrogen (due to cross-linking) from polyethylene. The rate of decrease in specific volume and the rate of increase in elastic modulus are much less for polystyrene than for polyethylene. It is thought that a lower rate of cross-linking is due to the presence of the phenyl group, which may function either to dissipate the radiant energy or to impose steric hindrance to cross-linking.

The phenolic polymer shows the greatest rate of gassing and deterioration in strength of these three polymers which contain phenyl groups. Lowered resistance to chain cleavage may be due to the presence of the phenyl groups connected directly as part of the polymer chain.

Aniline formaldehyde polymer shows greater gassing and loss of strength than polystyrene. The structure of aniline formaldehyde polymer may be derived from that of polystyrene if part of the carbon of the polymer chain is replaced by nitrogen. This substitution is thought to result in lowered resistance to chain cleavage.

The gassing rate of polystyrene is less than the rate of hydrocarbon evolution of polyethylene. Measurements for polystyrene were made for only one exposure period, since relatively long exposure is required to produce measurable quantities of gas. It is therefore uncertain whether the gassing is proportional to the radiation exposure. It is not known how the rates of diffusion of hydrocarbons in polystyrene and polyethylene compare. For these reasons, it is not altogether certain that polystyrene is more resistant to chain cleavage than polyethylene; however, the very low gassing rate and the low rate of change in specific volume show a low rate of cross-linking for polystyrene.

Mixtures of polystyrene and styrene-butadiene copolymer (Pliotuf and Royalite plastics), which are softer and more flexible than unmodified polystyrene, show a rate of hardening (likely due to cross-linking) of the same order as the rate of hardening of polyethylene; however, the rate of gassing is much lower than the rate of gassing of

polyethylene. The low gassing rate may be due to the absorption at double bonds of part of the hydrogen from cross-linking.

Lower gassing rates are given by mineral-filled phenolic, alkyd, and melamine plastics than by unfilled phenolic, alkyd, and melamine polymers, but the rate is not greatly changed when the amount of mineral filler is increased in elastomers. The mineral filler may function to stabilize the hard materials by dissipating energy which would otherwise damage the polymer. This evidently does not occur in soft materials.

DISCUSSION OF RESULTS

Most irradiations were conducted in the maximum-flux region of the ORNL Graphite Reactor, where thermal-neutron, fast-neutron, beta, and gamma radiation are present. Beta radiation results from absorption of thermal neutrons by the sample container and by elements which are present in the plastics and elastomers. For most of the materials tested, the absorption coefficient for thermal neutrons is low enough so that the major portion of the damage comes from fast-neutron and gamma radiation. The product of the thermal-neutron flux in neutrons/cm^2·sec and the exposure time in seconds, the nvt, is used to measure the radiation exposure, since it is readily measured by the activation of cobalt foils. The neutron-flux spectrum is given in an ORNL report (*2*).

For materials of the composition $(CH_2)_n$, calorimetric measurement (*3*) of the energy absorbed from both fast-neutron and gamma radiation gives 1.0×10^9 rep in an exposure of 1.0×10^{18} nvt. Of this, about 70% is from fast-neutron radiation and 30% is from gamma radiation (*1*).

Similar effects for both fast-neutron and gamma radiation are to be expected for organic materials which are damaged by ionizing radiation. Protons ejected from hydrogen atoms by fast neutrons cause ionization and excitation of atoms in their path in a manner similar to that of secondary electrons produced by gamma radiation.

Although most of the changes in physical properties described here were produced in the maximum-flux region of the ORNL Graphite Reactor, a number of comparative studies were made with other types of radiation. The sources of neutron-free gamma radiation that were used included Co^{60} (photons of 1.25-Mev average energy) and Au^{198} (0.3-Mev photons), which were produced by the activation of gold and cobalt in the reactor. Qualitatively, the changes produced by gamma radiation and reactor radiation are the same. Quantitatively, within a sensitivity of about a factor of 2, equivalent changes are produced in many properties for the same energy absorption by both types of radiation. The low sensitivity is partly the result of poor statistics due to the small number of samples which were irradiated with the gamma sources (limited irradiation space was available) and possibly the result of energy dependence of the radiation-produced changes. Because of the limited irradiation space available, exposures to gamma radiation employed in the study were less than 10^9 rep.

The level of intensity of radiation from Co^{60} was varied from 10^4 to 10^6 rep by shielding the source with water. Within this range, no pronounced intensity effect was detected, but the changes produced were dependent upon the total energy absorbed. The level of intensity employed for the Au^{198} irradiations was not varied, since it was very low. (The half life of Au^{198} is very short; therefore it was necessary to replace this source once a week with a freshly irradiated source. The log mean intensity was about 2×10^4 rep.)

The most intense source of radiation employed was obtained by wrapping in cadmium the materials which were irradiated in the reactor. The $Cd^{113}(n,\gamma)$ reaction with thermal neutrons produces gamma radiation in addition to that which is normally present in the reactor. The total energy absorption both from fast-neutron and gamma radiation is increased three- to eightfold by the cadmium, depending upon the composition of the material.

With most materials, irradiations conducted in oxygen and in helium gases give similar changes. (An exception is stretched rubber, which shows more damage in oxygen because of ozone attack.)

Ionizing radiation produces changes in organic materials by breaking the chemical bonds between atoms. If the broken bond is in the main polymer chain, chain-cleavage results. If the broken bonds are between carbon atoms of the main chain and attached side atoms or groups which are not connected directly in the main chain, either unsatu-

ration or cross-linking between adjacent polymer chains may result.

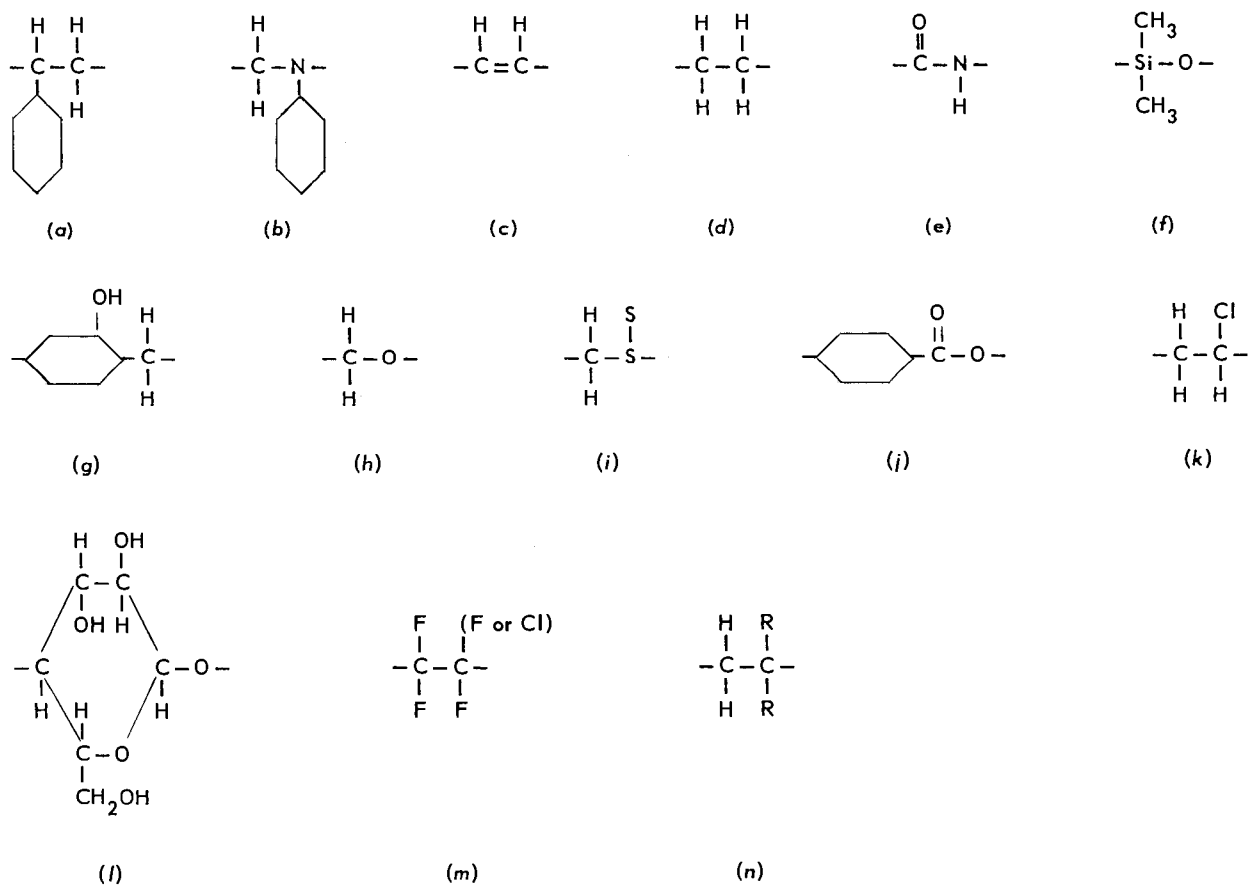
For polyethylene plastic, which has the structure of the unsubstituted paraffin chain, $(CH_2)_n$, cross-linking rather than chain cleavage is the predominant process. This is evidenced by increase in hardness, tensile strength, and density (*1,4*).

Certain other polymers are observed to lose strength and to become either soft or brittle when subjected to radiation exposures too short to produce much change in polyethylene. In most instances, the rate of gas evolution of these materials is even less than it is for polyethylene. The hardness is either decreased or little changed, and there is small change in density. The most pronounced change is a decrease in tensile strength. It is speculated that the mechanism for damage of polymers which show radiation stability of lower order than that of polyethylene is predominantly by chain cleavage.

Other linear polymers may be considered to have the paraffin-chain structure of polyethylene, but with substitutions. This outlook offers the advantage that the effect of the substituted groups on radiation stability may be determined by comparing the stabilities of the other plastics with the stability of polyethylene. In Chart 15, the chemical groupings present in the polymers studied are ranked in order of radiation stability. The ranking is not precise. There is often uncertainty as to the relative order of groupings which rank close together; however, a very large difference exists in the stability of groupings which are spaced far apart. A discussion of the determination of the stability of the groupings follows.

Group *a* is the repeating unit in the structural formula of polystyrene. Polystyrene shows the best stability of all the unfilled polymers tested. A comparison of group *a* with group *b* suggests that the greatly increased stability of polystyrene

CHART 15. CHEMICAL GROUPINGS RANKED IN ORDER OF RADIATION STABILITY



over polyethylene is due to the presence of the phenyl.

Polystyrene plastics are hard and rigid. As is discussed in Chapter 3, soft materials which are mixtures of polystyrene with other polymers do not have the high order of radiation stability of unmodified polystyrene. Apparently the same forces which make polystyrene hard and rigid impede the cross-linking process (which hardens soft aliphatic structures). In Chapter 7, it is shown that the amount of gas evolved by the polystyrene-containing mixtures is less than that for polyethylene; yet in Chapter 2 the rate of hardening is shown to be as great for the mixtures as for polyethylene. The rate of gas evolution of most elastomers is also less than the rate of gas evolution for polyethylene, although in Chapter 1 the rate of hardening of the elastomers is shown to be as great as that of polyethylene. It is speculated that polystyrene-containing mixtures and unsaturated elastomers may cross-link with less gas evolution than polyethylene.

Group *b* is the repeating unit in the structural formula of polyaniline formaldehyde. Again the stability is attributed to the bulky, benzene-ring–containing side groups.

Group c is present in the structural formulas of many of the elastomers. Since all the elastomers with the exception of butyl rubber and Thiokol show approximately the same order of stability (though the amount of unsaturation is different) and since the elastomers become hard at about the same exposure as polyethylene, group c is given about the same rank as group *d*.

Group *d* is the repeating unit in the structural formula of polyethylene.

Group e is present in the structural formula of Nylon. Since Nylon shows the same order of stability as polyethylene, group e is ranked close to group *d*.

Group *f* is the repeating unit in the structural formula of Silastic. It is ranked close to groups *d* and e, since Silastic shows the same order of stability as most other elastomers.

Group *g* is the repeating unit in the structural formula of phenol formaldehyde polymer in which the benzene ring is a part of the linear polymer chain (rather than attached as a side group as in polystyrene). Since unfilled phenol formaldehyde plastic crumbles after exposures which only harden polyethylene, the presence of the benzene ring as part of the main polymer chain is thought to increase the probability of chain cleavage. (This is in contrast to polystyrene in which the benzene ring is present as a side group.)

Group *h* also is taken to have less stability against chain cleavage than *d* has. Radiation produces softening in polyallyl diglycol carbonate in which the ratio of oxygen to carbon atoms in the main chain is about 1:2, while Selectron 5038 with a ratio of 1:4 shows hardening like that of group *d*. Softening occurs also in polyvinyl formal and polyvinyl butyral in which oxygen is present as part of a chain which bridges the main polymer chain.

Group *i* is present in Thiokol to the extent that the ratio of carbon atoms to sulfur atoms is about 1:1. Thiokol is unchanged in hardness after radiation exposure which hardens other elastomers; however, the tensile strength of Thiokol is decreased. It is thought that the constancy in hardness results from a balancing effect of cross-linking and chain-cleavage processes.

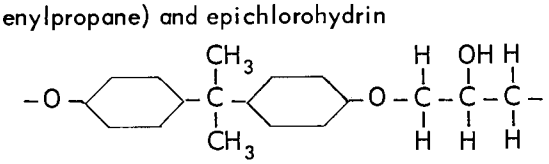
Dacron contains the *j* grouping; the predominant radiation change is embrittlement.

Group *k* is the repeating unit of polyvinyl chloride; the predominant effect of irradiation is evolution of HCl. Polyvinyl chloride materials soften initially, but finally they harden.

The repeating unit in the structural formula of cellulose is group *l*. That this structure is sensitive to chain cleavage is shown by the rapid embrittlement of cellulosic plastics.

Group *m* is the repeating unit in the structural formulas of Teflon and fluorothene, materials which become brittle and crumble apart at relatively short exposure. Evidently resistance to chain cleavage is poor.

Group *n* is the repeating unit in the structural formulas of polymethyl methacrylate, butyl rubber, and polyalphamethyl styrene. Butyl rubber becomes a viscous fluid under irradiation. Polymethyl methacrylate and polyalphamethyl styrene are embrittled, and not much change is shown in Rockwell hardness until embrittlement progresses to the extent that breakage occurs when the major load is applied during the test. These polymers with quaternary carbon atoms show very low stability against chain cleavage. An exception to the rule of instability for quaternary carbon atoms is shown by a polymer of bisphenol A (2,2-parahydroxyphenylpropane) and epichlorohydrin



which shows better stability than group *g*. Here two of the groups attached to the quaternary carbon atom are phenyls which are part of the main polymer chain.

The resistance of hard plastics with structures *g* and *h* is greatly improved for materials containing mineral filler. Hard and rigid polystyrene (with structure *a* above) shows little change in properties after an exposure of 3×10^{10} rep when sufficient energy has been absorbed to break all the chemical bonds in the substance (*1*).

Soft materials which contain mineral filler and soft materials which have aromatic side groups do not show improved resistance to hardening over unfilled or aliphatic soft materials. None of the soft materials tested show a high order of radiation stability. Though the hardness of Thiokol and certain (butyl rubber–natural rubber) mixtures is not greatly changed, tensile strength and elongation are decreased.

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Appendix

TEST PROCEDURES FOR ELASTOMERS

CONDITIONING

After specimens are conditioned for at least 24 hr at 25°C and 50% RH, dimensional measurements are taken. The specimens are conditioned again after irradiation.

TENSILE PROPERTIES

Description:

Dimensions of the test specimen are shown in Fig. A1, and the cutting dies are shown in Fig. A2. A Baldwin Southwark universal testing machine (Fig. A3) was used with a Baldwin extensometer and Scott grips (Fig. A4) for testing nonrigid plastic materials. The sensitivity of the load indicator is about 0.2 pound. For elastomers which stretch at least 3%, the speed of testing is the rate of travel of the platen-adjusting motor, about 10 in./min; however, for materials embrittled by irradiation so that the elongation is less than 3%, the rate of loading is reduced in order to prevent failure by impact at the start of stressing. For materials with less than 3% elongation, the speed of testing is 400 lb/min.

Procedure:

1. Measure the thickness of the test specimen before irradiation. Mark off 1-in. gage marks.
2. Place the specimen in the grips of the testing machine, using care to adjust it symmetrically so that tension will be distributed uniformly over the cross section. Place the extensometer on the center portion of the specimen.
3. Record the stress-strain curve; test until rupture.
4. Ten minutes after the specimen is broken, fit the two pieces together and carefully measure the distance between gage marks.

Report:

1. Tensile strength (psi) = breaking load/original cross-sectional area.
2. Ultimate elongation (%) = 100(distance between gage marks when the break occurs minus 1 in.)/1 inch.
3. Set at break (%) = 100(distance measured in Procedure 4 minus 1 in.)/1 inch.

COMPRESSION SET

Description:

Compressive-set tests are intended to measure the ability of rubber compounds to retain elastic properties during prolonged action of compressive stress. For the purpose of these tests, compressive set shall be considered as the residual decrease in thickness of a test specimen measured 30 min after removal from a suitable loading device (Fig. A5) in which the specimen had been subjected to compressive deformation for a definite time and under specific conditions of load and temperature. Two types of tests are employed here.

Test A

The standard specimen described in ASTM-395-49T is cut from blocks of material about ½ in. thick by means of a sharp circular die having an inside diameter of 1.129 ± 0.001 inches. Specimens are tested under constant load at 70°C. The test is made after the specimens are irradiated.

Procedure:

1. Measure the thickness, t_0, of the sample before irradiation.
2. After irradiation, place the sample in the center of the compression set jig and apply a load of 400 pounds. The rate of application of load is approximately 400 lb/min, and a stress-strain curve is taken during application of the load.
3. Screw down the loading nuts until movement is detected on the ram pacer of the testing machine.
4. Remove the jig from the machine and place in an oven at 70°C for 22 hours. Before inserting the test specimen in the compression jig, the jig is preheated overnight at 70°C and it is not kept out of the oven for more than 20 minutes.
5. After the heating period, remove the compression jig from the oven and immediately remove the test specimen from the jig.
6. Place the test specimen on a wooden table top and allow to cool for 30 minutes.
7. Measure the final thickness, t_f, at the center of the specimen.

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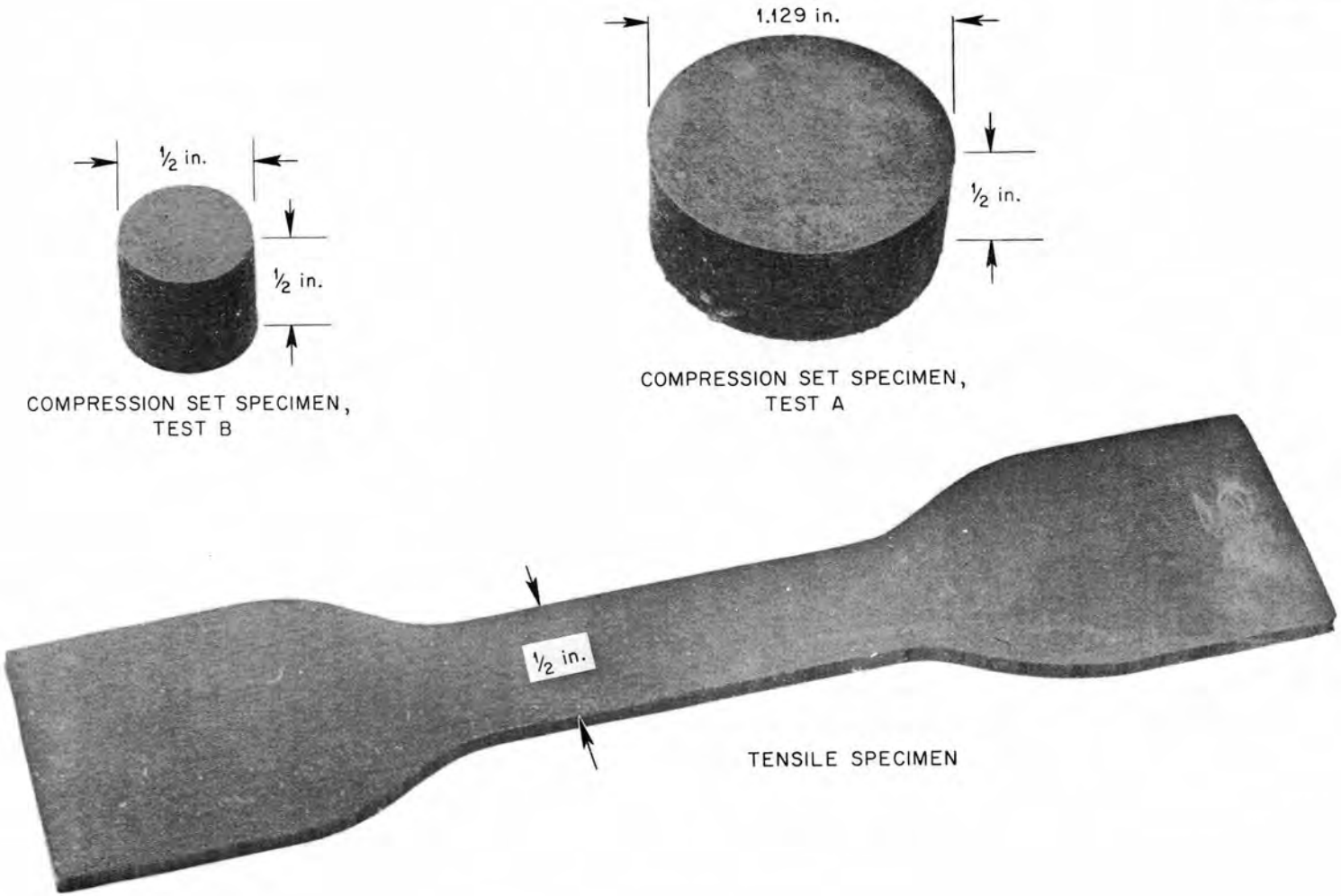

Fig. A1. Test Specimens.

Fig. A2. Specimen Cutting Dies.

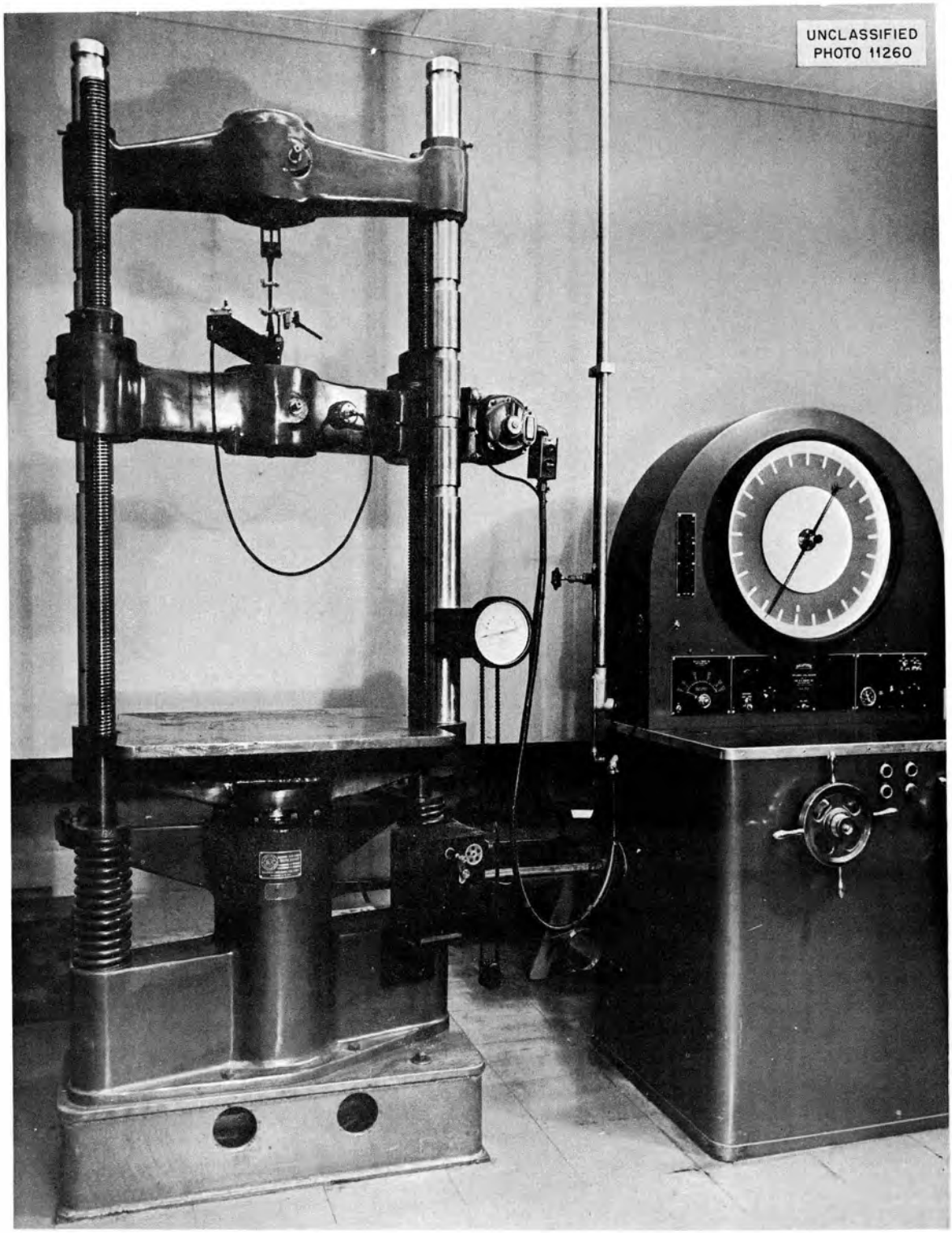

Fig. A3. Universal Testing Machine.

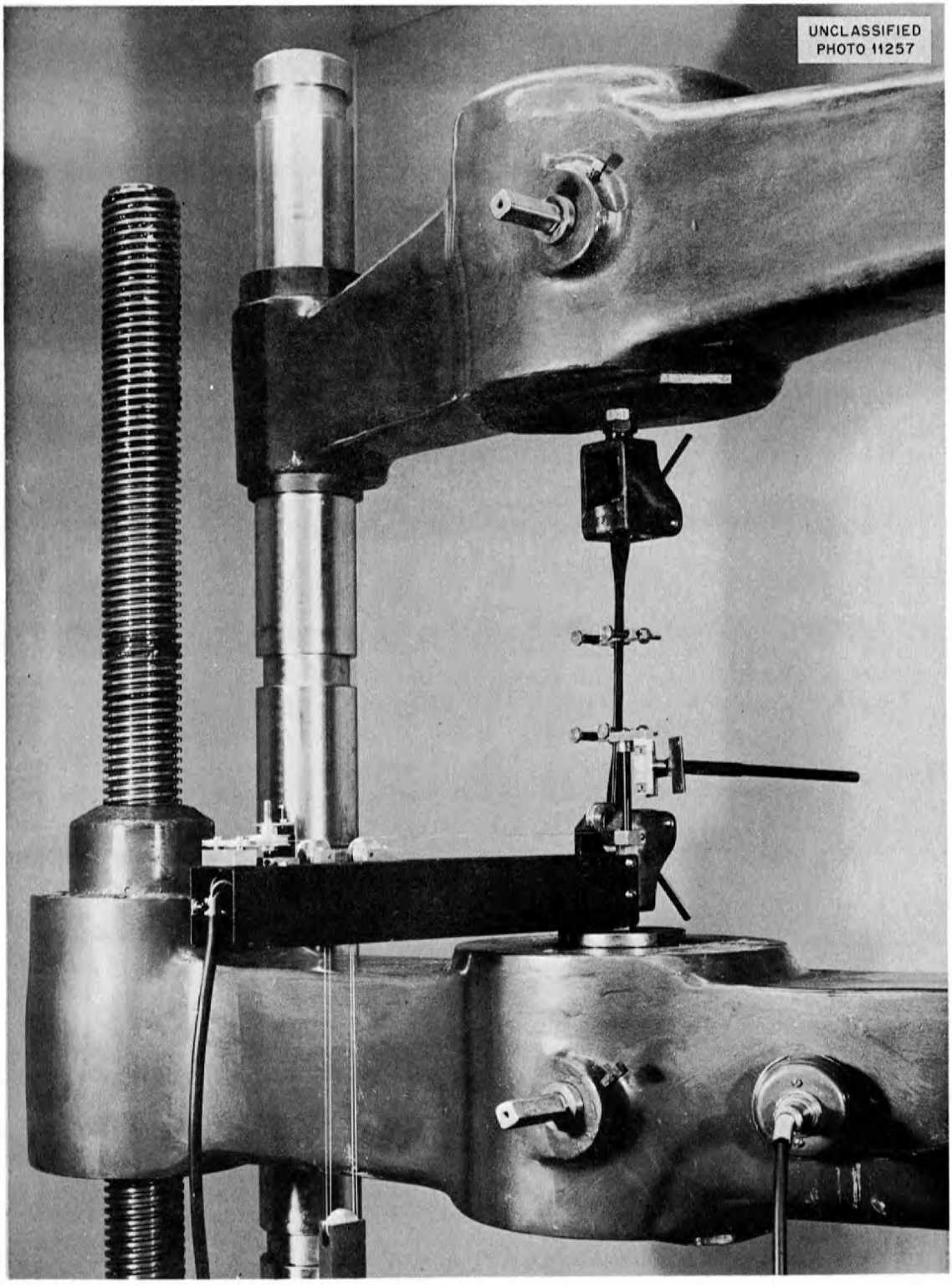

Fig. A4. Grips and Extensometer Used for Testing Nonrigid Plastics and Elastomers.

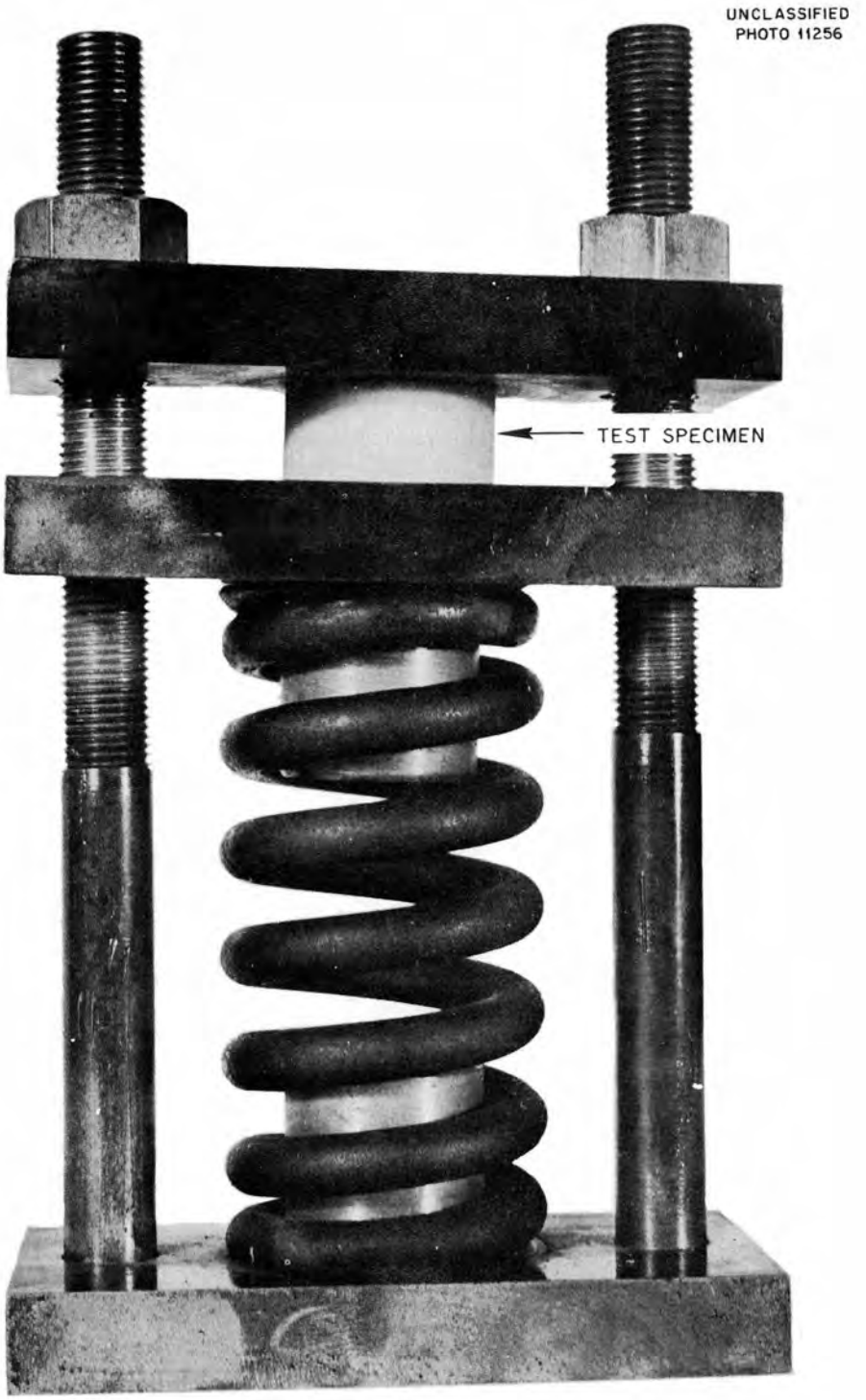

Fig. A5. Jig for Compression Set Test A.

Report:

1. Record load at failure if failure occurred.
2. Record the thickness of the sample before and after compression.
3. Compression set (%) = $100(t_0 - t_f)/t_0$.

Test B

In this test, the specimen is stressed during irradiation. Due to space limitations, the diameter of the specimens is ½ inch. The thickness is about ½ inch. This test is made under constant deflection (rather than under constant load as in test A).

Procedure:

1. Measure the thickness, t_0, of the test specimens.
2. Place the specimens in the jig (Fig. A6) and tighten the jig so that the spacer rings fit tightly against the separator plates. This compresses the specimen to ⅜ inch.
3. Irradiate the specimen while in the jig.
4. Remove the test specimen and measure the final thickness, t_f, 30 min after removal.

Report:

The percentage recovery is given by

$$\left(\frac{t_f - \frac{3}{8}}{t_0 - \frac{3}{8}}\right) \times 100 \ .$$

SHORE DUROMETER HARDNESS (A MODIFICATION OF ASTM-D676-49T)

Description:

This method covers the test for determining the indentation of rubber by means of a Shore durometer (Fig. A7). Specifications for the durometer are given in ASTM-D676-49T. The durometer has a presser foot from which protrudes a spring-loaded indentor. The distance that the indentor penetrates when the presser foot is brought into contact with an elastomer is read on the scale of the instrument. A zero penetration gives a reading of 100.

Hardness was measured either on compression set test specimens or on two thicknesses of tensile specimens (it was first determined that similar results were obtained in either case for the materials tested).

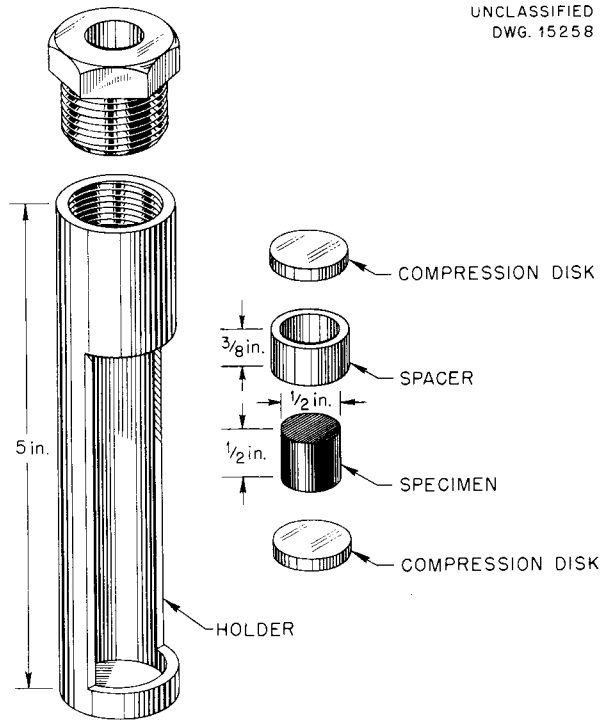

Fig. A6. Jig for Compression Set Test B.

Procedure:

1. Place the test specimen on the table of the instrument and lower the presser foot of the durometer parallel to the surface of the specimen and centered on the specimen. Lower the instrument as rapidly as possible without shock. The test pressure applied is just sufficient to ensure firm contact of the presser foot and the test specimen.
2. The durometer indentation reading is taken immediately after firm contact has been established between the presser foot and the specimen (maximum reading).
3. Take three readings and average. .

SHORE ELASTICITY

Description:

The elastometer is like the durometer except for the indentor which is needle-like and is not spring-loaded. After the presser foot is brought into contact with the elastomer, the indentor is forced into the elastomer and released. The distance the indentor is forced back due to the resilience of the elastomer is read on the scale of the instrument. If the needle is forced all the way back, the reading is 100; if it is not forced back at all, the reading is zero.

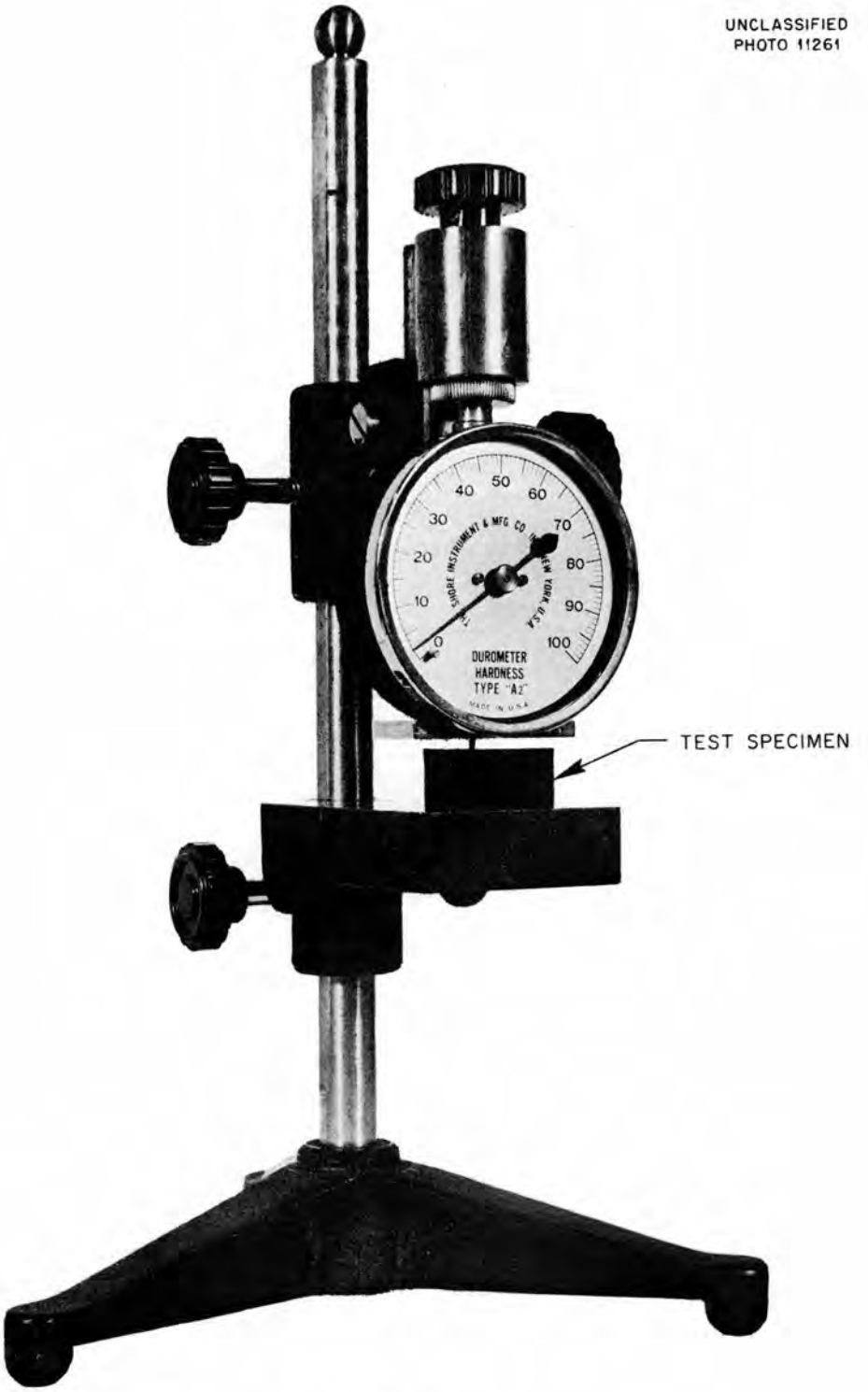

Fig. A7. Durometer Hardness Tester.

Procedure:

1. Place the test specimen on the table of the instrument and lower the presser foot of the elastometer until it is in firm contact with the specimen.

2. Force the indentor into the elastomer rapidly, release it, and record the scale reading.

3. Take three readings and average.

OTHER TESTS

Specific gravity, change in weight, change in thickness, dielectric strength, and volume resistivity were determined on test A compression-set specimens before the compression-set test. Rockwell hardness was taken on irradiated elastomers which gave a Durometer hardness of over 95. The procedures for these tests are the same as those for the plastics and are given in ORNL-928 (*1*).

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*The other plastics mentioned in this report are described in ORNL-928.