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UCRL-51222

**IRRADIATION OF A POLY-M-CARBORANYL
SILOXANE AND SOME RELATED COMPOUNDS**

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MS. date: May 4, 1972

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IRRADIATION OF A POLY-M-CARBORANYL SILOXANE AND SOME RELATED COMPOUNDS

Abstract

The number of gas molecules evolved for 100 eV of absorbed dose (G-value) was obtained for the neutron and ^{60}Co γ -irradiation of a poly-m-carboranyl siloxane formulation, and for the neutron irradiation of o-carborane and isopropyl o-carborane. A poly-dimethyl siloxane rubber was also irradiated. The carborane moiety adds stability to the silicone chain and to the aliphatic chain; however, it is not as effective in this respect as the

aromatic ring. The G-values are: poly-m-carboranyl siloxane—0.93, poly-dimethyl siloxane—2.4, o-carborane—1.09, and isopropyl o-carborane—1.37. The latter value can be compared with the corresponding G-values for benzene—0.06, isopropyl benzene—0.245, and polyethylene—2-5.

Some heating experiments were also performed on irradiated and un-irradiated poly-m-carboranyl siloxane.

Introduction

Poly-m-carboranyl siloxanes constitute a new class of polymers with excellent high-temperature properties. In these polymers, m-carborane units are regularly spaced along a poly-dimethyl siloxane chain; the polymer investigated in this study has two dimethyl siloxane units for each m-carborane, and has been described in the literature¹⁻³ by the code names SiB-2 or Dexsil-201.

It is of interest to obtain a preliminary evaluation of the irradiation stability of these polymers and compare it to that of some related materials, such as pure o-carborane, isopropyl o-carborane, aromatic compounds, and a conventional polysiloxane rubber, Y-3602 (Union Carbide). The stability to neutron irradiation was of particular interest, since

thermal neutron capture by the boron-10 leads to disruption or gross change of the carborane cage structure. Since there was some uncertainty about the absolute radiation dose during neutron irradiation as well as interest about the relative effects of neutron and γ -irradiation, the poly m-carboranyl siloxane polymer was also irradiated with a cobalt-60 source.

For the purpose of this preliminary evaluation of irradiation stability, the G-values for gas evolution* were compared. Thermogravimetric analyses of irradiated and virgin polymers were also obtained.

*G-value is the number of gas molecules evolved for 100 eV of absorbed dose.

Experimental

MATERIALS

The poly-m-carboranyl siloxane (Dexsil) is usually compounded with an iron oxide filler which enhances the high-temperature air stability; however, due to neutron activation this filler would give us handling problems. The formulation selected (Table 1) has 49.6 wt% silica filler (Min-U-Sil 5M). The chemical structure of Dexsil-201 is¹

where the $\text{C}_2\text{B}_{10}\text{H}_{10}$ stands for the m-carborane nucleus.

Impure o-carborane was obtained from the Thiokol Co. and purified at Lawrence Livermore Laboratory (LLL) to 98-99% purity. The isopropyl o-carborane was also prepared by Thiokol. The sample

Table 1. Dexsil-201.

Formulation ^a	
Dexsil-201	100 pts.
Min-U-Sil (5M)	100 pts.
Luperco CST ^b (50% DCBP)	1.2
Cure	5 min at 230°F
Post cure:	16 hr at 212°F
	8 hr at 300°F
	2 hr at 500°F

^aAs supplied by Olin Mathieson.

^b50% dichlorobenzoylperoxide in a silicone fluid.

was a colorless liquid of about 99% purity. The Y-3602 silicone rubber of Union Carbide is a poly-dimethyl siloxane cross-linked with isocyanate and filled with 25 wt% silica.

IRRADIATION

The neutron irradiation experiments were carried out in the Livermore Pool-Type Reactor (LPTR) in the R-1 pneumatic tube station. A small polyethylene cylinder, "the rabbit," containing the sample is shot to a position near the core of the reactor. At the completion of the irradiation, the "rabbit" containing the sample is shot out of the tube with compressed air. The transit time is about 1 sec; thus with irradiation times of 1-5 min, timing accuracy was adequate.

The γ -irradiations were carried out at the LLL ^{60}Co irradiation facility.

Sample size was governed by two factors. First, in order to measure the volume of gas produced easily and provide

an adequate sample for mass spectrographic analysis, it was necessary to generate between 0.2-1 cm³ (STP) of gas. Second, it was decided that 10% of the sample would be the maximum amount of allowable destruction. Original sample sizes were calculated by estimating the neutron flux and the G-values.

The samples were prepared for irradiation by sealing them in evacuated quartz vials. The vials were then placed in standard rabbits to be shot in the pneumatic tube. A combination of rigid and flexible foam was used to protect the samples from shock.

After irradiation, the glass vials were placed inside a vacuum system and broken open using a sample breaker. The volume of the evolved gas was measured using a standard volume and a MKS Baratron^R pressure measuring device. The gas was then collected and analyzed by mass spectrometry. All of the samples were handled in this fashion, although slightly different quartz vials were used to accommodate the liquid and crystalline samples.

With the samples of Dexsil and the silicone rubber, it was found that it was best to cut the sample into small chunks to minimize self-attenuation. Thick, single-plate samples were tried and yielded a smaller G-value, indicating a smaller absorbed dose throughout the sample. The samples never exceeded 1 cm³ in volume, thus leaving 3 or 4 cm³ for gas collection. Some data were also obtained on the composition of the gases evolved by heated (600°C) and irradiated and heated Dexsil.

CALCULATION OF ABSORBED DOSE

γ-Dose

The γ-dose rate as measured in the reactor with LiF thermoluminescent dosimeters is 7×10^7 (±30%) R/hr in the R-1 tube. Within this accuracy, one can assume that the absorbed dose is 1 rad/R for all materials. This assumption, as well as the uncertainty in the dose rate, are important only in the calculation of absorbed dose in the silicone rubber; for the carborane compounds, the neutron capture by ¹⁰B dominates the energy deposition. The γ-dose rate during the ⁶⁰Co irradiation of Dexsil-201 was 19.2 Mrad/hr and the total dose is known within 5%.

Neutron Dose

The neutron fluxes in the R-1 pneumatic tube location were monitored several times during the irradiations, using the cadmium-gold foil activation method. The activity induced in 0.5 wt% Au-Al alloy is used as a measure of the neutron flux. The flux of neutrons having energies below 0.18 eV (thermal) is deduced by comparing the activity induced in a bare Au-Al alloy foil with that induced in a similar foil shielded with Cd foils. The data in Table 2 show the individual measurements; average values are:

$$\begin{aligned}\phi_{\text{total}} &= 22.0 \times 10^{12} \text{ n/cm}^2 \text{ sec} \\ \phi_{\text{epithermal}} &= 10.5 \times 10^{12} \text{ n/cm}^2 \text{ sec} \\ &\quad (\text{above } 0.18 \text{ eV}) \\ \phi_{\text{thermal}} &= 11.5 \times 10^{12} \text{ n/cm}^2 \text{ sec}.\end{aligned}$$

For the calculation of absorbed dose from neutron interactions, we followed the method of Cheek and Linnenborn.⁴

Neutron irradiation deposits energy in a system by two mechanisms: (1) Scattering—elastic collisions with fast neutrons,

Table 2. Neutron flux measurements.

Total Au foil $\times 10^{-12}$	Epithermal Au + Cd foils $\times 10^{-12}$	Thermal $\times 10^{-12}$	Samples irradiated same day
21.5	10.2	11.3	N-010, N-011
22.4	11.0	11.4	N-015, N-016, N-018
21.8	10.7	11.1	
22.6	10.5	12.1	N-019, N-022
22.0	10.1	11.9	N-020, N-023
			N-021, N-024
			N-025
22.5	11.1	11.4	—
21.0	9.78	11.22	N-026, N-029
			N-027, N-034
			N-028
<u>Averages</u>			
22.0	10.5	11.5	
Average cadmium ratio—2.098			

and (2) capture reactions—neutron capture which predominantly occurs with thermal neutrons. The dose due to the two mechanisms is calculated separately.

With both calculations, a major problem is knowing the neutron spectrum. Following Cheek and Linnenbom, we assumed that the neutron energy distribution in the LPTR can be described by an epithermal component ($10^{-6} < E < 2$ MeV) and a fission energy component ($2 \text{ MeV} < E$). The energy distribution of the epithermal component is given by:

$$N(E) = k_1/E; \text{ for } 10^{-6} < E$$

$$\leq 2 \text{ MeV with } K_1 = 0.06517;$$

and the energy distribution of the fission neutrons is described by

$$N(E) = 0.4839 \sinh \sqrt{2E} e^{-E} \text{ for } E > 2 \text{ MeV.}$$

The above energy distributions dominate the energy deposited by scattering; the neutron capture by boron is predominantly in the thermal region.

Scattering

It is assumed that each element i in a compound m scatters independently, and the contribution to the dose due to scattering is

$$s \bar{D}_m = \sum_i i s \bar{D}_i,$$

where i is the mass fraction of element i in the sample and $s \bar{D}_i$ is a weighed energy contribution per unit mass of element i which includes the effect of neutron energy spectrum, the scattering cross section, and the average energy loss per collision.

The total dose is then this rate multiplied by the fast flux. When normalized to a fast flux of $10^2 \text{ n/cm}^2\text{-sec}$, the energy deposited by fast neutron scattering is given in Table 3 together with the γ -dose. Boron contains approximately 19% of ^{10}B isotope which has a very high thermal neutron capture cross section ($\sigma = 3850$ barns). The reaction is

Table 3. Reactor irradiations.

Dose due to n and γ scattering (for $\phi_{th} = 11.5 \times 10^{12}$ n/cm ² sec)			
Material	Neutron dose (rad/sec)	γ dose ^a (rad/sec)	Total scattering (rad/sec)
Dexsil-201	5.52×10^3	1.9×10^4	2.4×10^4
Silicone rubber	5.49×10^3	1.9×10^4	2.4×10^4
Isopropyl carborane	6.46×10^3	1.9×10^4	2.5×10^4
Carborane	6.12×10^3	1.9×10^4	2.5×10^4

^a Assume absorbed dose to be 1 rad/R for all materials.

Table 4. Dose due to boron-10 (n, α) reaction ($\phi_{th} = 11.5 \times 10^{12}$ n/cm² sec)

Material	Cross section (cm ⁻¹)	Dose (rad/sec)	Dose (eV/mole-sec)
Dexsil-201 ^a	13.5	5.57×10^5	6.08×10^{22}
Silicone rubber	—	—	—
Isopropyl carborane	22.6	10.4×10^6	12.1×10^{22}
Carborane	31.0	13.2×10^6	12.0×10^{22}

^a For the unfilled rubber.

$^{10}\text{B} + n^1 = ^4\text{He} + ^7\text{Li} + 2.79 \text{ MeV}$. The 2.79 MeV are partitioned into a 0.48-MeV γ and 2.31-MeV kinetic energy of the ^4He and ^7Li fragments. The local energy deposition from the γ can be neglected and the local deposition calculated from

$$R = E \phi_{th} \Sigma$$

where E is the local energy deposited per capture, 2.31 MeV; ϕ_{th} is the thermal neutron flux* and Σ is the macroscopic cross section given by

$$\Sigma(\text{cm}^{-1}) = \frac{\rho N_A}{M} \gamma \sigma$$

* It was assumed that the thermal neutrons measured with the Cd and Au foils have an effective energy consistent with the thermal neutron capture cross sections given in the literature.

where

N_A = Avogadro's number,

ρ = density,

γ = mass fraction of ^{10}B ,

σ = (n, α) cross section, and

M = molecular weight.

Table 4 gives the energy deposition from thermal neutron capture in the different materials.

In addition to the (n, α) reaction, there are some atoms which have (n, γ) reactions. The contribution in our case is very small, of the order of one-hundredth the contribution due to scattering. A comparison of Tables 3 and 4 shows that the scattering contribution is negligible in samples which contain boron.

For the purposes of all the subsequent calculations, the thermal neutron flux was assumed to be a constant for all irradiations, 11.5×10^{12} n/cm²

sec; the scatter in the G-values was not particularly improved by using the individual flux measurements given in Table 2.

Results

The G-values,* i.e., total moles of gas evolved per unit absorbed doses (Tables 5 through 11), are as follows:

	G-value*
Dexsil-201	0.93 (0.92 from the γ irradiations)
Y-3602	2.4
o-carborane	1.09

* Calculated to a filler-free basis for the two rubbers, Dexil and Y-3602.

Isopropyl carborane 1.37

While the difference in G-values for γ and neutron irradiation of Dexsil-201 is well within experimental error, different decomposition mechanisms must apply, as evidenced by the difference in gas compositions (Table 6). The G-values obtained on Y-3602 are quite consistent with literature data; thus, if we consider the

Table 5. Dexsil-201—irradiation data.^a

Sample No.	Exposure time (min)	Weight (g)	Gas evolved (STP cm ²)	Absorbed dose (Mrad)	G (molecules/100 eV)	Remarks
N-001	2.4	0.1561	1.378	800	0.953	
N-007	2.4	0.1584	1.916	800	1.31	
N-013	2.4	0.1652	1.322	800	0.864	
N-015	2.0	0.1485	1.145	668	0.999	
N-016	3.0	0.1588	1.663	1000	0.921	
N-019	2.0	0.1611	0.945	668	0.760	Thick sample, self-attenuation
N-020	2.0	0.1581	1.127	668	0.923	
N-021	2.0	0.1572	1.093	668	0.900	
Average G value 0.953						
Average G, excluding N-007 and 019 0.927; S = 0.046						
γ -001	—	0.1861	1.457	605	0.940	
γ -002	—	0.1922	1.437	605	0.897	
γ -003	—	0.1751	1.334	605	0.915	
Average G value 0.917; S = 0.023						

^a Values of G and absorbed dose are calculated for the unfilled rubber. Density of Dexsil—1.03 g/cm³.

Table 6. Dexsil-201.

Compound	Typical radiolytic gas composition ^a mole (vol) %			
	γ irradiation	n irradiation	Heating to 600°C	n-irradiation + heating
Hydrogen—H ₂	35.2	63-69	58	33-41
Methane—CH ₄	56.5	22-24	21	44-46
Ethane—C ₂ H ₆	7.73	5-6		2
Propane—C ₃ H ₈	0.33	—		
Butane—C ₄ H ₁₀	0.11	0.3		
Isopentane—C ₅ H ₁₂	0.05	N. A.		
Trimethylsilane—(CH ₃) ₃ SiH	0.03	N. A.		
Tetramethylsilane—(CH ₃) ₄ Si	0.04	0.3-0.6	15	9-20
cm ³ of gas/g (2.0-min reactor irradiation)		7.1	32	30-57

^aIn the initial survey the mass spectrometer results were only examined for major constituents.

Table 7. Y-3602 silicone rubber—irradiation data.^a

Sample No.	Exposure time (min)	Weight (g)	Gas evolved (STP cm ³)	Absorbed dose (Mrad)	G (molecules/100 eV)	Remarks
N-010	3.0	0.9996	0.1899	4.3	2.5	
N-22	5.0	0.9856	0.2732	7.2	2.2	
N-024	5.0	0.8071	0.2527	7.2	2.5	
N-026	5.0	0.8852	0.2773	7.2	2.5	
N-027	5.0	0.8256	0.2917	7.2	2.8	
N-011	5.0	1.0547	0.2725	7.2	2.1	
N-023	5.0	1.0950	0.3579	7.2	2.6	
N-025	5.0	0.8409	0.2363	7.2	2.2	
N-028	5.0	0.8550	0.4098	7.2	3.8	Omit from averages
Average G					2.4	S = 0.23

^aThe values of G and absorbed dose are calculated for the unfilled rubbers.

Density of Y-3602—1.15 g/cm³.

volume of CO₂ + CH₄ evolved per unit dose, we obtained 0.011 cm³/g Mrad as compared with 0.012 cm³/g Mrad reported by Klein and Mannal⁵ on General Electric's SR-32 silicone resin. The G-values indicate that the carborane nucleus, which

provides the high-temperature stability of Dexsil-201, also provides a measure of additional irradiation stability; a factor of 2 between the G-values of the unfilled rubbers formulated into Dexsil-201 and Y-3602. One can compare the radiation

Table 8. Y-3602 silicone rubber—
typical radiolytic gas composition
(7 samples).

Compound	Vol%
CO ₂	0.3-0.7
H ₂	30-36
Methane CH ₄	36-44
Ethane C ₂ H ₆	18.5-21.7
Propane C ₃ H ₈	0.09-0.2
Butane C ₄ H ₁₀	0.2-0.4
Acetone C ₂ H ₆ CO	0.2-8.2
Tetramethyl silane	0.03-0.1

The H₂/CH₄ ratio varied between 0.70
and 0.86; the C₂H₆/CH₄ ratio varied be-
tween 0.50 and 0.54.

stability of carborane derivatives with
that of benzene derivatives⁶:

	G Gas molecules/ 100 eV	Compound	G Molecules/ 100 eV
o-carborane	1.09	Benzene	0.059
Isopropyl carborane	1.37	Isopropyl benzene	0.245
Propane (total G-value)	5.4		
Butane (total G-value)	5.6		
Polyethylene	2-5		

While the carborane nucleus adds to the
radiation stability, it is not quite as ef-
fective as the aromatic benzene nucleus.

A few heating experiments were per-
formed on Dexsil to compare the amounts
of gas evolved and gas compositions under
the following set of conditions:

1. Irradiation only
2. Heating to 600°C
3. Neutron irradiation followed by
heating to 600°C.

The composition and amounts of gas
evolved under the three different treat-
ments, as given in Table 6, show that the
mechanisms of decomposition and total
gas volumes are quite different for the
three different treatments.

An attempt was made to compare the
weight losses on heating of irradiated and
un-irradiated material. The results,
shown in Fig. 1, indicate a completely
different pattern of decomposition. The
un-irradiated material shows two well de-
fined decomposition steps; they probably

Table 9. Simple carborane compounds—irradiation data.

Sample No.	Exposure time (min)	Weight (g)	o-carborane		G (molecules/100 eV)
			Gas evolved (STP cm ³)	Absorbed dose (Mrad)	
N-006	1.0	0.1332	3.46	949	1.18
N-030	1.0	0.2099	3.57	791	0.92
N-031	2.0	0.1554	6.71	1582	1.17
Average G					1.09
Density of o-carborane 1.0					
Sample No.	Exposure time (min)	Weight (g)	Isopropyl carborane		G (molecules/100 eV)
			Gas evolved (STP cm ³)	Absorbed dose (Mrad)	
N-008	1.0	0.1704	2.99	623	1.21
N-009	2.0	0.1662	7.04	1246	1.46
N-032	1.0	0.1824	3.76	623	1.42
N-033	2.0	0.1778	7.19	1246	1.39
Average G					1.37
Density of isopropyl o-carborane 0.925					

Table 10. o-carborane — radiolytic gas composition (3 samples).

Compound	Sample No.	
	N-006 (Vol%)	N-030 (Vol%)
H ₂	93.9	94.2
CH ₄	3.1	2.8
CO ₂	0.1	0.01
C ₂ H ₆	0.3	0.4
C ₃ H ₈	0.1	0.1
C ₄ H ₁₀	0.4	0.7
C ₆ H ₁₄	2.0	1.6
C ₆ H ₁₂	0.1	0.02
G-value	1.18	0.92

Table 11. Isopropyl carborane — radiolytic gas composition.

Compound	Sample No.	
	N-008 (Vol%)	N-009 (Vol%)
H ₂	93.4	76.8
CH ₄	5.6	11.3
Other	1.0	11.9
G-value	1.21	1.46

correspond to the loss of one hydrogen molecule (below 400°C) and a methane group (below 575°C) per repeating chain unit.

The irradiated material has essentially a continuous range of decomposition products.

Fig. 1. Comparative TGA run on irradiated and un-irradiated Dexsil-201.

Acknowledgments

The majority of the experimental work shown herein was done and coordinated by Stephen Cunningham during the summer of

1968. It could not have been done without the excellent help and cooperation from people in Analytical Chemistry and the

LPTR. Richard and Patricia Crawford and Elinor Smathers in Analytical Chemistry, and Willard Burns at the LPTR were particularly helpful. Robert Valentine and Ted Jessop obtained the TGA data. Dr. Richard Pearson sup-

plied the samples of simple carborane derivatives, and was most helpful in the planning of the experiment. The γ -irradiation results were obtained by Dr. Richard E. Bozak during the summer of 1971.

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**Printed in USA. Available from the National Technical
Information Center, National Bureau of Standards,
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