



Triple-shape memory polybenzoxazine resins and their composites

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ABSTRACT

Shape memory polymer (SMP) as a new type of smart material can be programmed into a temporary shape by external excitation. Benzoxazine is a novel thermosetting resin with excellent heat resistance, high glass transition temperature (T_g) and mechanical properties. Here, triple-shape memory polybenzoxazines with high T_g were obtained by copolymerization of phenol/polyetheramine with phenol/furanamine benzoxazines. Electrically driven composites were prepared using multi-walled carbon nanotubes, and the SMP electrically driven function was achieved by forming a complete and continuous conductive permeable network inside the composites, shape recovery can be completed in 15 s at 60v. Furthermore, at high temperatures the carbon residue rate is increased to 45 % at 800 °C, demonstrating the high performance of electrically driven shape memory polymer composites. The realization of the triple and electrically induced shape memory properties of shape memory polybenzoxazines broadens the way for their application in extreme high-temperature environments in aerospace and aviation.

1. Introduction

Shape memory polymer (SMP) has made significant progress in recent years due to its ability to actively respond to external stimuli and change its state [1–4]. With self-awareness, self-formation and variable stiffness properties, SMP shows great potential and value in aerospace, smart wearable, flexible robotics, biomedical and other applications [5–8]. Multiple-shape memory refers to the existence of multiple metastable states of SMP in a single shape memory cycle period [9–11]. At present, the typical method to realize multiple shape memory characteristics is to widen the transition temperature range of the material or introduce multiple independent discontinuous transition states into the material [12].

Benzoxazine resin has excellent thermal and mechanical properties and has a wide range of applications [13–15]. The relatively mature shape memory polymers, such as epoxy resin and polystyrene, have poor heat resistance, a large change in curing volume, and a low T_g in aerospace and other fields [16,17]. Polybenzoxazine (PB) has a flexible molecular structure, a high glass transition temperature (T_g), good thermal stability, a small change in curing volume, and low hygroscopicity. In shape memory effect, the cross-linked network formed between polymer units can be used as a hard chain segment with fixed

shape. In 2013, Erden et al. proposed the blending mechanism of thermoplastic polyurethane (PU) and polybenzoxazine [18]. The benzoxazine monomer was dissolved in the polyurethane prepolymer synthesized by phenyl isocyanate (MDI) and polytetramethylene glycol (PTMG) and finally cured to polymerize the benzoxazine into PB. The PB segment can be regarded as the hard segment of shape memory thermoplastic polyurethane (SMPU), which improves the shape memory performance, and the shape fixation rate and recovery rate reach 96.6 % and 93 % respectively. The material transformation temperature was raised from 51°C to 91°C, and the recovery stress increased by 91 % to 13 MPa. Schäfer et al. introduced terminal functionalized poly (phenyloxazine) ϵ -Caprolactone (PCL) is used as soft chain segment [19]. Since the toluene sulfonate end group is favorable for polymerization of benzoxazine, the curing temperature is reduced to 180°C, which solves the disadvantage of high polymerization temperature of benzoxazine. With the covalent incorporation of modified PCL into the benzoxazine structure, PCL contains a large number of flexible molecular segments, which can easily form a loose polymer network. The increased activity of molecular segments reduces cross-linking density, the polymer network is widened, and the rigidity of the polymer network is reduced. It shows the best shape fixation and recovery ability at the content of 80 wt%. Rimdusit et al. studied PB/epoxy SMP with improved mechanical

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properties and thermal stability based on previous work [20]. The rigid molecular structure and stronger intramolecular/intermolecular force of benzoxazine lead to the gradual increase of the crosslinking density of the blend, and the T_g increases from 47°C to 119°C. Prathumrat et al. realized the triple shape memory process in the blended resin [21]. Polybenzoxazine contains a large number of benzene ring structures, which makes the molecular chain extremely rigid, resulting in too brittle material performance. Due to the presence of phenolic hydroxyl and tertiary amine groups, strong intermolecular/intramolecular hydrogen bonds are formed, resulting in the formation of polymer cross-linking networks [13]. When flexible chain segments are introduced into the polybenzoxazine (PB) network, the corresponding polybenzoxazine will exhibit shape memory effect when the transition temperature is above the appropriate temperature.

In our work, we created a series of multifunctional triple-shape memory (TSM) polybenzoxazine with excellent properties such as high glass transition temperature, mechanical and thermal stability. By adjusting the ratio of two different benzoxazines, the molecular structure of benzoxazine with triple-shape memory effect was obtained. The conductive shape memory polybenzoxazine composites were prepared by combining multi-walled carbon nanotubes with shape memory polybenzoxazine. To realize the shape memory effect under electric drive, a continuous and stable conductive seepage network is formed in the composite system, by adjusting the doping ratio of conductive filler. To expand its variety and application scenarios, triple-shape memory polybenzoxazine composites with excellent overall performance were obtained.

2. Materials and methods

2.1. Materials

Phenol/polyether amine benzoxazine (P-pea) and Phenol/furfuramine benzoxazine (P-fa) were the monomers of benzoxazine, and benzoxazine was synthesized in two steps with toluene as the solvent. Phenol, polyformaldehyde, polyether amine, furfuramine, chloroform, toluene, anhydrous sodium sulfate, and multi-walled carbon nanotubes are all examples of organic compounds.

2.2. Preparation of P-pea and P-fa

Phenol/polyether amine benzoxazine was prepared by two-step method. The reaction process is shown in Fig. 1. In the P-pea group, weigh 0.05 mol of polyether amine D230, and 0.02 mol of paraformaldehyde, and dissolve them in 50 ml of toluene solution. In the P-pf group, 0.1 mol of furan amine and 0.2 mol of paraformaldehyde were weighed and dissolved in 50 ml of toluene solution. Two groups of experiments were stirred in an ice water bath for 60 min, phenol/toluene solution was added dropwise, the temperature was raised to 95°C, and the reaction was stirred by reflux for 24 h. After reaction, wash the crude product three times with NaOH solution and distilled water to remove the unreacted monomer or by-product. Dehydrated sodium sulfate is dried and evaporated under reduced pressure to remove toluene, and dried for 10 h to obtain pale yellow oily liquid P-pea and P-fa, with yields of about 76.2 % and 71.5 % respectively.

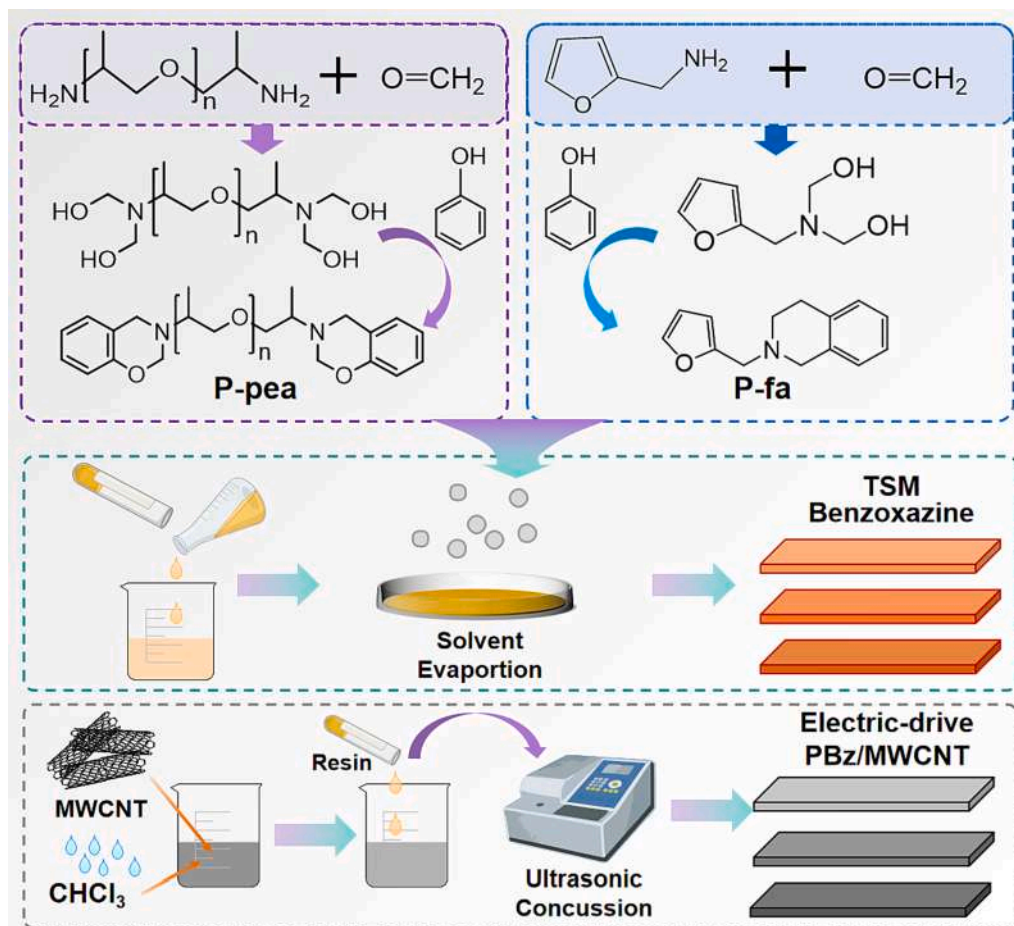


Fig. 1. The manufacturing of triple-shape memory benzoxazine and electrically driven composites.

2.3. Preparation of sample

Benzoxazine precursor is prepared by blending P-pea and P-fa monomers according to different molar ratios. The ratio is set to 5: 1, 5: 2, 5: 3, 5: 4, 5: 5, prepared PBz5-1, PBz5-2, PBz5-3, PBz5-4, and PBz5-5 front drive. Then vacuum curing was carried out according to the curing procedure in the reference literature, with the following procedures: 140 °C/2h, 160 °C/2h, 180 °C/2h, and 200 °C/3h to obtain a dark reddish brown semi-bio-based polybenzoxazine [22]. The preparation process of filled shape memory polybenzoxazine composite is shown in Fig. 1. Multi-walled carbon nanotubes (MWCNT) with a length of 10–30 nm and purity of > 95 % were selected to fill the polybenzoxazine resin matrix. Weigh multi-walled carbon nanotubes with mass fractions of 4 wt%, 6 wt%, 8 wt% and 10 wt% respectively, and prepared benzoxazine films by tape casting. Ultrasonic oscillation treatment was used to disperse the MWCNT solution, and MWCNT solutions of different mass concentrations were added to chloroform solvent. Slowly pour into the resin for blending and stir for 24 h, followed by 12 h of ultrasonic oscillation treatment. Try to improve the dispersion of MWCNTs as much as possible and reduce their degree of aggregation. MWCNT-filled shape memory benzoxazine film was cured at 140 °C/2h, 160 °C/2h, 180 °C/2h, and 200 °C/3h to obtain black MWCNT-filled PBZs

(MWCNT/PBz).

2.4. Chemical and structural characterization

NMR (^1H NMR and ^{13}C NMR) testing benzoxazine monomer was dissolved in a deuterated chloroform solution, and ^1H NMR scanning was performed to characterize the molecular structure of the synthesized material. Fourier transform infrared spectroscopy (FT-IR) can be used to analyze the molecular structure of materials. The corresponding relationship between wavelength and light transmittance can be converted into the content of specific groups in materials, to achieve qualitative or quantitative analysis of molecular structure. Differential Scanning Calorimetry (DSC) outputs a heat flow difference versus temperature curve under programmed temperature control conditions to characterize the thermodynamic or kinetic properties of a material such as heat of reaction, transition temperature, and crystallization rate. Use NDJ-8S to conduct viscosity-temperature and viscosity time tests on benzoxazine resin prepolymers. The heating rate is 1 °C/min, and viscosity data is recorded every 30 s.

Dynamic thermo-mechanical properties test (DMA) measures the energy storage modulus, loss modulus and loss angle tangent of the material. The prepared test sample size is a uniform strip of 30 mm *

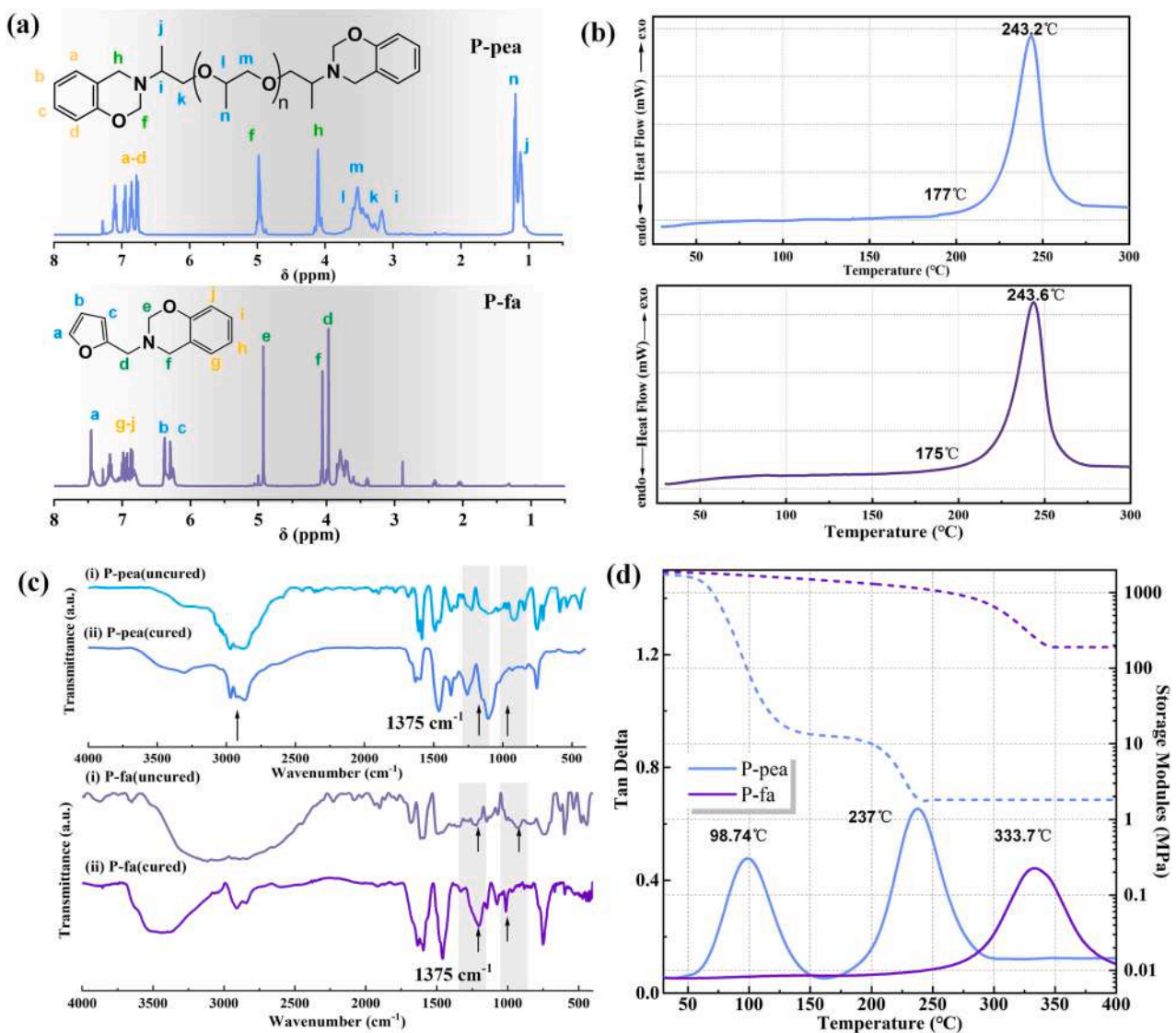


Fig. 2. (a) ^1H NMR spectra of P-pea and P-fa; (b) DSC curve of P-pea and P-fa; (c) FTIR spectra of P-pea before and after curing, P-fa before and after curing; (d) DMA curve after P-pea and P-fa curing.

3mm * 2mm, and the test temperature range is from room temperature to 400 °C, with a heating rate of 5 °C/min and a frequency of 1 Hz. Scanning electron microscopy (SEM) allows for the acquisition and analysis of electrons, which can yield information on the morphological characteristics of polymer sections, the distribution of dispersed phases, and dimensions. Four-point probe measurement method for resistivity testing of prepared carbon nanotube-filled electro shape-memory polybenzoxazine samples. The ablation performance of the sample was evaluated using the GJB323A-96 standard oxygen acetylene test, with an oxygen flow rate of 1512L/h and a flame heat flux density of 4190 kW/m².

3. Results and discussion

3.1. Material characteristics

The benzoxazine resin was characterized by ¹H NMR, as shown in Fig. 2(a). The corresponding chemical shifts of P-pea benzoxazine monomers are 4.98 ppm (f) and 4.11 ppm (h), and the resonance absorption peaks come from the methylene protons in O-CH₂-N and Ar-CH₂-N on the oxazine ring. 3.58 ppm (l), 1.20 ppm (n) and 3.52 ppm (m) are the characteristic peaks of hydrogen protons on the polyether amine segment, respectively. The methylene resonance absorption peak on the benzene ring appears between 6.87 and 7.20 ppm. At the same time, the ratio of the integral areas of the three hydrogen proton characteristic peaks f: h: i of benzoxazine is 1.94:2.09:0.95, which is close to the theoretical ratio of 2:2:1, proving the synthesis of the target product. The ¹H NMR characterization of P-fa benzoxazine monomers showed that the characteristic peak of the methylene in O-CH₂-N on the oxazine ring appeared at 4.94 ppm, and the methylene proton resonance absorption peak in Ar-CH₂-N appeared at 4.07 ppm (f). The multiple signal peaks 7.20 ppm (i), 6.99 ppm (h), 6.94 ppm (g) and 6.87 ppm (j) in the range of 6.87–7.20 are the characteristic peaks corresponding to the proton on the disubstituted benzene ring. The corresponding characteristic peak of the methylene proton of O-CH₂-C on the furan group is 7.47 ppm (a), and the chemical shifts of the other two furan ring protons are 6.31 ppm (c) and 6.39 ppm (b), respectively. The characteristic peak of the methylene proton connected to the furan ring appears at 3.82 ppm (d), and the characteristic peak near 3.6 ppm (m) is the absorption peak of the amino proton on the residual furylamine. The reaction temperatures of PBz5-0 and PBz5-1 resins are 243.6 °C and 247.2 °C, respectively. The DSC test results of P-pea are shown in Fig. 2(b). The curve shows that the starting position and peak position of Bz5-0 resin are 175 °C and 243.6 °C, respectively. The starting position and peak position of Bz5-1 resin are 180 °C and 247.2 °C, respectively, and the peak position corresponds to the maximum polymerization reaction temperature. It determines the ring opening and curing reaction activity of the oxazine ring, so the polymer can be studied according to the same curing procedure.

The infrared spectrum analysis results of benzoxazine resin after temperature rise curing reaction are shown in Fig. 2(c). The characteristic peaks at 844 cm⁻¹, 921 cm⁻¹, 1033 cm⁻¹ and 1226 cm⁻¹ of oxazine ring all disappeared, indicating that the ring opening of oxazine ring was fully involved in the polymerization reaction. The characteristic peak of the intermolecular hydrogen bond produced by the hydroxyl group is 3303 cm⁻¹, while the characteristic peak of the phenolic hydroxyl group produced following oxazine ring opening is 1375 cm⁻¹. It is concluded that the oxazine ring in benzoxazine opens after being heated, resulting in intermolecular crosslinking polymerization. The characteristic peak of oxazine ring in the target product is 935 cm⁻¹. At the same time, the vibration peak of the C–O–C of oxazine ring appears at 1220 cm⁻¹, and the vibration peak of the C–N–C bond appears at 1147 cm⁻¹. Based on this characteristic peak information, it can be determined that P-pea benzoxazine resin has been synthesized. There are two separate peaks in the tanδ curve of loss angle of the material. The first transition peak is at 98.74 °C, which is caused by the dynamic performance of the polyether amine chain segment, and the second transition peak is near 237 °C. The

decrease in transition temperature compared with P-fa is due to the decrease in the rigidity of the polymer network caused by the introduction of flexible backbone. The appearance of multiple tanδ peaks in the material indicates the existence of two transition temperatures and reversible states of the molecular network, and it can be inferred that P-pea has a triple shape memory effect. The DMA test results of P-fa are shown in Fig. 2(d), and the P-fa transition temperature is 333.7 °C. The tanδ curve of P-pea shows two separated peaks, the first transition peak is at 98.74 °C, caused by the dynamic performance of the polyether amine chain segment, and the second transition peak appears near 237 °C, caused by the dissociation and chelation of strong hydrogen bonds in the polymer network. The decrease in transition temperature relative to phenol/furylamine polybenzoxazine is due to the introduction of flexible main chains, which leads to a decrease in the rigidity and hydrogen bond content of the polymer network.

Thermogravimetric analysis can typically be used to ascertain the decomposition temperature and residual carbon content of materials. As illustrated in Fig. 3(a, b), the thermogravimetric curve of PBz resin can be observed. The thermal decomposition temperature of the polymer is observed to be higher than 320°C, and the carbon residue rate increases from 26.78 % to 31.88 % with the increasing proportion of P-fa. P-fa benzoxazine has more functional groups than other benzoxazines, which increases the crosslinking density of the network and improves the stability of the molecular chain segment, which makes the cured product more heat resistant. We mix benzoxazine monomers with different functional groups and then perform ring-opening polymerization. Due to the different characteristics of the rigid groups between different monomers, chemical and physical cross-linking occurs between them, improving material performance. Fig. 3(c, d) shows the thermogravimetric curve of polybenzoxazine composites filled with MWCNT with different mass contents. With the increase of MWCNT content, the initial decomposition temperature of the composite is significantly higher than that of PBz5-2 resin, doped with 8 wt%. The 5 % thermal decomposition temperature of the MWCNT composites is 302°C. The decomposition rate of 4 wt% composite material in the curve is the highest. As the doping amount of MWCNT increases, the decomposition rate of the composite material gradually decreases at high temperatures, due to the inability of MWCNT to decompose at high temperatures. The connection between polymer molecules is reinforced due to the role of MWCNT, which acts as a strengthening agent, thus resulting in the gradual release of small molecules in the second stage and a decrease in mass loss. In Fig. 3(e), it can be seen that with the increase of doping content, the carbon residue rate of the composite gradually increases when it reaches 5 wt%. In the vicinity, it gradually tends to a stable value, about 45 ~ 47 %, as shown in Fig. 3(f). This is attributed to the fact that the thermal decomposition mass loss of carbon nanotubes increases in the total loss when there is an excessive enrichment on the surface, and the increase in the carbon residue rate caused by a slight increase in doping content is not significant.

3.2. Mechanical performances

The DMA test was used to analyze the change rule of the storage modulus and loss factor tangent value of polybenzoxazine, to obtain the dynamic mechanical property and transition temperature of the cross-linked network. The DMA test curve shows multiple tanδ peaks in the PBz, indicating that the polybenzoxazine resin has a triple-shape memory effect, as shown in Fig. 4(a, b). The appearance of the peaks suggests that there are two transition temperatures and reversible states in the molecular network, confirming the triple-shape memory effect [23]. With the increase of the content of phenol/furylamine benzoxazine, the original low transition temperature peak gradually shifts to the right. Flexible segments have less of an impact on the molecular chain activity in polymer networks with higher levels of crosslinking. With the increase of the content of P-fa, the triple-shape memory performance gradually decreases. In particular, PBz5-2 has an excellent

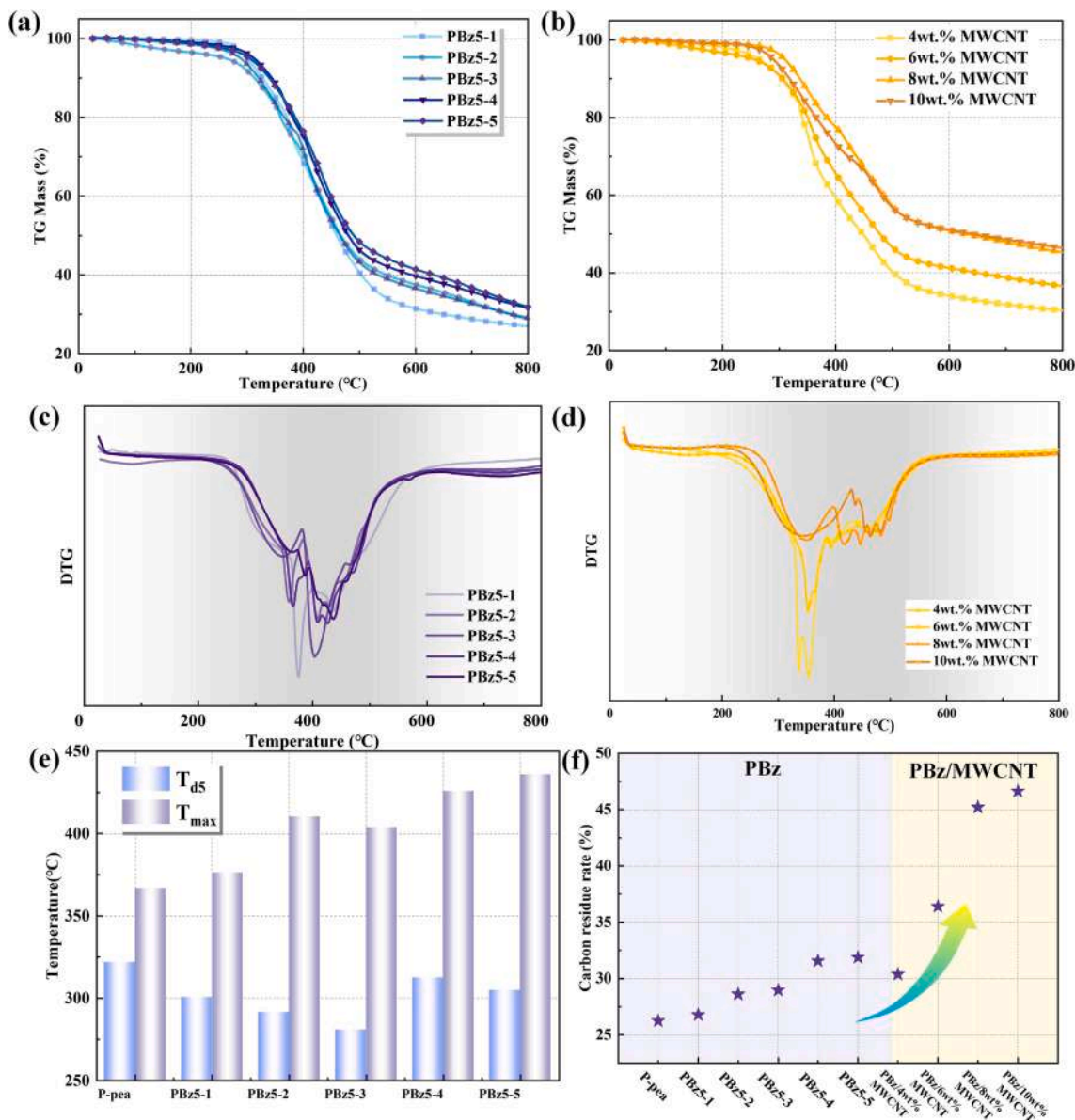


Fig. 3. (a) Thermogravimetric curve of PBz system; (b) Thermogravimetric curves of MWCNT/PBz composites with different contents; (c) Differential thermographic curve of PBz system; (d) Differential thermographic curve of MWCNT/PBz system; (e) High-temperature mass loss rate of PBz system; (f) High-temperature carbon residue rate of all samples.

triple-shape memory effect.

Fig. 4(c, d) shows the change curves of storage modulus and loss tangent of electro-induced shape memory polybenzoxazine with different doping ratios of MWCNT. It can be seen from the figure that with the increase of MWCNT content, the storage modulus of the composite gradually increases from 2371 MPa to 5408 MPa. Due to their large aspect ratio, multi-walled carbon nanotubes can strengthen the polymer matrix by connecting molecular chains and bearing loads. As a result of the significant improvement in the mechanical characteristics of composites filled with MWCNTs, the conductivity and electro-induced shape memory features of polybenzoxazine can also be realized while improving the mechanical properties and application possibilities of the material. The electro-induced shape memory polybenzoxazine composite's T_g peak change demonstrates that the value of T_g falls from 176 °C to 145 °C as the filling content of MWCNT increases. With the increase of doping content, as the particle content increases, particles will aggregate and occupy more free volume in the polymer, resulting in an increase in free volume, an increase in the degree of freedom of the

chain segment, and a relative decrease in T_g .

3.3. Ablation resistance

The tensile properties of the polybenzoxazine resin at room temperature are shown in Fig. 5(a). With the increase of P-fa content, the toughness of the resin increases from 1.6 % to 9.8 %, however, the strength gradually decreases. As the content of P-fa increases, due to the synthesis of P-fa from polyether amine D230 containing flexible segments, flexible segments are introduced into the polybenzoxazine molecular network, greatly enhancing the activity of the molecular segments. The toughness of the resin is greatly improved. The mechanical strength of polybenzoxazine with different P-fa content is shown in Fig. 5(b). The tensile strength decreases from 78 MPa to 52 MPa, while all of them are above 2 GPa according to the dynamic modulus data from the DMA test. After the shape memory polybenzoxazine resin was fractured at room temperature, its cross-section was characterized by scanning electron microscopy. Fig. 5(c, d) shows

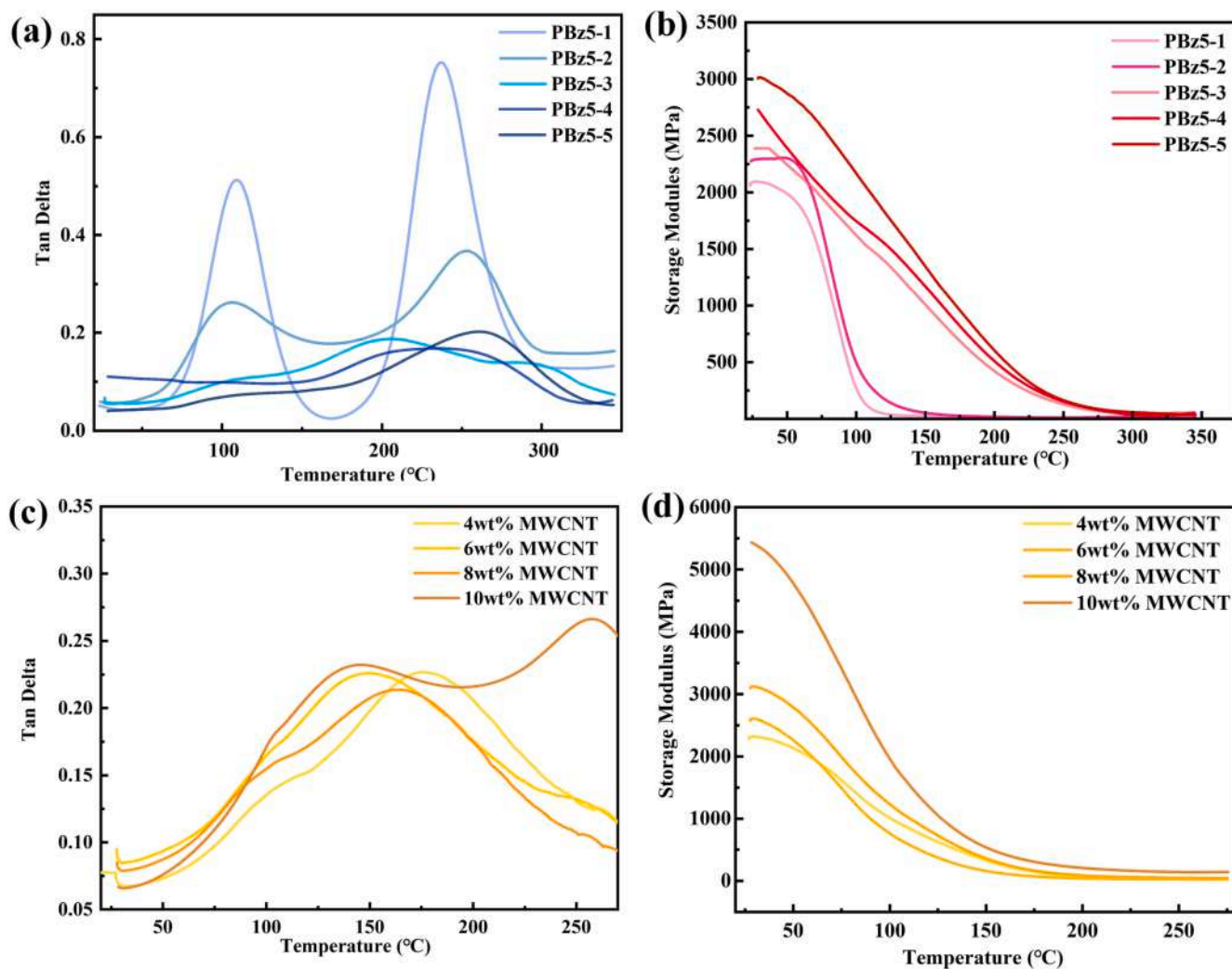


Fig. 4. (a, b)DMA test curve of PBz system, (c, d) DMA test curve of MWCNT/PBz composites.

the fracture morphology of P-pea polybenzoxazine resin. It can be seen that the sample section is in the form of a ladder fracture, the section is smooth, the cracks are approximately linear distribution, and the arrangement is orderly, showing a typical brittle fracture morphology. The section morphology shown in Fig. 5(e) is the fracture morphology of P-fa benzoxazine resin. The sharpness of the crack is relatively low, and the fracture surface is rougher than the brittle fracture surface, showing a strong and tough feathery fracture surface feature on the whole. The brittleness of shape memory polybenzoxazine resin is reduced and there is certain plastic deformation. To realize the shape memory function of polybenzoxazine resin, polyether amine soft chain segments were introduced into the network, and the toughness was enhanced. During the stretching process, the flexibility of the complex network increased, resulting in intermolecular slip, and the cross-section showed a morphology of high strength and high toughness. The shape memory polybenzoxazine resin after high-temperature oxidation treatment has differences in heat loss and quality, indicating that its antioxidant properties are different. Fig. 5(f-h) illustrates the surface morphology of polybenzoxazine with three different copolymer proportions after being subjected to high-temperature oxidation. The results indicate that as the cross-linking density increases, the ablation area on the polymer surface decreases, and the oxidation ablation pits formed on the polymer surface with a high P-fa content are relatively small, which is in line with the trend of the polymer mass damage rate.

3.4. Triple-shape memory behaviors

The oxazine ring splits during the benzoxazine resin's curing process, and phenolic hydroxyl groups then attack to take over the ortho position of a different benzoxazine benzene ring, resulting in chain growth. The benzoxazine resin with a single oxazine ring undergoes curing polymerization to form two distinct polymer network structures, as illustrated in Fig. 6(a). Dual network polymers containing two different network types have a triple shape memory effect. Based on the DMA test results, as the proportion of P-pea and P-fa changes, the transition from two separated transition peaks gradually transitions to a wide transition peak, which also proves that the sample has an excellent triple shape memory effect. Simultaneously, a second reversible switch segment was incorporated into the P-pea molecular chain segment, resulting in the formation of triple-shape memory properties, as depicted in Fig. 6(b). The DMA results show that there is a progressive transition from two separated transition peaks to a broad transition peak, indicating a triple shape memory effect, as the ratio of P-pea and P-fa is changed. As an illustration, a P-pea resin sample was heated at 250 °C for 2 min, then given a bending deformation, and after cooling and being fixed, it was heated at 120 °C for 2 min and similarly given a secondary deformation until it was fixed. At high transition temperatures, the mobility of molecular chains is significantly higher, and their structural deformation and fixation abilities are stronger. The time taken for different parts of the sample to reach the recovery temperature varies, resulting in a rapid recovery under the effect of entropy elasticity in 60 s. As the storage

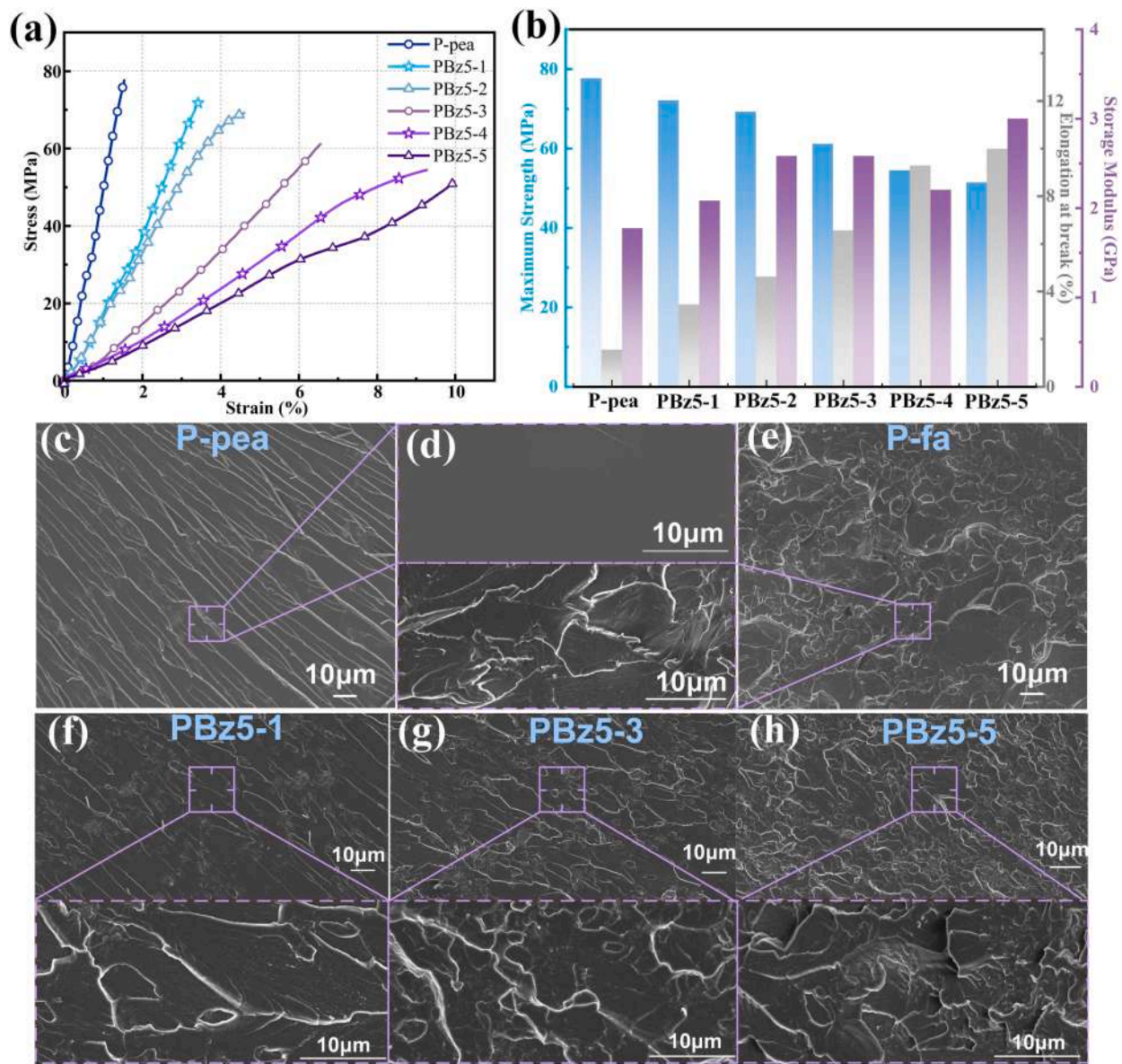


Fig. 5. (a) Tensile stress–strain curve of PBz system, (b) Mechanical properties of PBz system, (c) Cross-sectional morphology of P-pea type polybenzoxazine (scale bar: 10 μm), (d) Enlarged cross-sectional morphology of polybenzoxazine (Scale bar: 10 μm), (e) Cross-sectional morphology of P-fa (Scale bar: 10 μm), (f, g, h) Cross-sectional morphology of P-Bz5-1, P-Bz5-3, P-Bz5-5 type polybenzoxazine (Scale bar: 10 μm).

strain is released almost completely, the recovery rate tends to slow down. For shape memory polymers with wide transition temperature intervals, this is typically caused by the overlapping of multiple discontinuous transition states or by the local variations in molecular structure (Fig. 6(c)). Therefore, the wide transition temperature interval is indicative of the presence of multiple transition states, i.e., multiple transition temperatures. As the transition temperature interval increases, the multiple-shape memory effect is also enhanced. The fugacity of PBz5-5 at the two transition temperatures can be fixed by applying external forces during cooling. After reheating to 120 $^{\circ}\text{C}$, the assigned deformation is partially released and further deformation is achieved at 250 $^{\circ}\text{C}$, as shown in Fig. 6(d). For shape memory polymers with wide transition temperatures, it is generally caused by the overlap of multiple discontinuous transition states or local differences in molecular structure at the micro-scale of the material. Therefore, within a wide transition temperature range, it can be regarded as the equivalent existence of multiple transition states, i.e. multiple transition temperatures. As the transition temperature interval becomes larger, its multiple shape

memory effect becomes more excellent. Taking PBz5-2 with a wide transition temperature range as an example, 120 $^{\circ}\text{C}$ and 250 $^{\circ}\text{C}$ were selected as two “separated” transition states.

3.5. Rapid heat- and electric-response

The preparation process of MWCNT-filled shape memory polybenzoxazine composites is shown in Fig. 7(a). PBz5-2 was chosen as the matrix material, and multi-walled carbon nanotubes were incorporated in varying mass concentrations to create composites with electrical conductivity. The viscosity test of the prepared mixed resin containing different MWCNT contents is shown in Fig. S1. As the content increases, the viscosity of the mixed resin solution gradually increases. This is because the surface of carbon nanotubes adsorbs more molecules and forms additional frictional resistance, thereby increasing the viscosity of the solution. Once the volume concentration of the conductive material reaches the critical value, the conductive material particles in the material system can come into contact or form a gap to form electrical

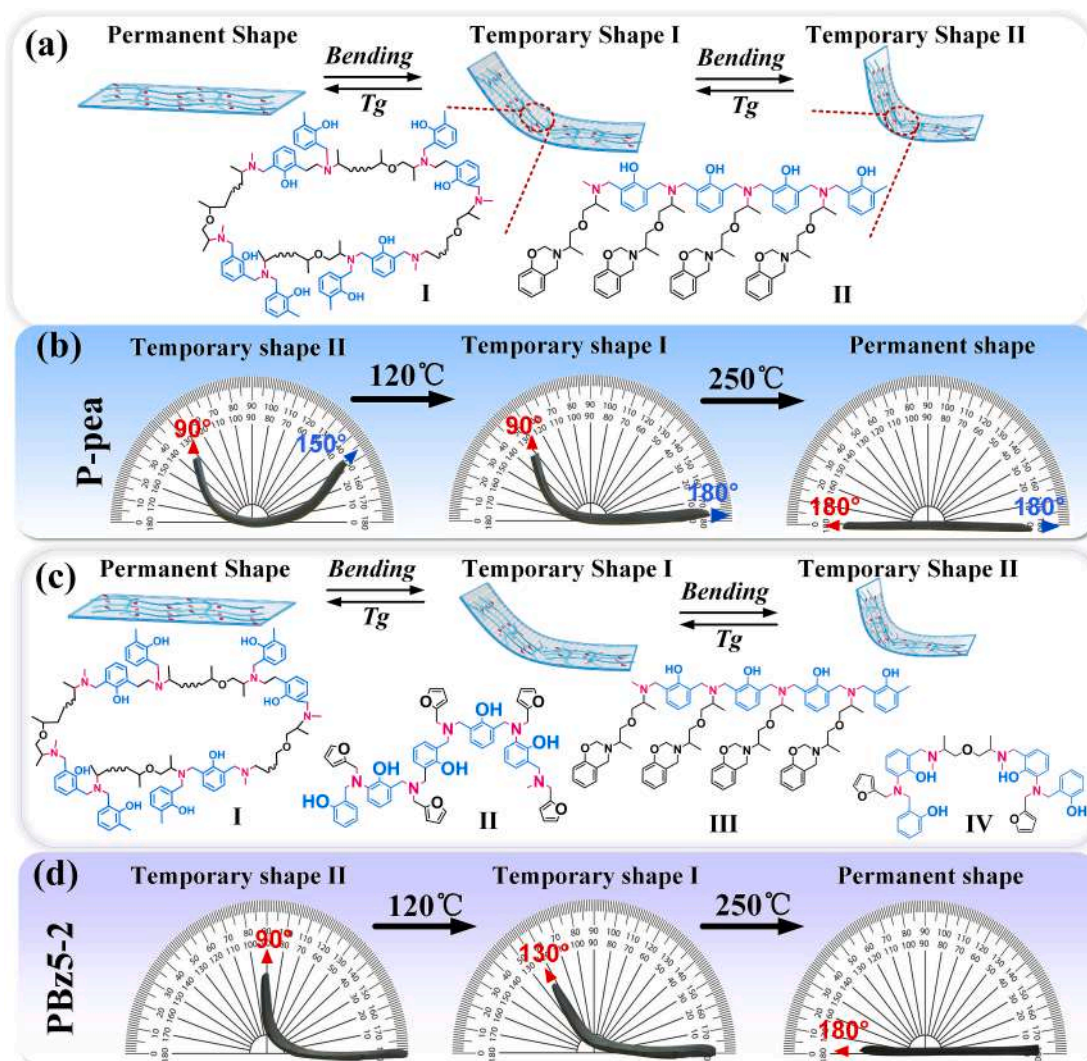


Fig. 6. (a, b) The triple shape memory effect of P-pea and the physical diagram of shape memory response; (c,d) The triple shape memory effect of PBz5-2 and the physical diagram of shape memory response.

equivalent bonding, thus forming a complete conductive network and rendering the composite material system conductive. As shown in Fig. 7 (b), when the content of MWCNT is low, the resistance of the composite is high, close to the property of an insulating polymer. When the content of MWCNT increased from 4 wt% to 10 wt%, the resistivity of the composite material decreased from 54 k Ω -cm to 25 k Ω -cm, a decrease of 53 %. As the content of MWCNTs increases, the electrical conductivity gradually increases and the resistance decreases. However, when the content is close to the percolation threshold, the conductive particles can form a continuous conductive network due to electron leap and tunneling effects when they come into contact with each other. The loss rate of the PBz under aerobic conditions at 400 °C decreased steadily from 21.13 % to 7.54 % in the pure P-fa resin as the P-fa type monomer content increased (resulting in an elevated crosslink density of the polymer network), as illustrated in Fig. 7(c). Under an aerobic environment of 400 °C, as the content of MWCNT increases, the carbon residue rate of the composite material gradually increases. This is due to the excessive enrichment of carbon nanotubes on the surface, the gradual increase in thermal decomposition temperature and a decrease in decomposition rate. At a constant voltage of 60 V, the 4 wt% WCNT/PBz5-2 composite began to regain its shape after 5 s of energization. However, the low heating efficiency and the presence of heat loss from the surface make it more difficult to raise the temperature of the material system to 160 °C. As a result, the shape could not be completely

restored to its original straight shape after 24 s, and the shape return rate was 76 %. The shape return process is depicted in Fig. 7(d). The conductivity of the composite system improved as the doping content increased from 10 % to nearly 83.3 %, and the shape recovery rate increased from 75.7 % to nearly 83.3 %, with shape memory recovery completed in 15 s at 60 V, indicating improved shape memory performance. With the addition of different MWCNT contents, the dispersion of MWCNT in the matrix can be obtained from SEM images, as illustrated in Fig. 7(c). It can be observed that there is no obvious agglomeration or aggregation phenomenon, indicating good dispersion.

Fig. 8(a) is a physical image of the oxygen acetylene experiment of polybenzoxazine. The results of oxyacetylene ablation on a cylindrical sample of pure PBz5-2 resin that was 10 mm thick and 30 mm in diameter. The bulk ablation rate was 0.079 and the line ablation rate of PBz5-2 was measured to be 0.103 during the ablation process, which lasted 10 s. The sample's surface was chapped following the ablation test, and as can be seen in Fig. 8(b), the surface essentially consisted of a flaky carbon layer that had been left behind. From the side of the sample, it can be seen that the carbon layer's thickness grows as the ablation process goes on. This is because the polymer side chains decompose more quickly than the polymer backbone, causing the carbon layer to form. Fig. 8 (c) depicted the 3D depth of field morphology of the sample after ablation. The image showed the chapping and roughness of the carbon layer, indicating that the thermal stress generated by the

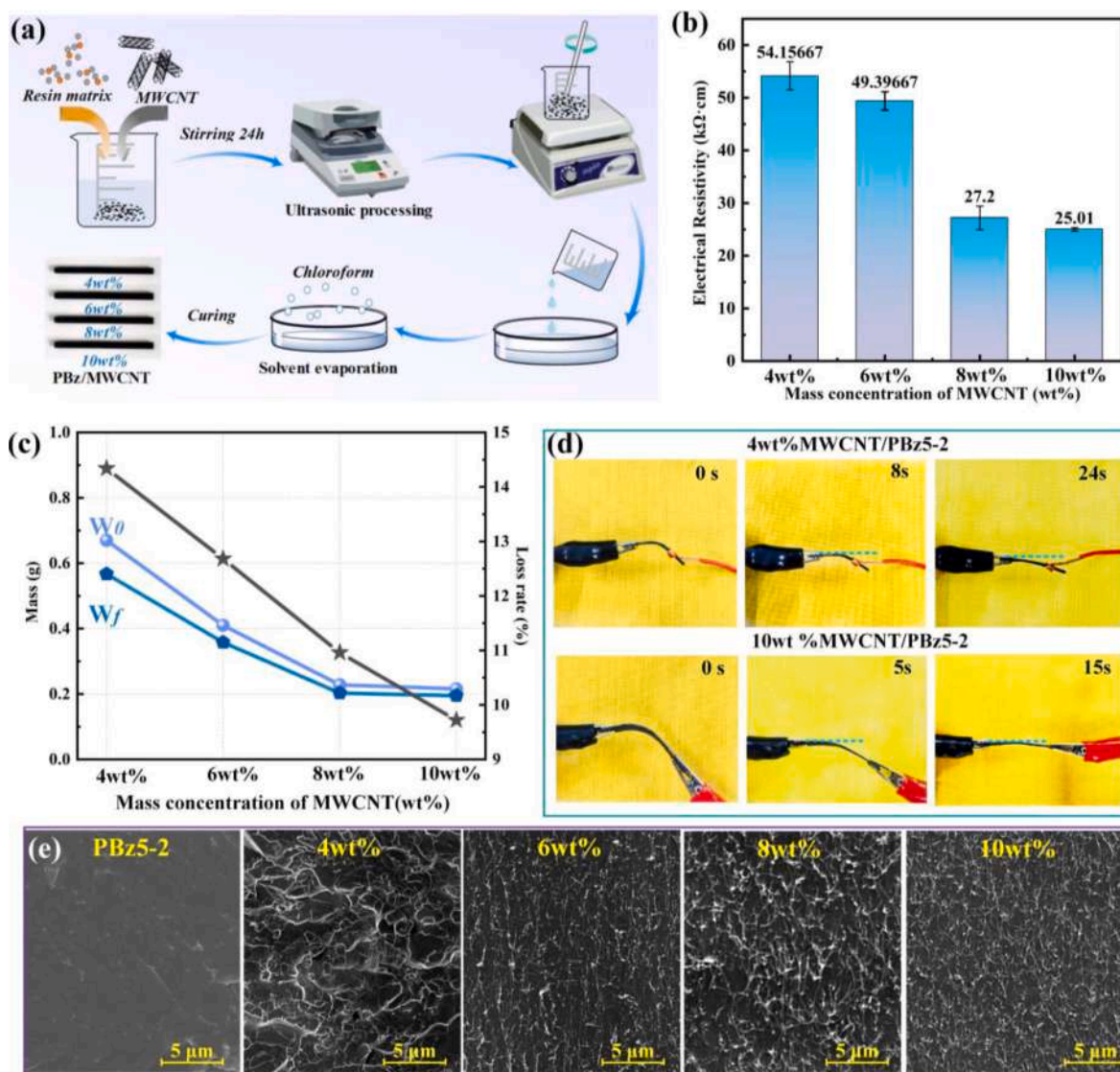


Fig. 7. (a) The fabrication process of composites of MWCNT/PBz; (b) Resistivity variation of the composites with different content of MWCNT; (c) High-temperature thermal stability of MWCNT composites with different content; (d) Conductive shape memory reversion process; (e) SEM images of composites with different contents of MWCNT.

temperature gradient in different parts of the material after the impact of high-temperature gas leads to the cracked surface of the carbon layer. In addition, there was no overall collapse of the sample after the oxygen acetylene test. This indicated that PBz5-2 can resist the stress and thermal stress effects generated during the ablation process. Even if the surface carbon layer fails to ablate, the material can still maintain its shape and integrity without being prone to collapse, providing a material foundation for ablative-resistant shape memory polymers.

Fig. 8(c) depicts the 3D depth-of-field morphology of the sample after ablation, which demonstrates that there is chafing and an uneven height of the carbon layer but that there is essentially no sample collapse following ablation. Fig. 8(d) shows the SEM image of the ablated sample, which can be classified into surface layer, interlayer, and innermost layer according to morphology. Under a flame with a high temperature of 2300 °C, the sample displayed ablation holes on the surface and bulges. The sample was nearly completely unharmed as it was probed further without coming into touch with a flame and as high temperature was transferred weakly layer by layer.

4. Conclusions

Polybenzoxazine with amine sources of polyetheramine and furfurylamine, respectively, was selected and analyzed for the toughening effect of flexible chain segments. With the increase of P-fa content, there is a gradual transition from separated double peaks to wide overlapping peaks to achieve the triple shape effect. The residual carbon rate reached 43.37 % due to its increased aromatic ring content and cross-link density. Based on the excellent comprehensive properties of PBz5-2 resin, electrically driven shape memory polybenzoxazine composites were prepared by introducing conductive multi-walled carbon nanotubes. The resistivity of the composite was reduced by about 44.9 %, and the mass loss rate of the sample with a 10 wt% filling rate was 9.72 %, enabling a dual-driven shape memory process with electrical and thermal excitation. When the doping content is 10 wt%, the shape recovery can be completed in 15 s at 60 V. MWCNT can improve the electric heating efficiency in two aspects to enhance the electrolytic shape recovery rate.

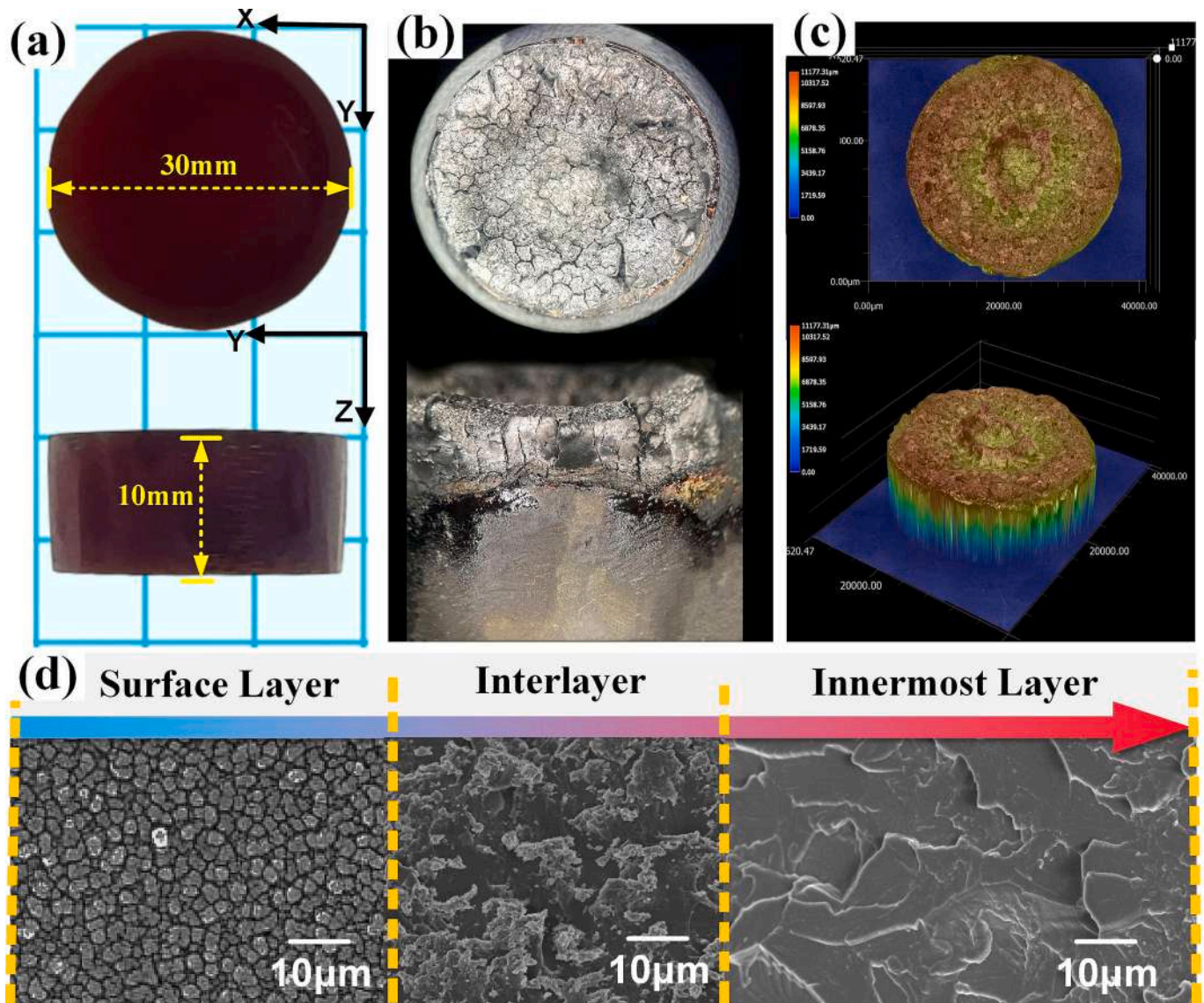


Fig. 8. (a) Physical image of ablation sample of PBz5-2; (b) Physical image of PBz5-2 after ablation; (c) 3D depth-of-field image of PBz5-2 after ablation; (d) SEM image of PBz5-2 after ablation.

CRediT authorship contribution statement

Lan Luo: Investigation, Methodology, Data curation, Visualization, Writing – original draft, Writing – review & editing. **Zhihong Niu:** Methodology, Validation, Resources, Project administration. **Rongxiang Hu:** Investigation, Validation, Project administration, Writing – review & editing. **Fenghua Zhang:** Investigation, Methodology, Validation, Resources, Project administration, Writing – review & editing. **Yanju Liu:** Conceptualization, Supervision, Project administration, Funding acquisition, Writing – review & editing. **Jinsong Leng:** Conceptualization, Supervision, Project administration, Funding acquisition, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.compositesa.2023.107910>.

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