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γ-ray irradiation effect on siloxane foam containning phenyl

HUANG Wei, FU Yi-Bei, XU Yun-Shu, BIAN Zhi-Shang, HE Mei-Ying

(*(Institute of Nuclear Physics and Chemistry. CAEP. Mianyang 621900)*)

Abstract The ^{60}Co γ radiation effect on spherical open-porous polymethylphenylvinyl siloxane foam was studied in different atmospheres at room temperature. The physical and chemical behaviors of unirradiated and irradiated materials were studied by SEM, FTIR, TG (thermal gravity analysis), GC/MS(gas chromatography and mass spectroscopy), etc. The present results indicate that the yields of gas products increase linearly with the dose increasing. Furthermore, some changes in material's microscopic form, composition, structure and mechanical property were observed, but the maximum thermal decomposition temperature of the sample alters little and the dose gives no effect on it.

Keywords Polymethylphenylvinyl siloxane foam, γ-ray irradiation, Radiation crosslinking, Radiation degradation

CLC numbers O644.2, TQ316

1 INTRODUCTION

Due to organic siloxane materials' resistance to acids and alkalis, antiweatherability, low temperature resistance and other advantages, they are widely used as wire, cable, sealing, cushion materials etc. Silicone rubbers and silicone foams used in the radiation ambient were studied in U.S.A, Japan, Great Britain and other countries[1~3]. The focus was about the effect of different radiation sources and dose rates on silicone rubber, fluorine rubber, natural rubber, etc. However, the damage of these materials and the changes in their structure and properties were not investigated. The behaviors of polymethylethyl siloxane foam used in γ radiation field was studied previously[4] and its radiation-resistance was found to be not very good. After irradiation at the dose of more than 2×10^5 Gy, the material suffered from radiation damage and the degradation was significant. As phenyl is better radiation-resistance, this work mainly concentrates the experimental research of polymethylphenylethyl siloxane foam and the purpose is to provide a technological basis for selecting better radiation-resistant materials. At present,

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there is no reference domestic and abroad on the relation between macroscopic properties and microscopic structure of polymethylphenylvinyl siloxane after and before irradiation.

2 MATERIAL AND METHODS

2.1 Material

Crude rubber was produced by Jilin Chemical Research Institute, and open-porous polymethylphenylethyl siloxane foam was processed by Institute of Structural Mechanics in CAEP (the China Academy of Engineering Physics).

2.2 Radiation

Radiation source was provided by the CAEP Cobalt Source Radiation Technology Co. Ld. The dose rate is 131~137 Gy/min and total dose is 10~1500 kGy.

2.3 Experiment methods

The sample was put into an ampoule glass bottle prepared specially with a branch tube attached so as to draw out the gas which was produced in the process of irradiation and sealed in the bottle at the state of high vacuum (1.2 Pa). This kind of sample is named as the sample in the vacuum. In another way, the air in the bottle was extracted to vacuum (1.2Pa), inert gas (pure N_2, 99.99% 2.67×10^4 Pa) was led into the bottle and the sample was sealed. This kind of sample is called the sample in inert atmosphere. The dose rate was kept constant (131~137 Gy/min) and the samples were irradiated at different doses.

2.4 Measurements and testing

The porous structures of samples' cross sections were analyzed by Scanning Electron Microscope (SEM)(Model S-250MK3). The change of sample's chemical structure was analyzed by Fourier Transformation Infrared Resonance (FTIR) (SYSTEM 2000, P.E.). The wavenumber range is 4000~400 cm^{-1}, scanning rate 0.5 cm/s, and resolution ratio 4 cm^{-1}. The weight-loss ratio of the sample was analyzed in nitrogen by Thermal Gravity Analysis Instrument (TGA7, P.E.). The rate of temperature increment is 10 ℃ /min. The temperature ranges from room temperature to 750°C. The gas products from the irradiated samples were analyzed by Gas Chromatography (HP6890) and Mass Spectroscopy (Finnigan MAT98 B-E)(GC/MS) using Hydrogen Flame Ignition Detector (HFID) and Thermal Conductivity Detector (TCD). The stress relaxation was determined by Electron creep/relaxation tester (CSS-237) at the temperature of 25°C and relative humidity of 55%.

3 RESULTS AND DISCUSSION

Fig.1 shows the microscopic structures of samples' cross sections after and before the irradiation. Before irradiation, the void in the sample is spherical and open-porous; After irradiation, the shape of spherical pore collapses.

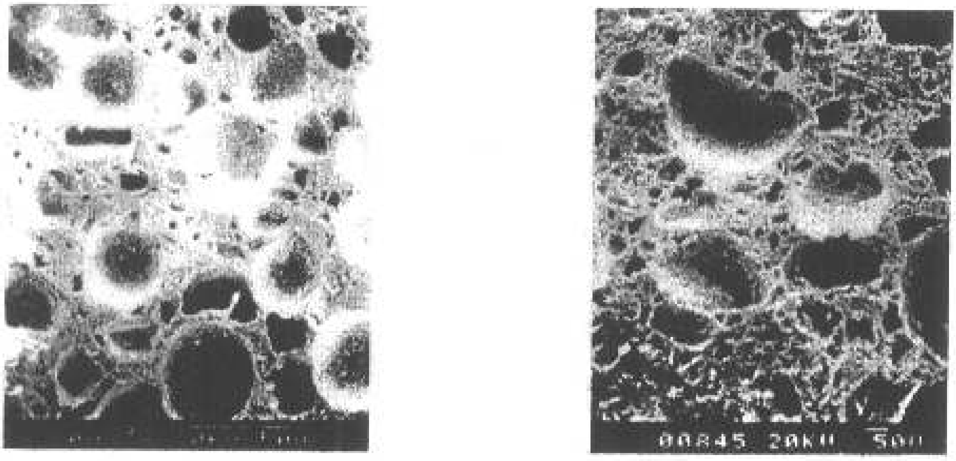

Fig.1 SEM photos of the samples

Left, unirradiated sample; Right, irradiated sample (1×10^6Gy)

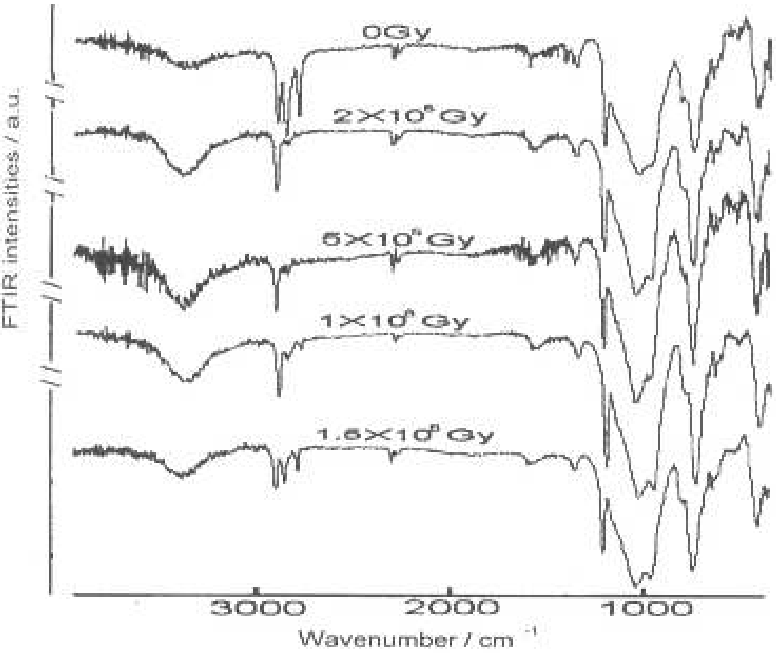

Fig.2 FTIR picture of the samples after and before the irradiation by ^{60}Co source (in air, at room temperature)

The FTIR built-up spectrum of the polysiloxane foam after and before the irradiation is shown in Fig.2. The positions of the same peaks in different spectra are alike, but the relative intensities of the same peaks are different. It is seen clearly from the figure that there is a triple-peak at the wavenumber of 2963 cm^{-1} in the spectrum of the unirradiated sample. The peak at this place changes into a single peak after the irradiation. However, the single peak transforms into a triple peak again when the dose gets to 1.5×10^6 Gy. The peak at 2963 cm^{-1} belongs to the stretching vibration of -CH_3 in the side chain. The peak at 1260 cm^{-1} is the bending vibration peak of -CH_3. The two peaks at 1020 cm^{-1} and 800 cm^{-1} are the characteristic peaks of Si-O unit. For Si-O peak at 800 cm^{-1} is relatively stable and there is little change in the position and intensity of it, the height of 800 cm^{-1} peak is chosen as the reference peak to calculate peak height ratios, and the relationship of peak (-CH_3 peak at 1260 cm^{-1} and Si-O peak at 1020 cm^{-1}) height ratios of the irradiated samples with the dose is discussed. As shown in Fig.3, the -CH_3 peak height ratio reduces with the dose rising, but the Si-O peak height ratio increases and then decreases.

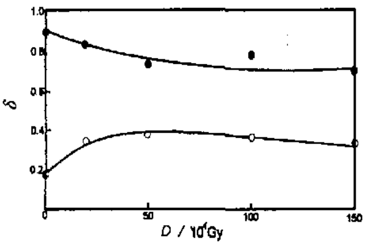

Fig.3 Si-O peak height ratio of the samples irradiated in different atmospheres at room temperature

● -CH_3, ○ -Si-O-

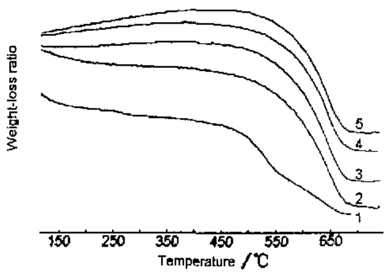

Fig.4 TG curves of the irradiated samples:
1. 0Gy, 2. 2×10^5 Gy, 3. 5×10^5 Gy,
4. 1×10^6Gy, 5. 1.5×10^6Gy

The TG curves of the unirradiated and irradiated samples are illustrated in Fig.4. Curve 1 corresponds to the unirradiated sample, and it is different from any other curves of the irradiated sample. It reflects the change of component and state in material after irradiation. Table 1 lists out the relation between the maximum thermal decomposition temperature of irradiated sample with the dose.

The result indicates that the dose has little effect on the maximum thermal decomposition temperature of polymethylphenylvinyl siloxane foam. Compared with the thermal property of polymethylvinyl siloxane[4], the former is superior to the latter.

Table 1 Relation between the maximum thermal decomposition temperature (°C) of the sample after irradiation and the doses ($\times 10^4$Gy)

Atmosphere	Dose			
	20	50	100	150
Vacuum	640	641	642	641
Inert gas	643	642	642	641

In general, the stress relaxation ratio of the crosslinked materials takes a decreasing trend with the dose increasing. But to polymethylphenylvinyl siloxane foam (in Fig.5), that is not the case. It decreases to a minimum point (about 1×10^6Gy), and then rises a little. The crosslinking and degradation simultaneously exist in the course of radiation. With increasing dose, radiation degradation becomes predominant and results in the reduction of stress relaxation ratio. It can be seen in Figure 5 that stress relaxation ratio increases a little. This is the characteristic of polysiloxane foam.

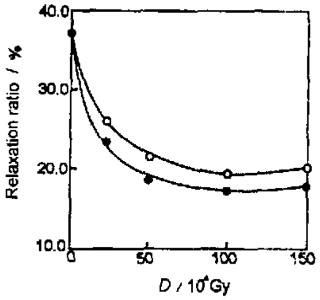

Fig.5 Stress relaxation ratio of the samples irradiated in different atmospheres and doses

○ In vacuum, ● In inert gas

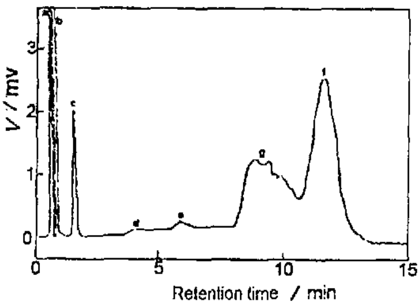

Fig.6 Gas chromatography of the sample irradiated at the dose of 5×10^5Gy in vacuum

a. CH_4, b. C_2H_4, c. C_2H_2, d. C_2H_6, e. C_3H_6, g. the stage of temperature increment

The gases produced by irradiation of materials were determined by GC/MS to be made up of hydrogen (H_2), methane (CH_4), ethylene (C_2H_4), silicone (CH_3SiOCH_3), acetylene (C_2H_2), ethane (C_2H_6), propylene (C_3H_6), etc. H_2 is detected by TCD, and other gases are detected by HFID detector. Figure 6 is the gas chromatography of the sample irradiated at the dose of 5×10^5 Gy. Using an external standard method, the outputs of H_2, CH_4 and C_2H_4 were analyzed quantitatively by GC. Fig.7 shows the influence of dose on the gas yield. With increasing dose, the content of gas increases linearly. Among the gases, the yield of C_2H_4 is high, that of H_2 is higher, and that of CH_4 is the highest. Furthermore, the gas content of material irradiated in inert atmosphere is less than that in vacuum. The reason may be that the inert atmosphere has some retarding function on the radiation degradation. During the irradiation degradation, the free radicals are produced and they have chance to bump each other and combine together. In N_2 atmosphere, the free radicals interact, and N_2 molegules also have probability to bump with the free radicals. So free radicals disappear more quickly and the yields of gases are less in N_2 than in vacuum.

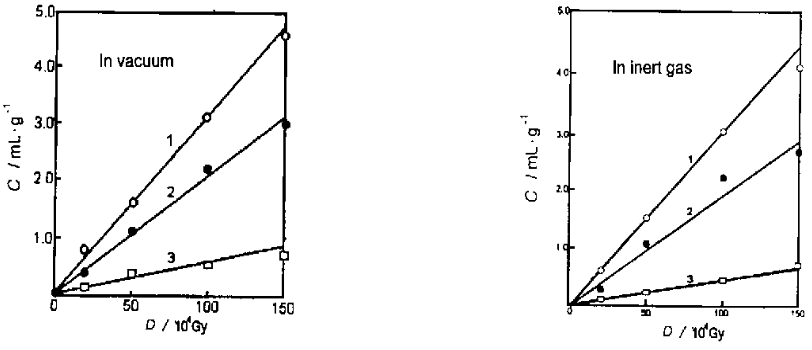

Fig.7 Relationship between the gas yield and the dose
1. CH_4, 2. H_2, 3. C_2H_4

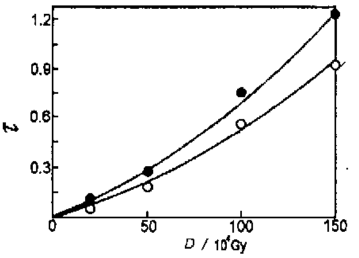

Fig.8 Yields of CH_3SiOCH_3
○ Irradiated in vacuum,
● Irradiated in inert gas

Since the standard reference material of CH_3SiOCH_3 was unavailable, CH_3COCH_3 was used as standard and the relative output of CH_3SiOCH_3 was calculated according to the response factor of CH_3COCH_3. Fig.8 shows that the relative output (τ) of CH_3SiOCH_3 increases with the dose rising and the quantity of CH_3SiOCH_3 in vacuum is more than that in inert atmosphere. This is similar to the increment of yields of H_2, CH_4 and C_2H_4. The only difference is that the increase of CH_3SiOCH_3 offsets line a little.

4 CONCLUSION

The spherical pore of polymethylphenylvinyl siloxane foam suffered from irradiation obviously. The fact is that the triple-peak of -CH_3 at the wavenumber of 2963 cm^{-1} begins from existence to disappearance and then reappearance in FTIR and the variance of -CH_3

and Si-O characteristic peaks indicates that the transformation of chemical structure of the sample after and before irradiation is dominated by radiation crosslinking and degradation. In the same condition, the contents of gases produced in ^{60}Co γ irradiation of polymethylphenylvinyl siloxane foam are put in the following order, $CH_4 > H_2 > C_2H_4$. The yields of these gases are improved with the dose.

The γ radiation dose has little effect on the maximum thermal decomposition temperature of polymethylphenylvinyl siloxane foam and the thermal stability of that is excellent.

The degradation tendencies of polymethylphenylvinyl siloxane foam irradiated in both vacuum and inert atmosphere show little difference, but the gas yield in inert atmosphere is less than that in vacuum, which illustrates that the inert gas has some inhibition effect on the radiation degradation.

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