

Effect of γ -Radiation on the Dynamic Mechanical Properties of Silicone Rubbers

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Synopsis

Dimethyl-, trifluoropropyl-, and high phenyl content polysiloxanes were irradiated in a ^{60}Co source to doses of 100 Mrad. The hardness of the specimens increased with dose. Crosslink density changes did not directly reflect the hardness changes. The crosslink density of the dimethyl polymer increased significantly and that of the trifluoropropyl polymer increased only slightly. There was a slight decrease in the crosslink density of the aromatic material. The storage moduli reflected the changes in crosslink density. Loss moduli of the dimethyl- and trifluoropropylpolysiloxanes initially decreased and then increased on continuing irradiation. Dynamic moduli of the high aromatic content polymer were essentially unchanged by the radiation. All the dynamic data were correlated by the WLF time-temperature relationship.

Radiation effects on silicone fluids and polymers have been extensively studied. Silicone rubbers are normally considered less radiation-resistant than the styrene-butadiene rubbers discussed in a previous paper.¹

The three polysiloxane systems used in this research are the Silastic 50 (a dimethylpolysiloxane), Silastic LS63 (methyltrifluoropropylpolysiloxane), and X3-0272 (an experimental stock of very high aromatic content). The fluorinated stock would be expected to be the least resistant to radiation² and the high phenyl content X3-0272 to be the most radiation-resistant.^{3,4} However it has also been reported that the compression set and swelling characteristics of Silastic LS63 were only slightly affected by exposure to ultraviolet energy, whereas other silicone systems were severely degraded.⁵ Also Dow Corning has a British patent⁶ claiming that the addition of small quantities of additives can make the fluoropropylpolysiloxanes resistant to 200 Mrad at 200°C. Measurements of compression sets⁷ of dimethyl, high phenyl content, and fluorinated silicone stocks showed that the set of the fluorinated material was much less than that of the others after exposure to 10 Mrad and that all three had about the same set after exposure to 100-1000 Mrad. Needless to say, the rating of materials according to radiation resistance is difficult. Wide variations in radiation effects in silicone systems have even been found between different batches of the same material.^{3,8}

Dimethylsilicone systems crosslink through methylene, silica to silica, and ethylene bonds, with the first two bonds predominating.^{9,10} Some branching has been noted in the irradiated liquid systems.¹¹ During irradiation silicone polymers have been reported to initially decrease then increase in hardness,^{3,12} initially increase in ultimate strength and then decrease,^{11,13} and initially decrease then increase in the dynamic modulus.¹⁴ The data indicate that scissioning and crosslinking reactions are both occurring during radiation exposure. The predominating reaction depends on the chemical structure, formulation, dose level, and probably other unknown variables. The crosslink structures are known for the dimethyl systems but the reaction mechanisms and the main chain scission reactions are not known.

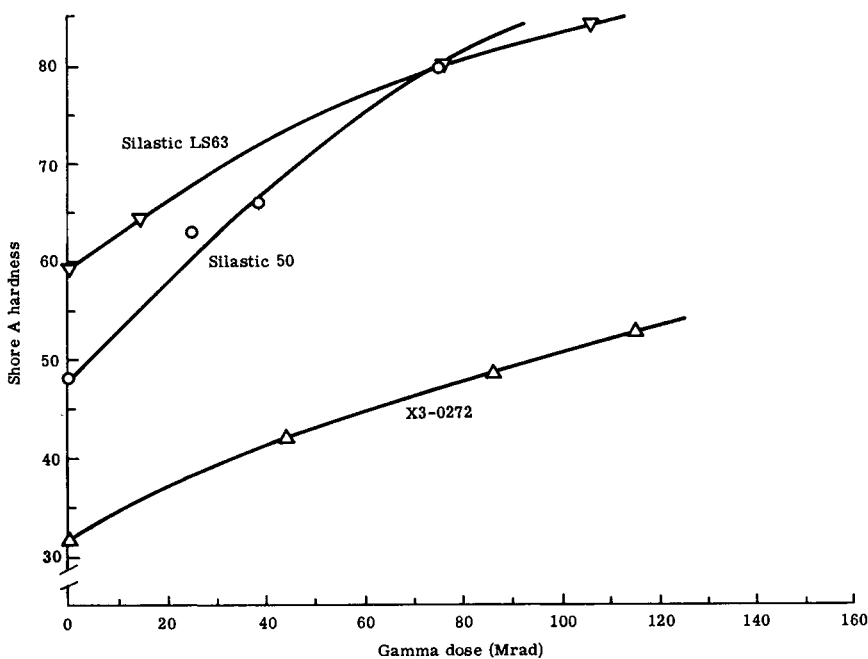


Fig. 1. Effect of γ -radiation on the hardness of silicone rubbers.

Details of the dynamic mechanical properties of silicone rubbers are not known at the present time. Shift factor values and the shape of the reduced modulus curves are not given in the literature. The loss modulus and storage modulus have been determined for silicone systems in two studies,^{15,16} but in each case, the storage modulus and the loss modulus could not be superposed using the same shift factor. One problem lies in the fact that the loss modulus is very low compared to the storage modulus and consequently is difficult to measure. Realistic superposition of both moduli were obtained at low temperatures in this research, but the loss modulus data scattered considerably at the high temperatures.

EXPERIMENTAL

Materials

The materials and formulation information were supplied by Dow Corning Corporation. Details are given in Table I.

TABLE I
Silicone Rubbers

	Silastic 50 ^a	Silastic LS63 ^a	X3-0272
Formulation information			
Polymer and plasticizer, wt.-%	72.2	73.5	75.0
Silica filler, wt.-%	24.6	36.0	25.0
Pigments, wt.-%	3.2	0.5	0.0
Polymer type ^b	Dimethyl	Methyltrifluoro- propyl	High phenyl
Cure information			
Curative	Luperco CST ^c or Cadox TS 50	Luperco CST ^c or Cadox TS 50	Luperco ASF ^d
Curative concentration, wt.-%	1.33	1.28	2.6
Cure temperature, °F.	480	400	None
Cure time, hr.	24	8	None

^a Trade name of Dow Corning Corporation, Midland, Michigan.

^b All contain vinyl groups for crosslinking.

^c 50% 2,4-Dichlorobenzoyl peroxide paste.

^d 40% Benzoyl peroxide paste.

Procedures

Samples were exposed to γ -radiation in an air atmosphere. After post-treatment, the dynamic shear moduli were measured by using a twin transducer apparatus. After mechanical testing, the hardness was measured and swelling tests performed. The procedures used throughout are the same as those described in a previous paper.¹

RESULTS AND DISCUSSION

Hardness

The γ -radiation increased the hardness of all the silicone rubbers as shown in Figure 1. The hardness of the dimethyl Silastic 50 is increased by 170% at 100 Mrad absorbed dose, the hardness of the X3-0272 by about 60%, and the hardness of the Silastic LS63 about 40%. The absolute change in hardness is approximately the same for the X3-0272 and the LS63.

Increased hardness of silicone rubbers exposed to radiation has been noted previously.^{3,12,17} However the results are frequently conflicting

and vary between different batches of the same material.³ Dimethylpolysiloxanes have been found to increase in hardness from 20 to 84%,¹⁷ and methylphenyl stocks from 20 to 30%^{12,17} after absorption of 100 Mrad of energy.

Crosslink Density

The volume fraction solvent in the swollen rubber, the solvent interaction parameters,¹⁸ the weight fraction sol, and the calculated crosslink densities are tabulated in Table II.

TABLE II
Effect of γ -Radiation on the Swelling Characteristics of Silicone Rubbers

Material	Gamma dose, Mrad	Volume fraction toluene in the swollen rubber	Inter-action parameter	Sol, wt.-%	Cross-link density, mole/cc. $\times 10^4$
Silastic 50	0.0	0.721	0.51	3.64	1.4
	25.2	0.627	0.60	2.60	1.7
	39.0	0.600	0.63	2.55	1.9
	75.7	0.483	0.74	1.49	2.4
Silastic LS63	0.0	0.229	1.14	1.86	4.8
	14.3	0.221	1.16	2.98	5.0
	76.9	0.214	1.18	2.94	4.8
	107	0.210	1.19	3.03	5.1
X3-0272	0.0	0.873	0.0	7.50	1.9
	44.1	0.829	0.26	7.53	1.8
	86.2	0.794	0.41	6.68	1.5
	115	0.773	0.45	6.01	1.5

The crosslink density values cannot be considered absolute since the solvent interaction parameters used in the calculations were not determined for these specific rubbers. The values used for calculating the crosslink densities of the X3-0272 are especially questionable, since the rubber was swollen to such a great extent. In this region of considerable swelling the actual solvent-interaction parameters are dependent on the solvent type and possibly on the chemical composition of the polymer.¹⁸

The crosslink density data plotted in Figure 2 show that the dimethyl material is readily crosslinked by γ -radiation, the Silastic LS63 may be slightly crosslinked, and the effect of radiation on the crosslink density of X3-0272 is questionable.

The sol content of the Silastic 50 decreases with increasing absorbed dose. The sol content of the Silastic LS63 however shows an increase which is an indication of degradation. This effect may be due to the increasing removal of the trifluoropropyl groups from the chain backbone or due to chain end scission. The isolated groups could be of too high a molecular weight to have been removed by the specimen treatment. The X3-0272 shows a

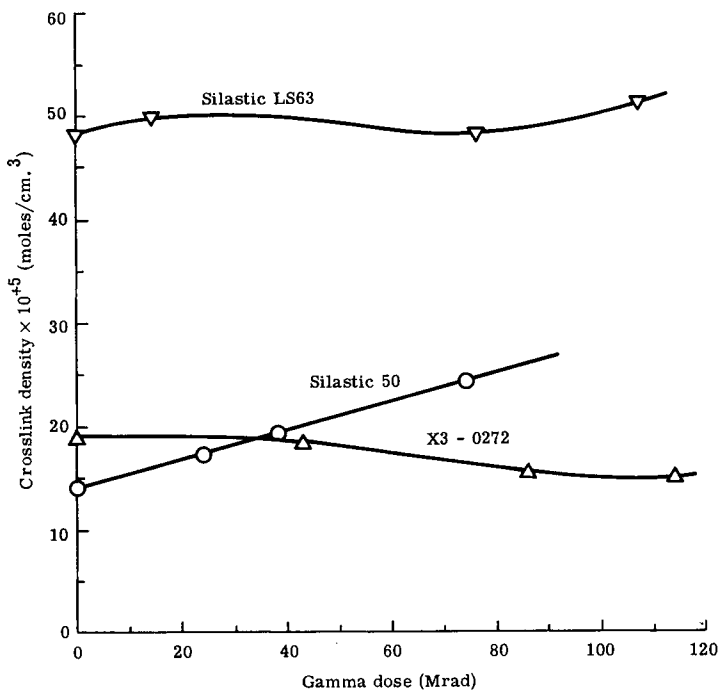


Fig. 2. Effect of γ -radiation on the crosslink density of silicone rubbers.

slight initial increase, then decrease in sol content. The increase could have been due to the formation of benzene and toluene by-products that have been found in other irradiation studies.¹⁹

G values for crosslinking, $G(\text{cl})$ of dimethylsilicone systems have been reported as 1.60,⁴ 2.3,²⁰ 2.5,^{21,22} and 3.0.¹⁰ For a $G(\text{cl})$ value of 2.5, the crosslink density change predicted for Silastic 50 would be 1.4×10^{-4} mole/cc. at 100 Mrad dose. The measured change in crosslink density for the Silastic 50 is approximately 1.3×10^{-4} mole/cc. at the 100 Mrad level which agrees with the calculated change.

Koike and Danno⁴ found that as the phenyl content of silicone liquids increased from 0 to 25%, the $G(\text{cl})$ decreased from 1.60 to 0.06. In other work Koike²⁰ has shown a decrease in $G(\text{cl})$ from 2.26 to 1.30 with the change from dimethyl- to dimethyldiphenylsilicones, and Jenkins²³ determined the $G(\text{cl})$ decreased from 2.83 to 1.62 by the addition of phenyl groups in filled dimethylpolysiloxane polymers. Consequently the high phenyl content X3-0272 would be expected to have a very low $G(\text{cl})$, which is experimentally found to be the case.

Storage Modulus

The effects of γ -radiation on the storage moduli of the three polymers are shown in Figures 3-5. The Silastic 50 modulus increased rapidly with dose, reflecting the change in crosslink density. The modulus of the

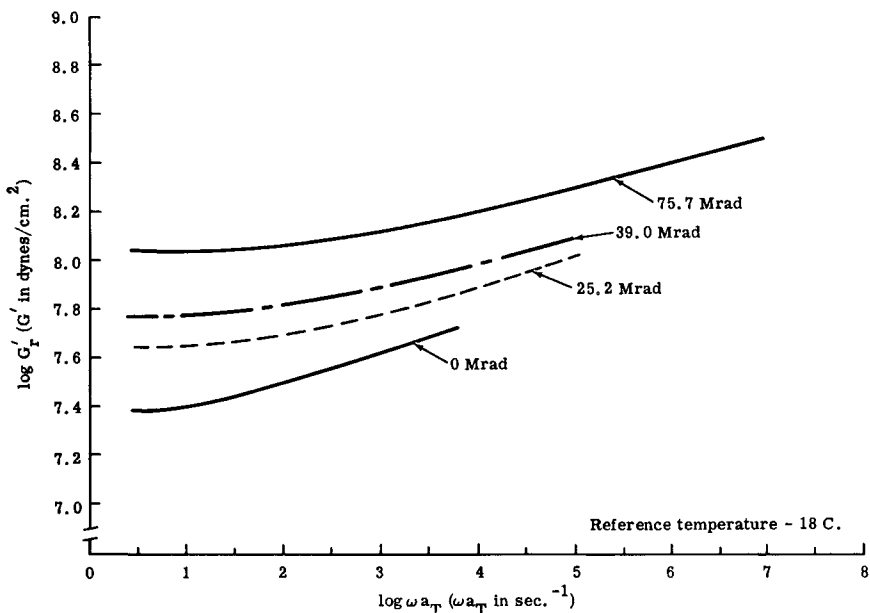


Fig. 3. Effect of γ -radiation on the storage modulus of silicone rubbers: Silastic 50.

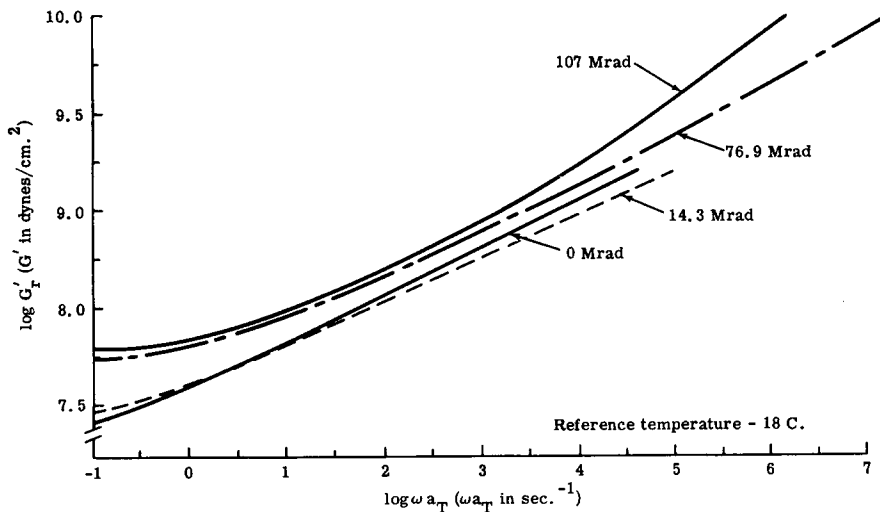


Fig. 4. Effect of γ -radiation on the storage modulus of silicone rubbers: Silastic LS63.

Silastic LS63 increased somewhat and the modulus of the X3-0272 was unchanged.

The LS63 rubber shows an initial decrease in storage modulus indicating a predominance of chain scission. This decrease does not appear in the hardness or crosslink density measurements but has been noted by Jenkins^{14,23} in dynamic tests.

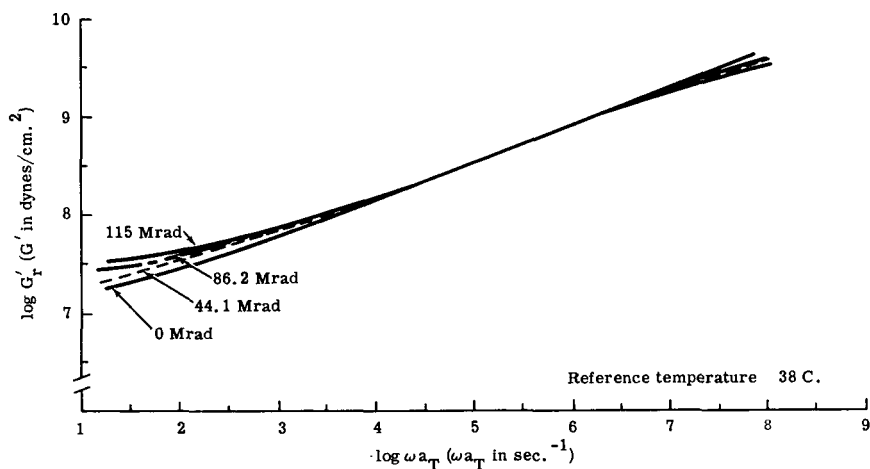


Fig. 5. Effect of γ -radiation on the storage modulus of silicone rubbers: X3-0272.

Loss Modulus

The loss modulus of the X3-0272 is unchanged by γ -radiation as shown in Figure 8. However the loss modulus of the Silastics 50 and LS63 initially decrease and then increase on continuing radiation exposure (Figs. 6 and 7).

The initial loss modulus decrease (lowering of the dynamic viscosity) suggests a chain-scission process. This decrease would be in agreement

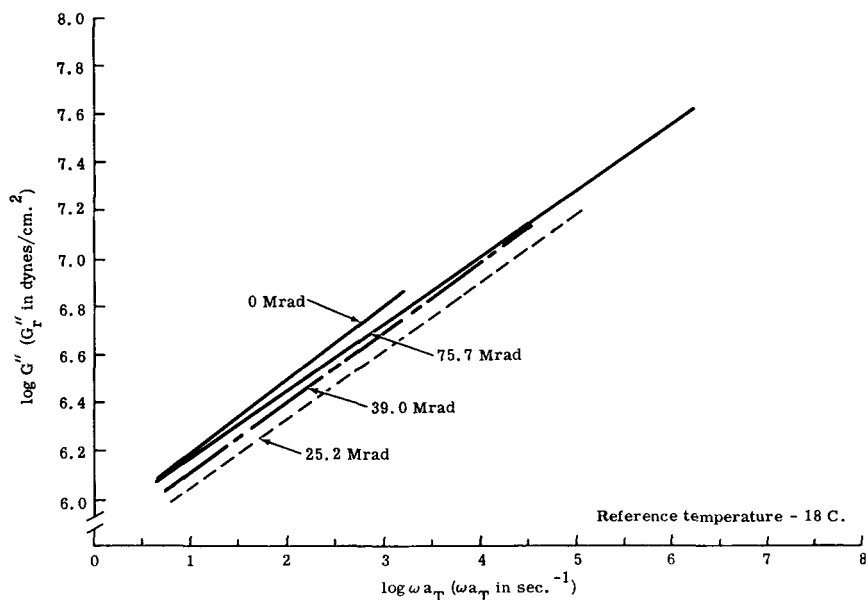


Fig. 6. Effect of γ -radiation on the loss modulus of silicone rubbers: Silastic 50.

with the change in storage modulus for the LS63 which was lowered in the initial radiation process. The decreases could be explained by the presence of residual trifluoropropyl groups or chain-end segments not removed by specimen treatment. The changes seen in the Silastic 50 cannot be readily

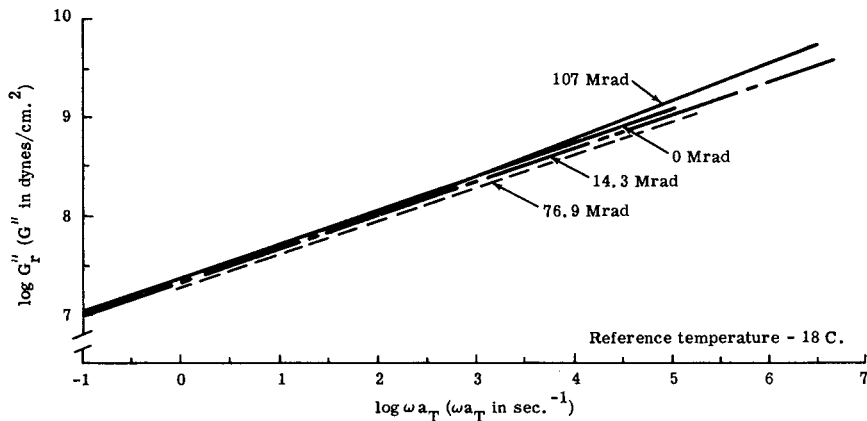


Fig. 7. Effect of γ -radiation on the loss modulus of silicone rubbers: Silastic LS63.

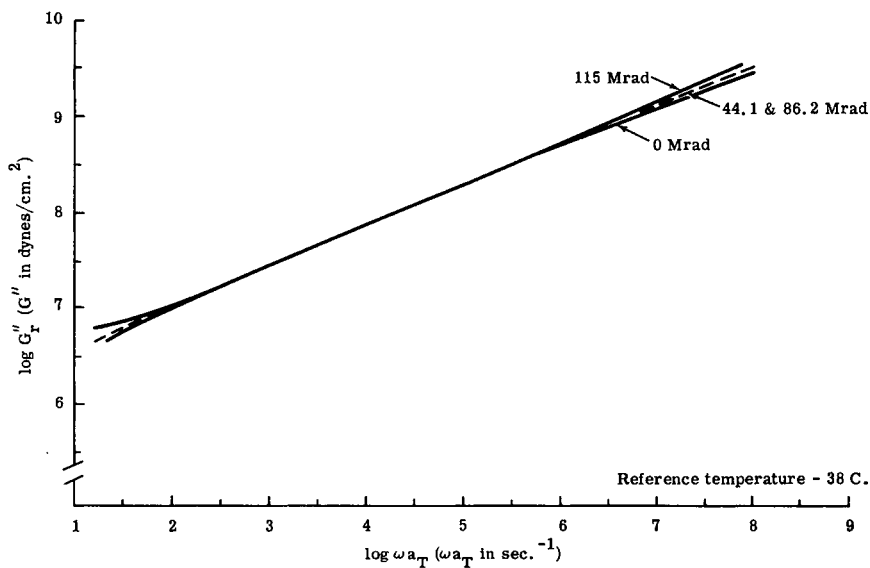


Fig. 8. Effect of γ -radiation on the loss modulus of silicone rubbers: X3-0272.

explained, since the low molecular weight decomposition fragments from dimethyl polymers should be removed by the specimen treatment. In addition, the storage modulus for the Silastic 50 increases. The possibility exists that chain fractures lead to entanglement couplings which act as crosslinks.

Loss Tangent

The loss tangent combines the storage and loss properties of a rubber. With these silicone systems which primarily crosslink, the loss tangent decreases with increasing radiation as shown in Figures 9-11.

The loss tangent of the Silastic 50 is significantly decreased by irradiation, the loss tangent of the LS63 is slightly decreased, and the loss tangent

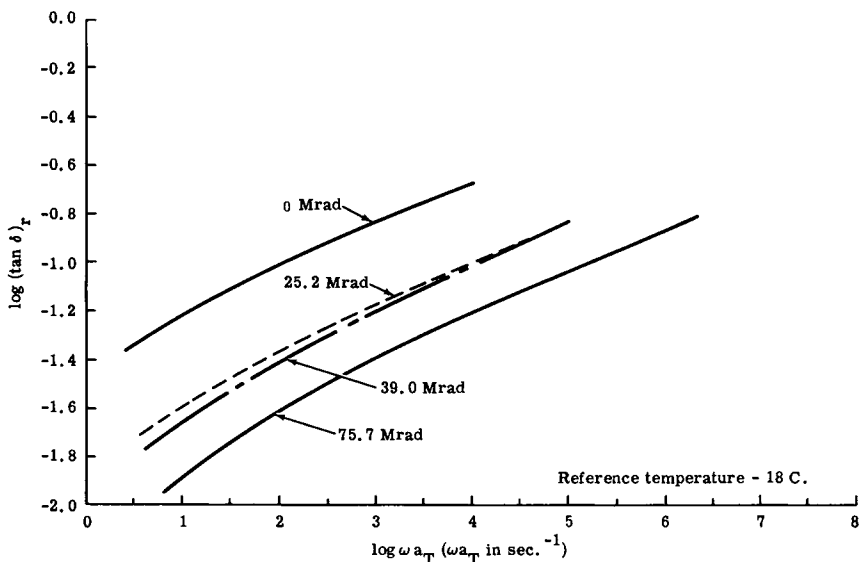


Fig. 9. Effect of γ -radiation on the loss tangent of silicone rubbers: Silastic 50.

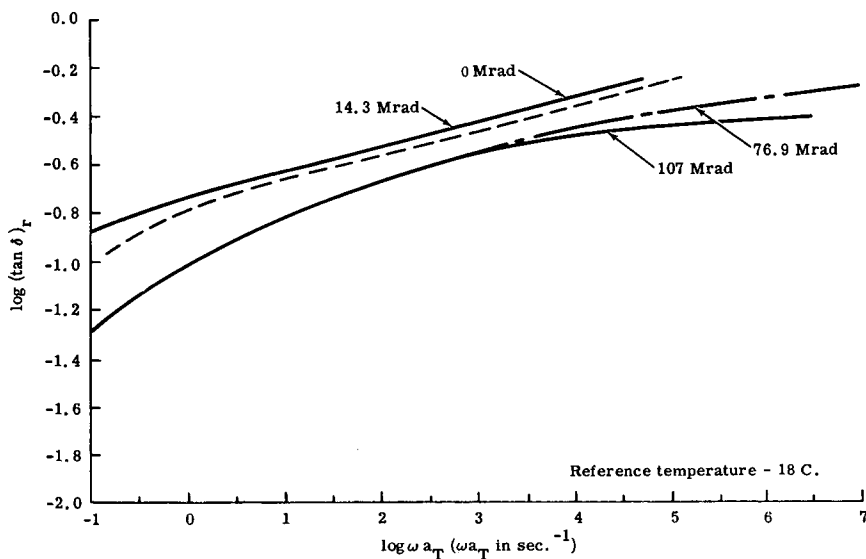


Fig. 10. Effect of γ -radiation on the loss tangent of silicone rubbers: Silastic LS63

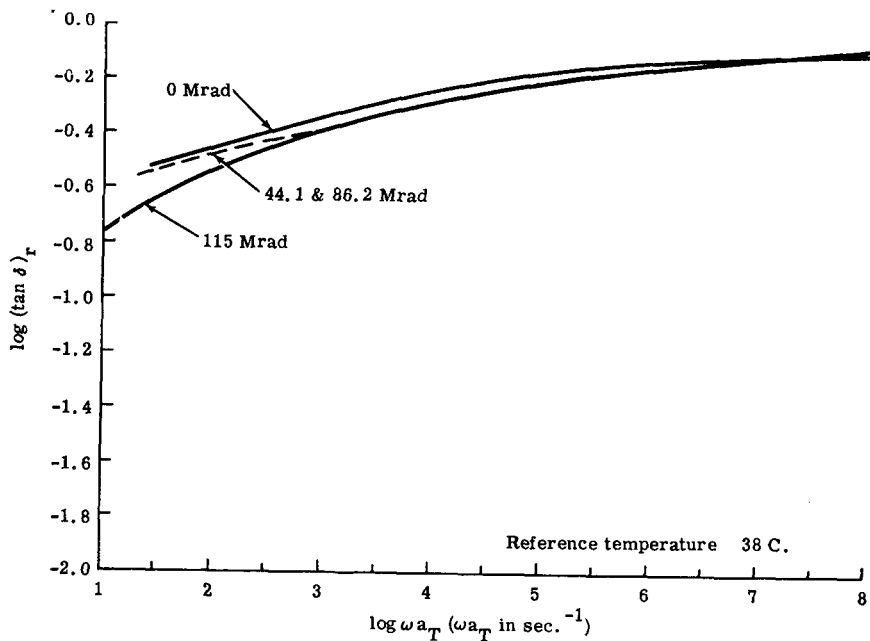


Fig. 11. Effect of γ -radiation on the loss tangent of silicone rubbers: X3-0272.

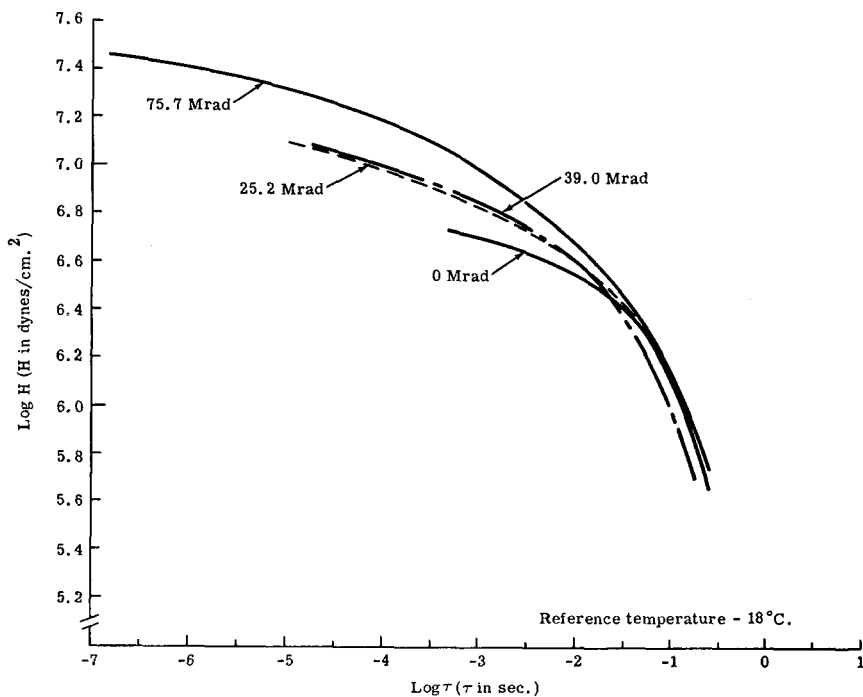


Fig. 12. Effect of γ -radiation on the relaxation spectra of silicone rubbers: Silastic 50.

of the X3-0272 changes very little. Jenkins²³ found no change in the loss tangent of irradiated silicone rubbers when the dynamic tests were performed during irradiation. The difference between the results of this research and that of Jenkins²³ could be due to post-irradiation crosslinking of the materials studied here.

Relaxation Spectra

The effect of γ -radiation on the relaxation spectra of the silicone rubbers is shown in Figures 12-14. The spectra are raised by irradiation effects as would be expected. However the spectra are not extended out to long times as was found in the case of the styrene-butadiene rubbers. This suggests that the molecular response is a different process for the two systems when mechanically deformed and/or when irradiated. Entanglement networks in the SBR could account for this difference.

Irradiation has little effect on the relative monomeric frictional coefficients. The coefficients are listed in Table III. This may be due to the overriding influence of the filler or again, perhaps due to the lack of an entanglement network formation.

Time-Temperature Shift Factors

The data in Figures 15-17 show the irradiation has little effect on the time-temperature relationships of the mechanical properties of silicone rubbers. This is expected for high molecular weight systems as these.²⁴

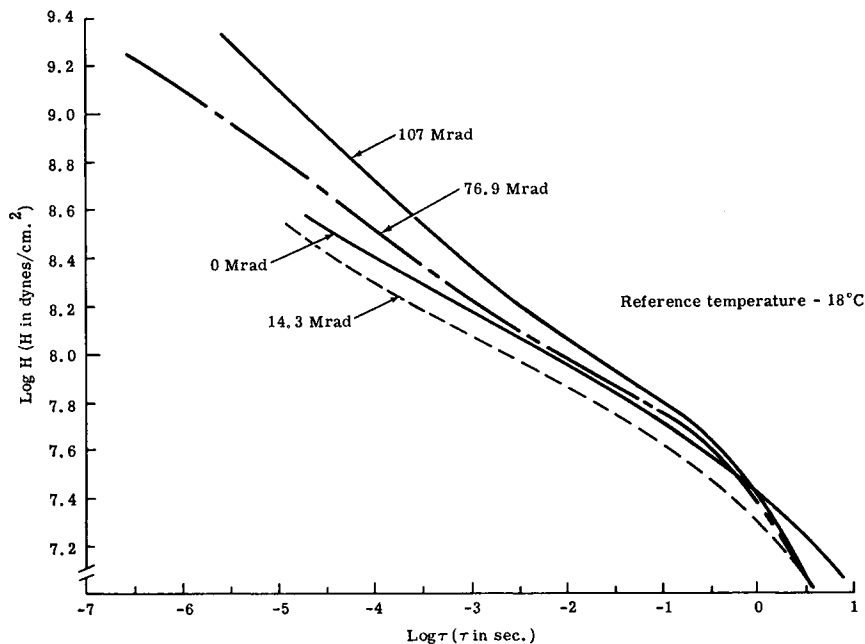


Fig. 13. Effect of γ -radiation on the relaxation spectra of silicone rubbers: Silastic LS63.

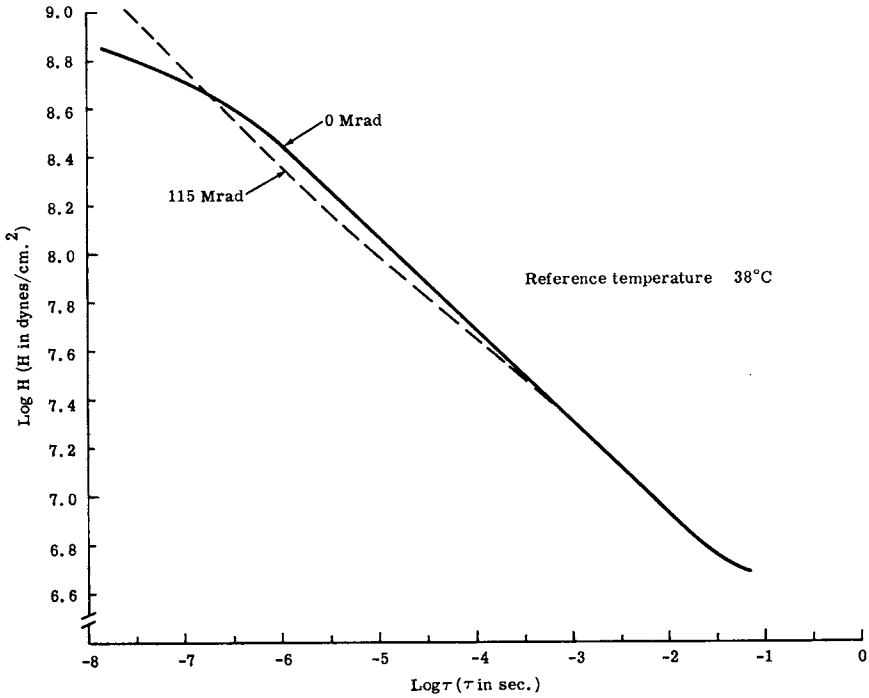


Fig. 14. Effect of γ -radiation on the relaxation spectra of silicone rubbers: X3-0272.

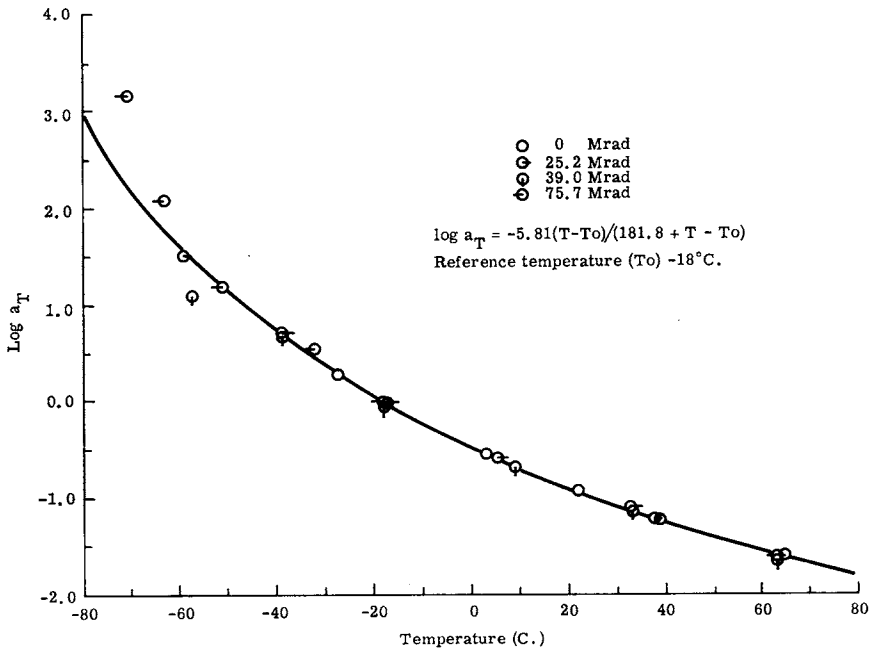


Fig. 15. Time-temperature shift factors of silicone rubbers: Silastic 50.

TABLE III
Relative Monomeric Frictional Coefficients of Irradiated Silicone Rubbers

Rubber	Irradiation dose, Mrads	Log τ	Log H	ζ_0 irradiated
				ζ_0 unirradiated
Silastic 50	0.0	-1.43	6.39	1.0
	25.2	-1.44	6.41	0.9
	39.0	-1.71	6.51	1.1
	75.7	-1.45	6.45	0.8
Silastic LS63	0.0	0.79	7.12	1.0
	14.3	0.25	7.20	2.4
	76.9	-0.25	7.51	4.4
	107	-0.20	7.53	1.5
X3-0272	All	No portion of the spectra had a slope of -0.5		

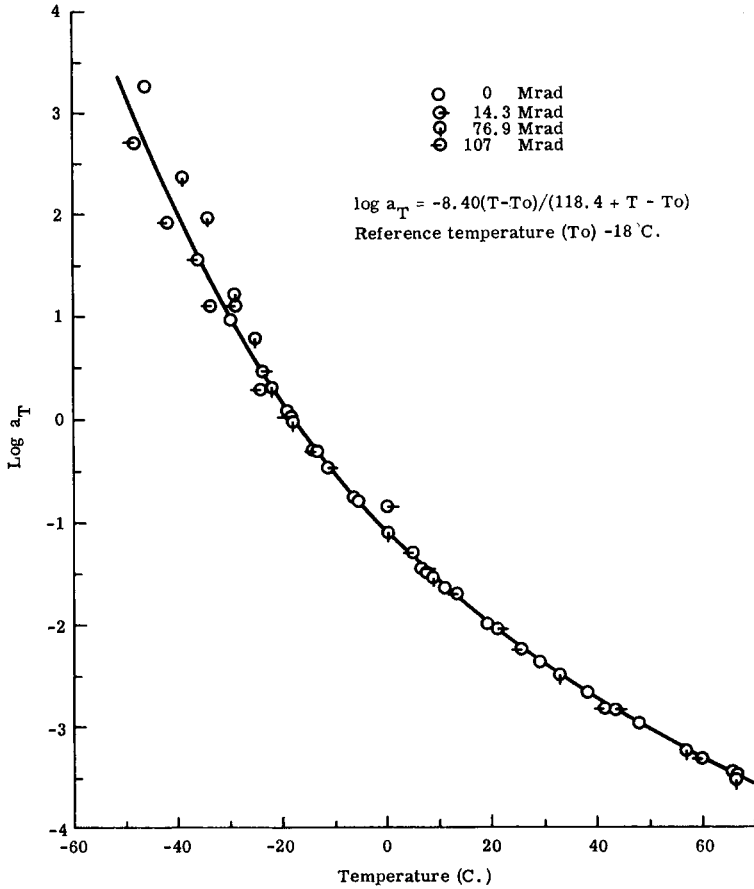


Fig. 16. Time-temperature shift factors of silicone rubbers: Silastic LS63.

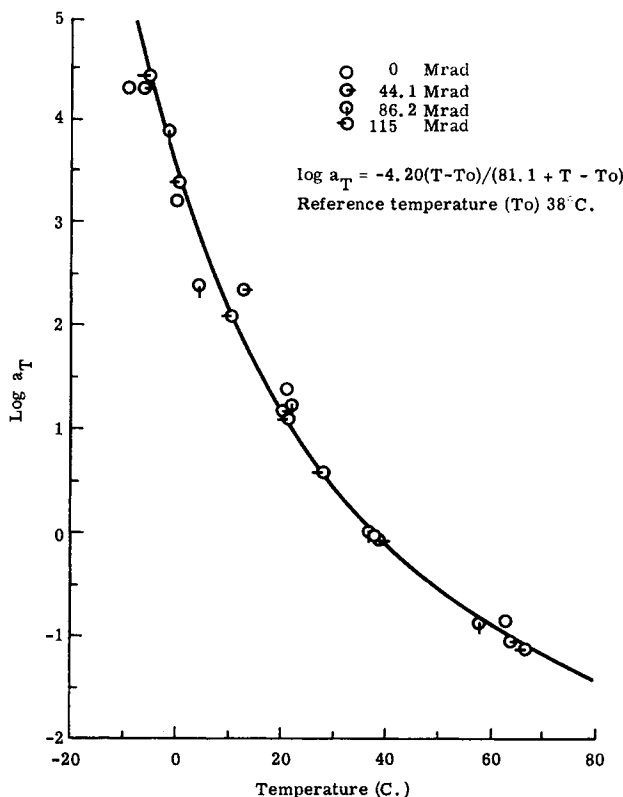


Fig. 17. Time-temperature shift factors of silicone rubbers: X3-0272.

The data can be correlated by the WLF equation.²⁵ The solid curves drawn in the graphs represent the WLF equation with parameters C_1 and C_2 derived from a least-squares analysis of the data.

The Williams modification²⁶ of the WLF equation has only one varying parameter, T_s . Glass transition temperatures are approximately 50°C. below the values for T_s .²⁵ Subtraction of 50°C. from the calculated values of T_s listed in Table IV give T_g values of -132°C. for Silastic 50, -80°C. for Silastic LS63, and -30°C. for the X3-0272. The estimated -132°C.

TABLE IV
Time-Temperature Relationships for Silicone Rubbers

Rubbers	Silastic 50	Silastic LS63	X3-0272
WLF equation			
Reference temperature, °C.	-18	-18	38
C_1	-5.81	-8.40	-4.20
C_2	181.8	118.4	81.1
T_s , °C.	-82	-30	20

for Silastic 50 agrees well with a reported²⁷ value of -123°C . for a dimethylpolysiloxane polymer. The value of -30°C . appears reasonable for the high phenyl content X3-0272, because increasing the phenyl content from 0 to 50% has been found²⁷ to increase T_g from -123°C . to -86°C .

CONCLUSIONS

Both scission and crosslinking reactions occur during the gamma irradiation of silicone rubbers. Dimethylpolysiloxanes predominantly crosslink as is evident in the measured changes in crosslink density and increase storage modulus. Scission reactions are also occurring as reflected in the initial decrease of the loss modulus on exposure to radiation. Scissioning and crosslinking reactions are approximately equivalent in the irradiated methyltrifluoropropylpolysiloxanes. Absorption of doses to 115 Mrad had essentially no effect on the crosslink density or dynamic mechanical properties of the aromatic-containing rubber, X3-0272. The aromatic structure is probably protecting the polymer chain. The high sol content (Table II) may also be influencing the response of the polymer to radiation.

This work was supported by the United States Atomic Energy Commission.

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Résumé

On a caractérisé des membranes à base de parlodion préparé par trempage dans des solutions de parlodion dans l'acétate d'isoamyle à des concentrations atteignant jusqu'à 3%. L'épaisseur de la membrane croît avec un accroissement de la viscosité de la solution dont on forme la membrane. Bien que la résistance des membranes croît avec l'accroissement de son épaisseur, la résistance spécifique ρ de différentes membranes n'était pas constante mais corissait avec une augmentation d'épaisseur et montrait une tendance à atteindre une valeur limite. Les effets de différents cations à la même concentration et pour un même cation à différentes concentrations sur les propriétés de la membrane ont été étudiés. Les membranes formées par trempages multiples dans la même solution et dans des solutions différentes de parlodion ont également été caractérisées, en ce qui concerne leur résistance électrique, leur capacitance et leur résistance spécifique. Toutes les solutions de parlodion en général, fournissaient des membranes, au second trempage, d'épaisseur accrue et de résistance également augmentée. Les trempages subséquents augmentent toujours l'épaisseur des membranes et leur résistance, excepté dans le cas de solutions à 0.25% qui produit une membrane d'approximativement la même épaisseur et même résistivité. Les techniques de trempage et d'étalement en vue de former la membrane ont été utilisées en vue d'introduire dans la matrice de parlodion de l'acide stéarique, de la phosphatidyl-L-sérine et du cholestérol, et les membranes lipidiques ainsi préparées ont été également caractérisées.

Zusammenfassung

Durch das Eintauchverfahren mit Parlodionlösungen in Isoamylacetat mit Konzentrationen bis zu 3% gebildete Parlodionmembrane wurden charakterisiert. Die Dicke der Membrane nimmt mit zunehmender Viskosität der membranbildenden Lösung zu. Der Membranwiderstand nahm zwar mit steigender Dicke zu, der spezifische Widerstand ρ der verschiedenen Membranen war jedoch nicht konstant, sondern stieg mit zunehmender Dicke an und zeigte eine Tendenz zur Erreichung eines Grenzwertes. Der Einfluss verschiedener Kationen bei gleicher Konzentration und des gleichen Kations bei verschiedenen Konzentrationen auf die Membraneigenschaften wurde untersucht. Weiters wurden Membrane, die durch mehrfaches Eintauchen in die gleiche Lösung oder in verschiedene Parlodionlösungen gebildet wurden, in Bezug auf ihren elektrischen Widerstand, ihre Kapazität und den spezifischen Widerstand charakterisiert. Alle Parlodionlösungen lieferten allgemein bei einem zweiten Tauchen Membrane mit erhöhter Dicke und erhöhtem Widerstand. Aufeinanderfolgendes Tauchen erhöhte die Membrandicke und den Widerstand mit Ausnahme des Falles einer 0,25%igen Lösung, welche eine Membran mit angenähert der gleichen Dicke und dem gleichen Widerstand lieferte. Das Tauchen und die Spreitungungsverfahren für die Membranbildung wurden zur Einführung von Stearinsäure, Phosphatidyl-L-serin und Cholesterol in die Parlodionmatrix benutzt und die so erhaltenen Lipoiden Membrane wurden charakterisiert.

Received November 10, 1965

Prod. No. 1319