

Effects of accelerated aging on thermal, mechanical and shape memory properties of cyanate-based shape memory polymer: I vacuum ultraviolet radiation



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ABSTRACT

Shape memory polymers (SMPs) are novel intelligent materials. Evaluation of the durability of SMPs in the complex environment of future space applications helps to optimize their incorporation in space-deployable structures. In this paper, we performed vacuum outgassing and ultraviolet (UV) radiation exposure tests on a cyanate-based SMP with a glass transition temperature of 206 °C. The cyanate-based SMP shows 1.04% of total mass loss and 0.01% of collected volatile condensable matter, as determined by vacuum outgassing tests. Vacuum UV radiation deepened the color of the surface, shown little effect on the thermal stability of the SMP sample. The irradiation induced some instability of the molecular structure within the material, and this effect was gradually strengthened with the increase of exposure time. However, UV radiation did not detectably change the mechanical properties of the cyanate-based SMP; the tensile strength and elastic modulus remained essentially constant at 66 ± 2 MPa and 1940 ± 80 MPa, respectively. The average shape fixity rate and average shape recovery rate before and after UV radiation were all above 97.6%, and the repeatability was satisfactory.

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1. Introduction

Shape memory polymers (SMPs) are novel intelligent polymer materials that can recover their original shape from a temporary deformation under a specific external stimulus [1,2]. The original shape was obtained when the material was initially prepared, by molding or mechanically machining, etc. The temporary shape can be obtained by a mechanical deformation, such as bending, stretching, twisting, and compressing from the original one. This temporary shape can be fixed and stable over long times at certain temperatures until an appropriate stimulus is applied to the polymer that drives it to recover the original shape [3]. The most common stimulus using to drive a SMP is heat. The thermal responsive SMPs possess a typical switching temperature (T_{sw}), which is usually based on a glass transition or a melting transition. Once the SMP was reheated above T_{sw} , the previous fixed temporary shape could be changed back to the original shape. This shape

memory effect of polymer is attributed to the entropy elasticity of the switching segments, which allows suppression and activation of the molecular mobility for shape fixing and recovery, respectively; and a crosslink network (either chemically or physically crosslinked) that sets the permanent shape [4]. For nearly 40 years, SMPs have enabled broad application prospects in areas such as heat shrinkable tubes [5], intelligent textiles [6], medical equipment and auxiliary equipment [7], photochromic materials [8], information carriers [9], intelligent molds [10], and aerospace deployable structures [11–13].

Cyanate resin is a thermosetting plastic that has a high glass transition temperature of up to 400 °C. In addition, cyanate resin also offers features such as low dielectric loss, low hydroscopic level and good thermal stability. These properties make cyanate ester a suitable material for electronic circuit board, dielectric coatings, high strength adhesives, aerospace composites and wave-transmitting materials [14]. Currently, research efforts on cyanate-based SMPs are focused mainly on aerospace deployable structures [15,16]. Epoxy resin and cyanate ester exhibit excellent compatibility and reactivity. Hence, epoxy resins are usually used as a modifier and toughening agent in preparing cyanate-based SMPs

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[17–21]. The CRG company has designed two types of cyanate-based SMPs; one is produced through a reaction between polyfunctional cyanate monomers and monofunctional cyanate ester monomers [22] and the other through a reaction between bi-functional cyanate monomers and active molecules that contain active hydrogen atoms [23]. Everhart et al. [24] developed a reusable heat smart shaft based on the shape memory cyanate manufactured by CRG. Our previous studies [25] investigated a series of cyanate-based SMPs using bisphenol A cyanate ester and two different modifiers, namely, polyethylene glycol and polybutadiene-acrylonitrile. This series of materials features an adjustable glass transition temperature (up to 255 °C) and excellent shape memory properties.

The synthesis of cyanate-based SMPs has been widely studied. However, to promote the practical application of cyanate-based SMPs based on theoretical and experimental research, many issues still need to be addressed. For example, the selection of SMPs for spacecraft construction requires the identification of candidate materials that can perform reliably in space. Understanding the effects of space on the materials is an important step in the selection of candidate materials [26,27]. The outer surfaces of space equipment are subject to factors such as high vacuum, the sun's radiation, thermal cycling, atomic oxygen, electron radiation and debris. High vacuum can induce degassing, evaporation, sublimation and decomposition of spacecraft materials. These effects may result in high-temperature surface-evaporated gas condensing on low-temperature surfaces, which can contaminate these surface and lead to changes in their physical and dielectric properties. Barnes [28] investigated the volatility of a thermoplastic carbon/polyether ketone composite material. Its total mass loss (TML) in vacuum is less than 0.02%, and the collected volatile condensable materials (CVCM) is less than 0.1%. This composite material meets the requirements of standards for TML and CVCM for vacuum outgassing of aerospace materials [29]. The in-orbit flight test data of the Apollo spacecraft also demonstrated that the volatility of small molecules of polymer materials in a high-vacuum sealed environment and material aging and degradation caused by this volatility were important factors that affected the safety of the sealed cabin [30]. Solar electromagnetic radiation also has an effect on polymer materials. In earth orbit, the solar constant is 1353 W/m², of which UV radiation accounts for approximately 8.7% (118 W/m²). Although UV radiation is only a small portion of solar electromagnetic radiation, its high photon energy can break chemical bonds and degrade material properties [31,32]. George et al. [33] and Smeenk et al. [34] reported that UV radiation has a significant effect on the optical properties of the polymer and can induce severe discoloration of the polymer matrix. These researches [28,30–34] all focused on traditional polymer materials rather than SMPs. In recent years, Leng et al. [35] investigated the property changes of an epoxy SMP under gamma-ray radiation. Arzberger et al. [15,16] characterized the vacuum outgassing of epoxy SMPs. However, except the works of Leng et al. [35] and Arzberger et al. [15,16], the adaptability of SMPs to space environment, which is the subject of the current paper, has been rarely reported.

In this work, we focus on the effects of high vacuum and solar radiation (specifically UV radiation) on thermal, mechanical and shape memory properties of cyanate-based SMPs. The effects of thermal cycling, atomic oxygen and electron radiation will be reported in our forthcoming work.

2. Experimental

2.1. Preparation of a cyanate-based SMP

Bisphenol-A cyanate ester monomer was purchased from

JiangduWuqiao Resin Factory, China. Polyethylene glycol (PEG) was supplied by Tianjin Guangfu Fine Chemical Research Institute, China. Materials were prepared according to the method reported earlier [25]. Cyanate ester monomer and PEG (71.4/28.6 w/w) were fully melted at 100 °C and then mixed with mechanical stirring for 20 min. To obtain a bubble-free pre-polymer, the mixture was degassed in a vacuum oven for 15 min and then injected into preheated glass molds. Three-step curing was performed at 120 °C for 2 h, 180 °C for 2 h and 210 °C for 5 h. Finally, a cyanate-based SMP sheet with a thickness of 2 mm was obtained.

2.2. Equipment and methods of space environmental exposure test

The outgassing property of the cyanate-based SMP in vacuum was tested first. The test was performed in an outgassing test environment using a DH series electric thermostatic incubator. A BP2110D high precision electronic balance (with an accuracy of 0.01 mg) was used to measure sample weight. The samples were kept at a constant temperature (23 °C) and humidity (50%) for 24 h. Samples were then vacuum outgassed for 24 h at 125 °C and a vacuum pressure of 4×10^{-4} Pa to 1×10^{-4} Pa with a collecting board condensation temperature of 25 °C. Finally, the samples were returned to a constant temperature of 23 °C and a humidity of 50% for 24 h. Two parameters, total mass loss (TML) and collected volatile condensable materials (CVCM), are regularly measured in the outgassing test. Total mass loss is defined as the total weight of the material that runs out of a specimen, which is maintained at a specific constant temperature and operating pressure for a specific period of time. The TML value is calculated from the mass of the specimen before and after the test and is expressed as a percentage of the initial sample mass. Collected volatile condensable materials is defined as the quantity of outgassed matter from a test specimen that condenses on a collector maintained in a specified constant temperature for a certain period of time. CVCM is expressed as a percentage of the initial specimen mass and is calculated from the condensate mass determined from the difference in mass of the collector plate before and after the test [29].

The vacuum-UV radiation environment experiments in this paper were performed using the Efficient UV radiation environment experiment system at Beijing Institute of Spacecraft Environment Engineering. The wavelength of radiation spectra using in the acceleration test were 200–400 nm with 5 times the solar constant. The pressure was lower than 1.3×10^{-3} Pa, and the exposure time was 600 h. The overall irradiation dose was 3000 equivalent solar hours (ESH; $1 \text{ ESH} = 1353 \text{ W/m}^2 \times 8.7\% \times 3600 \text{ s} = 4.2 \times 10^5 \text{ J/m}^2$). Samples were taken after every 200 h (1000 ESH) and referred to as SMCR-0ESH, SMCR-1000ESH, SMCR-2000ESH, and SMCR-3000ESH.

2.3. Characterization methods

Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, SPECTRUM ONE, Perkin Elmer Corporation, US) was used to characterize the chemical structure of the cyanate-based SMP. Thin film samples were used in a test spectrum range of 4000–650 cm⁻¹ with a 4 cm⁻¹ resolution and scan times of 8.

UV–vis spectroscopy measurements were conducted by UV–vis. spectrophotometer (UV-2600, Japan) in the wavelength range from 1100 nm to 250 nm, in transmission mode, taking the air as reference.

Dynamic mechanical analysis (DMA) of the cyanate-based SMP was performed using a DMS Q800 (TA Corporation). Stretching mode was selected for this test at 1 Hz, and a minimum dynamic force of 0.1 N was used. The amplitude was 10 μm, and the test temperature range was 25 °C–350 °C with a heating rate of 3 °C/

min. Samples were shaped by a high speed engraving machine to the dimensions of $20 \times 3 \times 1 \text{ mm}^3$.

Thermogravimetry analysis was performed using a TGA/DSC1 (Mettler-Toledo, Switzerland) thermal gravimetric analyzer. Powder samples were prepared by filing the bulk samples. The sample weights were approximately 8–10 mg. Tests were performed at a heating rate of $10 \text{ }^\circ\text{C}/\text{min}$ in a flowing nitrogen atmosphere within the temperature range of $25 \text{ }^\circ\text{C}$ – $800 \text{ }^\circ\text{C}$.

The static tensile test was carried out with the Zwick/Roell Z010 universal machine with a stretching rate of $5 \text{ mm}/\text{min}$ at room temperature. Tensile specimens were cut from a polymer plate using high speed engraving machine. The sample size was taken from the ASTM standard D638, type IV.

The cycling shape memory behavior of the elastomer was characterized on a DMA Q800 in controlled-force mode using a three-point bending fixture. The sample size was $30 \times 3 \times 1 \text{ mm}^3$. Under the controlled-force mode, the instrument itself records the real-time force, deflection (displacement of the control point) and temperature of each preset process. For the cycle N , the initial displacement was recorded as D_{n0} , the displacement after loading the downward force of 0.1 N at $210 \text{ }^\circ\text{C}$ was recorded as D_{n1} , the fixed displacement after cooling to $50 \text{ }^\circ\text{C}$ and unloading was recorded as D_{n2} , and the displacement after recovery at $210 \text{ }^\circ\text{C}$, which is also treated as the initial displacement of the cycle $N+1$, was recorded as $D_{(n+1)0}$. The shape fixity rate R_{nf} and shape recovery rate R_{nr} of the cycle N were calculated using the following equations:

$$R_{nf} = \frac{D_{n2} - D_{n0}}{D_{n1} - D_{n0}} \times 100\% \quad (1)$$

$$R_{nr} = \frac{D_{n2} - D_{(n+1)0}}{D_{n2} - D_{n0}} \times 100\% \quad (2)$$

3. Results and discussion

3.1. Outgassing test in a vacuum environment

The mass loss of polymer material in vacuum is an important evaluation criterion to determine whether the material can be used as an aerospace material. The requirement for an aerospace material is that its TML does not exceed 1.00% in a vacuum and its CVCM does not exceed 0.1% [29].

The TML and CVCM values of the cyanate-based SMP obtained from tests in a vacuum environment were 1.04% and 0.01%, respectively. Most material loss occurred from the desorption of surface-adsorbed gases, the release and separation of gases dissolved in the material and the release of penetrating gases. The CVCM value of the cyanate-based SMP (0.01%) fully met the criteria of the standard (less than 0.1%), whereas the TML value (1.04%) exceeded the standard limit by 0.04%. The excess of 0.04% for this parameter corresponds to a material outgassing effect that could cause high-temperature-surface-released gases to condense on and potentially contaminate the low-temperature surfaces of the spacecraft. Thus, the material requires further degassing treatment to reduce the volatile material content to less than 1.0% before its incorporation as a spacecraft material.

3.2. Effect of vacuum UV radiation on chemical structure

First, we observed the effect of different exposure durations of UV radiation on the surface color of the cyanate-based SMP. Fig. 1 shows the sample surface color changing from bright yellow (before irradiation) to brown yellow (after irradiation). The color

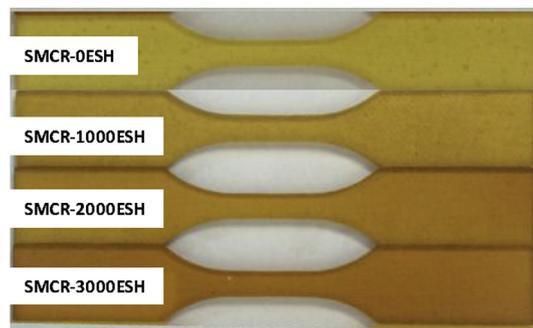


Fig. 1. Image of the cyanate-based SMP before and after UV radiation.

gradually deepened as the UV radiation dose was increased. Fig. 2 shows UV–visible transmittance spectra of the cyanate-based SMP with various durations of UV exposure in the wavelength range from 250 to 1100 nm . All the SMP samples could block the UV light below 400 nm , and the transparency decreased with the increasing UV exposure time in the visible region. In detail, the transmittance of 600 nm wavelength of light decreased from 70% (0ESH) to 64% (1000ESH), 57% (2000ESH), 51% (3000ESH), respectively. This implies that exposure to UV radiation may result in color and transmittance change of the material and is consistent with earlier reported observations [36].

Some changes in physical properties of UV exposed polymers, such as discoloration, have been directly related to chemical changes [37]. The cyanate-based SMP contains large amounts of benzene rings and benzene-like triazine rings from the cyanate ester monomer and the curing reaction. These two functional groups each exhibit a high bonding energy ($>2000 \text{ kJ}/\text{mol}$). The cyanate-based SMP also contains C–O bonds (bond energy $326 \text{ kJ}/\text{mol}$) from the polyethylene glycol and the cyanate ester monomer. The IR spectra of the cyanate-based SMP before and after UV radiation (Fig. 3) indicate that most of the characteristic peaks, including the two triazine rings at 1558 cm^{-1} and 1356 cm^{-1} remained unchanged. However, a new characteristic peak appeared at 1718 cm^{-1} in the spectra of UV exposed SMP samples, which corresponds to the C=O stretching vibration peak [38]. This peak was much more striking when the UV exposure time went up to 600 h (3000 ESH). The appearance of the C=O bond after UV radiation was supposed to be attributed to the breaking of one end of low-bond-energy C–O after exposure to UV radiation, which

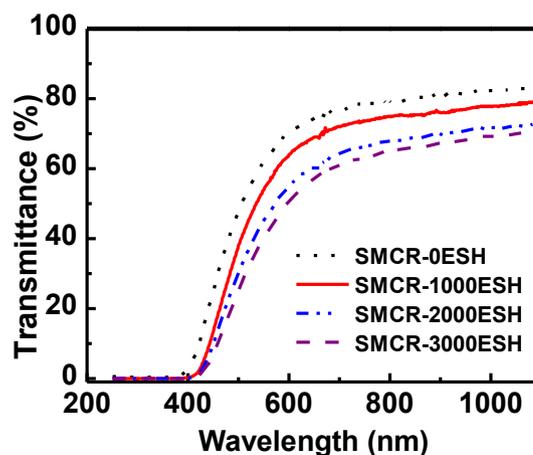


Fig. 2. UV–visible transmittance spectra of the cyanate-based SMP with various durations of UV exposure.

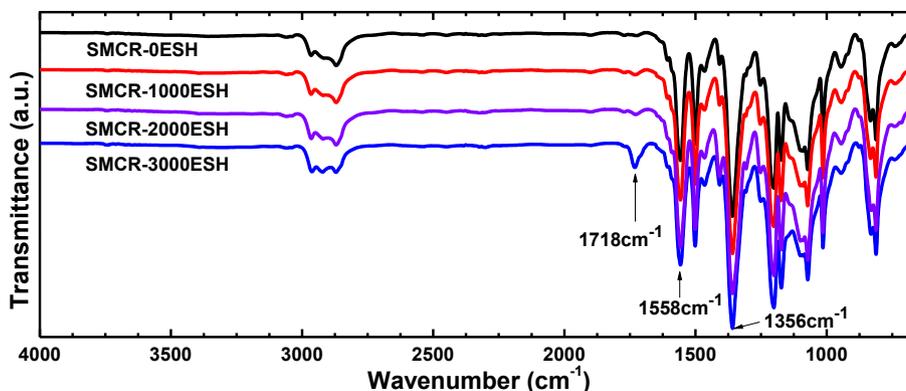


Fig. 3. FTIR spectra of the cyanate-based SMP before and after UV radiation.

generated carbonyl groups C=O with much higher bond energy (728 kJ/mol), resulting in a lower molecular weight of the system. The other end of the breaking C–O bonds would connect to each other, resulting in a crosslinking reaction in the system. This reaction mechanism was consistent with previous report that moieties such as $-\text{CH}_2\text{NH}-$, $-\text{CH}_2\text{O}-$, or $\text{COCH}=\text{CH}-$ are oxidation-sensitive and enhance radical formation [39]. This finding indicated that although the main net points of crosslinking network, the benzene ring and benzene-like triazine rings, was unchanged, there were some other crosslinking and degrading reactions occurred within the material. The effect of UV radiation on the material's chemical structure can be summarized as follows: With the increase of irradiation time, the effects of UV radiation were gradually strengthened, resulting in the change of molecular structure. Crosslinking, degradation, breaking of weak bonds and formation of more stable chemical bonds may be involved in the complex photo-chemical process. Because there was only one characteristic peak (1718 cm^{-1}) in the FTIR spectra obviously changed after the UV radiation, we could not precisely define the detailed chemical reactions. Fortunately, the mechanical properties analysis in a later part of this paper demonstrates that these reactions do not significantly alter the material's mechanical properties.

3.3. Effect of vacuum UV radiation on thermal stability

Fig. 4 shows that thermal gravimetric (TGA) curves of the

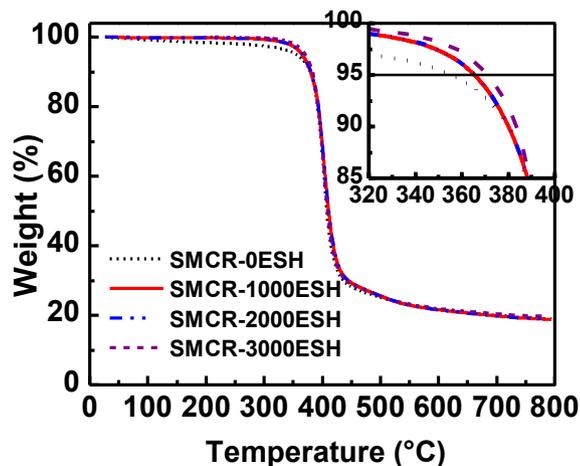


Fig. 4. Thermal gravimetric curves of the cyanate-based SMP before and after UV radiation.

cyanate-based SMP before and after UV radiation essentially overlapped for the testing temperature range. The char yield at $800\text{ }^\circ\text{C}$ for all four samples was 19%, indicating the UV radiation has no effect on the thermal stability, including thermal decomposition rate or final char yield. The only difference between the TGA curves before and after UV radiation is the initial thermal decomposition temperature (the temperature at which the sample weight drops to 95%). With increasing irradiation dose, the initial thermal decomposition temperature increased by about $10\text{ }^\circ\text{C}$. The reason is that there exist some unreacted small molecules, impurities, absorbed water from the air and carbon dioxide in the original unexposed sample. These small molecules escape from the sample because of the pressure induced by vacuum UV radiation. Thus, higher purity cyanate-based SMP remains. Because of the high degree of chemical crosslinking and three dimensional network structure, the initial thermal decomposition temperatures for all the samples are above $356\text{ }^\circ\text{C}$, which is the evidence of the excellent heat resistance of the cyanate-based SMPs [40].

3.4. Effect of vacuum UV radiation on mechanical properties

Fig. 5 compares the mechanical properties between the cyanate-based SMP samples before and after UV radiation. The tensile strength remained at 66 MPa within 2 MPa standard deviation after UV radiation. As the irradiation dose increased, strain at break of the four samples was $7 \pm 1\%$, $6 \pm 1\%$, $7 \pm 1\%$ and $6 \pm 1\%$, respectively. These values lie between 5% and 8%. The tensile modulus of the material did not decrease even after 3000 ESH UV radiation. The

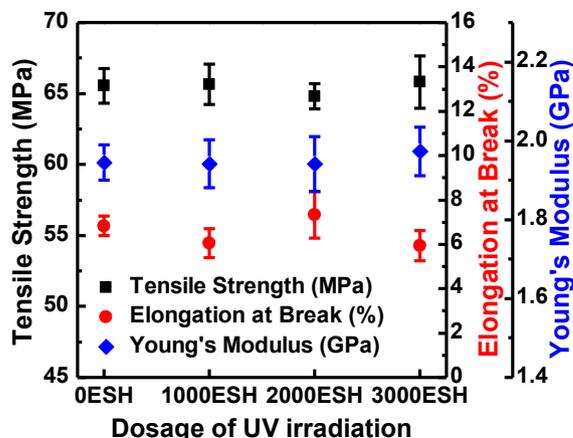


Fig. 5. Mechanical properties of the cyanate-based SMP before and after UV radiation.

average elastic modulus was above 1940 MPa, and the standard deviation was less than 80 MPa. This result indicates that UV radiation induces minimal changes to the chemical bonds inside the polymer. Similar result was reported by Shimamura et al. [41] and George et al. [33], they found that UV radiation only affects a thin layer of the surfaces and has little impact on mechanical properties. Accordingly, the changes that are induced involve only a few functional groups and small molecule impurities near the surface of the cyanate-based SMP; thus, they have no detectable effect on the major molecular structure of the polymer and no detectable effect on the overall mechanical properties of the material.

3.5. Effect of vacuum UV radiation on $\tan \delta$ and storage modulus

The loss modulus is commonly used to express the polymer deformation energy lost or converted to heat, which corresponds to the damping. The storage modulus describes the elastic recovery ability of the polymer material after deformation. It represents the energy stored in the elastic deformation of a viscoelastic material. The storage modulus is essentially the Young's modulus. The ratio of the loss modulus to the storage modulus is defined as the loss factor, $\tan \delta$. The change of $\tan \delta$ reflects the viscoelastic characteristics of the molecule [42].

Fig. 6 shows the DMA curves of the cyanate-based SMP before and after UV radiation. The storage modulus curves of the cyanate-based SMP before and after UV radiation are overlaid at room temperature. This result is consistent with the above mechanical analysis in that the tensile modulus of the materials displays no significant difference before and after irradiation. The peak of $\tan \delta$ curves did not significantly change with 1000 ESH and 2000 ESH irradiation compared to the sample before irradiation. However, the peak of $\tan \delta$ curves moves to the lower temperature, from 206 °C to 197 °C, when the irradiation dose reached 3000 ESH. SMCR-3000ESH also exhibited a lower storage modulus at high temperature (>150 °C) than that of the other samples. Although infrared analysis and mechanical property analysis indicate that UV radiation did not show significant effect on the chemical structures, the breaking of the unstable bonds (C–O) may result in lower crosslinking density. Thus, the change of $\tan \delta$ peak temperature and storage modulus might result from a possible degradation to smaller molecular weight chains which is going to plasticize the materials [43]. Thus, we could also find that the intensity of $\tan \delta$ peak of SMCR-3000ESH show the highest value among all the

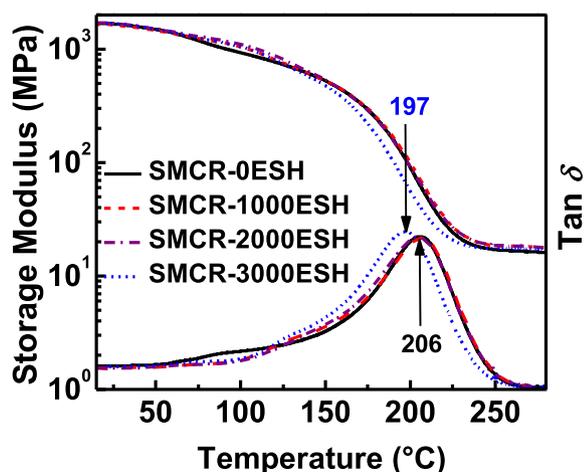


Fig. 6. Storage modulus and loss factor ($\tan \delta$) of the cyanate-based SMP before and after UV radiation as functions of temperature.

samples, which also implies a lower crosslinking density [37].

3.6. Effect of vacuum UV radiation on shape memory behavior

It is expected that if an SMP were used in a space deployable structure, a long flight would precede arrival at the expansion location. In other words, the SMP would be exposed to radiation in space before its shape memory function is exploited. Hence, investigation on the effect of irradiation in space on the shape memory function of the cyanate-based SMP is of great necessity.

The shape memory properties of unexposed sample (a) SMCR-0ESH and post-exposed sample (b) SMCR-3000ESH are characterized and shown in Fig. 7. Samples were first heated to 210 °C (4 °C above the glass transition temperature), and a 0.1 N force was applied to shift the midpoint. The shape was fixed after cooling and the force withdrawn. Samples were heated to 210 °C again to complete a shape memory cycle. Calculations indicated that the shape fixity rates of three shape memory cycles were 97.8%, 97.9% and 97.1% for sample SMCR-0ESH with an average shape fixity rate of 97.6%. The shape recovery rates were 96.9%, 97.0% and 99.0% with an average shape recovery rate of 97.9%. The shape fixity rates of three shape memory cycles were 97.8%, 97.9% and 98.0% for sample SMCR-3000ESH with an average shape fixity rate of 97.9%. The shape recovery rates were 98.2%, 98.8% and 98.9% with an average shape recovery rate of 98.6% (Table 1). It can be concluded that the shape fixity and recovery rates of the cyanate-based SMP are not significantly altered by 3000 ESH UV radiation. The average shape recovery rate increased by 1% compared to the control sample. The test repeatability is excellent. These findings indicate that UV radiation has no harmful effect on the shape memory properties of the cyanate-based SMP. In addition, Fig. 7 shows a gradual increase of the displacement at a given loading force from the first to the last cycle on SMCR-3000ESH. As we analyzed in the DMA test, the UV radiation might cause the degradation to smaller molecular weight chains which is going to plasticize the material [43]. So we suppose that the UV degradation might be the origin of that effect. The degradation of the polymer to lower molecular weight might to some extent endow some plasticization which will endow ratcheting deformation (cyclic creep) accumulates [44,45], in other words, higher displacement at the same loading force during the cyclic test.

4. Conclusion

The effects of UV radiation were investigated in terms of microscopic morphology, chemical composition, mechanical properties, $\tan \delta$ and thermal properties. Outgassing tests in a vacuum environment indicated that the TML of the cyanate-based SMP in vacuum was 1.04%, slightly higher than the standard limit of 1.00%. The materials require a degassing treatment before use in space. UV radiation deepened the sample surface color and lowered the transmittance of the visible light. With the increase of irradiation time, the effects of UV radiation were gradually strengthened, resulting in the change of molecular structures. Degradation, breaking of weak bonds and formation of more stable chemical bonds may be involved in the complex photo-chemical process. UV radiation has no effect on the thermal stability of cyanate-based SMPs, including thermal decomposition rate or final char yield. The tensile strength remained within $66 \text{ MPa} \pm 2 \text{ MPa}$ with an average elastic modulus of $1940 \pm 80 \text{ MPa}$. The DMA curves shows that the sample exposing to 3000ESH UV radiation exhibits a lower crosslinking density which may result from the UV degradation of the polymer. The average shape fixity rate and shape recovery rate of samples before and after UV radiation were each above 97.6%. The rates improved after irradiation, and the repeatability was

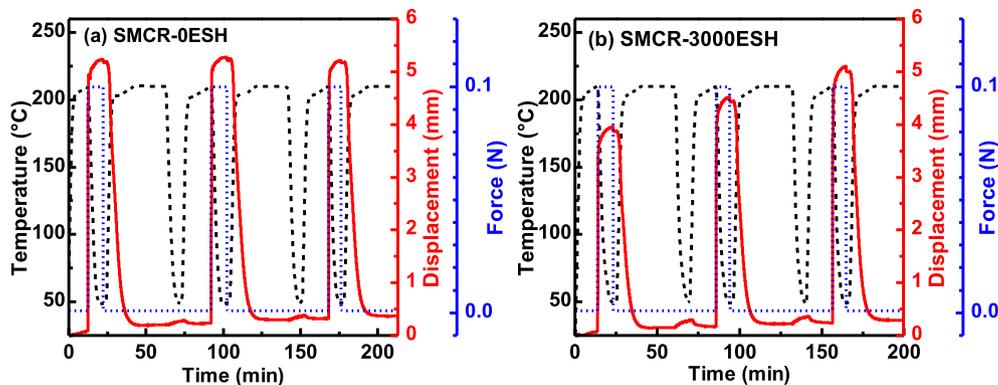


Fig. 7. Effect of UV radiation on the shape memory effect of the cyanate-based SMP (a) SMCR-0ESH, (b) SMCR-3000ESH.

Table 1

Shape fixity rate (R_{if}) and shape recovery rate (R_{nr}) of the cyanate-based SMP before and after UV radiation.

Sample	N	1	2	3	Average
SMCR-0ESH	$R_{if}(\%)$	97.8	97.9	97.1	97.6
	$R_{nr}(\%)$	96.9	97.0	99.0	97.6
SMCR-3000ESH	$R_{if}(\%)$	97.8	97.9	98.0	97.9
	$R_{nr}(\%)$	98.2	98.8	98.9	98.6

satisfactory. Overall, vacuum UV radiation has an insignificant effect on the performance of the cyanate-based SMP due to its stable three dimensional network structure.

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