

Shape memory polyimide composites with high storage modulus and high glass transition temperature

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Abstract

Shape memory polymers (SMPs) are smart materials that can be programmed to change shape under external stimuli, whereas the low storage modulus limit the application of them. Herein, carbon fabric (CF) reinforced shape memory polyimide composites (SMPIs) with high storage modulus were manufactured via hot pressing molding process. Firstly, we synthesized one kind of thermoplastic shape memory polyimide (SMPI) with glass transition temperature of 205°C by the two-step high-temperature solution polycondensation. In addition, the triamine was added in the SMPI system as a crosslinking agent to form the thermosetting SMPI with different crosslinking degree. In order to improve the storage modulus of SMPI, the CFs with three layers were embedded in thermosetting SMPI matrix. The storage modulus of the obtained SMPIs was as high as 26 GPa. The glass transition temperature and thermal decomposition temperature of SMPIs were up to 213°C and 505°C, respectively. Moreover, the shape fixation rate and recovery rate of SMPIs were both more than 94%. These SMPIs with high storage modulus is of great significance, proving more application potential in many fields such as aerospace.

Keywords

Shape memory polyimide, composites, high storage modulus, high glass transition temperature

Highlights

- (1) A series of shape memory polyimide (SMPI) was designed and the transition temperature and storage modulus of SMPIs were greatly increased by introducing triamine as a crosslinking agent.
- (2) High storage modulus shape memory polyimide composites with low-porosity were prepared via hot pressing molding process.
- (3) These composites have high fixation rate and high recovery rate in a fast recovery speed, and show higher thermal decomposition temperature and glass transition temperature.

deformation temperature controllability etc. (Herath et al., 2019; Lin et al., 2014; Ratna and Karger-Kocsis, 2008; Sun et al., 2016; Xiao et al., 2017; Xie et al., 2016). SMPs have been widely used in aerospace, bio-medicine, intelligent textile, and soft robot field.

For SMPs, the glass transition temperature (T_g) is used as the point, around which material gradually deformed in general. In space environment, materials are usually used between -160°C and 120°C . As for SMPs, the T_g of them was usually 50°C higher than the temperature of circumstance, and the peak width of T_g is narrow, in order to guarantee the shape recovery process will not be triggered untimely (Li et al., 2011). For different environmental conditions, the most recent works that to research and develop SMPs with gradient

1. Introduction

Shape memory materials refers to the material that can recover its original shape through external stimuli, such as heat, electricity, and magnetism (Sealy, 2019). Shape memory materials include polymers, alloys, ceramics, and gels (Lendlein and Kelch, 2002). Among them, SMPs have advantages of variable stiffness, low cost, low density, high strain, easy processability, and

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and controllable T_g are important to highlight. In contrast to traditional low T_g ($<150^\circ\text{C}$) SMPs, high-temperature SMPs can be used under harsh space environmental condition, with a wide application potential, such as space expandable structure, intelligent engine propulsion systems, high-temperature drives, and sensors. With excellent comprehensive properties, aromatic polyimides (PI) have been used in aerospace, electronics, automotive, and other fields. Based on properties as high T_g , good mechanical properties, great thermal stability, excellent radiation resistance, shape memory polyimide (SMPI) can be stimulated to change shape, which has great application potential for the field of high temperature SMPs. Although SMPIs have been widely reported in the literature, their mechanical properties sometimes are not ideal to meet the requirements of the aerospace field (Gao et al., 2017).

In recent years, high storage modulus of SMP have attracted the attention of researchers. The storage modulus of SMPI is around 1–3 GPa, which is not enough in aerospace applications (Chang and Wu, 2006; Huang et al., 2019; Jiang et al., 2013; Yuan et al., 2011). Meanwhile, the strength of SMPI is relatively low, and there is also problem of low recovery strain at high temperatures. All these problems limit the application of SMPs in many fields. In order to solve this problem, the use of SMP as matrix material and reinforced fibers as second-phase material was chosen to prepare shape memory polymer composite (SMPC), resulting in a lower density, better mechanical properties and shape memory performance of these materials (Hu et al., 2005; Mu et al., 2018; Wei et al., 2015). At the same time, the defects of SMPs are relatively brittle and low modulus. To further develop applications of SMPs, it is necessary to prepare SMPCs with better thermomechanical performance and shape memory effect.

In this work, we used ether-contained diamine and trifluoromethyl-contained dianhydride as monomer materials respectively, as well as different ratios of crosslinking agent with triamino group, to synthesize a series of thermoplastic and thermosetting SMPIs. The introduction of carbon fabric (CF) as the reinforcement material can greatly improve the storage modulus (to about 26 GPa) of shape memory polyimide composites (SMPICs) and enhance shape memory properties of these composites, which were manufactured via hot pressing molding process. The effects of different proportions of crosslinking agent and CF on the properties of the material, such as T_g , storage modulus, thermal decomposition temperature and elongation at break, were studied. The aim was to broaden the application fields of SMPIs and SMPICs, and provide experimental basis for further application of high-temperature SMPIs and SMPICs using in aerospace field in the future.

2. Experimental

2.1. Materials

Dianhydride monomer 2,2-bis(phthalic anhydride)-1,1,1,3,3,3-hexafluoroisopropane (6FDA) (98%), and crosslinking agent tris(4-aminophenyl)amine (TAPA) (97%) were purchased from Aladdin Co.. Diamine monomer 1,3-bis(3-aminophenoxy)benzene (APB) ($>99\%$) were purchased from Shanghai Guchuang Chemical New Material Co., Ltd.. Crosslinking of thermoplastic SMPI was performed with ether-contained diamine and trifluoromethyl-contained dianhydride, while thermosetting SMPIs contained 1%–4% triamine as a crosslinking agent for adjusting the crosslinking density. Dimethylacetamide (DMAc) of chromatographic purity and analytically pure toluene were from Tianjin Guangfu Fine Chemical Research Institute. Chloroform and hydrogen peroxide were analytical grade from Sinopharm Chemical Reagent Co., Ltd.. 55-NC was used as mold release agent from Shenzhen Xinhualiang Technology Co., Ltd.. T300-type twill CF was from Toray Industries. All raw materials were used as received.

2.2. Polymerization

The chemical equation for the synthesis process of SMPI is presented in Figure 1. The formation of the polyamic acid of the thermoplastic polyimide and thermal imidization are shown as the main line. The branch is the synthesis of crosslinked network after the addition of the triamine as a crosslinking agent to obtain the thermosetting polyimide. First, the diamine monomer APB was added to aprotic polar solvent DMAc and ventilate with nitrogen as an inert shielding gas in a three-necked flask, which was then stirred for 30 min at room temperature giving a uniform diamine solution. Add 6FDA of fluorinated dianhydride monomer in batches, each addition is 10 min. Continue stirring at room temperature for 20 h, anhydride-terminated polyamic acid (PAA) solution was synthesized through this solution polycondensation step. The crosslinking agent TAPA, which the total number of amino functional groups in the diamine monomer APB and the crosslinking agent TAPA is equal to the total number of anhydride group functional groups in the dianhydride monomer 6FDA, was added to the anhydride-terminated PAA solution. Then a crosslinking agent terminated PAA solution was synthesis after stirring at room temperature for 6 h. The PAA solution was placed in a vacuum oven drying for 2 h at 60°C to be defoamed. The defoamed PAA solution was poured onto a horizontal glass substrate, and then the temperature of oven was programed at 50°C for 1 h, 100°C for 2 h, 150°C for 2 h, 175°C for 1 h, 200°C for 1 h, 250°C for 1 h, and 300°C for 1 h for the thermal imidization reaction. After the thermal imidization, the

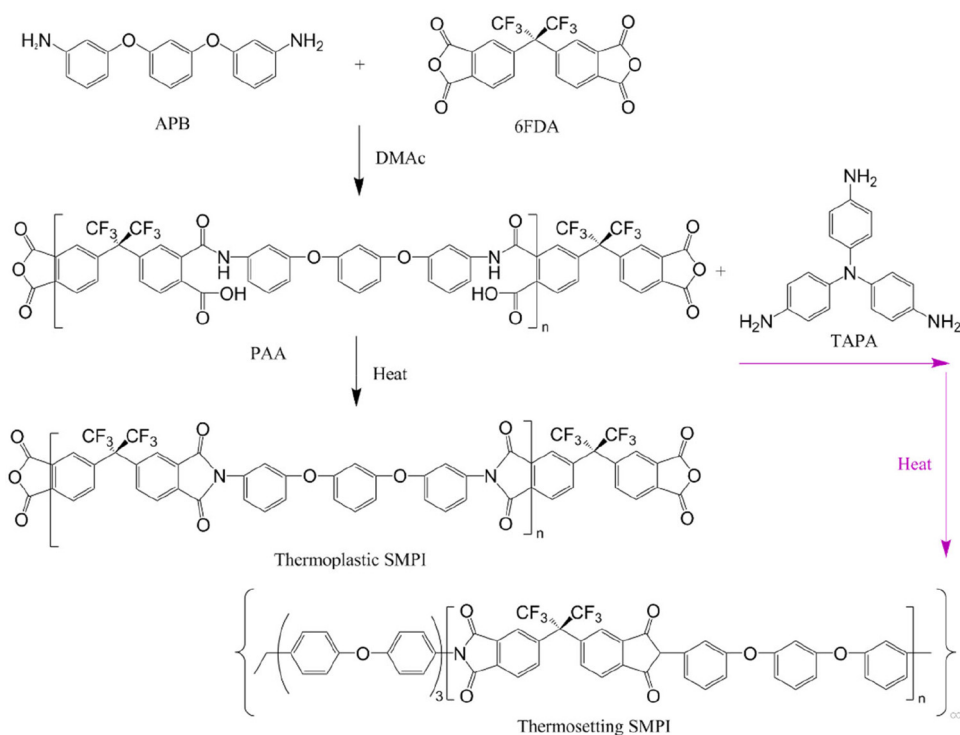


Figure 1. The chemical equation for the synthesis process of SMPI. Main line is the synthesis of the polyamic acid of the thermoplastic polyimide and thermal imidization. Branch is the formation of crosslinked network after the addition of the crosslinking agent.

Table 1. Raw material ratio and mechanical properties of SMPI.

No.	Dianhydride (mol)	Diamine (mol)	Percentage of crosslinking agent (%)	T_g (°C)	Tensile strength (MPa)	Elastic modulus (MPa)	Elongation at break (%)
PI-0	0.02	0.02	0	205.4	68.74	708.66	9.70
PI-1	0.0197	0.02	1	210.6	84.96	1019.93	8.33
PI-2	0.0194	0.02	2	210.8	93.12	1400.30	6.65
PI-3	0.0191	0.02	3	212.2	99.00	1561.51	6.34
PI-4	0.0188	0.02	4	213.4	100.33	1613.02	6.22

sample was cooled to room temperature. The glass substrate was immersed in distilled water to make the polyimide film fall off, the film was cleaned with distilled water, and then the cleaned film was dried in an oven at 100°C for 3 h. Membranes with crosslinking agent percentages of 0%, 1%, 2%, 3%, and 4% were prepared and expressed as PI-0, PI-1, PI-2, PI-3, PI-4, respectively. Table 1 lists the theoretically expected raw material ratio and experimentally obtained mechanical properties of SMPI samples.

2.3. Preparation of composites

The process flow for preparing SMPIC is shown in Figure 2. PAA impregnated fiber prepreps were prepared by coating the PI-0 and PI-4 PAA solution on twill CF, and dipped for 12 h. Samples were placed in aluminum foil containers, which were placed in the

120°C oven for 8 h to volatilization the solvent and the shape memory polyimide molded prepreps were obtained. Four layers of prepreps were put in the mold and close the mold. The mold was placed on the pre-heat hot press at 180°C for 30 min. After preheating, hot press machine was deflated 10 times and gradually pressurized to 10 MPa. Then the mold was heated up to 250°C for crosslinking 2 h, and finally up to 280°C for a post-cure of 30 min. After natural cooled to room temperature, demolded, and air-dried, thermoplastic and thermosetting shape memory polyimide composite materials were obtained. Performance parameters of CF used are shown in Table 2.

2.4. Characterization

Fourier Transform Infrared Spectrometer (FT-IR) was recorded by the Spectrum One infrared spectrometer

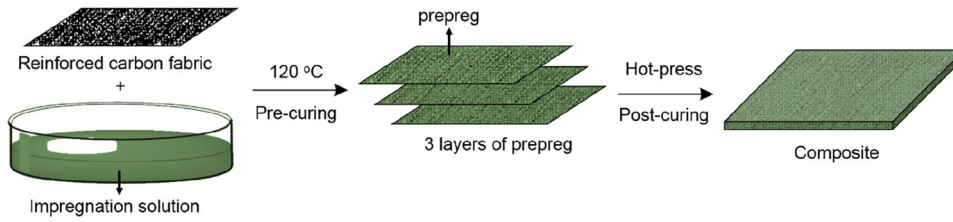


Figure 2. The process flow for preparing SMPIC.

Table 2. Carbon fabric performance parameter.

Type	Number of filaments in a bundle	Density of warp and weft (bundle/25 mm)	Mass per unit area (g/cm ²)	Thickness (mm)
T300	3000	12.5	198	0.25

which was produced by Perkin Elmer Instruments Co., Ltd.. The test parameter was 4000–450 cm⁻¹ wavelength range, four scans, and the 4 cm⁻¹ instrument resolution.

Four reagents with different polarities were selected for the swelling test: water (10.2), N,N'-dimethylacetamide (6.4), chloroform (4.4), toluene (2.4). The film sample was cut into a rectangular shape, with the original weight m_0 . Sample was put in the solvent and immersed for 24 h. The sample after swelling was gently removed, the solvent on the surface of the sample was absorbed, and the mass m after swelling was weighed to obtain. The swelling degree Q was calculated using the mass method of formula 1 (Chung et al., 2019).

$$Q = \frac{m - m_0}{m_0} \quad (1)$$

Thermogravimetric analyzer (TGA) and differential scanning calorimetry (DSC) were used on Mettler-Toledo TGA/DSC STAre System under a N₂ flow environment from 25°C to 800°C/280°C at a 10°C min⁻¹ heating rate, to get the thermal changes and the thermal stability of SMPI and SMPIC.

Conventional dynamic mechanical analysis (DMA) (TA Instruments Q800) was carried out for the storage modulus and shape memory properties of SMPIC. The DMA test for film samples was performed in the tensile mode with a pre-strain of 0.05%, a frequency of 5 Hz, from 25°C to 280°C at a heating rate of 3°C min⁻¹. The size of film samples was 30 × 5 × 0.1 mm³. The DMA test for composite samples was performed in the three-point bending mode with a frequency of 5 Hz, from 25°C to 280 °C at a 3°C min⁻¹ heating rate. The size of composite samples was 55 × 8 × 1 mm³.

Uniaxial tensile test was conducted on Zwick electronic universal material testing machine. Measuring

range of the force sensor was 10 KN, and the extensometer was used to determine the strain during the test. ASTM-D 882-10 and ASTM-D638 were used as the test standards for SMPI and SMPIC, respectively. The experimental conditions of SMPIs were as follows: room temperature (25°C), tensile rate of 1 mm/min and sample size of 80 × 8 × 0.15 mm³. The test conditions of SMPICs were as follows: room temperature (25°C), tensile rate of 1 mm/min and sample size selected according to Type-IV standard.

To measure resin content and porosity of the composite samples, a mixed solvent of 1:1 volume ratio of concentrated sulfuric acid and 30% hydrogen peroxide was used. The sample with the mass of W_c and the volume of V_c was heated to reflux for 2 days. The mass of CF after drying was W_f . ρ_f and ρ_r represent the carbon fiber density and the resin density, respectively. The resin content R_{con} and the porosity V_{void} of the composite sample were calculated according to formulas (2) and (3) respectively (Hussain et al., 2013).

$$R_{con} = \left(1 - \frac{W_f}{W_c}\right) \times 100\% \quad (2)$$

$$V_{void} = 1 - \left(\frac{W_f}{V_c \rho_f} + \frac{W_c - W_f}{V_c \rho_r}\right) \quad (3)$$

In shape memory performance test, the strip sample was heated to a temperature above T_g , folded to a U shape, kept the load until the sample cools to room temperature. We recorded the deformation of the sample as L_i . After the external load stop applying, the deformation was recorded as L_f , the angle of the deformation was recorded as θ_f . The shape fixation rate (R_f) is the ratio of these two deformations, as shown in equation (4). The sample was reheated to above T_g and we recorded the angle after recovery as θ_r , the recovery time as t . The shape recovery rate (R_r) is the difference

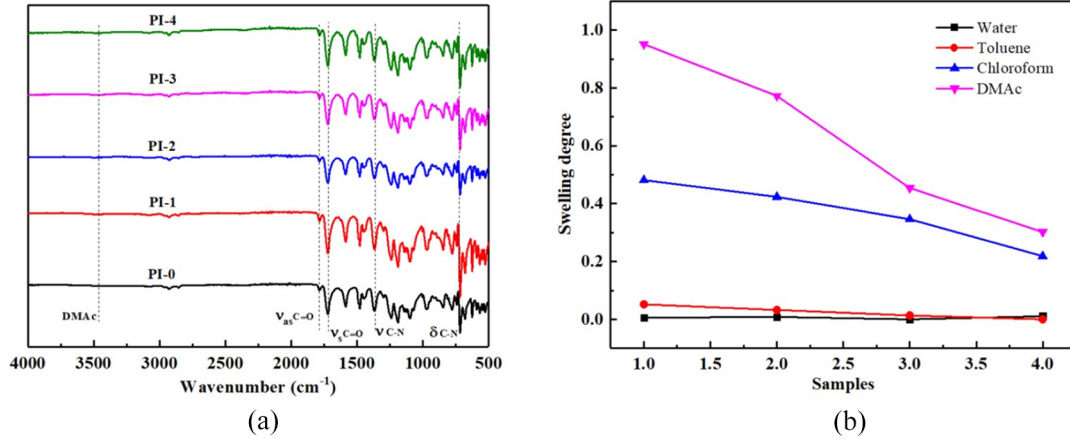


Figure 3. (a) FTIR spectrum of SMPI and (b) swelling performance curves of the SMPI series prepared in different solvents. The abscissas 1–4 correspond to samples with a crosslinker content of 1%–4%.

between θ_f and θ_r over θ_f , as shown in equation (5). The above process was repeated with three samples, and the average test value was taken as the final results (Lendlein and Kelch, 2002).

$$R_f = \frac{L_i}{L_f} \quad (4)$$

$$R_r = \frac{\theta_f - \theta_r}{\theta_f} \quad (5)$$

3. Results and discussion

3.1. Molecular structure

Figure 3(a) shows the infrared spectrum of the SMPI series synthesized in this work. The infrared spectroscopy shows that there are obvious absorption peaks at 1775 and 1720 cm⁻¹, and these two absorption peaks correspond to asymmetrical and symmetrical C=O bond stretching vibration in the imide group, respectively. Characteristic absorption peak at 1370 and 725 cm⁻¹ represents the stretching vibration C-N bond and the bending vibration C=O bond in imide group, respectively. Further analysis of the infrared spectrum shows that there are no characteristic absorption peaks of C=O in amic acid near 1715 and 1650 cm⁻¹ which corresponds to asymmetric and symmetric stretching vibration. At the same time, there is no characteristic absorption peak of asymmetric stretching vibration and symmetric stretching vibration of the CO-NH group in the amic acid around 1550 and 1360 cm⁻¹. There is no characteristic absorption peak of the solvent at 3463 cm⁻¹, which can prove that the solvent has completely evaporated during the thermal imidization process. Based on the above three-step analysis, there is no characteristic absorption peak of amic acid and solvent on the infrared spectrum, and the characteristic absorption peak corresponding to the imide ring group can be clearly observed. It indicates that the

polyimide synthesized has been completely imidized and no solvent remains, which can prove that the polyimide has been successfully prepared (Kong and Xiao, 2017; Qiu et al., 2017). Besides these, the addition of different content of crosslinking agent of the SMPI has no significantly difference in infrared spectroscopy, indicating that the change in the crosslinking agent content did not cause changes in the characteristic absorption peak of polymer chemical bond and functional group.

Figure 3(b) is the swelling performance curve of the SMPI series prepared with different solvents in this work. As shown in this figure, as the crosslinking agent content of TAPA increases, the degree of crosslink increases, the degree of swelling of the sample with the same solvent gets smaller. As for the length of the polymer segment is reduced, the reduced flexibility of the molecular network makes it more difficult for small solvent molecules to enter the polymer crosslinking network. Samples with different solvents have different swelling phenomena. In toluene and water, the swelling phenomenon of the sample can hardly observe, while in N,N'-dimethylacetamide, the swelling phenomenon is obvious. This is as a result of the incompatible polarity of the solvent. DMAc is a strong polar solvent, and the affinity of it with the sample is stronger, so that the rate of penetration of solvent molecules into the polymer network is greatly accelerated. Therefore, the swelling performance of the sample with DMAc is better.

According to the formula above, the resin content of the thermoplastic SMPIC prepared in this paper is 32.3% and the porosity of it is 1.8%; the thermosetting SMPICs have the resin content of 34.5% and the porosity of 2.1%.

3.2. Mechanical properties

As shown in the stress-strain curve in Figure 4(a), the tensile strength of the SMPI films prepared in this

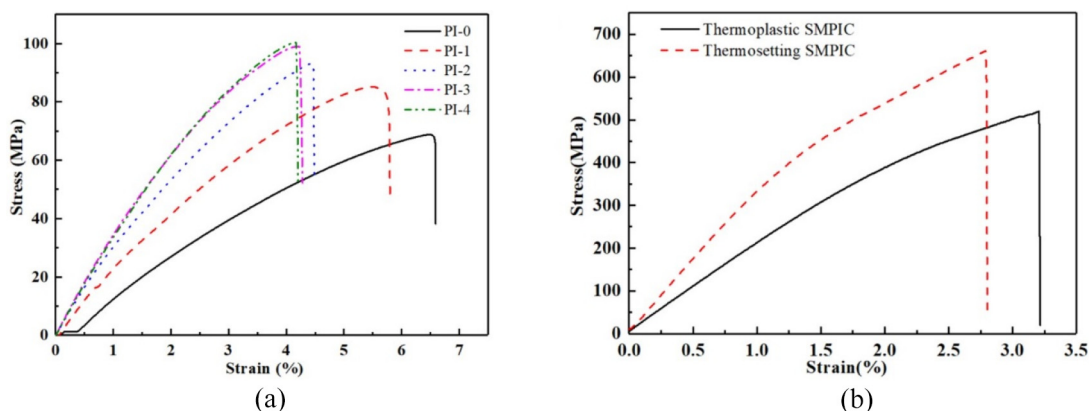


Figure 4. Stress-strain curves: (a) SMPI films and (b) thermoplastic and thermosetting SMPICs.

paper are 68–100 MPa, the elastic modulus of them is 0.7–1.6 GPa, and the elongation at break is 6.2%–9.7%. This indicates that these SMPICs are typical hard and tough polymers. The SMPICs prepared in this work, due to the presence of the side-trifluoromethyl group in the main-chain of the molecule, were destroyed the ordered arrangement of the main-chain structure, making the material exhibit a lower elastic modulus. But these materials have better mechanical strength and toughness. At the same time, as the crosslink density increases, the tensile strength and elastic modulus of these materials gradually increase, and the elongation at break gradually decreases. After the introduction of the crosslinking agent, the material undergoes a crosslinking reaction, and the polymer molecular structure changes from the previous linear structure to a crosslinked three-dimensional network structure, generating a thermosetting polymer. The crosslinking point acts as a stationary phase in the thermosetting polymer molecular network, can keep the shape of the polymer fixed and carry a certain load. After the introduction of a moderate crosslinking agent, the tensile strength and the elastic modulus of the polymer increased, also the crosslinking density. By the way, the increase in crosslinking points caused by the increase in crosslinking density also reduced the toughness of the SMPICs, making the SMPICs brittle. On the other hand, it will reduce the mechanical properties of the SMPICs. Table 1 summarizes the tensile strength, elastic modulus, and elongation at break of SMPI and SMPIC.

The stress-strain diagram of SMPICs shows carbon fabric reinforced composite materials are typical hard and strong, and their stress-strain curves change linearly, as shown in Figure 4(b). The results above further prove that when polyimide is filled into bidirectional CF, a large amount of stress is effectively transferred from the polyimide matrix to the CF (Likitaporn et al., 2018; Liu et al., 2004). As can be seen, the CF reinforced thermoplastic, thermosetting SMPICs prepared

in this experiment have tensile strength of 520–661 MPa, elongation at break of 2.79%–3.20%, and elastic modulus of 16–23 GPa. Compared with the matrix resin, the tensile strength and the elastic modulus of SMPICs are significantly improved, the elongation at break of them are significantly reduced. Tensile strength and elastic modulus of the thermosetting composites have been increased by 127% and 146%, respectively, compared to the thermoplastic SMPIC. The reason is that after the introduction of the crosslinking agent, the molecular structure crosslinked of the material forms a three-dimensional network structure. This feature of the molecular structure makes the thermosetting SMPICs have higher rigidity and lower elongation at break, which shows better mechanical properties. The results show CF as the material framework can effectively enhance the resin strength (Likitaporn et al., 2018; Liu et al., 2004) and can reduce the elongation at break (Hine et al., 2014).

3.3. Thermomechanical properties

Figure 5(a) is the DSC scanning chart of the SMPI with different crosslinking agent contents. T_g of the prepared SMPI series are all above 205°C (as shown in Table 1), and the T_g of the samples with the content of the crosslinking agent TAPA show positive correlation. From the molecular motion view, factors that lead to a mobility increase in molecular segments will reduce T_g . From another point of view, T_g will increase with the cause of a mobility decrease of molecular segments. For thermosetting polymer, polymer molecular with three-dimensional network structure is formed by the adding of crosslinking agent. As for molecular segment is limited by crosslinking point, the movement ability of the segment decreases with the decrease flexibility of the segment and the increase crosslinking density. As a result, the T_g of the sample gradually increases. In addition, compared with the thermoplastic PI-0 without crosslinking agent, T_g of thermosetting samples

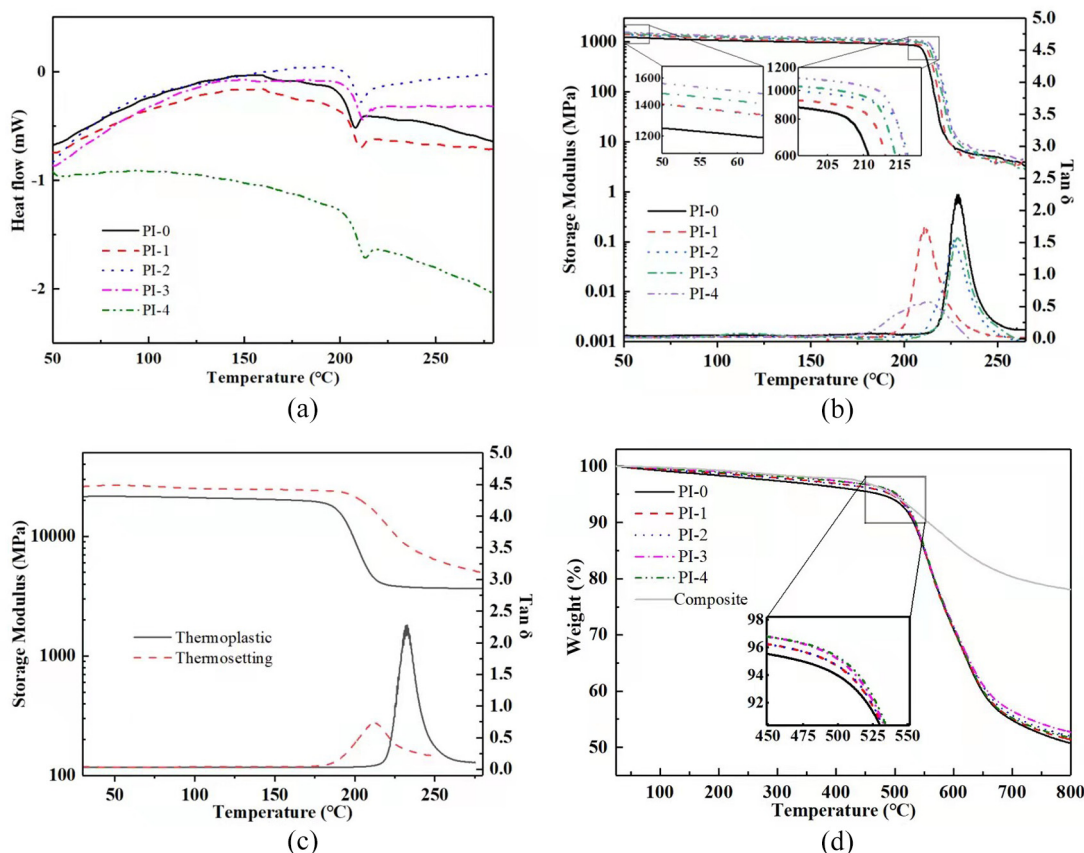


Figure 5. (a) DSC scanning chart of SMPI with different crosslinking agent contents, (b) storage modulus and loss factor curves of SMPI, (c) storage modulus and loss factor curves of SMPIC, and (d) thermal weight loss curves of SMPI.

increased by 5°C–11°C after the crosslinking agent was added. T_g increases gradually, which is related to the greater flexibility of the triamine as a crosslinking agent used in this work.

The storage modulus (E') of SMPI and SMPIC materials slowly decreases with increasing temperature in the glass-state, but E' drops sharply during the glass transition (Figure 5(b) and (c)). The storage modulus of the series of SMPIs at $T_g - 20^\circ\text{C}$ (glass state) and $T_g + 20^\circ\text{C}$ (rubber state) are 1.25–1.56 GPa and 2.73–4.88 MPa. The sharp drop in storage modulus is beneficial in achieving excellent shape memory effects. Compared with thermoplastic PI-0 without crosslinking agent, with the increase of crosslinking density, the storage modulus of the thermosetting SMPIs prepared in this paper increased by 113%, 115%, 115%, 125% at 50°C, which shows crosslinking improves the mechanical properties of the material.

The storage moduli of SMPICs are 22–26 GPa and 4–7 GPa at $T_g - 20^\circ\text{C}$ and $T_g + 20^\circ\text{C}$ respectively, which are much higher than that of SMPI. The storage modulus of the thermoplastic and thermosetting SMPICs at 50°C are significantly improved compared to the matrix resin, and are both increased by 17 times. The higher storage modulus at the glass state shows the

material has a higher cohesive energy and less creep during deformation, which make the material have a relatively better shape fixation ability. When the temperature increases to about glass transition temperature, the storage modulus of the material drops sharply. When the matrix material is in the rubber state on the high temperature platform, the composite material still maintains high mechanical properties. Compared with the relatively low storage modulus of the matrix resin on the high temperature platform, the storage modulus of the composites are significantly higher after the CF is introduced into the composites. This phenomenon solves the problem that the matrix material SMPI has insufficient mechanical properties when deformed. This ensures that when the material is deformed, it has enough mechanical properties and can generate sufficient driving force. So that, the space structure made by these SMPICs can meet the requirements of strength and stability during the whole process from the beginning of deformation to the recovery of shape.

3.4. Thermal stability

Figure 5(d) shows the curves of the thermal decomposition of the SMPIs and SMPIC as a function of

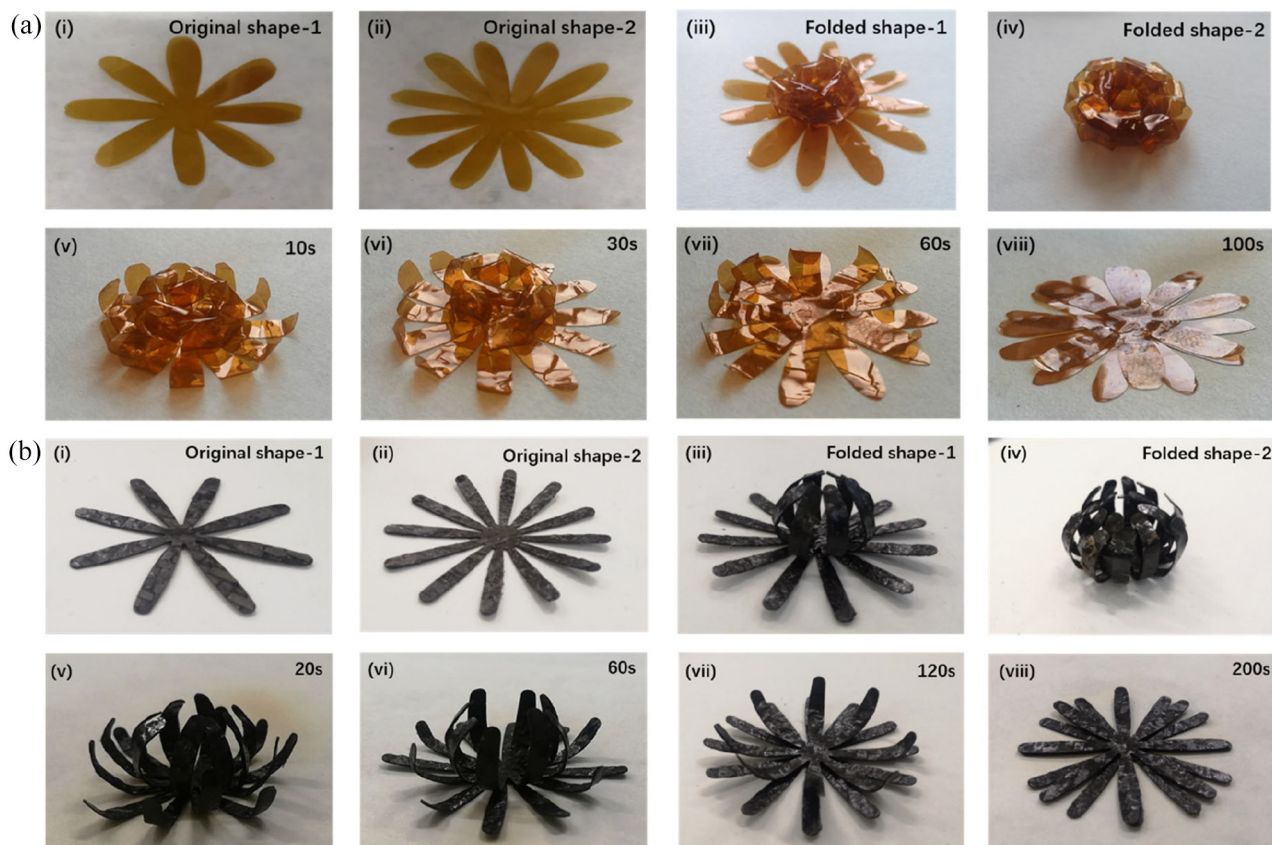


Figure 6. (a) Shape recovery process of PI-0, (i) First original shape, (ii) second original shape, (iii) first folded shape, (iv) second folded shape, (v) shape recovery with 10 s, (vi) shape recovery with 30 s, (vii) shape recovery with 60 s, (viii) shape recovery with 100 s and (b) shape recovery process of thermoplastic SMPIC, (i) first original shape, (ii) second original shape, (iii) first folded shape, (iv) second folded shape, (v) shape recovery with 20 s, (vi) shape recovery with 60 s, (vii) shape recovery with 120 s, (viii) shape recovery with 200 s.

temperature. The temperature at which the change of weight reaches 5% is usually regarded as the decomposition temperature (T_d). The T_d of thermoplastic and thermosetting SMPIs are 475°C and 495°C–505°C, respectively. It can be proved that the addition of the crosslinking agent slightly improves the thermal stability and the SMPIs have good thermal stability. The T_d of SMPIC is higher than that of SMPI, as for the CF greatly improves the thermal stability. At 800°C, the solid residue of SMPIC is higher than that of SMPI, indicating that the CF as a thermal coating can effectively reduce the escape rate of high-temperature decomposition and further improve the heat resistance of the materials (Yuan et al., 2014).

3.5. Shape memory performance

Figure 6(a) shows the shape recovery process of the thermoplastic PI-0 prepared in this experiment at $T_g + 20^\circ\text{C}$. The flower with eight leaves is original shape 1 as shown in Figure 6(a) and (i), and the flower with 12 leaves is original shape 2 as shown in Figures 6(a) and (i), respectively. The original shape 1 were

curled at $T_g + 20^\circ\text{C}$. Curled original shape 1 placed on original shape 2 is called folded shape 1 as shown in Figures 6(a) and (i). Curled original shape 1 wrapped with curled original shape 2 is called folded shape 2 as shown in Figures 6(a) and (i). Shape recovery process is the SMPI bud unfold at $T_g + 20^\circ\text{C}$ as shown in Figure 6(a) and (v). The SMPI series prepared in this experiment have the R_f of above 97% and the R_r of above 95%, which can be seen in Figure 7(a). The storage modulus of SMPI is several hundred times higher in the glass state than that in the rubber state, and its huge difference can effectively freeze the segment motion during cooling and fix the temporary shape with a high R_f (Qiu et al., 2017). Compared with the thermoplastic SMPI, the thermosetting SMPIs have more rigid molecular structure and smaller creep. Thermosetting SMPIs have smaller irreversible deformation during the shape recovery process, thus showing better shape memory performance.

Shape recovery time of the SMPIs prepared in this work were 30, 35, 37, 34, 38 s, respectively. As we can see, the SMPIs prepared can achieve shape recovery within 40 s. With the increase in the content of

crosslinking agent, the shape recovery speed shows a downward trend, which is mainly caused by two reasons. On the one hand, with the increase of crosslinking density, the number of dynamic networks in the polymer molecular structure decreases, which further limits the movement of molecular chains and makes the movement of molecular segments more difficult. On the other hand, polymers with low crosslinking density have a relatively low glass transition temperature.

When discussing the shape memory mechanism of shape memory polymers, bi-stable theory is usually used for analysis. Bi-stable theory believes that in shape memory polymers, there are two stable phase states, in which the molecular chain acts as a reversible phase, which acts to sense and respond to external excitations and produce deformation. The crosslinking points between the molecular chains caused by physical crosslinking or chemical crosslinking act as a stationary phase, which plays a role in maintaining and remembering the initial shape of the material. When subjected to external stimuli, the reversible phase can respond to the stimulus, thereby generating elastic deformation and storing the strain energy. At the same time, the stationary phase is still in the glass state and can only produce a certain degree of plastic deformation. The stationary phase in thermoplastic SMPI mainly is the intertwined polyimide macromolecular chains. For thermosetting SMPI, tris(4-aminophenyl)amine also acts as a crosslinking agent. On the other hand, tris(4-aminophenyl)amine in thermosetting SMPI also acts as a chain extender. At the molecular scale, the three-dimensional network structure formed by chemical covalent crosslinking is similar to physical crosslinking. Compared with thermoplastic material, thermosetting ones exhibit better shape memory performance, which is mainly due to the deformation process damage the former physical crosslinking integrity.

So far, the commonly used low-temperature to medium-temperature transition ($T_g < 150^\circ\text{C}$) temperature SMPs usually have a flexible molecular backbone in the molecular structure. The relatively high T_g ones, such as polyimide, cyanate, polyether ether ketone, etc., have a relatively high rigidity molecular backbone composed of benzene ring and flexible bonding units (such as ether bonds, etc.). With the preparation of diamine and dianhydride by the polycondensation reaction, the SMPIs in this work is prepared by using the ether-bond-contained diamine and hexafluoroisopropyl-group-contained dianhydride as monomer materials respectively in the molecular structure. The hexafluoroisopropyl group and ether bond in the molecular skeleton of the material system provide a certain flexibility for the highly aromatic polyimide structure, and the molecular chain plays a role of reversible phase in it.

At the same time, polyimide has a large number of aromatic functional groups, in which π - π bond interaction has an important effect on polyimide. The π - π

bond interaction is a non-covalent interaction and a conjugation between aromatic functional groups. It has great application potential for self-healing materials, supramolecular chemistry, and biochemistry. The π - π bond interaction has an important effect on the shape memory properties of the material. On the one hand, it can play the role of physical crosslinking points, which increase the number of that in the molecular structure, and then affect the shape recovery. On the other hand, in the shape memory process, it can also fix the orientation of the molecular backbone, so that the material has a relatively higher shape fixation rate. In addition, the SMPIs prepared from 1,3-bis(3-aminophenoxy)benzene and 4,4'-(hexafluoroisopropylene) diphthalic anhydride in this work also showed good performance of the shape recovery rate, which may be due to the relatively high rigidity of the main chain of the SMPI molecules prepared, and easy to produce π - π bond interaction between the molecular chains.

Figure 6(b) shows the recovery process of the shape memory behavior of the thermoplastic SMPIC prepared. The process of shape fixing and shape recovery is the same as that of SMPI in Figure 6(a). The SMPICs prepared have R_f above 94% and R_r above 95%, as shown in Figure 7(b). The CF reinforced SMPICs still has good shape memory performance. Compared with the SMPIs, the shape fixation rate of SMPICs is slightly reduced. As for when the composite is bent and deformed, the CF trends to recover. Moreover, the storage modulus of the composites in the rubber state are only several times higher than that in the glass state. The smaller difference between them leads to a decrease in its shape fixing ability.

The shape recovery speed test shows the shape recovery process slows down after the introduction of CF, as for the shape recovery time for thermoplastic and thermosetting SMPICs were 90 s and 95 s, respectively. As for the CF hinders the movement of the polyimide molecular chain during the shape recovery process. Compared to thermoplastic SMPIC, thermosetting SMPICs require longer time to achieve shape recovery. It is mainly because the chemical crosslinking point restricts the movement of molecular chain segments, and it requires more energy to achieve shape recovery. For spatial unfolding structures such as shape memory hinges, the relatively slow shape recovery process can avoid structural damage caused by quickly unfolding. Therefore, according to different application conditions, the shape recovery rate can be controlled by material design.

4. Conclusions

In summary, thermoplastic and thermosetting shape memory polyimide (SMPI) with gradient crosslinking degree were synthesized by two-step high-temperature

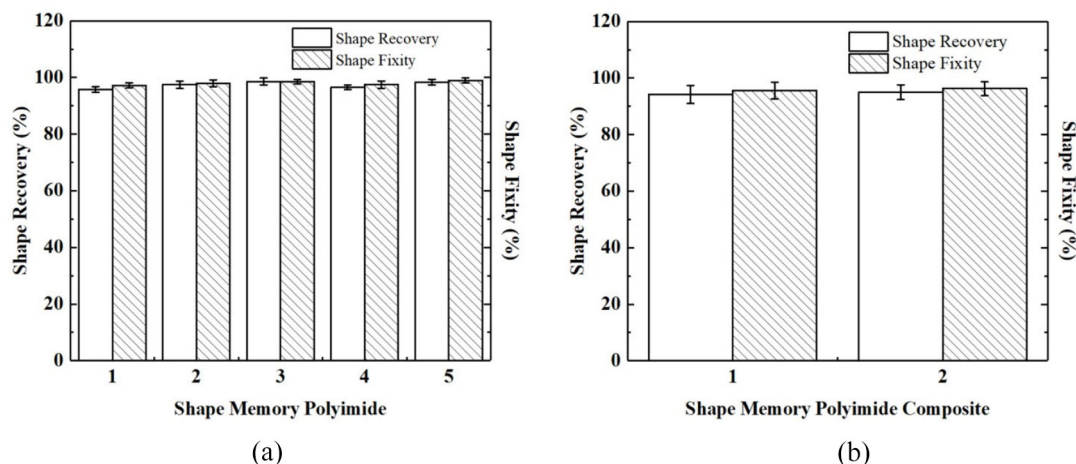


Figure 7. Shape recovery rate and shape fixed rate chart of: (a) SMPI and (b) SMPIC.

solution polycondensation. The storage moduli of thermoplastic SMPIC at 50°C and $T_g + 20^\circ\text{C}$ are 17 and 1465 times of their matrix materials, respectively. The introduction of triamine as a crosslinking agent made the thermosetting SMPI with different crosslinking degree. Compared to the thermoplastic SMPI, the storage modulus of the thermosetting SMPIs increased by 125%. The CF reinforced SMPIC with a high storage modulus of 26 GPa and T_g of 213°C was fabricated via hot pressing molding process. The storage moduli of thermosetting SMPICs at 50°C and $T_g + 20^\circ\text{C}$ rubbery state are 16 times and 1500 times of their matrix materials, respectively. These results indicated that the CF greatly improved the mechanical modulus of SMPIs. The SMPICs exhibited shape fixation rate of above 94% and shape recovery rate of more than 95%. The shape recovery process took less than 100 s. These high storage modulus SMPICs have potential applications in smart materials and structures.


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