



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 micro-structure, 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 ($T_g \sim 255.1.0$ °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, tan δ)	Storage modulus (MPa, 25 °C)
SMCP0	100/0/0	213.5 \pm 3.2	226.8 \pm 2.2	3436 \pm 45.1
SMCP1	83.33/16.67/0	228.7 \pm 4.8	241.3 \pm 1.2	2771 \pm 47.3
SMCP2	83.33/0/16.67	245.5 \pm 5.6	255.1 \pm 4.0	3014 \pm 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 \times 5 \times 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 \times 10 \times 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 $R_f = 180^\circ - \theta_s / 180^\circ$ and $R_r = \theta_r / 180^\circ - \theta_s$, 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

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