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Effects of combined neutron and gamma irradiation upon silicone foam

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ABSTRACT

The total dose effect of combined fast-neutron beam and ^{60}Co γ-ray radiation on silicone foam in air and nitrogen were investigated, respectively. The results show that foam hardening occurs and crystallization of polymer matrix decreases with increasing dose. Gas chromatograph was used to identify the kinetics of volatile products generating, which generally increase with increasing total dose. The study indicates that combined neutron and gamma irradiation would influence silicone foam property obviously during the investigated dose range.

1. Introduction

Silicone foams, also called silicone rubber foams, are prepared from the mixture of catalysts, fillers, and blowing agents into a high-molecular-weight, linear siloxane polymer (Landrock, 1995), in which polysiloxane matrix has Si–O bonds in the main chain and organic groups such as methyl, ethyl, or benzyl in the side chains. Since Si–O bond has a high dissociation energy, approximately 30% greater than the C–C bond (Johnson and Tubolsky, 1954), polysiloxane has good stability during lifetime. Silicone foam has combined the virtues of organic and inorganic materials, possessing good mechanical properties with reduced density (Jawhar et al., 2014). It has therefore been applied extensively in extreme environments, such as aerospace and nuclear power plants where complicated radiation exist.

Previously, gamma radiation effects of polysiloxanes (Charlesby, 1954; Hill et al., 2001; Maxwell and Balazs, 2002; Warrick, 1955), silicone rubbers (Hall and Patel, 2006; Labouriau et al., 2015a; Maxwell et al., 2003; Palsule et al., 2008; Stevenson et al., 2001; Traeger and Castonguay, 1966; Zhang et al., 2006), and silicone foams (Chen et al., 2015; Huang et al., 2002; Sui et al., 2013) have been studied with dramatic physical or mechanical property changes. Maxwell and co-workers investigated the thermal, mechanical, and segmental dynamics properties of silica-filled polysiloxane foams exposed to gamma (γ) rays with dose ranging from 30 kGy to 3800 kGy at 83.33 kGy min^{-1}, (Maxwell et al., 2003). Labouriau et al. reported on the hardening effects of exposing silica-reinforced polysiloxane foams to moderate doses of gamma irradiation (less than 250 kGy at 60 Gy min^{-1}) (Labouriau et al., 2015b). The effect of different radiation sources such as γ-rays (Maxwell and Balazs, 2000), neutrons (Hu et al., 1999), and electron beams (Huang et al., 2010) on silicone foams has also been reported, respectively.

However, it is still a concern of the materials under combined neutron and gamma irradiation. As neutrons may cause different effects in polymeric materials compared to gamma-rays with the same released dose due to their high linear energy transfer, the synergistic interaction of neutrons and gamma-rays was unclear. Sandia National Laboratory reviewed combined gamma and neutron irradiation effects on epoxies in 2012, suggesting no concerns exist for the Epon 828-1031/DDS system with a total fast-neutron fluence of ~10^{12} n cm^{-2} and a γ dose of ~500 Gy (White and Bernstein, 2012). For silicone foams, limited publication is available regarding combined neutron and gamma irradiation to the best of our knowledge.

In this study, we present irradiation effects of filled silicone foam under combined fast neutrons and γ-rays in the presence of air and nitrogen, respectively. We examine changes in mechanical properties, morphological structure, crystallinity, and the chemical structure of composite foams from a macro- to microscopic scale. The quantitative kinetics of volatile products generating was also investigated. It is expected that these results could provide a new thought to assess the lifetime of such materials being used in complex radiation-containing environments.

2. Experimental

2.1. Materials

Silicone foam were prepared through previous reported method (Shi et al., 2007; Shi et al., 2008). These materials were prepared by a peroxide cure of silica-filled (~30% filler) methyl vinyl silicone rubber, catalyzed by dibutyltin dilaurate, foamed using N,N′-dinitrosopenta-

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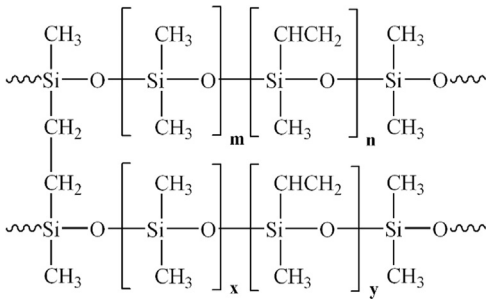

Fig. 1. Network structure of polysiloxane.

methylenetetramine (hydrogen blowing agent), cross-linked using dicumyl peroxide and benzoyl peroxide, washed in water, and post-vulcanized to form a silicone foam with a typical nominal density of 0.50 g cm^{-3} and in the form of ~2-mm-thick sheets. The network structure of the principal component, polysiloxane, is shown in Fig. 1.

2.2. Irradiation

The combined irradiation of neutron and gamma were kept at a constant ratio. The China Fast Burst Reactor II (CFBR II) at the Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, was used as a neutron source at a neutron fluence rate of ~10^9 cm^{-2} s^{-1} in steady power mode. γ irradiation was provided by a ^{60}Co source at a 10 Gy min^{-1} at the same institute.

Table 1 shows samples irradiated with γ and then neutron under different conditions. The X axis of Figs. 2, 3, 4, 5, 6, 8, 9, 10 and 11 is the absorbed γ dose for the constant ratio of neutron and gamma irradiation (0.17–0.18 10^{12} n cm^{-2} kGy^{-1}).

2.3. Characterization

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

Scanning electron microscopy (SEM, ZEISS EVO 18 special edition) was used for porous morphology surface analysis of the silicone foams at an acceleration voltage of 15 kV.

Two-dimensional X-ray diffraction (2D-XRD) studies were performed at room temperature on a Bruker D8 Discover diffarctometer which is configured in parallel beam geometry with Cu Kalpha radiation (wavelength of about 1.5418 Å).

Differential scanning calorimetry (DSC, TA-Q100) analyses were performed by cooling the sample at 30 °C min^{-1} to −90 °C from room temperature. The sample temperature was held isothermal for 5 min. The sample was then heated from −90 to 120 °C at 3 °C min^{-1}, kept at 120 °C for 5 min to erase any thermal history, and cooled to −90 °C at 3 °C min^{-1}, under a 50 mL min^{-1} nitrogen gas flow.

Table 1
Accelerated aging conditions for silicone foams.

Samples	Atmosphere	γ Dose (kGy, 10 Gy min^{-1})	Neutron fluence (10^{12} cm^{-2})
1	Nitrogen	7.8	1.36
2		26	4.76
3		39	7.14
4		52	9.52
5	Air	7.8	1.36
6		26	4.76
7		39	7.14
8		52	9.52

A ^{29}Si-solid-state nuclear magnetic resonance (NMR) cross-polarization spectrum was obtained using a Brüker AV 300, at 59.62 MHz, 5000 r s^{-1}, and with a cross-polarization time of 8 ms.

Solvent swelling experiments were performed by a two stage swelling process as reported previously (Chien et al., 2000; Flory and Rehner Jr, 1943; French and Division, 1980; Roggero et al., 2016). Initial sample (~200 mg) was submerged in excess of toluene (20 mL, Keshi, AR) until equilibrium, following by 5 mL ammonia (28 wt%, Cuicr, AR) added to the toluene solution, to break the hydrogen-bonding interaction between the silanols on the filler and the siloxane polymer. The equilibrium weight of each sample in toluene/ammonia mixture was recorded as the swollen weight. The samples were dried in vacuum at ambient temperature and weighed again. The average molecular weight between crosslinks was calculated by Flory-Rehner equation (Flory and Rehner Jr, 1943):

$$M_c = \frac{-V_s \rho_p (\nu_f^{1/3} - \nu_f/2)}{\ln(1-\nu_f) + \nu_f + \chi \nu_f^2} \quad (1)$$

where V_s is the molar volume of toluene (106.5 mL mol^{-1}), ρ_p is the polymer density (0.99 g cm^{-3}), $^{\nu}_f$ is the volume fraction of polymer in the sample at equilibrium swelling, and χ=0.465 is the Flory-Huggins polymer-solvent interaction parameter.

Volatile products were analyzed quantitatively by gas chromatography (HP 6890) using an external standard method with negative-pressure sample injection. Tube volumes were measured, and samples were removed for further characterization.

3. Results and discussion

3.1. Mechanical property changes during radiation

The chemical structures of silicone foams are easily affected by radiation, such as the polymer-filler interaction, crosslinking density, functional groups and et al. These changes might contribute to their properties. The mechanical measurements were performed to obtain the tensile strength and elongation at break results for silicone foams irradiated under combined neutron and gamma rays in nitrogen and air, respectively (Fig. 2). In inert gas, the tensile strength first increase and then decrease slightly with increasing accumulated dose, while adverse tendency appears in air. Interestingly, the tensile strength in both atmospheres show similar values at the highest dose, and are slightly greater than that of the reference samples. Meanwhile, the increase of irradiated dose affected mechanical properties of silicone foam inducing a remarkable decrease of elongation at break as compared with non-irradiated samples, which may be attributed to increased crosslinking density (Aliev, 1999). It should be noted that the decrease of elongation at break in air (21.9%) was less than that in nitrogen (37.5%), meaning the effectiveness in air by the combined neutron and gamma irradiation was less in comparison with the irradiation in nitrogen.

3.2. Morphological structures of control and irradiated materials

The morphologies of the control and irradiated silicone foams are observed by SEM, as shown in Fig. 3. The silicone foams show two types of cell structures, with scale ranging from several to hundreds of micrometers, respectively. The surface of large cells tends to shrink with increasing dose. The atmosphere influence could be detected by comparing Fig. 3 B and D, where the cells is more smooth after irradiation in air than nitrogen.

The mechanical property characterization shows that the elongation at break decreases with increasing dose. Information on molecule structure and mobility was further estimated by more refined methods. To confirm whether defects are likely to emerge around the filler, the