Electron-Beam-Induced Radiation Effects on Siloxane Foam

Wei Huang, Xiaoling Gao, Jie Xiong, Liangping Xiong, Yunshu Xu, Yibei Fu*

Summary: Two types of siloxane foam were irradiated by an electron beam at room temperature. Changes in the chemical structure of the samples were determined by Fourier-transform infrared resonance. The gaseous products from the irradiated samples were analyzed by gas chromatography and mass spectroscopy. Electron spin resonance was used to analyze the free radicals, and the compression properties were determined by a universal material tester. The results indicated that the effect of absorbed dose on the mechanical properties of polymethylvinyl siloxane foam was more pronounced than that for polymethylphenylvinyl siloxane foam. The yield of gases evolved from the radiation degradation of polymethylvinyl siloxane foam was higher than that from polymethylphenylvinyl siloxane foam. The free-radical signal from polymethylphenylvinyl siloxane foam was stronger and lasted longer than that from polymethylvinyl siloxane foam after irradiation.

Keywords: electron beam; polymethylvinyl siloxane foam; polymethylphenylvinyl siloxane foam; radiation effect

Introduction

Siloxane foam is very widely used, especially in the fields of aviation, cosmonautics, electronics, and electricity. It is usually used in the form of cable, sealing or cushioning material. Previous work[1–3] has focused on the irradiation of siloxane materials, and the effect of different radiation sources was discussed. In our earlier work,[4] the behavior of polymethylvinyl siloxane foam in a gamma-radiation field was discussed. Our results indicated that the radiation-resistance properties of polymethylvinyl siloxane foam were poor, the damage to the material irradiated with a dose of more than 2×10^5 Gy arising mainly from radiation degradation. In this paper, the effect of electron-beam irradiation on polymethylvinyl siloxane foam (PMVSF) and polymethylphenylvinyl siloxane foam (PMPVSF) has been studied.

Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900
E-mail: huangwei839@126.com

Materials and Methods

Materials

PMVSF and PMPVSF with open pores were processed by the Institute of Structural Mechanics in the China Academy of Engineering Physics. Each sample was put into a specially prepared glass bottle with an airway attached so as to draw out gas. Then the atmosphere in the bottle was vacuum extracted (1.2 Pa) and the bottle was sealed to keep the sample under vacuum. If the sample was to be kept in air, the bottle was directly sealed.

Experimental Part

A Van de Graaff accelerator was provided by the Nuclear Institute of Science and Technology, Sichuan University. Its energy was 2 MeV, and the electric current was 0.25 mA. The dose rate was changed by adjusting the electron energy and current, and the voltage was alternating. Intermittent radiation was adopted to scatter the heat produced. The dose rate was determined by

a thermoluminescence dosimeter, which was calibrated by the standard dosimeter at Shanghai Applied Radiation Institute, Shanghai University.

The samples were analyzed by Fourier-transform infrared resonance (FTIR) using a SYSTEM 2000, P.E. apparatus. The wavenumber was in the range 4000 to 400 cm^{-1}, the scanning rate was 0.5 cm/s with a scanning order number frequency of 100 times and a resolution ratio of 4 cm^{-1}.

Volatile products from the irradiated samples were collected by a negative-pressure device devised by our research group. These products were analyzed by gas chromatography (HP6890) and mass spectroscopy (Finnigan MAT98 B-E)(GC/MS).

The free-radical signal was determined by electron spin resonance (ESR) using a Bruker ESP 300E apparatus. The X-band range of the microwave bridge was 9∼10 GHz, and the actual frequency was 9.79 GHz.

The compression properties of the samples were measured by a universal testing machine (Instron 1196), and the stress relaxation by an electron creep/relaxation tester (CSS-237) at 25 °C and 55% relative humidity.

Results and Discussion

FTIR Analysis of the Irradiated Siloxane Foam

The built-up FTIR spectra of PMVSF and PMPVSF before and after irradiation are shown in Figure 1. The peak positions in the different spectra are the same, but the relative intensities of the peaks are different. It can be clearly seen that there is a triple peak around 2963 cm^{-1} in the spectra of the samples; it belongs to the stretching vibration of methyl (-CH_3) in the side chain. The peak at 1260 cm^{-1} is the bending vibration of -CH_3. The peaks at 1020 cm^{-1}

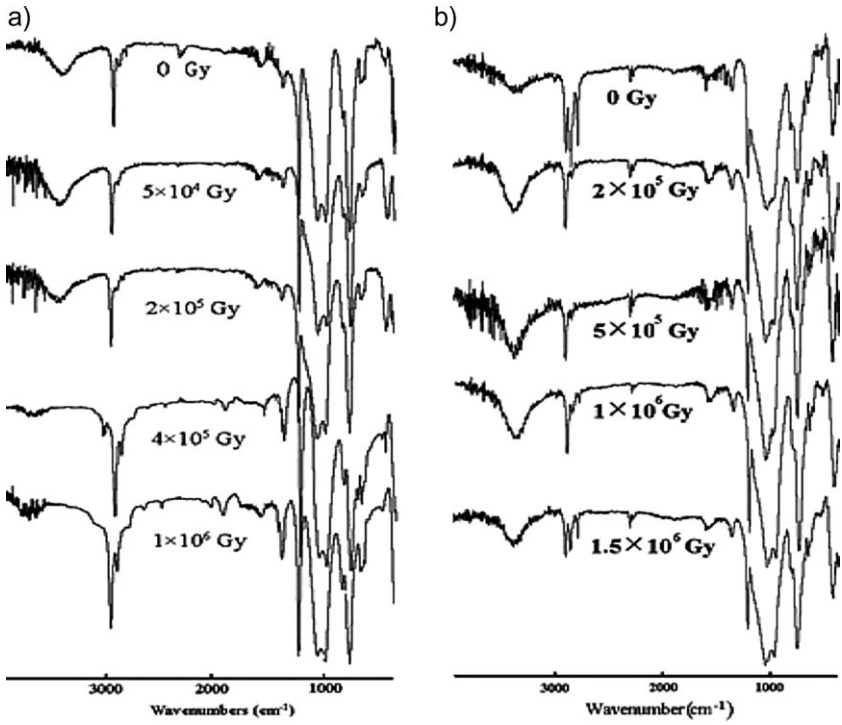

Figure 1.
FTIR spectra of samples irradiated in air (dose rate = 5×10^4 Gy/min.) a. PMVSF, b. PMPVSF.

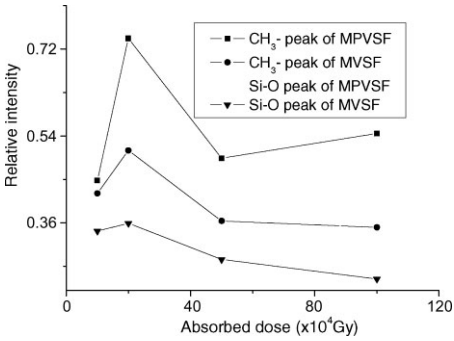

Figure 2.
Relative intensities of the -CH_3 peak and Si-O peak of the irradiated samples (dose rate = 5×10^4 Gy/min.).

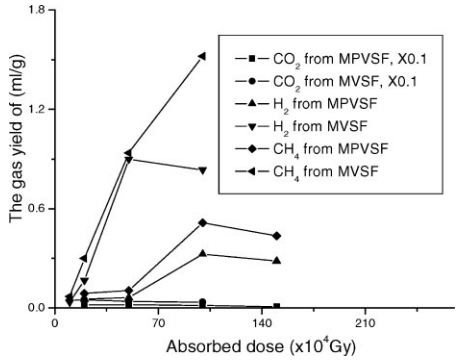

Figure 3.
Gas yield of PMVSF and PMPVSF irradiated in vacuum at different absorbed doses (dose rate = 1.2×10^5 Gy/min.).

and 800 cm^{-1} are characteristic of the Si-O unit. As the Si-O peak at 800 cm^{-1} is relatively stable and with little change in its position and intensity, its height is chosen as the reference peak for calculating the peak-height ratio, and the relationship between the peak-height ratio (-CH_3 peak at 1260 cm^{-1} and Si-O peak at 1020 cm^{-1}, respectively) of irradiated samples and the absorbed dose is discussed below.

Figure 2 shows the relative intensities of the -CH_3 and Si-O peaks of the irradiated samples as a function of absorbed dose. The relative intensity of the -CH_3 peak in PMVSF and PMPVSF increases up to a maximum at a dose of 2×10^5 Gy, then drops. The relative intensity of the -CH_3 peak in PMPVSF is higher than that of PMVSF, because PMPVSF contains phenyl, which can absorb radiation energy so as to protect the side groups on the long chains in the polymer. The relative intensity of the Si-O peak of PMVSF is higher than that of PMPVSF at low doses, but the relative intensity of the Si-O peak of PMPVSF increases rapidly above 6×10^5 Gy, and it becomes much larger than that of PMVSF. This shows that the Si-O main chain of PMPVSF is resistant to high doses of radiation.

Effect of Dose and Dose Rate on the Gases Evolved from Irradiated PMVSF and PMPVSF

The gases evolved from the irradiated samples were determined by GC/MS. Figure 3 gives the gas yield of PMVSF and PMPVSF for different absorbed doses. It shows that the gas yield increases with increasing absorbed dose. Among the evolved gases, the increase in the amount of CH_4 is the most obvious, there is less H_2, and the amount of CO_2 evolved is the least. PMVSF evolves more gas than PMPVSF, which indicates that the radiation resistance of PMVSF is inferior to that of PMPVSF. The gas yield of PMPVSF irradiated at the dose of 1×10^6 Gy is highest, and it drops a little at the dose of 1.5×10^6 Gy due to the radiation damage of samples.

Figure 4 shows the gas yield of samples irradiated at different dose rates. It can be seen that the CO_2 yield of PMPVSF is very

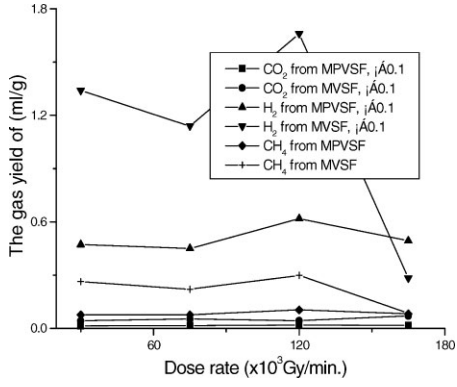

Figure 4.
Gas yield of PMVSF and PMPVSF irradiated in vacuum at different dose rates (absorbed dose = 2×10^5 Gy).

low; in other words, the dose rate has little effect on the CO_2 yield of PMPVSF. However, PMVSF is sensitive to the dose rate up to 1.2×10^5 Gy/min.

Analysis of Free Radicals in the Irradiated Samples

Figures 5 and 6 show the ESR spectra of PMVSF and PMPVSF irradiated in vacuum at different absorbed doses. It can be seen that the signals in the ESR spectra of samples irradiated at different absorbed doses are similar, but the signal intensities of the free radicals are different. The radical signal of samples irradiated at high doses is stronger, which demonstrates that the irradiated samples contain more radicals. The signal intensity of PMPVSF is stronger than that of PMVSF.

The lifetime of the free radical in PMVSF is very short, and its signal disappears after one day, but the free radical in PMPVSF lasts much longer. Figure 7 shows the ESR spectra of irradiated PMPVSF at different storage times. The signal of the free radical fades with increasing storage time, because free radicals bump and combine one another along with the time going on. After 20 days, the free-radical signal of PMPVSF has almost disappeared.

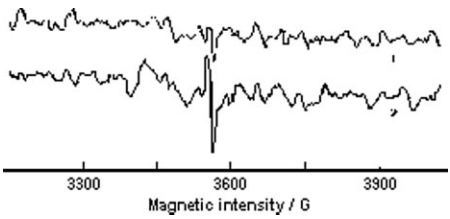

Figure 5.
ESR of PMVSF irradiated in vacuum 1: 5×10^4 Gy; 2: 2×10^5 Gy.

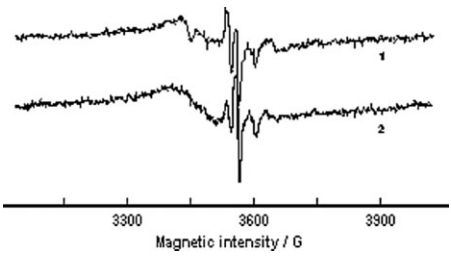

Figure 6.
ESR of PMPVSF irradiated in vacuum 1: 5×10^4 Gy; 2: 2×10^5 Gy.

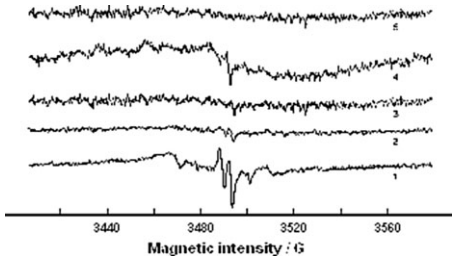

Figure 7.
ESR of PMPVSF irradiated in vacuum at different storage times (absorbed dose $= 5 \times 10^4$ Gy) 1: 0; 2: 5 days; 3: 10 days; 4: 15 days; 5: 20 days.

Mechanical Properties of Irradiated Samples

Figure 8 shows the compression stress–strain curves of samples irradiated in air. It can be seen that the stress–strain curves of PMPVSF samples are close together, whereas those of PMVSF are disperse. This indicates that the effect of dose on the compression property of PMPVSF is weak for the given dose range. Figure 9(a) shows the relationship between the irradiated sample's stress-relaxation ratio and the dose. It can be seen that the stress-relaxation ratio of PMPVSF is higher than that of PMVSF.

In general, the stress-relaxation ratio of irradiated samples increases with increasing absorbed dose, and then decreases. Crosslinking and degradation take place simultaneously during irradiation. At low doses, radiation crosslinking plays an important role in the increase of a sample's stress-relaxation ratio. With increasing dose, radiation degradation becomes predominant and results in a reduction of the stress-relaxation ratio. The stress-relaxation ratio of PMVSF has a maximum value at a dose of 2×10^5 Gy, while that of PMPVSF is a maximum at a dose of 5×10^5 Gy. This indicates that the radiation resistance of

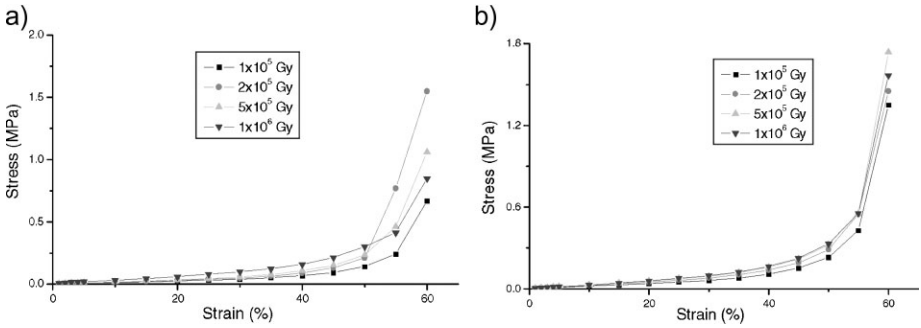

Figure 8.
Compression stress–strain curves of samples irradiated in air at different doses (dose rate $= 5 \times 10^4$ Gy/min.) a. PMVSF, b. PMPVSF.

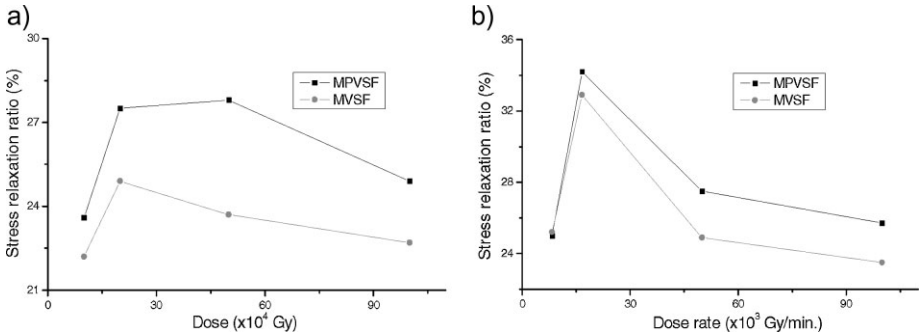

Figure 9.
The stress-relaxation ratio of samples irradiated in air, a. the effect of dose (dose rate $= 5 \times 10^4$ Gy/min.), b. the effect of dose rate (absorbed dose $= 2 \times 10^5$ Gy).

PMPVSF is superior to that of PMVSF. Figure 9(b) shows the relationship between the stress-relaxation ratio of the irradiated samples and the dose rate. The stress relaxations of PMVSF and PMPVSF change in a similar way, and the stress-relaxation ratio of PMPVSF is higher than that of PMPVSF.

Conclusion

1) The relative intensity of the methyl peak in PMPVSF is higher than that in PMVSF.
2) Several types of gases evolve from the irradiated samples, the gas yield of PMVSF being more than that of PMPVSF. Relatively speaking, the yields of H_2 and CH_4 are both much larger than that of CO_2.
3) The signals in the ESR spectra of samples irradiated at different doses are similar, but the signal intensity of PMPVSF is stronger than that of PMVSF, and the lifetime of PMPVSF's free radical is much longer.
4) The compression properties of PMPVSF are superior to those of PMVSF in the given dose range. On the whole, PMPVSF has better radiation-resistance properties.

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