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γ -rays radiation resistant shape memory cyanate ester resin and its composites with high transition temperature

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Abstract

Shape memory polymers (SMPs) as a kind of functional material have attracted great attention in aerospace field. High temperature resistant, high mechanical strength and space environment resistant materials are needed in practical applications. In this paper, the cyanate ester resin with a high glass transition temperature 219.4 °C and a high storage modulus 2.14 GPa was fabricated. The effect of different dose of γ -rays radiation on shape memory cyanate ester (SMCE) resin was investigated. Compared to the SMCE resin, the storage modulus of the irradiated SMCE who underwent 1000 KGy radiation increased 2.6% and the stretching strain exceeded 44.5%. The shape recovery rate of SMCE reached up to 99.6% and that of the irradiated SMCE is 98.8%. Moreover, carbon fiber fabric reinforced cyanate-based composites were prepared via a sandwich mold perfusion method for increasing resin's strength and load, whose shape recovery time was shorter than that of SMCE. Thermosetting SMPs and their composites with high transition temperature and good irradiation resistance performances is expected to play an important role on spacecraft in the future.

Supplementary material for this article is available online

Keywords: shape memory polymer, high transition temperature, cyanate ester, γ -rays radiation, carbon fiber fabric reinforced composites

(Some figures may appear in colour only in the online journal)

Introduction

Human exploration of aerospace is becoming more and more frequent with the social progress and technological development. However, the environment of outer space is extremely awful, as in-orbit spacecrafts are caught in high and low temperature, UV radiation [1], charged particle radiation [2], γ -rays radiation [3, 4], atomic oxygen [5, 6], neutron [7] and space debris inevitably. As all we know irradiation will speed up ageing and shorten the life of polymers. Among them, γ ray is an electromagnetic wave whose wavelength is less than 0.01 nm and energy is very high. γ -ray radiation has a greater influence on thermodynamic properties of materials than other electromagnetic irradiations. The interactions of ionizing radiation with polymers can generate reactive intermediates, for instance ions, free radicals and excited states [8]. These intermediate reactions can result in the accumulation of small molecular products, which can greatly affect the materials' thermodynamic, chemical and physical properties [9]. Hence, polymer materials used for spacecrafts are bound to meet the requirements of excellent thermal performance and mechanical property as well as irradiation resistance.

Shape memory polymer (SMP) is a novel smart material, which can change shapes from a temporary form to the original shape under a specific external stimulus. Compared to shape memory alloy, SMP reveals significant advantages, including light weight, low cost and simple preparation process, vividly providing the great potential and the bright prospect in the aerospace sector. As a promising substitution to traditional materials, SMP has been widely used in various fields, such as aerospace, automotive, electronic, construction and so on. Cyanate ester (CE) resin is a typical high-performance thermosetting resin owning many favorable properties, such as low dielectric constant, cure shrinkage rate and moisture absorption, high glass transition, thermal resistance and irradiation resistance, as well as excellent mechanical properties [10–12]. Effects of UV and γ -rays radiation on thermal, mechanical as well as shape memory properties of epoxy-based and cyanate-based SMPs have been reported [13–15].

In brief, polymer material performances are determined by the degree of the chain cross-linking, decreasing the gas permeability [16]. But the chain scission is destruction of cross-linking structure or destruction of macro-molecule network structure. In addition, chain scission and chain crosslinking can synchronize in the irradiation process and both of them can change the properties of the material. But ultimately, one of them may be dominant over the other. Therefore, comprehending the behavior of polymers after high-energy radiation is important for predicting the lifetime of polymer materials. To improve polymer's resistant radiation, composite materials that glass fibers reinforced [17, 18], graphene doped [19, 20], carbon fibers [21, 22], carbon nanotubes [23, 24] and halloysite reinforced [25, 26] were studied. It can be seen that those carbon materials are researchers' favorite additives to perfect the irradiation resistance.

Our research is distinct from the above ones. Small molecular products and volatile products come mainly from side chain scission during the irradiation process. Therefore, linear molecules with active groups and high stability were selected as modifier agents to CE resin. In our study, two agents were added in the CE matrix to improve its toughness. The CE resin and γ -rays irradiated CE resin specimens were tested by DMA, DSC, and TGA. Different layers of carbon fiber fabrics reinforced CE composites were prepared and showed super excellent mechanical property and irradiation resistance, which was expected to be used for complex structure units in aerospace engineering.

Experimental

Materials

Bisphenol A cyanate ester monomer (BACEM) was purchased from Jiangsu Wuqiao Resin Factory, China. The bis (hydroxy)-terminated and bis(epoxy)-terminated polyethers (R_m -OH and R_n -CH₂CH₂O) were purchased from Sigma-Aldrich. Carbon fiber fabric was from Weihai Guangwei Composites Co. Ltd, China. Carbon fiber fabric (Twill, 3 K, 200 g m⁻²) was from TORAY, Japan.

Preparation of shape memory CE and their composites

BACEM was melted at 120 °C in a beaker. Then, the modifiers, $R_{\rm m}$ -OH and $R_{\rm n}$ -CH₂CH₂O, were added into the BACEM with stirring continuously for 30 min to obtain a uniform prepolymerized solution. Next, the solution was injected into a preheated glass mold, which was cured at 150 °C for 2 h, 180 °C for 2 h and 210 °C for 3 h at a heating rate of 0.25 °C min⁻¹. Finally, cyanate-based SMP sheets were obtained.

Carbon fiber fabric was spread in the mold. The other steps are the same as above. Finally, carbon fiber fabrics reinforced cyanate-based SMPs were obtained.

Space environmental exposure test

First, degassing was performed to confirm if the material can work as aerospace components. Samples were placed in a vacuum chamber with a 2×10^{-4} Pa pressure and a 125 °C temperature for 24 h. The total mass loss was 0.81% which did not exceed the standard value of 1.00%. The collected volatile condensable material was 0.04% which did not exceed the standard value of 0.1%. Then, the vacuum γ -rays radiation environment experiments were performed at Heilongjiang Academy of Sciences (Harbin, China). The CE resin was exposed to the different intensity of γ -rays. The γ rays radiation dose is 10 KGy, 100 KGy and 1000 KGy respectively. The dose growth rate is 5 Gy s⁻¹.

Characterizations

The cyanate-based SMP was performed by attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR, Perkin Elmer Corporation, US). Powdered samples were tested with a test spectrum range of $4000-400 \text{ cm}^{-1}$ and 4 cm^{-1} resolution.

Dynamic mechanical analysis (DMA) of shape memory cyanate ester (SMCE) and its composites were characterized using a DMA Q800 apparatus (TA Corporation) with a frequency of 1 Hz and an amplitude of 20 μ m in the stretching mode. The sample was shaped as a rectangle whose size was 25 mm × 4 mm. Three-point bending mode was used for testing shape memory cycles and glass transition temperature of CE composites.

Thermogravimetry analysis (TGA) was carried out using a thermal gravimetric analyzer (Mettler-Toledo, Switzerland). Granular samples were tested from 25 °C to 800 °C with a 10 °C min⁻¹ ramp rate under nitrogen atmosphere.

The mechanical properties of tensile standard samples (ASTM D638, Type IV) before and after γ -rays radiation were tested using an Instron 5500R universal Testing Machine (Instron Corp., USA) with a load cell of 5 kN. Tensile tests were carried out at the elongation rate of 1 mm min⁻¹ at room temperature.



Figure 1. As-prepared SMCE resin and their CFFR composites.

Shape memory property

The shape fixity rate (R_f) and shape recovery rate (R_r) of the cycles were calculated using the following equations [27]:

$$R_{\rm f} = \frac{\varepsilon}{\varepsilon_{load}} \times 100\%$$
$$R_{\rm r} = \frac{\varepsilon - \varepsilon_{rec}}{\varepsilon} \times 100\%$$

where ε is the fixed strain after cooling and load removal. ε_{load} is the maximum strain under load, and ε_{rec} is the strain after recovery.

Results and discussion

The CE resin samples with diverse mass ratios (20/5/1, 20/5/3, 20/5/5) of CE monomer, $R_{\rm m}$ -OH and $R_{\rm n}$ -CH₂CH₂O were prepared, which was named as CE^a, CE^b and CE^c as shown in figure 1(b₁)–(b₃). The CE^b specimens underwent three different radiation doses, 10 KGy, 100 KGy and 1000 KGy, respectively. These irradiated specimens were referred to as CE^b10, CE^b100 and CE^b1000, which were exhibited in figure 1(a₁)–(a₃). The as-prepared CE composites based on CE^b were abbreviated to CE^bC¹, CE^bC² and CE^bC³ in figure 1(c₁)–(c₃). Among, superscripts 1, 2 and 3 mean the number of carbon fiber fabric layers.

Compared to CE^{b} specimens, the irradiated specimens are light in color. The higher the radiation dose, the lighter the color is. The color of $CE^{b}10$ is distinctly deep than $CE^{b}100$ and $CE^{b}1000$ whose colors are almost the same. The sort of change suggests that the material is ageing when it is exposed to 10 KGy dose of γ -rays, which is inevitable for polymer materials. The change may be caused by the scission of chains, both side chains and main chains. Actually, side chains are easier to break than the main ones. Linear chain without side chains has more advantages against γ -rays. That was the reason why we selected R_{m} -OH and R_{n} -CH₂CH₂O as modifiers.

The modifiers, R_m -OH and R_n -CH₂CH₂O, have different roles in resin curing. *R* is a symbol of the main chain without side chains, whose performance is stable. As shown in figure 2(i), the self-crosslinking reaction of BACEM is performed during the heating process. Three –CN groups are polymerized generating a 1,3,5-triazine group whose structure is highly symmetrical resulting in the frangibility of pure cyanate ester material [28]. The main purpose of adding $R_{\rm m}$ -OH is to increase the steric hindrance of the self-crosslinking reaction of -CN groups and then to reduce the probability of the reaction. That can effectively improve the toughness of the CE material. Rn-CH2CH2O contains a lot of end-epoxy groups. The main purpose of adding R_n -CH₂CH₂O is to react with -CN group and 1,3,5-triazine group as shown in figures 2(ii) and (iii). So that the self-crosslinking degree of -CN groups and generation of 1,3,5-triazine groups reduce [29, 30]. We consider a reaction between the hydroxy and end-epoxy group in figure 2(iv). The reaction can be progressing successfully under acidic or alkaline condition. More, it also can start to react when the temperature is higher than 200 °C and. The reaction can proceed but is slight and slow, because the highest curing temperature of SMCE is 210 °C.

FT-IR spectra are used to analyze the changes of characteristic functional groups of the SMCE resin. Figure 3(a) exhibits the FT-IR spectra of BACEM, pristine CE (PCE) resin and CE resin. PCE resin is generated through heatcuring of BACEM. Modifiers are added into BACEM, and CE^b resin is obtained after heat-curing. For the FT-IR curve of BACEM, the two peaks at 2275 and 2237 cm^{-1} can be put down to the typical signs of -CN groups [31]. For the curve of CE^{b} resin, the two peaks at 1564 and 1366 cm⁻¹ can be attributed to 1,3,5-triazine groups [12]. There are peaks of two kinds of groups in the FT-IR curve of PCE. The -CN groups in PCE are not completely consumed in the process of thermal curing. Compared PCE resin and CE resin, it is obvious that the residual -CN groups react with the modifiers in the thermal curing process [32]. Obvious peaks at 2967 cm^{-1} and 2871 cm⁻¹ is corresponding to C-H stretching vibration in $-CH_3$ and $-CH_2$, respectively. The peak at 1106 cm⁻¹ is due to C-O-C stretching vibration in the curve of CE^{b} . $-CH_{3}$ group is from CE, -CH₂- and C-O-C groups are from $R_{\rm m}$ -OH and $R_{\rm n}$ -CH₂CH₂O. In addition, a new peak occurs at 1694 cm^{-1} because of -C=N- stretching vibration.

FT-IR spectra of radiated CE resins with different amounts of γ -rays are demonstrated in figure 3(b). Before being irradiated, the peaks of the wavenumbers at 1564 and 1366 cm⁻¹ are clearly present and assigned to the 1,3,5-triazine groups. There are no new peaks formed and no significant changes in peak intensity after γ -rays radiation, which indicates that the SMCE resin is irradiation resistance.

The mechanical property of the CE resin is performed by DMA. Figure 4(a) displays storage modulus and tan δ with temperature spectra of CE resins. Glass transition temperature (Tg) defined as the temperature corresponding to the maximum tan δ value shifts to lower temperature as the modifier content increases, which is 219.7 °C, 203.1 °C and 164.3 °C, respectively. The addition of $R_{\rm m}$ -OH increases the stereo-hindrance among active functional groups in CE resin and can lead to the decreasing of Tg value and storage modulus. Figure 4(b) shows the contrastive spectra of CE^b resin before and after exposing to γ -rays. It is clear that when γ -rays dose increases to 1000 KGy, the storage modulus of the CE resin only slightly increases from 1.86 to 1.91 GPa at 25 °C. The CE^b1000 sample also exhibits a lower storage modulus from



Figure 3. FT-IR spectra of (a) CEM, pristine CE resin and CE^b resin; (b) SMCE resin with different dose of γ -rays.

4000

800

CE

CE^b10

CE^b100

CE^b1000

3200

2400

Wavenumber(cm⁻¹)

80 °C to 210 °C than that of the other three samples. With increasing γ -rays dose, Tg of CE^b decreases from 203.1 °C to 189.4 °C [33]. The decreasing can be put down to the break of chemical bonds of side chains in CE resin during irradiation leading to defects. The defects initiate in CE resins may result in a local stress concentration under external forces [9]. In

CEM

PCE

CEb

4000

296 287

3200

2275 2237

2400

Wavenumber(cm⁻¹)

1564

1600

other words, CE resin is easier to be destroyed where there are defects.

1600

800

TGA is used to research the effect of γ -rays radiation on the thermal stability of the SMCE resin. Figure 4(c) shows the TGA curves of both non-irradiated and irradiated specimens at different γ -rays doses. DTG curves reveal the specimens' mass change rate in figure 4(d). The temperature of 5 wt%



Figure 4. (a), (b) Storage modulus and Tan δ values versus temperature of CE resin and irradiated CE resin; (c), (d) thermal gravimetric and DTG curves of the SMCE resin before and after γ -rays radiation.



Figure 5. (a) The mass rate of CE resin before and after irradiation; (b) tensile test curves of non-irradiated and irradiated cyanate ester at RT.

weight loss is defined as initial thermal decomposition temperature (T_i) and that of fastest quality reduction is maximum decomposition rate temperature (T_m) . From the results, *T*_i is 364.7 °C, 366.2 °C, 363.7 °C and 358.7 °C, respectively, which is in a downtrend. When the temperature is above 420 °C, these TGA curves show some distinct differences, and the CE^b1000 sample is the most obvious. The high final thermal decomposition temperature demonstrated that the SMCE resin possessed excellent heat resistance. The char yield of all four samples is 20.9%, 20.8%, 20.3% and 19.3% at 800 °C, respectively. Remarkably, it is noted that the char yield gradually decreases with the increasing of radiation dose. All the above results indicate that the higher γ -rays dose can result in the weakening of thermal stability of the SMCE resin. Moreover, as we know that polymer materials with a higher crosslinking density usually demonstrate a better mechanical property and thermal stability. Hence, the irradiation of high-energy γ -rays can damage the cross-linked structure of the SMCE resin, which decreases the crosslinking density and thermal stability of the SMCE resin.

The mass is increased after irradiation and the mass rate rise with the increasing of γ -rays dose. The mass rate is under 0.27% when it is exposed in 1000 KGy γ -rays. The deformation curves of cyanate ester before and after γ -rays radiation are shown in figure 5(b). It is clear that stretching stress is almost linear with stretching strain in the early stage of the curves before and after γ -rays radiation. Then the stretching stress rise to a maximum value and drop suddenly at last. The stretching strain is 5.89%, 5.86%, 6.12% and 8.51%, which increase slightly with the increasing γ -rays dose. That is to say the SMCE resin has certain tolerantability to 1000 KGy γ rays. The similar improvement of ILSS is also obtained in the study [25]. They claim that 1,3,5-triazine ring of cured cyanate ester resin has excellent γ -rays radiation resistance.

Pure CE resin has a high crystallinity feature because of highly symmetrical structure of 1,3,5-triazine group. Pure CE



Figure 6. Shape memory cycle tests and shape recovery process of the SMCE resin (a), (c) CE^b, (b), (d) CE^b1000.

resin usually exhibits a typical brittle failure, but toughened CE resin does quasiductile behavior. A platform area occurs in the stress-strain curves and it is associated to necking symmetric propagation and elastic deformation at almost constant stretching stress. That is because it shows a balance of stretching stress and internal stress. The internal stress is from molecular chains orientation and crystallinity of the CE resin, and the molecular orientation occurs both in the crystalline and the amorphous phase [34]. Plasticizer-filling and particles-filling have a big impact on stress-strain curves of composites [35]. Sphaerocrystal in CE resin is stretched into spheroidicity in the elastic deformation stage. The crystal is destroyed where defect exist. Molecular chains are rearranged, oriented and recrystallized [36] where the stretching stress can be maintained.

SMP will expose to γ -rays in space before it works. Hence, researches about the effect of γ -rays radiation on the shape memory function of the SMCE resin are essential. The shape memory properties of non-irradiated specimen MCE^b and irradiated specimen CE^b1000 are tested and demonstrated in figure 6. The specimen is heated to 210.0 °C with 60 MPa stress applied to stretch it. The shape is fixed after cooling and then the stress is unloaded. During unloading, the shape usually has a slight rebound. The specimen is heated to 210.0 °C again and recover to its original shape. The process above is a shape memory cycle.

In figures 6(a) and (b), three shape memory cycles are tested. Their maximal strain for sample CE^b is 4.18%, 4.19% and 4.21%, respectively. Calculations indicate that the $R_{\rm f}$ is 99.8%, 99.9% and 99.1%, respectively. Their average $R_{\rm f}$ value is 99.6%. The $R_{\rm r}$ is 99.5%, 99.8% and 99.5%,

respectively. Their average R_r value is 99.6%. Their maximal strain for sample CE^b1000 is 3.95%, 3.91% and 3.83%, respectively. The R_f is 99.7%, 99.6% and 99.3%, respectively. The average R_f value is 99.5%. The R_r is 99.6%, 98.3% and 98.5%, respectively. The average R_r value is 98.8%. The average R_r value droped by 0.8% compared to that of the common specimen. The data show that the test repeatability is excellent. We can conclude that the R_f and R_r of the SMCE resin are not significantly altered after undergoing 1000 KGy γ -rays.

Figures 6(c) and (d) show shape recovery courses of a box-shaped structure and a clamshell-shaped structure (attached files: video 1 and video 2 is available online at stacks.iop.org/SMS/28/075039/mmedia). The hot plate is heated to 210.0 °C first. Then the structure is laid on the hot plate and the course starts. The temporary shape recovers to its initial shape with the increasing temperature of the structure. Recover time of the box-shaped structure is less than 3 min and 20 s, and that of the clamshell-shaped structure is 4 min and 35 s. These results explain that γ -rays radiation has no obvious effect on the shape memory properties of the SMCE resin.

Figure 7(a) shows the storage modulus and $\tan \delta$ with temperature spectra of carbon fiber fabrics reinforced CE resin, CE^bC² and CE^bC³, whose Tg is 200.9 °C and 194.2 °C, respectively. Their storage modulus is over 5.0 GPa at room temperature. CE^bC² and CE^bC³ have lower glass transition temperature than CE resin. Maybe it is the result of a combination of the following three factors. Carbon fiber would hinder the formation of cross-linking points in CE resin resulting in a decreasing of crosslinking degree and T_g value.



Figure 7. Carbon fiber fabrics reinforced cyanate ester resin: (a) storage modulus and $Tan\delta$ values versus temperature of CE^bC^2 and CE^bC^3 ; (b) shape memory test of CE^bC^2 ; (c), (d) shape recovery process of CE^bC^2 .

Then, CE^bC^2 and CE^bC^3 have a better thermal conductivity than pure CE resin. Its glass transition temperature may shift towards the low temperature zone during the testing process. Finally, an interface is formed between carbon fibers and cyanate ester resin. In order to obtain smooth and starched surface of the fabric, the carbon fibers are coated with a thin layer of epoxy resin in their production process. CE can interact with the epoxy resin generating cross-linking points or ntermolecular forces which make some contribution to glass transition temperature.

The specimen, CE^bC^2 , is heated to 200.0 °C again to return to its original shape. The bending strain is up to 1.29% when the stress is 1.2 MPa in figure 7(b). Calculations indicate that the R_f of the shape memory cycle is 94.9%. The R_r is 98.6%. The recovery processes of the composites are shown in figures 7(c) and (d) (attached files: video 3 and video 4). The recovery time of the box-shaped structure is 2 min and 52 s and that of the clamshell-shaped structure is 3 min. Compared to pure CE resin structure, the shape recovery time of carbon fiber fabric reinforced composite structure is shorter. The reasons for which are excellent thermal conductivity of carbon fiber and increasing restoring force due to carbon fibers filling. The greater the restoring force, the shorter the shape recovery time [37].

Conclusion

We prepared a heat resistant and radiation resistant SMCE resin, BACEM as the raw material, $R_{\rm m}$ -OH and $R_{\rm n}$ -CH₂CH₂O as modifiers. The specimens went through γ -rays radiation whose dose was as high as 1000 GKy. The effects of different γ -rays dose on their thermal and mechanical properties, cross-linking density as well as changes of chemical bonds are analyzed. There was no significant effect on the properties of the SMCE resin. To improve the material's strength, multilevel carbon fiber fabric was immersed in CE resin. The test results showed that carbon fiber fabric reinforced cyanate-based composites exhibited good mechanical properties and shape memory effects, which is suitable for aerospace applications.

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