

Radiation Effects on Methyl Vinyl Polysilicone Foam

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ABSTRACT: The effects on methyl vinyl polysilicone foam of ^{60}Co γ -ray radiation at room temperature was studied in air, *in vacuo*, and in an inert gas atmosphere. The unirradiated and irradiated samples were analyzed by Fourier transform infrared spectroscopy, scanning electron microscopy, pyrolysis gas chromatography/mass spectroscopy, and thermogravimetric analysis, and the gas products after radiation were analyzed by gas chromatography/mass spectroscopy. The changes of the gel fraction, compression properties, and the stress–relaxation ratio with dose for irradiated samples were observed. The results show that the

second crosslinking reaction in the polysilicone after chemical crosslinking took place at a low dose (2×10^5 Gy), but radiation degradation was predominant, with the dose increasing step by step. The mechanical properties of polysilicone foam gradually became low grade after it was irradiated by any dose in excess of 2×10^5 Gy. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 3437–3441, 2003

Key words: radiation; compression; crosslinking; degradation

INTRODUCTION

Silicone rubber has many virtues, such as cold resistance, antiweatherability, and excellent insulating properties.^{1–3} It is widely used for wire cables, sealing, and cushion materials, among others.^{4,5} One article on silicone rubber irradiated by γ -ray radiation appeared early in 1957.⁶ This article mainly commented on the radiation-resistance ability of several silicone rubbers, and their gross dose range of radiation resistance was determined. Since 1980, there have been more studies on silicone rubber used in the radiation field in the United States, Japan, Germany, England, and other locations.^{7–12} The focus has been on the effect of different radiation sources and dose rates versus silicone rubber, natural rubber, fluorine rubber, and so on, but they have not touched on the damage to these materials and changes in their microscopic structure. Until now, there has been no detailed study of radiation effects on open-porous silicone rubber foam. In this study, the chemical structure of methyl vinyl silicone foam after γ -ray radiation and its gas products were comprehensively analyzed, and the internal relations between the structure and properties of the materials after and before radiation were studied.

EXPERIMENTAL

Materials

Open-porous methyl vinyl polysilicone foam was from the Institute of Structural Mechanics, Academy

of Engineering Physics, Mianyang, China. The additives in the foam were carbon black, ZnO, and Fe_2O_3 .

Radiation

The radiation source was provided by Cobalt Source Radiation Technology Co., Ltd. (Mianyang, China). The dose rate was 131–137 Gy/min., and the total dose was 10–1000 kGy.

Measurement and testing

The porous structure of each sample's section was analyzed by scanning electron microscopy (SEM; model KYKY-2800, Scientific Instrument Corp., Chinese Academy of Sciences, Beijing, China), and the porous size and dispersity were studied with a 570 Analysis Instrument of Picture and related computer software, Beijing Corp. of Analytic Instruments, Beijing, China.

The samples were analyzed by Fourier transform infrared spectroscopy (FTIR; System 2000, Perkin Elmer, Norwalk, CT). The wavenumber range was $4000\text{--}400\text{ cm}^{-1}$, the scanning rate was 0.5 cm/s , the scanning order number frequency was 100 times, and the resolution ratio was 4 cm^{-1} .

The quality–loss ratio of the samples was analyzed in nitrogen by thermogravimetric analysis (TGA; TGA7, Perkin Elmer). The rate of temperature increase was 10°C/min .

The gel fractions of samples were measured by the Soxhlet extraction method. The samples were dried to a constant weight (W_0) and then placed in a Soxhlet vessel and extracted in xylene. After extraction, the residues were dried in a vacuum oven to a constant

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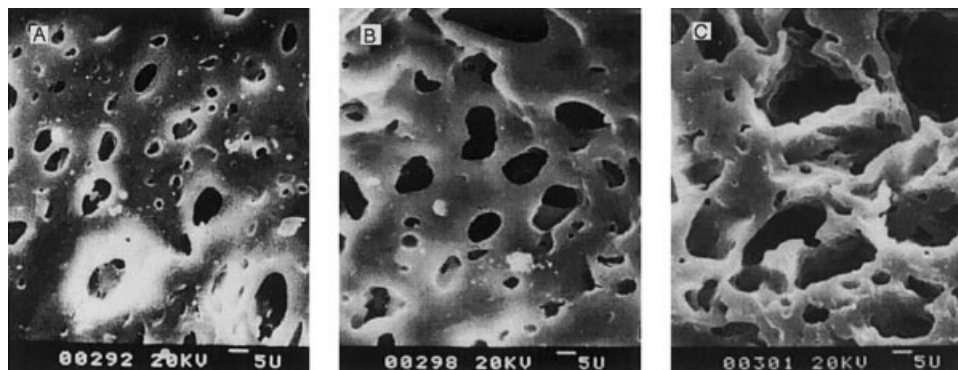


Figure 1 SEM micrographs of samples at room temperature in air: (A) unirradiated sample, (B) sample irradiated at 4×10^5 Gy, and (C) sample irradiated at 1×10^6 Gy.

weight (W_1) at 50°C and were then weighed to determine the gel fraction (g) with the following equation:

$$g = \frac{W_1 - W_2}{W_0 - W_2}$$

where W_2 is the total quantity of fillers or other additives that are insoluble in xylene.

The samples were also analyzed by gas chromatography (GC; HP6890) and mass spectroscopy (MS; Finnigan MAT98 B-E, Germany). The pyrolysis machine was a model CDS2000.

The compression properties of the specimens were determined with a universal testing machine (Instron 1196, Changchu, China), and the stress relaxation was determined with an electron creep/relaxation tester at a temperature of 25°C and a relative humidity of 55%.

RESULTS AND DISCUSSION

Porous changes of methyl vinyl silicone foam before and after radiation

Figure 1 shows the microscopic structure of the sample sections before and after radiation at different doses. The porous size and dispersity are random in the photos. When the samples were irradiated at a higher dose, the porous size became bigger, and the completeness of the porous wall was destroyed. The porous sizes of the unirradiated sample and the one irradiated at a dose of 1×10^6 Gy were determined; the former was $4.564 \mu\text{m}$, and the latter was $7.005 \mu\text{m}$.

FTIR analysis of the methyl vinyl polysilicone foam before and after radiation

The FTIR built-up spectra of the polysilicone foam after and before radiation are shown in Figure 2. The spectra were similar in the position of the same peak for the different samples, but the relative intensity of the same peak was different. The bending vibration of $-\text{CH}_3$ was at 1260 cm^{-1} . The characteristic peaks of the Si—O unit

were at 1100 , 1020 , and 800 cm^{-1} . The nonplanar rocking vibration absorption peak of the C—H bond partly coincided with the 800 cm^{-1} peak. The peak at 2963 cm^{-1} belonged to the stretching vibration of $-\text{CH}_3$ in the side chain, and there was little change in the position and intensity of $-\text{CH}_3$. As a result, the height of the 2963 cm^{-1} peak was chosen as a reference. Figure 3 shows the relationship of the peak (1020 cm^{-1} Si—O) height ratio of irradiated samples with the dose. There was a large difference in the samples' Si—O peak height ratio after radiation in different atmospheres, especially in air. The Si—O peak height ratio decreased sharply along with the dose due to the interference of oxygen in air. However, *in vacuo* and in inert gas, the Si—O peak height ratio increased and then decreased. At first, the Si—O—Si chain was strengthened with the dose, but when it was exposed to a higher dose radiation, the main chain was gradually damaged due to degradation.

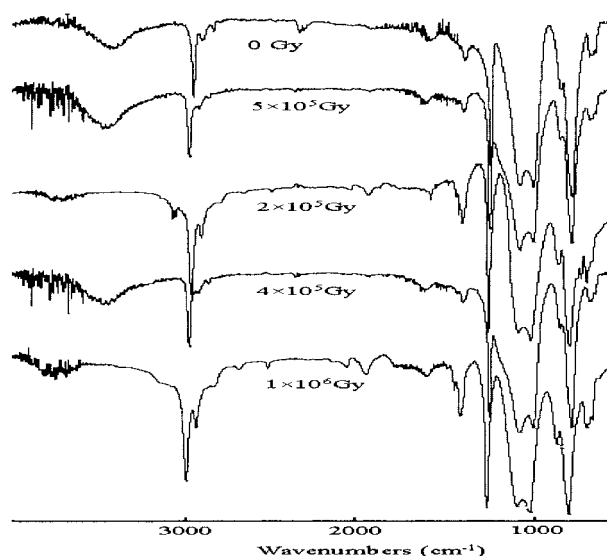


Figure 2 FTIR of samples before and after radiation in air at room temperature.

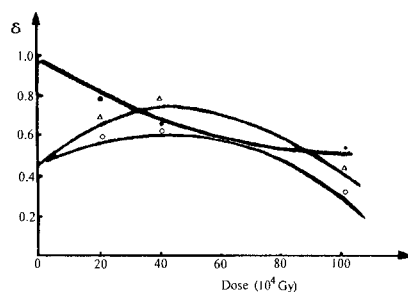


Figure 3 Si—O peak height ratio of samples irradiated in different atmospheres at room temperature: (●) in air, (▲) in inert gas, and (○) *in vacuo*.

Thermal analysis of the samples before and after radiation

The thermal stability of the samples before and after radiation was studied by TGA. The initial resolution temperature can be affected by many factors, including as the sample's state and experimental conditions. Therefore, the resolution temperature corresponding to the maximum quality-loss ratio (T_{\max}) was chosen and is discussed. The T_{\max} of samples irradiated in different doses in the three atmospheres is plotted in Figure 4. With increasing dose, the T_{\max} of samples in air gradually decreased and stabilized after radiation at a dose of about 4×10^5 Gy. This could be attributed to the fact that the diffusing rate of oxygen into foam was quicker than the consumption rate of adsorbed oxygen and that the residual oxygen accelerated the decomposition of samples when irradiated and led to the decrease in T_{\max} . However, when the dose was increased to eliminate the absorbed oxygen in the pores and after the elimination arrived at a limit, the oxygen disturbance reached another limit, and the curve platformed at high doses. However, the radiation results *in vacuo* and in inert gas were much different than those in air. At the initial stage, T_{\max} increased with increasing dose, and the thermal steadiness of samples was improved. However, later T_{\max} gradually decreased with further increasing dose. The thermal steadiness of the corresponding sample be-

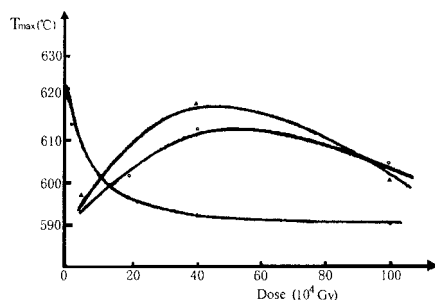


Figure 4 T_{\max} values of the samples after radiation as a function of the dose: (●) in air, (▲) in inert gas, and (○) *in vacuo*.

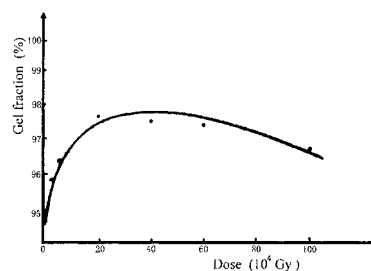


Figure 5 Gel fraction of silicone foam irradiated in air at room temperature.

came low, but it was still higher than that of the sample irradiated at the same dose in air.

Relationship between the gel fraction of the samples and the dose

Figure 5 shows the change in the gel fraction of the sample irradiated in air. At the beginning, the gel fraction of the sample took on a rising trend. The reason was that a second crosslinking took place after chemical linking, that is, additional radiation linking. The gel fraction of the silicone foam attained a maximum at a dose of 2×10^5 Gy. Then, with the dose further increasing, the gel fraction of sample decreased. This indicates that the crosslinked silicone foam was in a saturation state due to decomposition from radiation. However, on the whole, the decomposition degree was not high. The gel fraction of the sample irradiated at a dose of 1×10^6 Gy decreased 2% or so compared with that of the sample irradiated at a dose of 2×10^5 Gy. This shows that methyl vinyl silicone foam had better radiation stability.

Gas products of samples after radiation and the reaction mechanism

The decomposition temperature in pyrolysis gas chromatography (PGC) after the nonirradiated sample and those irradiated in different doses were analyzed by TGA was defined as 600°C. The sample was placed in the PGC/MS sample vessel, and the temperature was increased to 600°C in 10 min. The gas products of the samples after thermal decomposition were analyzed. In the low district of MS, the gas products of the nonirradiated sample through thermal decomposition were the same as those of the irradiated sample through radiation decomposition. Some of the products were H_2 ($m/e = 2.1$ and 1.1), CH_4 ($m/e = 16.2$, 15.2 , and 14.2), and CH_3SiOCH_3 ($m/e = 73.3$ and 57.3 ; see Fig. 6 for more details). This shows that the decomposition mechanism resulting from radiation was similar to that resulting from thermal decomposition with some other peaks in the high district. The objects attacked by decomposition were often the points of

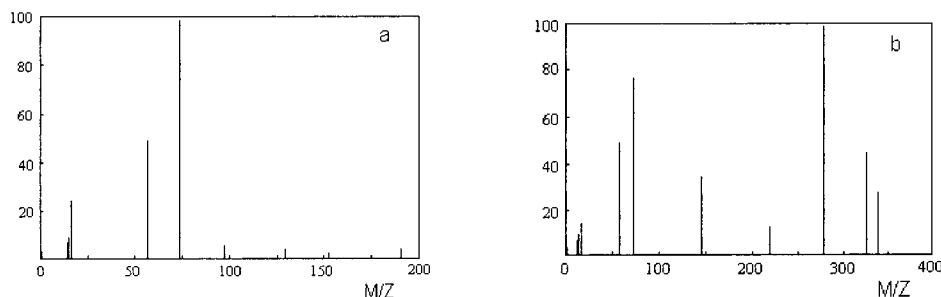
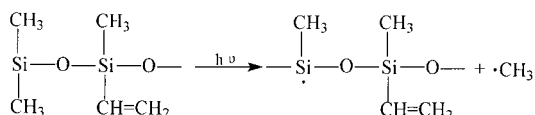


Figure 6 MS of gas products from the degradation of samples at different conditions: (a) after irradiation and (b) after thermal resolution (at room temperature, dose = 1×10^6 Gy, and resolution temperature = 600°C).

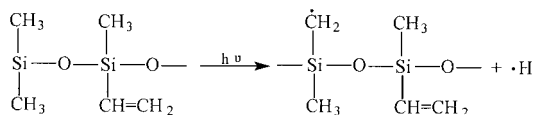
weakness in the chemical long chain, such as in low bond-energy positions and side chain positions.

According to the FTIR of irradiated samples and the MS of gas products, the decomposition mechanism of silicone was deduced as follows:

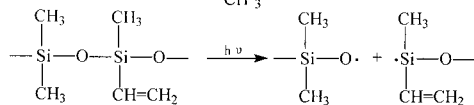
1. The formation of the methyl free radical. For example



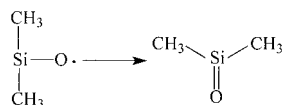
2. The formation of a hydrogen free radical. For example



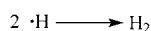
3. The formation of $-\text{Si}(\text{CH}_3)_2\text{O}\cdot$. For example



4. The formation of $\text{CH}_3\text{SiOCH}_3$. For example



5. The formation of H_2 . For example



Variance in the mechanical properties of the samples before and after radiation

Figure 7 shows the relations of the compression properties of the samples irradiated in air and the dose. The

flat area in the curve expanded after the dose was increased. However, the sample irradiated up to 1×10^6 Gy was easily compacted. This proved that the resilience of the sample was not very good before radiation, but after radiation, the resilience was improved, and the hardness of sample was increased. With further increasing dose, the brittleness of sample rose, and the elasticity dropped. There was no apparent change in the stress relaxation curves, and they flattened out after 12 h. However, the stress relaxation ratio had some characteristic variance. As shown in Table I, the relaxation ratio decreased after radiation in air, but *in vacuo* and in inert gas, it first decreased and then increased.

CONCLUSIONS

The SEM of silicone foam showed that the porous wall was damaged in different degrees after radiation. The mean aperture of sample had a further increment along with the dose.

With the γ -ray dose rate and the dose range, the crosslinking and degradation reactions of the silicone foam took place simultaneously. These two reactions played adverse roles in the structure and properties of samples. From the gel fraction curve, this change was clear, especially in air. The gas products of radiation reaction were mainly H_2 , CH_4 , and $\text{CH}_3\text{SiOCH}_3$.

The result of GC/MS analysis indicates that the gas products of samples through thermal decomposition

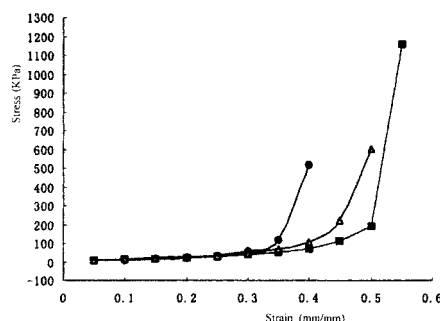


Figure 7 Compression stress-strain curve of samples irradiated at different doses: (●) 0, (△) 2×10^5 , and (■) 1×10^6 Gy.

TABLE I
Relationship Between the Stress Relaxation Ratio (%) of
Samples Radiated in Different Atmospheres and at
Different Doses

Atmosphere	Dose ($\times 10^4$ Gy)			
	0	20	40	100
Air	27.9	26.7	10.7	9.94
Vacuum	27.9	19.9	9.0	17.0
Inert gas	27.9	12.2	15.0	16.1

at 600°C and through γ -ray radiation degradation were the same at the low district of the proton-ion peak in MS. So, we concluded that the mechanisms of these two group reactions were similar.

The variation regularity of the Si—O peak height ratio in FTIR of irradiated samples with the dose was not same in different atmospheres. In air, the Si—O peak height ratio of the samples decreased continuously with increasing dose. However, *in vacuo* and in inert gas, a maximum of the Si—O peak height ratio appeared, and the height decreased after this due to the oxygen effect on the reaction. The thermal stability of samples irradiated in air decreased a little, but that of the samples irradiated *in vacuo* and in inert gas increased with the dose and decreased afterward. The whole trend was that the thermal stability of samples irradiated in the latter two atmospheres was superior to that irradiated in the former atmosphere.

The main reaction was radiation crosslinking below 2×10^5 Gy. Radiation decomposition played a great role at an excess of 2×10^5 Gy. Correspondingly, the mechanical properties of polysilicone foam changed from excellent to low grade.

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