Synthesis and characterization of high temperature cyanate-based shape memory polymers with functional polybutadiene/acrylonitrile

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ABSTRACT

New thermosetting shape memory cyanate polymers (SMCPs) modified with polybutadiene/acrylonitrile (PBAN) were synthesized and compared with polyethylene glycol (PEG)-modified SMCPs for integration into the family of high temperature shape memory polymers with controllable glass transition temperatures (T_g) used in the aerospace industry. The materials were characterized in terms of microstructure, thermal properties, mechanical properties and shape memory properties by Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetric analysis, dynamic mechanical analysis, and tensile tests. Differing from the SMCP with PEG, the new cyanate-based shape memory polymer with PBAN (T_g ~255.1.0 °C) had better shape memory properties and higher thermal stability (relatively high initial degradation temperature and high char residue value at 800 °C). Both of the SMCPs with PBAN and PEG displayed exceedingly high glass transition temperatures over 241.3 °C and higher toughness than unmodified polycyanurate. These qualities render them desirable candidates as matrices in polymer composites, particularly for space applications.

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1. Introduction

Shape memory polymers (SMPs) are a type of smart material possessing the capability of recovering their original shape upon the application of an external stimulus [1,2]. With huge development potential, the application of polymer matrix shape memory materials has spanned various areas such as foam [3,4], sensors [5], biomedical devices [6,7], micro-systems [8], smart textiles [9] and deployable space structures [10,11]. SMPs can usually be categorized into either thermoplastic or thermoset types. Research on shape memory polymers have been widely developed both on the thermoplastic SMPs and thermoset SMPs. Thermoplastic SMPs always display the attribute of considerable recoverable deformation and high breaking elongation, and thermoset SMPs always display high shape fixity and recovery ratio with quick response [12]. By understanding the relationship between the composition, structure, properties and shape memory behavior, great effort has been made toward broadening SMP applications in the next generation of smart structures. Various kinds of SMPs have been developed with facile tailoring of T_g, including epoxy-based SMPs [13] (T_g range from 44 °C to 93 °C [14–16] or from 37 °C to 96 °C [17]), polystyrene-based SMPs (T_g range from 52 °C to 69 °C [18] or from 63 °C to 74 °C [19]), and thermosetting polyester-based SMP with T_g around 32 °C [20].

Although previously reported SMPs have excellent shape memory properties, the narrow working temperature range greatly limits their application in the aerospace industry. Materials used in deployable space structures must have good adaptability in the complicated and severe space environment, characterized by high vacuum, ionizing radiation, UV radiation, atomic oxygen, plasma, meteoroids, debris, thermal cycles and electrostatic charge. However, ultra-high and ultra-low temperature thermal cycles are first and foremost a crucial problem for space structures. For example, for the MESSENGER spacecraft, during normal spacecraft operation around the planet, the solar arrays will experience at least 278 eclipse cycles, during 28 of which the temperature will vary from −100 °C to +150 °C at a rate of 70 °C/min. During an attitude anomaly, the structural portion of the panel could reach 270 °C in the event the arrays are at planet perihelion, which means that the materials need to be potentially capable of withstanding short-term temperatures as high as 270 °C [21]. Considering structural safety and environment factors, the raw materials, i.e. SMPs, should

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exhibit both an admirable shape memory effect and excellent thermomechanical properties. McClung, who inducted bismaleimide (BMI) resin into the ranks of SMP [22] in 2011, synthesized a series of novel polyaspartimide-urea based shape memory polymers with a tunable glass transition temperature of 110 °C–164 °C [23], and Koerner reported a shape memory polyimides system which exhibits excellent high temperature (220 °C) shape memory performance with fast recovery times [24]. More shape memory systems with much higher glass transition temperatures are still required.

Compared with epoxy resin (EP) and bismaleimide resin (BMI), cyanate resin possesses excellent thermal and thermomechanical properties, dielectric properties, and absorption performance, and has been used as an insulation material [25,26], in high-frequency copper-clad laminates [27], and solar array substrate panels [21]. Recent studies have focused on the shape memory effect of cyanate resin, mainly because of the high glass transition temperatures obtained due to its highly crosslinked, typical three-dimensional polycyanurate network. Tong et al. formed shape memory cyanate ester copolymers via the reaction of a multifunctional cyanate ester and a mono functional cyanate ester with a controllable glass transition temperature over 150 °C [28]. Biju et al. reported a shape memory polymer based on a cyanate ester-epoxy-poly(tetramethyleneoxide) co-reacted system; the T_g values were 72 °C, 94 °C, and 100 °C with different molar ratios of the diglycidyl ether of bisphenol A and phenol telechelic poly(tetramethyleneoxide) [29]. In our previous work, a series of shape memory cyanate polymers (SMCPs) were prepared using cyanate ester and a variable content of a linear modifier polyethylene glycol (PEG). The prepared SMCPs had a high glass transition temperature above 156.9 °C [30]. The present work illustrates a unique combination of the shape memory effect and an increased high glass transition temperature to introduce a new thermosetting SMCP modified by polybutadiene/acrylonitrile (PBAN). The T_g of the novel cyanate-based SMP was adjusted to 253.0 °C with the introduction of PBAN.

2. Experimental section

2.1. Materials synthesis

The bisphenol-A cyanate ester (BACE) was purchased from Jiangdu Wuqiao Resin Factory, China. Polyethylene glycol (PEG) was supplied by Tianjin Guangfu Fine Chemical Research Institute, China. Polybutadiene/acrylonitrile (PBAN) was supplied by Zibo Qilong Chemical Industry Co., Ltd, China. All chemicals were used as received without further purification.

The compositions of the blend system with BACE, PEG or PBAN are listed in Table 1. The bisphenol-A cyanate ester and PEG were fully melted and the PBAN was preheated to 100 °C before mixing. To obtain a bubble-free pre-polymer, the mixtures were degassed in a vacuum oven for 15 min and then injected into preheated glass molds composed of two slides separated by a silica gel rod spacer. Three-step curing was performed at 120 °C for 2 h, 180 °C for 2 h, and 210 °C for 5 h. Finally, SMCPs sheets with a thickness of 3 mm were obtained.

Table 1
Composition and thermomechanical properties of the SMCP blend system (average values and standard deviations).

Sample no.	Mass fraction of BACE/PEG/PBAN	T_g (°C, DSC)	T_g (°C, tanδ)	Storage modulus (MPa, 25 °C)
SMCP0	100/0/0	213.5 ± 3.2	226.8 ± 2.2	3436 ± 45.1
SMCP1	83.33/16.67/0	228.7 ± 4.8	241.3 ± 1.2	2771 ± 47.3
SMCP2	83.33/0/16.67	245.5 ± 5.6	255.1 ± 4.0	3014 ± 57.6

2.2. Characterization

Fourier transform infrared spectroscopy (FTIR, Nicolet AVATAR 360) was used to investigate the variations of the chemical structures using KBr pellet, in the wave length range of 4000–400 cm^{-1} at a resolution of 2 cm^{-1}. Differential scanning calorimetry (DSC, NETZSCH STA 449 C) measurements were used to characterize the change in the thermal properties of the polymers from 25 °C to 300 °C at a heating rate of 10 °C min^{-1}. The glass transition temperature (T_g) values were obtained as the inflection temperatures in the DSC curves. Dynamic mechanical analysis (DMA, NETZSCH Q800) experiments were conducted in tension mode. Samples with dimensions of 30 × 5 × 1 mm were used. All runs were performed at 5 Hz and 0.05% strain, and the specimens were heated in a hot chamber at a constant rate of 5 °C min^{-1} from 25 °C to 300 °C. The tensile stress-strain tests were carried out on a Zwick/Roell Z010 (Zwick GmbH & Co. KG) instrument equipped with an extensometer at room temperature. Standard dog-bone samples (ASTM D638, Type IV.) for the tensile test were cut by a laser from the polymer sheet and strained at a speed of 5 mm/min. Thermogravimetric analysis (TGA, METTLER TOLEDO TGA/DSC 1) was carried out from 25 °C to 800 °C at a constant heating rate of 10 °C min^{-1} under flowing nitrogen.

The shape memory behaviors were examined by a bending test using rectangular strip specimens (60 × 10 × 1 mm) as the permanent shape. The schematic representation of the bending test is shown in Fig. 1. The specimens were heated up to $T_g + 40$ °C in an oven and held for 1 min for full heating. Then the strip specimens were elastic and they were slowly pushed into a 'U' shape aluminum mold with another aluminum bar by applying a constant force. They were subsequently cooled to room temperature with the mold constrained for 20 s to fix the temporary shape. Then the specimens were released from the 'U' shape mold. The deformed specimens were again heated up to $T_g + 40$ °C and the shape recovery process was recorded by a video recorder. Due to the high operating temperature, wearing heat insulation gloves is necessary during this test. The shape recovery angle was determined by measuring the θ angle between the straight ends of the bent specimen. The shape fixity ratio (R_f) and the shape recovery ratio (R_r) were calculated as $R_f = 180°-\theta_s/180°$ and $R_r = \theta_r/180°-\theta_s$, where θ_s represents the slack or released angle after cooling and mold removal, while θ_r is the recovered angle. In addition, the shape recovery speed was evaluated by determining the time to full recovery, T_r. In order to test the reproducibility of shape memory behavior between different samples, the shape memory bending tests were carried out with three comparative specimens of each SMCP sample.

3. Results and discussion

3.1. FTIR analysis of the SMCP chemical structure

Cyanate resins are a unique class of chemicals that contain highly reactive cyanate functional groups (-OCN). These resins cure via a cyclotrimerization reaction, in which three cyanate functional groups form a triazine ring. This mechanism creates a very high crosslink density in the cured material, producing the excellent thermomechanical properties of these thermosetting resins. An FTIR analysis of all the SMCP samples and the bisphenol A cyanate ester (BACE) was performed. Compared to pure BACE, the FTIR spectra of SMCPs in Fig. 2 show the appearance of a characteristic absorption peak at 1369 cm^{-1} (the triazine ring concomitant peak), increased width and intensity of the peak at 1560 cm^{-1} (the triazine ring peak), and almost complete disappearance of the cyanate ester peak at 2235-2273 cm^{-1}. These results indicate that
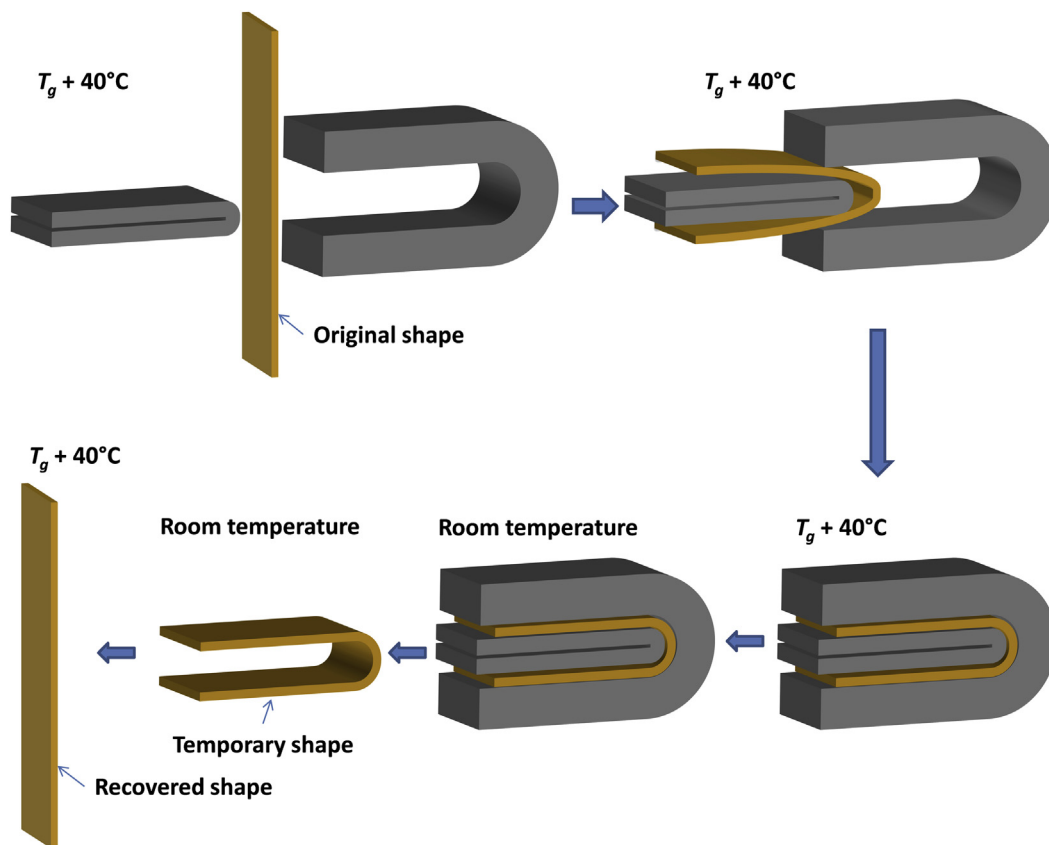
Fig. 1. The schematic representation of the shape memory bending test.

the formation of a triazine ring by cyclotrimerization of cyanate ester groups occurred during the synthesis reaction of SMCPs. It should be noted that the carbon–nitrogen triple bond (−CN) originated from PBAN, confirmed by the appearance of a characteristic absorption peak at 2216 cm^{-1}. The FTIR analysis showed that the SMCP modified with both PEG and PBAN presented excellent networks and higher conversion than unmodified SMCP0.
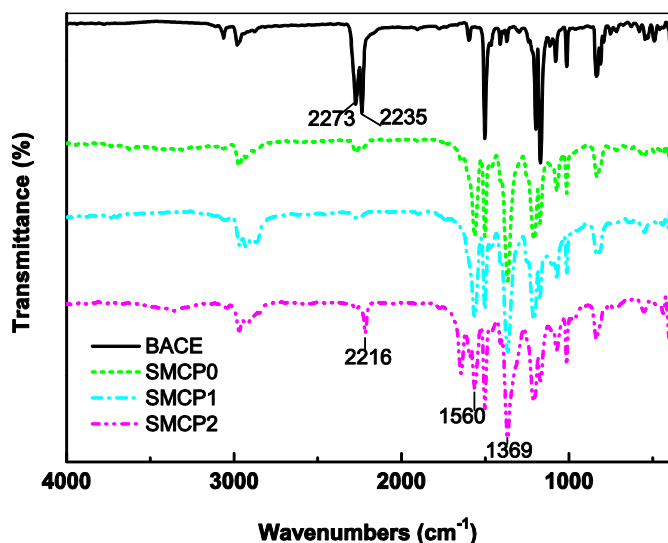
3.2. Thermogravimetric analysis

TGA in nitrogen was used to investigate the thermal stability of PEG, PBAN and SMCP samples from 25 °C to 800 °C. One typical thermogravimetric curve of all the SMCP samples and modifiers were shown in Fig. 3, with specific temperature and char residue values corresponding to each curve in the same color. The average
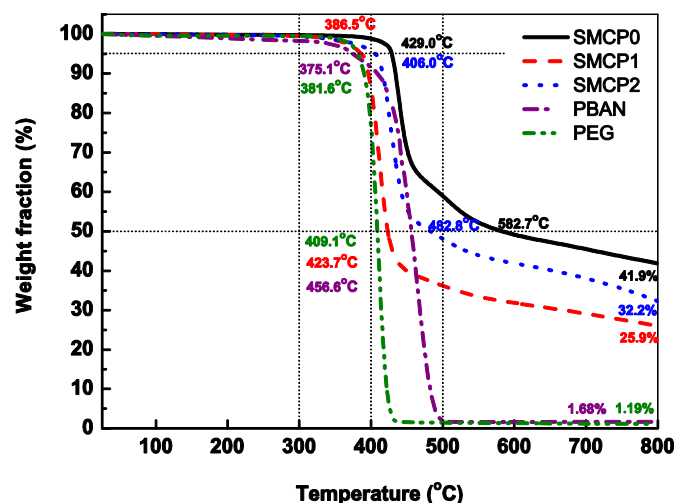

Fig. 2. FTIR spectra of SMCPs and the pure bisphenol A cyanate ester (BACE).

Fig. 3. Thermogravimetric curve of SMCPs.

Table 2
The average values and standard deviations of the thermo degradation properties.

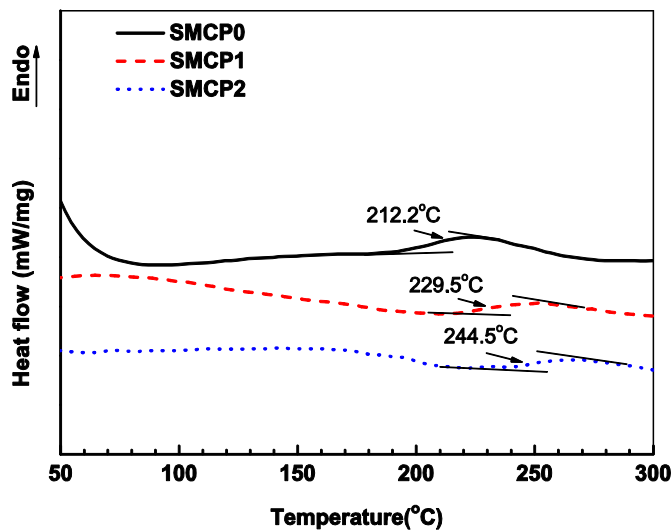| Sample no.	Temperatures at 5% weight loss (°C)	Temperatures at 50% weight loss (°C)	Char residue value at 800 °C (%)
PEG	381.3 ± 0.24	409.0 ± 0.14	1.07 ± 0.12
PBAN	379.7 ± 3.1	452.5 ± 5.1	1.19 ± 0.33
SMCP0	431.5 ± 2.2	584.8 ± 2.9	42.4 ± 1.6
SMCP1	385.1 ± 2.7	429.8 ± 5.6	24.6 ± 0.89
SMCP2	400.5 ± 5.5	478.7 ± 3.1	30.1 ± 1.93

Fig. 4. DSC thermogram of SMCPs.

values and standard deviations of the temperatures at which 5% and 50% weight loss and the char residue value at 800 °C were evaluated for all the samples (Table 2). The average temperatures at which 5% weight loss was observed were 431.5 °C, 385.1 °C, and 405.5 °C for synthesized SMCP0, SMCP1, and SMCP2, respectively. The average temperatures at which 50% weight loss was observed were 584.8 °C, 42.8 °C, and 478.7 °C, respectively. The average char residue value of the SMCPs at 800 °C was 42.4% (SMCP0), 24.6% (SMCP1), and 30.1% (SMCP2). It is shown that the initial
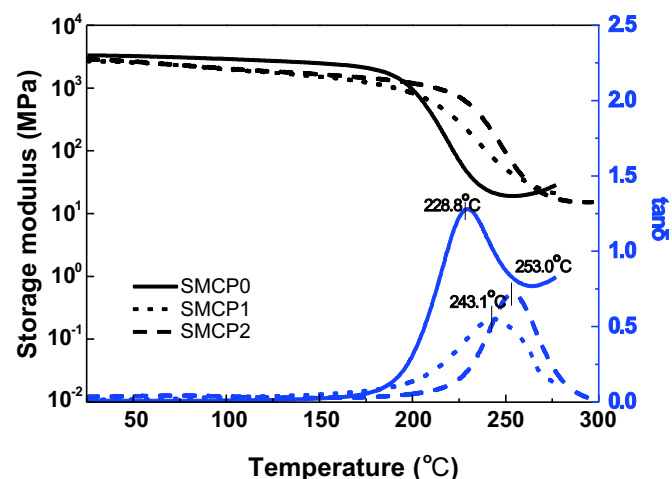

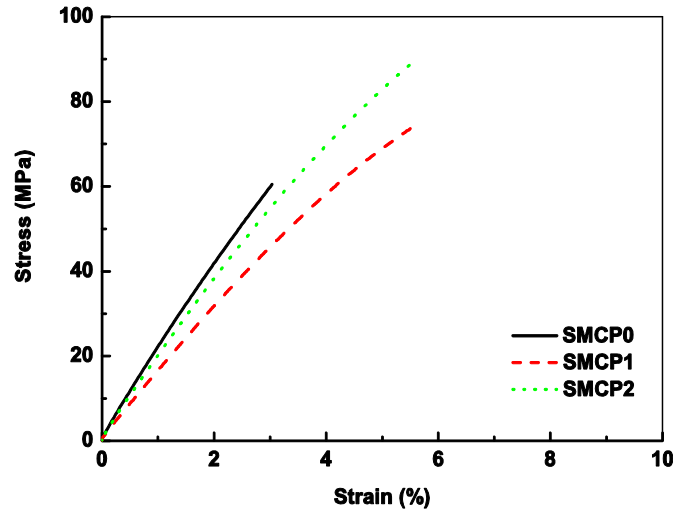**Fig. 5.** Storage modulus and tanδ curves of SMCPs.

Fig. 6. Tensile stress–strain curves of SMCPs.

degradation temperatures were all well above 300 °C, indicating that the SMCPs remained thermally stable at high temperatures. In general, the SMCPs could be used at high temperatures above their T_g without significant thermal degradation. As the thermal stability of higher carbon content polycyanurate is much higher than that of the modifier, the introduction of PEG and PBAN resulted in reduced thermal stability. However, this effect was much smaller with PBAN than that with PEG. As shown in Table 2, the 5% and 50% weight loss temperatures of SMCP2 in average were 15.4 °C and 48.9 °C higher than those of SMCP1, and the relative char residue value of the SMCPs at 800 °C was 5.5% higher.

3.3. Differential scanning calorimetry analysis

The typical DSC thermograms of our SMCP samples with marked T_g are shown in Fig. 4, and T_g of the sample was 212.2 °C, 229.5 °C, and 244.5 °C for SMCP0, SMCP1, SMCP2, respectively. Comparing SMCP2 with SMCP1, the T_g was increased by 15 °C (16.8 °C in average, Table 1) by introducing PBAN rather than the same amount of PEG. It was demonstrated in our previous study [30] that the T_g of SMCP can be altered by controlling the amount of PEG. The increase of T_g could be explained by the activity of the cyclotrimerization reaction and the homogeneity of the system. The cyclotrimerization reaction is enhanced when the modifier, either PEG or PBAN, plays the role of catalyst. Furthermore, the reaction system shows better homogeneity and stability when the modifier, PBAN, possesses analogous functional groups with those

Table 3
Shape memory behavior of the first five shape memory cycles for SMCPs samples.

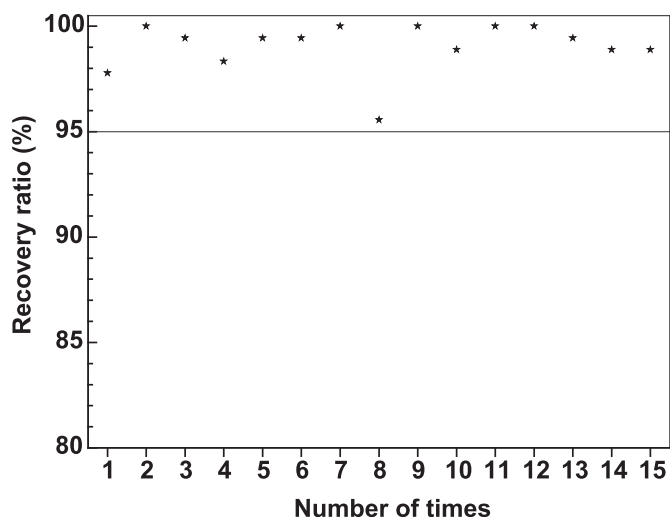| Shape memory polymers	Shape memory results	1st	2nd	3rd	4th	5th
SMCP0	R_f (%)	98	99	97	99	100
	R_r (%)	99	97	95	96	97
	T_r (s)	45	35	50	65	60
SMCP1	R_f (%)	99	98	100	100	99
	R_r (%)	97	95	98	96	99
	T_r (s)	27	15	17	15	18
SMCP2	R_f (%)	99	98	100	98	99
	R_r (%)	98	100	99	98	99
	T_r (s)	14	18	15	17	27

Fig. 7. Shape recovery ratios for 15 consecutive shape recovery processes of the specimen SMCP2.

of BACE. The analogous functional groups refer in particular to the −CN of PBAN and the −OCN of BACE.

3.4. Dynamic mechanical analysis

Characterization by dynamic mechanical analysis (DMA) provides data on the storage modulus and tanδ (Fig. 5, Table 1). The storage modulus curve depicts the stiffness of the material with respect to temperature. The steep decline in the curve represents the temperature range over which the polymer softened. Fig. 5 shows that all the samples presented two plateaus, i.e. at a low temperature with a modulus around 2−4 GPa, corresponding to the glassy state, and at a high temperature with a modulus around 10−100 MPa, corresponding to the rubbery state of the shape memory polymer. Large and sharp drop in the storage modulus around the glass transition always demonstrates the excellent shape memory effect of the materials [17]. The elastic ratio, which is defined as the glass/rubber modulus ratio, is often quoted to estimate the magnitude of modulus change when the polymer undergoes shape recovery. The maximum point of the tanδ curve is an estimate of T_g in this study. As the temperature is increased, the polymer molecules begin to obtain greater and greater energy, allowing some internal mobility in the material's structure. The average T_g of the SMCPs in the tanδ curves were observed at 226.8 °C, 241.3 °C, and 255.1 °C for SMCP0, SMCP1, and SMCP2, respectively. The storage modulus of SMCP2 at 25 °C was about 243 MPa higher than that of SMCP1, also indicating good mechanical properties. Furthermore, the storage modulus of all the samples from the DMA results began to decrease at about 175 °C, suggesting that these shape memory polymers possessed enough structural stability to be used in high temperature conditions.

3.5. The mechanical properties of SMCPs

High strength and a high modulus are basic requirements for aerospace materials. The tensile stress−strain curves of the SMCP samples are shown in Fig. 6. The tensile strength of the samples was 60.5 MPa, 75.1 MPa, and 89.1 MPa, with elongation at break at 3.04%, 5.68%, and 5.53% for SMCP0, SMCP1, and SMCP2, respectively. Although the elastic modulus decreased, the addition of the modifier increased the toughness of the polymers significantly. The

tensile strength and elastic modulus of SMCP2 with PBAN were higher than those of SMCP1 with the same amount of PEG. These results also show that the mechanical properties of SMCPs are equivalent to the mechanical properties of engineering plastics, and SMCPs are extremely promising smart structural materials for high temperature aerospace applications.

3.6. Shape memory behaviors of SMCPs

The shape memory behavior of the first five shape memory cycles for SMCPs samples are described in Table 3. It could observed that the recovery time was no longer than 65 s, mostly in the range of 15−30 s, indicating that all samples achieved shape recovery in a short period of time. This feature is quite distinctive and necessary for SMCPs under high temperature conditions, because the SMCP material should not remain in a high temperature environment for a long period of time in order to avoid serious thermal degradation. The results show that the recovery speed of SMCP1 and SMCP2 was a little faster than SMCP0, which could be explained by the relative homogeneity of their chemical structure and network density. According to the experimental data, R_f and R_r for the first five shape memory cycles for the SMCPs were all greater than 95%, and nearly reached 100% for one or two shape memory cycles. In addition, the recovery ratios were not significantly affected by the variation of the modifier, indicating that SMCPs modified with PEG and PBAN could all possess high recovery ratios. This property is very beneficial for practical material selections. In order to test the reproducibility of shape memory behavior between different samples, the shape memory bending tests were carried out with three comparative specimens of each SMCP sample. Looking at the first five shape memory cycles for each specimen, the error range of the shape fixity ratio (R_f) and shape recovery ratio (R_r) was all within 1−5%, not only for different specimens of SMCP2 but also for SMCP0 and SMCP1. The error range of full recovery time (T_r) was up to 50%, but all specimens could recover their original shape within 90 s after full heating. As for SMCP1 and SMCP2, it took no more than 40 s for different specimens. However, SMCP0, i.e. the cured BACE without modifier, has a lower recovery speed in all the shape memory bending tests, which indicated the necessity of introducing the modifiers into this cyanate-based shape memory polymer system.

The shape memory behavior of SMCP2 was investigated in detail for 15 cycles of the shape recovery process. The results show that the recovery ratio of SMCP2 was greater than 95% after 15 trials, and the average ratio was up to 99% (Fig. 7). The recovery ratio fluctuation was mainly due to the accumulation of deformations after several cycles. In spite of the small fluctuation, the samples exhibited excellent shape memory behavior. As shown in Fig. 8, SMCP2 recovered its initial shape after the fifth shape memory cycle within 27 s, showing good shape memory properties.

4. Conclusions

A series of shape memory cyanate polymers were synthetized using a bisphenol A cyanate ester and various modifiers, i.e. PEG and PBAN. The thermal properties and shape memory behaviors of the shape memory cyanate polymers were investigated in detail. The new thermosetting shape memory cyanate polymer (SMCP) modified with polybutadiene/acrylonitrile (PBAN) was as competent as robust high temperature shape memory polymers for use in the aerospace industry due to its high glass transition temperature (T_g ~255.1.0 °C), good shape memory properties and high thermal stability (relatively high initial degradation temperatures and high char residue value at 800 °C). The SMCPs modified with PBAN and PEG displayed exceedingly high glass transition temperatures over
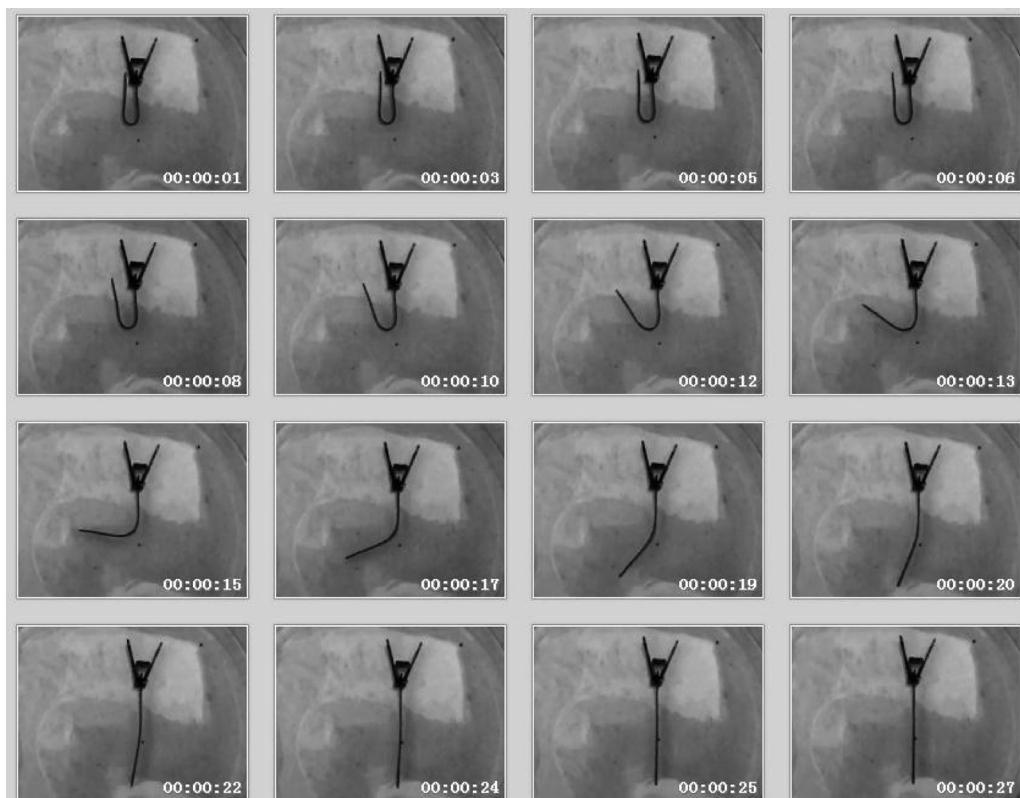
Fig. 8. Shape memory process of SMCP2 (the fifth cycle).

241.3 °C and higher toughness than unmodified polycyanurate, rendering them good candidates as matrices in polymer composites, particularly for space applications.

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