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Degeneration and damage mechanism of epoxy-based shape memory polymer under 1 MeV electron irradiation

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ABSTRACT

The degradation behaviors of epoxy-based shape memory polymer (SMP) after 1 MeV electron irradiation were investigated in the paper. It was founded that the shape fixity rate remained almost no changed at approximately 99.6% while the shape recovery rate decreased rapidly from its original 98.6% to 85.9% with increasing fluence up to 200×10^{14} cm^{-2}, which could be owned to the partial cleavage of the cross-linked network of epoxy-based SMP after irradiation. Further research found that the irradiation-induced scissions of the crosslinked network took place as a result of the debonding of the weak aliphatic C-O and C-N groups.

1. Introduction

As a kind of new intelligent structural materials, shape memory polymers have the advantages of self-controllable expansion, large recoverable strain, low density, indicating great potential in space deployable structures. Since the 1970s, there appear various kinds of shape memory polymers, including mainly thermoplastic polyurethane [1], polycaprolactone [2] and thermosetting epoxy-based polymers [3], polystyrene polymers and so on. Among them, the epoxy-based SMP has the talents of more stable structure, good thermal stability, making it more suitable for smart space deployable structures. However, the space environment is extremely complicated and harsh, including high vacuum, atomic oxygen, radiation environment of high-energy particles, etc.. Among them, particle irradiation is thought as the most severe one to damage the materials, especially the sensitive polymers. Therefore, it is necessary to study the performance and damage mechanism of epoxy-based SMP under the particle irradiations.

So far, the radiation damage of epoxy resin has mainly focused on the thermal degradation [4], outgassing properties [5], etc. The results indicated that epoxy resin show to some degree sensitive to the space irradiation. However, few studies were reported on the degradation behaviors of shape memory properties of irradiated epoxy resin as shape memory polymers. Leng et al. [6,7] studied γ-ray and UV irradiation damage on shape memory properties, showing that the epoxy-based SMP possessed unique anti-irradiation performance while the glass transition temperature decreased no more than 10%. But to the author's knowledge, there is no more information found to investigate on the behaviors and damage mechanism of energetic particle irradiation on epoxy-based SMP. It is known that the space particles include mainly electrons, protons appearing as spectra with a large energy range, from radiation belts and solar cosmic radiation [8]. It is obvious that different particles show different interaction behaviors with the irradiated materials. However, there include some similar damage mechanisms on the materials. In this case, people could apply some specific particle radiation (such as 1 MeV electron accelerator [9]) to simulate equivalently the irradiation damage from the orbital particles. This paper aims to study the degradation and damage mechanism of 1 MeV electron irradiation on shape memory properties of epoxy-based SMP.

2. Experimental

The tested epoxy-based SMP was provided by Shanghai Institute of Aerospace System Engineering, and the main components confirmed by infrared spectroscopy (see Fig. 1(a)) were diglycidyl ether of bisphenol A (DGEBA) cured with amine curing agent. The irradiation test was carried out in a Van der Graff electron accelerator. The specimens with a thickness of 0.5 mm were irradiated by 1 MeV electrons to fluences of 5, 10, 50, 100, 200 ($\times 10^{14}$ cm^{-2}) at room temperature in ambient. The programming process, as illustrated in details in Fig. 1(b) was employed to

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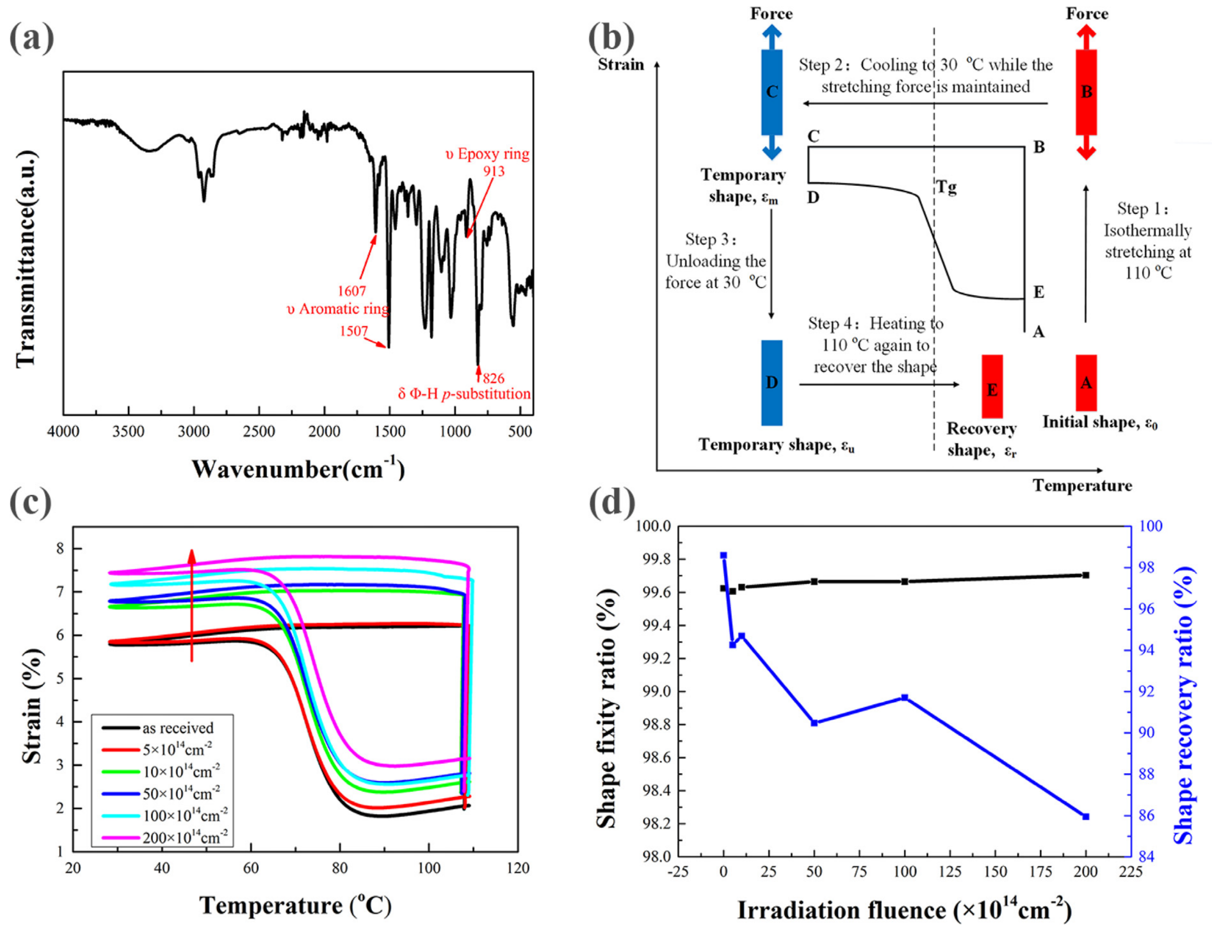

Fig. 1. (a) Infrared spectroscopy of the unirradiated epoxy-based SMP (b) schematic diagram of shape memory effect (c) shape memory behavior and (d) properties of epoxy-based SMP.

evaluate the shape memory performance of unirradiated and irradiated specimens in terms of shape fixity rate (R_f) and shape recovery rate (R_r). It was stress-controlled, carried out on a DMA Q800 (TA instrument) in film tension mode. The instrument itself records the real-time stress, strain and temperature of each process. Also using this instrument, dynamic mechanical analysis (DMA) was carried out to determine the glass transition temperature (T_g, hence defined as the peak temperature of the tan δ spectrum). All runs were performed at 1 Hz at temperature ranged from 30 °C to 110 °C with a heating rate of 4 °C/min. Electron paramagnetic resonance (EPR) spectra were measured in ambient to investigate the electron-irradiation induced free radicals in specimens using an A200 spectrometer (Bruker Instrument).

3. Results and discussion

Fig. 1(c) displays the shape memory behavior of epoxy-based SMP after irradiation. R_f and R_r were calculated using the following equations [10]:

$$R_f = \varepsilon_u/\varepsilon_m \tag{1}$$

$$R_r = (\varepsilon_u - \varepsilon_r)/(\varepsilon_u - \varepsilon_0) \tag{2}$$

where ε_0, ε_m, ε_u and ε_r represent the initial strain at 110 °C, the strain before unloading the tensile stress of 0.1 MPa at 30 °C, the fixed strain after unloading the tensile stress and the one after recovery at 110 °C, respectively.

The unirradiated epoxy-based SMP specimen showed wonderful shape memory properties, with the shape fixity rate of 99.6% and shape recovery rate of 98.6% (Fig. 1(d)), respectively. On one hand, the shape fixity rate remained almost no changed at approximately 99.6% after 1 MeV electron irradiation up to 200 × 10^{14} cm^{-2}. This is similar to that in the literature reported by Ref. [11]. The reason could be discussed by the following results.

On the other hand, the shape recovery rate decreased sharply from the as-received 98.6% to 85.9% after irradiation (see Fig. 1 (d)). Obviously, there was a significant degradation after electron irradiation in terms of shape recovery rate. It should be noted that the result that the shape recovery rate decreased sharply after 1 MeV electron irradiation is quite different from those reported in the literatures [10,11]. The reason would be analyzed as following.

In order to further explore the mechanical degradation mechanisms of the electron irradiated SMPs, DMA experiments were carried out for the tested samples. Fig. 2 presents the storage modulus and Tan δ of epoxy-based SMP after irradiation as a function of temperature, respectively. On one hand, the elastic ratio defined as the rubber to glass modulus ratio (E'_r/E'_g) is often used to estimate the shape fixity rate using the equation as below:

$$R_f \approx 1 - E_r/E_g \tag{3}$$

It can be seen that there was a large and sharp drop in the storage modulus around glass transition, although there are some minor changes of the storage modulus for both the glass and rubber states in the samples. Actually, the glassy modulus was three orders of magnitude larger than the rubbery modulus (Fig. 2(a))