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What is This?
Effect of the γ-radiation on the properties of epoxy-based shape memory polymers

Jinsong Leng¹, Fang Xie², Xuelian Wu¹,³ and Yanju Liu²

Abstract
In this article, the epoxy-based shape memory polymers were exposed to simulated γ-radiation environments up to 140 days for an accelerated irradiation. The influence of γ-radiation on thermal and mechanical properties was evaluated by differential scanning calorimetry, dynamic mechanical analysis, and tensile test. The glass transition temperatures (Tg) determined by differential scanning calorimetry and dynamic mechanical analysis decreased no more than 10%, and the shape recovery speed became a little faster after γ-radiation of 1 × 10⁵ Gy. The tensile strength and elastic modulus could, respectively, maintain 26 MPa and 1.36 GPa after being irradiated by 1 × 10⁶ Gy radiation, showing great potential in aerospace structural materials.

Keywords
Shape memory polymer, epoxy-based shape memory polymer, γ-radiation

Introduction
Shape memory polymers (SMPs) are materials responding to external stimulus to change their shapes after a programmed process (Behl and Lendlein, 2007). The shape memory effect (SME) of SMPs can be triggered by heat, electric field, light, magnetic field, moisture, and even some chemical solutions (Gall et al., 2005; Huang et al., 2005; Luo and Mather, 2010; Mohr et al., 2006; Small et al., 2005). In recent researches, the mechanisms of the SME have been investigated deeply. Several deformation constitutive models were developed to describe the thermally triggered SME (Ge et al., 2012; Qi et al., 2008), thermo- or chemoresponsive SME (Huang et al., 2012), multi-SMEs (Yu et al., 2012), and so on. The mechanical properties of SMPs vary over a wide range due to their diverse and tunable chemical structures. Main chemistries raw materials of SMPs include polyurethane (Tobushi et al., 1992), polystyrene (Xu et al., 2010), epoxy (Leng et al., 2009b; Rousseau and Xie, 2010), polycaprolactone (PCL) (Alvarado-Tenorio et al., 2011), poly(methyl methacrylate) (PMMA) (Zhao et al., 2011), and perfluorosulfonic acid (PFSA) (Xie, 2010; Xie et al., 2010). SMPs have common advantages of traditional polymers, such as lower cost and weight and less complicated processing and programming. Compared with shape memory alloys, SMPs possess higher deformation capability and higher recoverable strain levels (Lendlein and Kelch, 2002). The fast programming process and biological compatibility of some kinds of SMPs have enabled their applications in medical devices (Lendlein and Langer, 2002; Nardo et al., 2011). Potential application for SMPs also lies in smart textiles (Hu et al., 2009), sensors (Kunzelman et al., 2008), actuators (Ma et al., 2013), and the deployable space structures (Barrett et al., 2007; Lan et al., 2009).

As an emerging class of smart structure and material, SMPs and their adaptability in the space environment attract more and more attention. Materials used for the deployable space structures must have good adaptability to the space environment (e.g. high vacuum, ionizing radiation, ultraviolet (UV) radiation, atomic oxygen atmosphere, plasma, meteoroids, debris, thermal cycles, and electrostatic charging). Among recent research about SMP performances in the simulated in-service environments, several works have reported the effect of
UV radiation (Fulcher et al., 2010; Lu et al., 2011; Tandon et al., 2010; Xu et al., 2011), xenon arc radiation (Tandon et al., 2009), electron beam radiation (Youssef, 2009), and so on. So far, some works have already been carried out to investigate the durability of the SMPs under γ-radiation, for example, on the thermoplastic bioabsorbable polymer-based SMPs in the medical level (Paakinaho et al., 2012; Yackacki et al., 2008). However, the SMPs have not fully exerted their technological potential applications in spatial deployment structure. In this case, there are numerous works to be done on γ-radiation performances of thermosetting SMP use in the space environment.

The γ-radiation is an electromagnetic radiation of high frequency, and consequently high energy. The electron and proton radiation degradation of materials are the primary factors to be concerned in addition to atomic oxygen and UV radiation. The nominal orbital environmental parameter of the space station truss structure for 30 years electron radiation is $10^4$ to $10^5$ Gy/min. Accelerated irradiation test of up to 140 days exposure to γ-radiation (up to $1 \times 10^6$ Gy) was conducted on the epoxy-based SMPs in this study to investigate the effect of γ-radiation on them. Differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), tensile test, and a “U”-shape bending test were carried out to measure the relevant thermomechanical properties and shape memory behaviors of the epoxy-based SMP before and after γ-radiation. All the radiation tests were conducted at room temperature in this current research. Given the complex and volatile space environments, it is only a baseline assessment of the durability of epoxy-based SMPs being considered as structural material substrates. The SMP behaviors under other individual factor (e.g. extremely high- or low-temperature condition) or the synergetic and additive effect of several factors will be conducted in our future work.

**Experimental**

The polymer matrix consists of an epoxy base resin, a curing hardener, and an active linear epoxy monomer. The linear monomer is composed of a long linear chain of C–O bonds. The epoxy resin and the linear monomer have an epoxy group number ratio of 1:1 in one molecule, a molecular weight ratio of 2:5, and a density ratio of 1:1. The resin and hardener are mixed with a weight ratio of 1:0.8, and linear monomer contents of 0, 5, 10, and 15 wt% were used for specimens SMP1, SMP2, SMP3, and SMP4, respectively. To obtain a bubble-free prepolymer, mixtures of epoxy resin, hardener, and linear epoxy monomer were degassed at a vacuum oven for 15 min and then injected into preheated glass molds composed of two slides separated by a silica gel rod spacer. After that, a three-step curing condition was performed at 80°C for 3 h, 100°C for 3 h, and 150°C for 5 h. After the curing process, the thermoset cross-linked network of the SMP products was obtained. The composition and preparation of the epoxy-based SMPs similar to this work have been reported in our previous study (Leng et al., 2009b).

The γ-irradiation is a highly penetrating technique that uses γ-rays from a radioactive Cobalt 60 ($^{60}$Co) isotope. In this study, the accelerated weathering conditioning was performed in a $^{60}$Co isotope exposure chamber under a limited atmospheric condition. During irradiation, the temperature in the exposure chamber was controlled to room temperature (25°C), and dosages of irradiation were $1 \times 10^5$ Gy and $1 \times 10^6$ Gy. Due to the limitation of the experimental time, the radiation rate is set to 5 Gy/min for accelerated irradiation, which is much higher than the nominal value. After exposure, the specimens of epoxy-based SMPs were examined for any visible damage and apparent color changes. Irradiation was performed by Heilongjiang Academy of Sciences (Harbin, China).

The DSC (NETZSCH DSC 204, Selb, Germany) measurements were employed to characterize the changes in thermal properties of the SMPs from 0°C to 200°C at a heating rate of 10°C/min. The glass transition temperatures ($T_g$) were identified as the shift in the baseline of the DSC curves.

The DMA (NETZSCH DMA Q800) experiments were conducted in a tensile mode. Samples with dimensions of $30 \times 5 \times 1$ mm$^3$ were prepared. All runs were performed at 5 Hz, and at temperature ranges from 25°C to 250°C at a heating rate of 5°C/min. The glass transition temperatures ($T_g$) were identified at the tan delta (tan δ) peak values in the DMA tests.

Isothermal quasi-static tension test was carried out on a Zwick Z010 (Zwick GmbH, Ulm, Germany) equipped with an extensometer at room temperature (20°C). Standard samples (ASTM D638, Type IV) for tensile test were cut by a laser cutter from the prepared SMP sheet and stretched at an elongation rate of 1 mm/min.

The shape memory behaviors of the SMPs before and after the irradiation were demonstrated through a “U”-shape bending test in the same condition. To compare shape memory behaviors before and after γ-radiation, the samples were cut from thin polymer sheets into rectangular strips (about $80 \times 10 \times 1$ mm$^3$), using it as the permanent shape. The straight bar-shaped samples were heated up to $T_g + 40$°C and held for 20 min for full heating, and then samples became elastic and were deformed to a “U”-shape easily under an external force. The deformed samples were cooled to room temperature to achieve a stiff state of SMPs, so that the temporary shape could be fixed when the samples were unloaded. After this programming
process, the sample maintained the “U” shape without loading. And the shape recovery process under different actuating temperatures ($T_g$, $T_g + 10^0C$, $T_g + 20^0C$, $T_g + 30^0C$, $T_g + 40^0C$) was recorded by a video recorder. Shape recovery angle is determined by measuring the angle between the straight ends of the bent specimen. The shape recovery ratio ($R_r$) was calculated as $R_r = \theta_r/\theta_b$, where $\theta_b$ represents the bending angle after cooling and $\theta_r$ the recovered angle. In addition, shape recovery speed was evaluated by the full recovery time $T_r$.

**Results and discussion**

**Effect of γ-radiation on surface profile**

As shown in Figure 1, the SMP color changes from transparent to yellow-green and dark-brown when exposed to increasing γ-radiation, but there is no visible damage to all the irradiated specimens.

**Effect of γ-radiation on thermal properties**

The equilibrium properties of epoxy-based SMPs determined by DSC and DMA tests are listed in Table 1 for a clear comparison. The glass transition temperatures ($T_g$) were identified as the shift in the baseline of the DSC curves. The $T_g$ of the samples confirmed by the DSC curves decreased by 7°C–15°C with an increase in irradiation dose. Since $T_g$ represents the onset of cooperative segmental motion, widely spaced cross-links will produce only a slight restriction on this motion. As the cross-linking density is increased, the restriction on molecular mobility becomes substantial, and much higher energy will be required to induce segmental motion ($T_g$ increases) (Ebewele, 2000). So, we could speculate that the cross-linking density of the networks decreased after a complex chemical reaction process by the irradiation of γ-ray.

**Effect of γ-radiation on dynamic mechanical properties**

DMA is a key technique to relate change in molecular motion with macro-properties for polymer materials. Figure 2 presents the storage modulus and tanδ as a function of temperature. The relationship between the dynamic stress and the corresponding strain provides the complex modulus, a real part (storage modulus) and imaginary part (loss modulus), and tanδ presents the ratio of the loss modulus to the storage modulus. It could be seen clearly that these SMP samples had two different elastic states with the change in temperature: glassy state and rubbery state. The region among two states is glass transition process. A large and sharp decrease in the storage modulus around glass transition could be seen in Figure 2 both before and after γ-radiation, which is crucial for a good shape memory material. The elastic ratio that is defined as the glass-to-rubber modulus ratio ($E_g/E_r$) is often quoted to estimate the magnitude of the change in modulus when the polymer undergoes shape recovery. A large elastic modulus ratio is beneficial for showing good shape memory capability, since it gives larger shape fixity upon cooling and realizes a larger strain with a small stress at high temperature. As is shown in Figure 2,

![Figure 1. Photographs of epoxy-based SMPs before and after γ-radiation. SMP: shape memory polymer.](image)

<table>
<thead>
<tr>
<th>Samples</th>
<th>Total radiation dosage (Gy)</th>
<th>$T_g$ by DSC (°C)</th>
<th>$T_g$ by tanδ (°C)</th>
<th>Amplitude of tanδ at $T_g$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SMP1</td>
<td>0</td>
<td>125.3 ± 2.3</td>
<td>162.8 ± 2.1</td>
<td>1.31</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^5$</td>
<td>119.6 ± 1.8</td>
<td>160.0 ± 1.1</td>
<td>1.32</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^6$</td>
<td>115.5 ± 1.9</td>
<td>150.3 ± 0.9</td>
<td>1.29</td>
</tr>
<tr>
<td>SMP2</td>
<td>0</td>
<td>113.8 ± 0.6</td>
<td>150.7 ± 1.3</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^5$</td>
<td>110.7 ± 1.2</td>
<td>147.8 ± 0.6</td>
<td>1.27</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^6$</td>
<td>106.4 ± 1.3</td>
<td>142.1 ± 0.8</td>
<td>1.59</td>
</tr>
<tr>
<td>SMP3</td>
<td>0</td>
<td>101.9 ± 0.9</td>
<td>137.9 ± 0.8</td>
<td>1.17</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^5$</td>
<td>100.3 ± 1.0</td>
<td>133.5 ± 1.9</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^6$</td>
<td>94.8 ± 2.5</td>
<td>131.5 ± 0.7</td>
<td>1.60</td>
</tr>
<tr>
<td>SMP4</td>
<td>0</td>
<td>73.1 ± 1.4</td>
<td>110.3 ± 1.5</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^5$</td>
<td>69.3 ± 1.7</td>
<td>105.3 ± 1.2</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>$1 \times 10^6$</td>
<td>58.2 ± 0.8</td>
<td>100.0 ± 0.7</td>
<td>1.75</td>
</tr>
</tbody>
</table>

SMP: shape memory polymer; DSC: differential scanning calorimetry; DMA: dynamic mechanical analysis.
γ-radiation had no obvious effect on the elastic modulus ratio in this study. After γ-radiation of $1 \times 10^5$ Gy, the storage modulus and tan δ curves slightly move to the lower temperature. As the storage modulus reveals the stiffness of the material, it could be noted that the stiffness of the polymer is stable after a low dose of γ-radiation. After γ-radiation of $1 \times 10^6$ Gy, the transition region of the storage modulus curves and the tan δ peaks moved to a lower temperature for about 5°C–12°C, less than 10%, also predicting the decrease of $T_g$. At the same time, the tan δ peaks in Figure 2 became higher and broader with the incremental radiation. The amplitude of tan δ peaks (Table 1) indicates the damp property of the polymer, and the width of the curve reveals the homogeneity of the segments in the network. In the case of SMP3, the tan δ peak value increased from 1.26 (0 Gy) to 1.75 ($1 \times 10^6$ Gy). A higher tan δ in general indicates that materials are more resistant to impact (or cracking) through better dissipation of mechanical energy (Lu et al., 2011). This phenomenon was gradually more obvious with the increasing linear monomer from SMP1 to SMP4. Then, it is obvious that after γ-radiation of $1 \times 10^6$ Gy, the homogeneity of the segments in the network was weakened. It is noteworthy that $T_g$ values obtained from the DMA (tan δ) were 30°C–40°C higher than those from the DSC test. The method of determining $T_g$ by DMA can cause disagreements, as at least five ways are in current use. Depending on the industry standards or background of the operator, the peak or onset of the tan δ curve, the onset of the storage modulus decrease, or the onset or peak of the loss modulus curve may be used. The values obtained from these methods can differ by up to 25°C from each other for the same run. In addition, a 10°C–20°C difference from the DSC is also seen in many materials (Menard, 2003). Since the value obtained from the peak of tan δ curve is generally the highest one among the above methods, the difference in $T_g$ values obtained from the DMA (tan δ) and DSC test is reasonable.

**Effect of γ-radiation on quasi-static mechanical properties**

To investigate the effect of γ-radiation on mechanical behaviors, tensile tests for the epoxy-based SMP samples before and after irradiation were all carried out at 20°C (Figure 3). Compared with non-irradiation

![Figure 2. DMA curves of the epoxy-based SMPs before and after γ-radiation.](image)

DMA: dynamic mechanical analysis; SMP: shape memory polymer.
samples, the tensile strength changed little after irradiation of $1 \times 10^5$ Gy. Tensile strength of SMP1, SMP2, and SMP3 decreased slightly with the rates from 2.2% to 11%, while that of SMP4 increased slightly with a rate of 2.3%. However, after $\gamma$-radiation of $1 \times 10^6$ Gy, the tensile strength of all samples reduced significantly, with the rates of 11%–51%.

Elastic modulus of epoxy-based SMPs before and after $\gamma$-radiation is shown in Figure 4. After irradiation of $1 \times 10^5$ Gy, only SMP1 saw a 5.3% decrease in elastic modulus, while the others increased by 2%–9.6%, and they all changed slightly. After irradiation of $1 \times 10^6$ Gy, the elastic modulus decreased significantly with the rates of 16%–47%. These results suggest that elastic modulus first increased slightly and then reduced significantly with an increase in $\gamma$-radiation.

Currently, there are no specific or uniform evaluation indicators for SMPs under radiation. In practice, the main method is to compare the mechanical properties of structural materials for aerospace before and after irradiation. In this article, the epoxy-based SMPs showed good resistance to irradiation of $1 \times 10^5$ Gy, and after being irradiated by $1 \times 10^6$ Gy radiation, the tensile strength and elastic modulus were above 26 MPa and 1.36 GPa, respectively, showing great potential in aerospace structural materials.

Effect of $\gamma$-radiation on shape memory properties

The shape recovery time under different actuating temperatures ($T_g$, $T_g + 10^\circ C$, $T_g + 20^\circ C$, $T_g + 30^\circ C$, and $T_g + 40^\circ C$) of the epoxy-based SMPs before and after $\gamma$-radiation is shown in Figure 5. It is worth noting that below $1 \times 10^5$ Gy $\gamma$-radiation, the shape recovery speed above the respective glass transition temperatures was faster than that without irradiation. As the shape switching temperature was set to match with $T_g$ when $T_g$ decreased after irradiation, the actuating temperature was correspondingly high. However, the recovery time became a little longer for the samples exposed to a dose below $1 \times 10^6$ Gy $\gamma$-radiation probably because the recovery force became much smaller due to the damage of large amount irradiation. But generally speaking, the recovery time after irradiation fluctuated slightly around the time before irradiation, and when the actuating temperature was high enough, for example, $T_g + 40^\circ C$, the recovery time was quite similar.

The shape recovery process of SMP4 at 100°C is shown in Figure 6, as an example. According to the experimental results, the shape recovery ratio of all the samples were greater than 95%, which means that the samples recovered nearly the full initial shape and $\gamma$-radiation has little effect on shape recovery ratio. Therefore, after $\gamma$-irradiation doses of $1 \times 10^5$ Gy and $1 \times 10^6$ Gy, the shape memory properties of epoxy-based SMPs are basically stable.

Conclusion

In this article, the thermomechanical properties and shape memory behaviors of the epoxy-based SMPs before and after $\gamma$-radiation were investigated systematically. The radiation source was $^{60}$Co, and the radiation dosage was $1 \times 10^6$ Gy for the first time. The influence of $\gamma$-radiation on thermal and mechanical properties of the SMPs was characterized by means of DSC, DMA, and tensile test. The shape memory behaviors of the SMPs before and after irradiation were demonstrated through a “U”-shape bending test. Although this work is only a baseline assessment of the durability of epoxy-based SMPs under $\gamma$-radiation, the results are quite instructive in selecting and evaluating material for aerospace structures. We may draw the
Figure 5. Time for recovery of the epoxy-based SMPs before and after γ-radiation. SMP: shape memory polymer.

Figure 6. Shape recovery process of SMP4 at 100°C. (a) Before radiation, (b) after $1 \times 10^5$ Gy, and (c) after $1 \times 10^6$ Gy. SMP: shape memory polymer.
following conclusions from this: (1) $T_g$ of the epoxy-based SMPs confirmed by the DSC curves decreased by 7°C–15°C with an increase in irradiation dose and the DNA test showed that the homogeneity of the segments in the network was weakened after exposure to the large amount of γ-radiation ($1 \times 10^6$ Gy). (2) The stiffness of the polymer is stable under a low dose of γ-radiation ($1 \times 10^5$ Gy), while the tensile strength and elastic modulus could, respectively, maintain above 26 MPa and 1.36 GPa under $1 \times 10^6$ Gy γ-radiation. (3) The shape recovery ratios of the SMPs were all above 95%. The recovery speeds of the irradiated specimens fluctuated slightly around that of non-irradiated ones, and the speed had little difference when the actuating temperature was high enough above $T_g$. The acquired good properties under irradiation successfully expanded the applications of epoxy-based SMPs in aerospace and other harsh environments.

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**References**


