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Dose rate effects of gamma irradiation on silicone foam

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ABSTRACT

The dose rate effects of gamma irradiation on silicone foam were confirmed by investigating the relationships between the dose rate and the structures-property of the materials. With accumulation of the dose, the elongation at break (E_b) decreases significantly, while the creep ratio slightly decreases and gas yield increases after irradiation in air, especially at lower dose rate. However, the main gas yields, including H_2 and CH_4, from samples irradiated in nitrogen do not increase linearly with reducing the dose rate. Furthermore, ESR spectra show that more radicals are generated at lower dose rate, indicating obvious dose rate effect. It is deduced that the dose rate effect is caused by the competition among the radical generation, reaction, and quenching rates.

1. Introduction

Silicone foams [1], are elastomeric foams from silicone rubbers with main components of polysiloxane, fillers and other additives. The characteristics of silicone foams are excellent temperature tolerance, chemical resistance, low density, and good elastic recovery properties due to their porous structures [2]. Hence silicone foams are engineered as thermal insulation and/or shock absorbents in various fields such as aerospace, electronics, marine, and nuclear facilities [3,4]. The aging effects and lifetime predictions of silicone foams have been investigated systematically, such as temperature [5,6], moisture [7], atmosphere [8], stress loading [9], radiation [10,11] and their interactions on aging [12]. Lawrence Livermore National Laboratory (LLNL) [13–15], Los Alamos National Laboratory (LANL) [16,17], Atomic Weapons Establishment (AWE) [7], and other researchers [18–20] have done respected works on radiation effects of silicone rubbers. The results show that ionizing effects induced by high energy radiation would change the structures of the materials, which may further influence the lifetime of the materials.

In the past, accelerated ageing methods with high dose rate and high doses have been utilized to study radiation effects of polymer materials, for saving research time and other resources. Limited publication on the dose rate effects of silicone foam is available probably due to extremely long experimental period. In fact, the foam is mostly used in low dose rate radiation environments. The material may undergo different mechanisms and changes at various dose rates. Then the lifetime prediction of a polymer material with aforementioned high-dose-rate method would be highly uncertain.

Dose rate effects on polymer materials such as polyethylene [21], EPDM [22], PVC [23], silicone rubber [24], and fluorosilicone rubber [25], have been explored. The corresponding mechanisms include intermediate species interactions, chain branching, and diffusion limited oxidation effects. The competition between oxygen diffusion and reaction as a function of the dose rate (formation rate of radicals) has been studied extensively [26–28]. Although the dose rate effect of silicone rubber has been investigated briefly, the detailed components, structure, microstructure, and properties of the investigated silicone rubbers [24] are quite different from silicone foam in this study (even though their main components are both polysiloxanes), whose dose rate dependence under irradiation is still unknown. Considering the actual low-dose-rate radiation environment, it is necessary to develop suitable characterization, evaluation and prediction methods to evaluate the radiation effects. In the present work, we have studied the mechanical properties, gas yield and chemical changes of silicone foam irradiated by gamma rays at a series of dose rates in the presence of nitrogen or air. The possible mechanisms are also proposed.

2. Experimental

2.1. Materials

Silicone foam was prepared by peroxide cure, foaming and post-vulcanization of silica-filled methyl vinyl silicone rubber with additives (hydroxyl silicone oil, dibutyltin dilaurate as catalyst, N, N′-dinitrosopentamethylenetetramine as blowing agent, and dicumyl peroxide and benzoyl peroxide as crosslink agent) as previously reported

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[18,19,29,30], with a typical nominal density of 0.50 g cm^{-3}, gel content of 3% and in the form of ~2-mm-thick sheets. The radical trapping agent, 2-methyl-2-nitrosopropane (MNP), was purchased from Sigma-Aldrich.

2.2. Irradiation

The gamma irradiation was provided by a ^{60}Co source at dose rates of 91.2, 9.14, and 1.80 Gy min^{-1}, with total dose up to 104 kGy at the Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics. The samples were cut into certain shapes and then sealed in glass tubes with air or nitrogen atmosphere.

2.3. Characterization

Volatile products were analyzed quantitatively by gas chromatography (HP 6890) with negative-pressure injection through a flexible tube fixed on the top of the glass tube, using an external standard method. Tube volumes were measured to calculate the gas concentration.

Tensile strength and elongation at break of samples were conducted with an Instron 1196 testing machine at a tensile rate of 50 mm min^{-1}. Five dumbbell-shaped samples of each group were tested for reproducibility.

Creep tests were performed with a NETZSCH 242 Dynamic Mechanical Analyzer using a tension holder at static force of 4 N with a sample size of 10.0 × 2.0 × 4.0 mm^3. The creep ratio was recorded after 30 min equilibrium. Dynamic thermomechanical analyses were performed using the same DMA equipment in the tension mode with 10.0 × 2.0 × 4.0 mm^3 rectangular samples too. The specimens were analyzed at a frequency of 5 Hz in a temperature ranging from −150.0 °C to 0 °C at a heating rate of 3.0 °C min^{-1}.

Electron spin resonance spectra (ESR) were recorded on a Bruker A200 spectrometer operating in X band with a microwave frequency of 9.85 GHz and a central magnetic field of 3512 G, at room temperature. Silicone foam samples were immersed for 24 h in MNP (as spin trap)/toluene solution at a concentration of 0.5%, then dried in oven prior to irradiation.

The molecular weights of the extracted samples were obtained on a PL-GPC 220 high temperature gel permeation chromatograph system with trichlorobenzene as solvent at concentration of about 0.2 wt%.

3. Results and discussion

The macroscopic mechanical performance was used to evaluate the irradiation effects (Fig. 1). A decrease in mean elongation at break can be observed for all irradiated samples. The low-dose-rate irradiation accelerates the degradation, especially at total dose above 50 kGy. The influence of irradiation atmosphere is also presented in the graphs. The elongation at break decreases more obviously for all samples in nitrogen, from 147% for the control to 44% for the sample irradiated at the dose of 104 kGy (1.80 Gy min^{-1}). The reduction in elongation at break indicates that the sample became brittle, that is, the samples go sooner beyond their elastic limits in practical application [31]. The elastic behavior was further measured by Dynamic Mechanical Analyzer at a set force and temperature recording the creep response of sample, and at a set frequency recording the dynamic response at various temperatures.

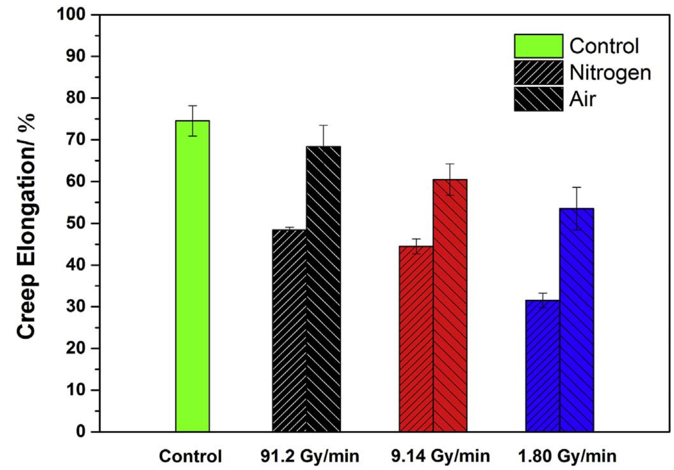

Fig. 2. The creep elongation ratio changes of silicone foam before (green plain) and after irradiation (104 kGy) in nitrogen (medium slash) and air (sparse backslash) at series dose rates (black-91.2 Gy/min; red-9.14 Gy/min; blue-1.80 Gy/min). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The creep percentages of the control and silicone foam irradiated at 104 kGy (various dose rates) in both nitrogen and air were recorded (Fig. 2). The creep ratio has decreased in both atmosphere to some content, indicating the change of chemical structure under irradiation. Further analyses show that the creep ratio of the samples decreases with reducing dose rate in both atmospheres. In nitrogen, the foam shows much lower creep ratio (31%) that in air (53%) at 1.80 Gy min^{-1}, which may be attributed to the crosslinking degree of network structures.

DMA was adapted with tensile mode to measure dynamic mechanical properties of the samples. The changes in the tan δ peak heights relate to transitions of the materials; an increase in the peak height may be related to chain scissions or reduction in crystallinity, resulting in increased chain mobility [32].

Fig. 3 shows E′, E″ and tan δ of the samples tested from −150.0 to

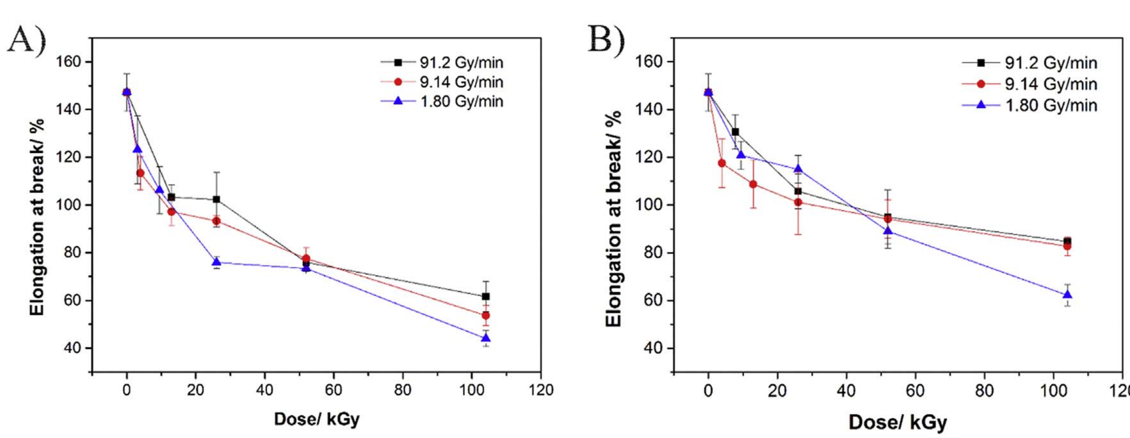

Fig. 1. Tensile elongation at break as a function of dose at a series of dose rates (square-91.2 Gy/min; circle-9.14 Gy/min; triangle-1.80 Gy/min) in nitrogen (A) and air (B).