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Fabrication and Characterization of Poly(9-vinylcarbazole)-Reinforced Epoxy Shape Memory Polymers

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Abstract: Shape memory polymers (SMPs) are smart materials capable of recovering their original shape in response to external stimuli, making them attractive for biomedical applications. Unfortunately, limited mechanical performance and single functionality hinder their utilization in load-bearing environments. To address this drawback, we incorporated poly(9-vinylcarbazole) (PVK) into the epoxy matrix to fabricate multifunctional SMP composites with improved mechanical performance. Uniformly dispersed PVK/epoxy composite films were successfully fabricated, and the effects of PVK content on the materials' properties were systematically evaluated. The results showed that PVK not only improved the mechanical strength of the composite films but also enabled a lower charge transfer resistance compared with the reference sample. Meanwhile, PVK had a minimal impact on the phase transition temperature and shape memory behavior of the epoxy matrix. *In vitro* biological evaluations demonstrated a low hemolysis rate and promoted the proliferation of mesenchymal stem cells (MSCs), indicating favorable blood compatibility and cytocompatibility. These findings suggested that PVK-reinforced epoxy-based SMP composites possessed a promising combination of mechanical performance, reduced charge transfer resistance, shape memory functionality, and biocompatibility for potential applications in biomedical fields.

Keywords : shape memory polymer; poly(9-vinylcarbazole); biocompatibility; composites.

1 Introduction

Smart materials, alternatively termed intelligent or stimuli-responsive materials, have drawn considerable research attention in scientific and engineering fields. Shape memory polymers (SMPs), among the most promising smart materials [1], can revert from a temporary shape back to their intrinsic permanent shape when triggered by external stimuli such as heat [2, 3], light [4], electricity [5], humidity [6], magnetic fields [7, 8], and pH levels [9]. Compared to other shape memory materials (e.g. shape memory alloys and shape memory ceramics), SMPs possess distinctive advantages including low density, high deformability, multi-stimulus responsiveness, ease of processing, and colorability [10, 11]. With these merits, the unique shape-shifting capabilities of SMPs have been exploited to advance a wide range of biomedical applications, involving cell and tissue scaffolds [12], orthopedic repair scaffolds [13, 14], vascular stents [15], drug delivery carriers [16], and so on.

SMPs can be categorized into two types: thermoplastic SMPs and thermoset SMPs [17]. Thermoplastic SMPs generally rely on physical crosslinks. Upon exposure to ambient moisture, they are susceptible to moisture, which results in unstable mechanical performance. In contrast, thermoset SMPs are constructed via chemical crosslinks and exhibit superior shape-memory, chemical, thermal, and mechanical properties compared with physically crosslinked SMPs. Epoxy resins have garnered considerable interest owing to their high strength, high elastic modulus, robust adhesion, excellent thermal stability, and solvent resistance [18]. Epoxy-based SMPs represent a typical class of thermoset SMPs with processability, and shape memory properties [19].

Doping strategy serves as an effective approach to tailor and enhance the

performances of epoxy SMPs [20]. Incorporating various functional reinforcements into shape memory polymer matrices can effectively improve their functionality and mechanical properties. Collado et al. doped graphene nanoplatelets (GNPs) into epoxy SMPs to endow them electrical and thermal conductivity [21]. Upon incorporating the highest GNPs loading, the composite delivered an electrical conductivity of 10^{-1} S/m together with a thermal conductivity 1.250 W/mK, which is remarkable taking the insulating behaviour of the polymer matrix into account. The introduction of rigid conjugated structures can also enhance the storage modulus of SMPs. Yan et al. [22] utilized the rigid conjugated structured resveratrol and 2,5-furandicarboxylic acid to fabricate SMPs, whose storage modulus are higher than those of reported shape memory fully biobased epoxy resin.

Poly(9-vinylcarbazole) (PVK) possesses pendant carbazole groups with π -conjugated structures, which endow the polymer with favorable hole-transporting capacity [23]. PVK has been widely used as hole transport layers (HTL) in light-emitting diode (LED) [24] and organic solar cells [25, 26] due to its favorable hole mobility. Although hole-transporting polymers such as PVK were originally developed for optoelectronic devices, their conjugated π -structures and photoelectric responsiveness enable them to be integrated into SMPs toward promising biomedical applications including organic bioelectronic interfaces [27].

In our previous study, we tailored an epoxy SMP whose glass transition temperature (T_g) was at around physiological temperature by adjusting the crosslink density and introducing chain flexibility [28]. Herein, based on our previous research,

PVK with varied mass fractions was incorporated into the epoxy-based shape memory polymer matrix to endow the SMPs with enhanced mechanical and electronic properties. The aromatic carbazole units of PVK enabled efficient π – π stacking, providing a feasible pathway to regulate the mechanical and electronic properties of epoxy-based shape memory composites. By optimizing the synthesis conditions, we fabricated PVK-doped epoxy SMPs (denoted as PVK/epoxy SMP) with uniform filler dispersion. Subsequently, we prepared a series of PVK-doped epoxy SMPs with different PVK loadings (from 0 to 1.2% wt.) that display excellent shape-memory performance. Upon PVK loading, the samples showed significantly improved mechanical strength and electrical properties, while exerting negligible effects on the phase transition temperature. *In vitro* biological evaluations demonstrated a low hemolysis rate and promoted the proliferation of mesenchymal stem cells (MSCs), indicating favorable blood compatibility and cytocompatibility. These findings suggested that PVK-reinforced epoxy-based SMP composites possessed a promising combination of mechanical performance, electrical property, shape memory functionality, and biocompatibility for potential biomedical applications.

2 Experimental Sections

2.1 Materials.

Poly(9-vinylcarbazole) (PVK) with average molecular weights (M_n) of 25 kDa and 90 kDa was obtained from Shanghai Bison Biochemical Technology Co., Ltd. Tetrahydrofuran (THF) was obtained from Sinopharm Chemical Reagents Co., Ltd. The diglycidyl ether of bisphenol A epoxy monomer (EPON 826) was purchased from

Yubang Technology Co., Ltd. The curing agent, poly(propylene glycol) bis(2-aminopropyl) ether (Jeffamine D230), was supplied by Huntsman Technology Co., Ltd. Neopentyl glycol diglycidyl ether (NGDE) was provided by Aladdin Biochemical Technology Co., Ltd. All chemicals were used as received without further purification.

2.2 Synthesis of PVK/epoxy SMP composites.

The PVK/epoxy SMP composites were prepared using a melt blending and thermosetting method. First, 3.84 g of EPON 826 was added to a glass sample bottle, which was then placed in an ultrasonic water bath heated to 55°C for ultrasonic treatment. This step fully softened the epoxy resin, improved its flowability, and eliminated air bubbles from the mixture. Separately, 2.16 g of NGDE and 2.3 g of D230 were added into glass sample bottles, mixed thoroughly, and also placed in the ultrasonic water bath for later use [29]. Next, varying amounts of PVK were weighed and dissolved in THF as the solvent. This solution was then subjected to ultrasonic treatment for thorough dispersion. Afterwards, 1 mL of THF was added to the degassed epoxy resin system, followed by 10 minutes of ultrasonic treatment. Once the system was well mixed, the prepared PVK solution in THF was gradually added to the epoxy resin system, and ultrasonication was continued for an additional 5 minutes. Finally, the NGDE and D230 blend was then added to the previous solution, followed by 5 minutes of ultrasonication until the mixture became uniformly clear. This clear solution was promptly transferred into a glass container preheated to 55°C and placed on a heating plate for further thermal treatment. The mixture underwent a three-stage heating process: initially held at 55°C for 2 hours; then the temperature was raised to 100°C

and maintained for 90 minutes; finally, it was increased to 135°C and kept for 70 minutes. The final sample was obtained immediately after demolding. The detailed composition of each component used in preparing the PVK/epoxy SMP composites is provided in Table 1.

Table 1 The amount of each component used in the preparation of PVK/epoxy SMP composites

	EPON 826 (mol)	NGDE (mol)	D230 (mol)	$\omega(\text{PVK})$
REF	0.01	0.01	0.01	0
PVK-0.3	0.01	0.01	0.01	0.3%
PVK-0.5	0.01	0.01	0.01	0.5%
PVK-0.8	0.01	0.01	0.01	0.8%
PVK-1.0	0.01	0.01	0.01	1%
PVK-1.2	0.01	0.01	0.01	1.2%

2.3 Scanning electron microscopy (SEM)

The microstructure and morphological properties of composites were characterized using scanning electron microscopy [30] (SEM, Merlin Compact, Carl Zeiss NTS GmbH, German) at an accelerating voltage of 10 kV after gold spraying. The epoxy SMPs were cut to a small size of 5×5 mm.

2.4 Gel content determination of PVK/epoxy SMP composites.

In the gel content determination experiment, the epoxy SMPs were cut into square specimens with dimensions of 5×5 mm, and their initial mass (m_1) was recorded. Each sample was then immersed in 10 mL of tetrahydrofuran (THF) and soaked continuously for 48 hours. Subsequently, the samples were placed in a vacuum drying oven at 70 °C

and dried until a constant mass was achieved, which was recorded as the final mass (m_2). To ensure the accuracy and reproducibility of the experimental data, each sample group underwent three parallel tests. The gel content (G) was calculated using the following formula:

$$G = \left(\frac{m_2}{m_1} \right) \times 100\%$$

2.5 Differential scanning calorimetry (DSC) measurement

The thermal properties of the films were analyzed using a program-controlled temperature thermal-enthalpy analyzer coupled with mass spectrometry (STA449F3-QMS403D, NETZSCH). All measurements were conducted under a nitrogen atmosphere. Samples were heated from ambient temperature to 150°C at a controlled rate of 10°C per minute.

2.6 X-ray diffractometer (XRD)

The crystalline structures of PVK/epoxy SMPs were systematically characterized using an X-ray diffractometer (XRD, SmartLab) at angles ranging from 5° to 60°, with a scanning rate of 5° per minute.

2.7 Mechanical properties of PVK/epoxy SMP composites.

Tensile tests were conducted on each group of composite films using an electronic universal testing machine (CMT-20, LG) to evaluate their mechanical properties [31].

2.8 Fourier transform infrared spectroscopy (FTIR) measurement

The chemical structures of PVK/epoxy SMPs were systematically characterized using a synchronous thermal-transmission reflectance spectrometer (STA8000 Frontier).

2.9 Shape-memory evaluation of PVK/epoxy SMP composites.

The sample was initially heated in a hot-water bath (60 °C), then an external force was applied to induce bending deformation. After deforming the PVK/epoxy SMPs into a predetermined shape, the samples were rapidly cooled in a 10 °C water bath for shape fixation. Afterwards, samples were reheated in a hot-water bath at 60 °C, above the glass transition temperature. The material's shape recovery process was then observed and documented.

2.10 Evaluation of the swelling properties of PVK/epoxy SMP composites.

Water immersion tests were performed to assess the water resistance of the composites. Changes in sample dimensions before and after immersion were adopted as the primary evaluation indicators.

2.11 Electrochemical Performance Testing

An electrochemical workstation was used to measure the electrochemical impedance spectra (EIS) of composite samples with different compositions during immersion in phosphate-buffered saline (PBS). The test employed a three-electrode system, with the composite sample serving as the working electrode, a platinum foil as the counter electrode, and a saturated calomel electrode as the reference electrode. Prior to testing, the sample was cut into 1 cm × 1 cm pieces and connected to the circuit via copper wires for EIS measurements. The experimental frequency scan range was set from 10^6 Hz to 10^{-2} Hz. The EIS data were fitted using an equivalent circuit in ZSimpWin software to obtain parameters such as resistance.

2.12 Hemolysis test

To evaluate the blood compatibility of the composite membrane, we conducted an *in vitro* hemolysis test using mouse cardiac blood cells. Fresh blood was collected from the mice and transferred to sterile test tubes. Sodium citrate solution was introduced to inhibit blood coagulation. The blood was washed with physiological saline and centrifuged to isolate the red blood cells. Subsequently, the samples were centrifuged at 1200 rpm for 15 minutes until the supernatant became colorless and transparent. The epoxy SMPs were cut into square specimens with dimensions of 1×1 cm. Deionized water was used as the positive control, whereas phosphate-buffered saline (PBS) acted as the negative control. The epoxy SMP sample was immersed in the red blood cell suspension and incubated at 37°C in a constant-temperature water bath for 4 hours. The color change of the supernatant was then observed. Each group was tested in triplicate, and absorbance was measured at 562 nm using a detection system. The hemolysis rate was calculated using the following formula.

$$hemolysis\ rate(\%) = \frac{A_t - A_n}{A_p - A_n} \times 100\%$$

A_t represents the absorbance value of the supernatant in the experimental group samples. A_n is the absorbance of the negative control group, and A_p is the absorbance of the positive control group.

2.13 MTT assay of PVK/epoxy SMP composites.

Bone marrow-derived mesenchymal stem cells (MSCs) from Sprague-Dawley (SD) rats aged approximately four weeks were used as the cellular model for cytotoxicity assays. The cellular compatibility of SMP samples without PVK (denoted as REF, used as a control) and with varying levels of PVK doping was determined using

the MTT (3-(4,5-dimethyl-2-thiazolyl)-2,5-diphenyl-tetrazolium blue) colorimetric assay. Succinate dehydrogenase in living cells, particularly in mitochondria, catalyzes the reduction of the yellow MTT reagent into insoluble blue-violet formazan crystals. When cells die, the loss of this enzyme activity prevents the production of formazan.

100 mg of each test sample were placed into separate centrifuge tubes. First, the samples were washed three times with ethanol, followed by three rinses with PBS. After washing, each sample was individually immersed in 10 mL of Dulbecco's Modified Eagle Medium (DMEM) supplemented with 1% penicillin-streptomycin antibiotics. The samples were subsequently incubated at 37 °C for 24 h under constant-temperature conditions. The final filtration was performed using a 22-micron syringe filter, and the target extract was collected. Mesenchymal stem cells (MSCs) were seeded at a density of 3×10^4 cells per well in a 96-well culture plate. Cultivation was conducted using DMEM supplemented with 10% fetal bovine serum (FBS) under conditions of 37°C and 5% CO₂ in an incubator, with continuous culture maintained for 24 hours. After the initial culture phase, the original culture medium was discarded and replaced with the extraction solution. Subsequently, the MSCs were cultured for an additional 1, 3, and 7 days, respectively. The culture medium was refreshed every two days. At the end of each culture period, 10 µL of MTT reagent was added to each well. And the plate was incubated for 4 hours under the same culture conditions to allow formation of MTT formazan crystals. The liquid was then discarded from the wells. Under light-protected conditions, 100 µL of dimethyl sulfoxide (DMSO) was added to each well. The plate was placed on a light-protected shaking incubator and shaken for 15 minutes to ensure

complete dissolution of the crystals. Finally, the absorbance at 490 nm was measured using a microplate reader [32]. Cell viability was calculated according to the following formula:

$$cell\ activity(\%) = \frac{A_s - A_0}{A_c - A_0} \times 100\%$$

A_0 denotes the absorbance of wells containing only cell-free medium. A_s is the absorbance of the experimental group, and A_c is the absorbance of the control group.

2.14 Live/Dead staining assay of PVK/epoxy SMP composites.

The MSCs were stained by the calcein-AM and propidine iodide (PI). Cells were suspended at a density of 4×10^4 cells per well. This suspension was seeded into a 24-well plate at 500 μ L per well and incubated for 24 hours under standard conditions at 37°C in a 5% CO₂ incubator. Following the initial incubation, the extraction solution was replaced in each group, and incubation continued for an additional 24 hours. Subsequently, a 1 μ g/mL working solution of calcein-AM and a PI staining solution were prepared and used to perform live/dead staining on the cells. The MSCs was then observed by fluorescence microscopy.

3 Results and Discussion

3.1 Fabrication of PVK/Epoxy SMP composites with uniformly dispersed PVK

There were four main components in the PVK/epoxy SMPs, whose chemical structures were showed in Figure 1a. In this system, rigid aromatic diepoxides (EPON 826) and flexible diepoxides (NGDE) acted as the building blocks for the matrix. Aliphatic diamine (Jeffamine D230, denoted as D230) functioned as a crosslinker. The epoxy–amine curing reaction led to the formation of a three-dimensional crosslinked

network (Figure 1b). As a rigid conjugated polymer with benzene rings, PVK was adopted as a functional filler. However, direct blending of PVK with EPON and NGDE cannot produce a homogeneous mixture, and tetrahydrofuran (THF) was introduced as a cosolvent. A three-dimensional crosslinked network was formed after melt mixing and subsequent thermal curing, converting the liquid mixture into a solid material (Figure 1c). Meanwhile, the aromatic rings of PVK molecules can interact with EPON 826 via π - π stacking interactions (Figure 1d).

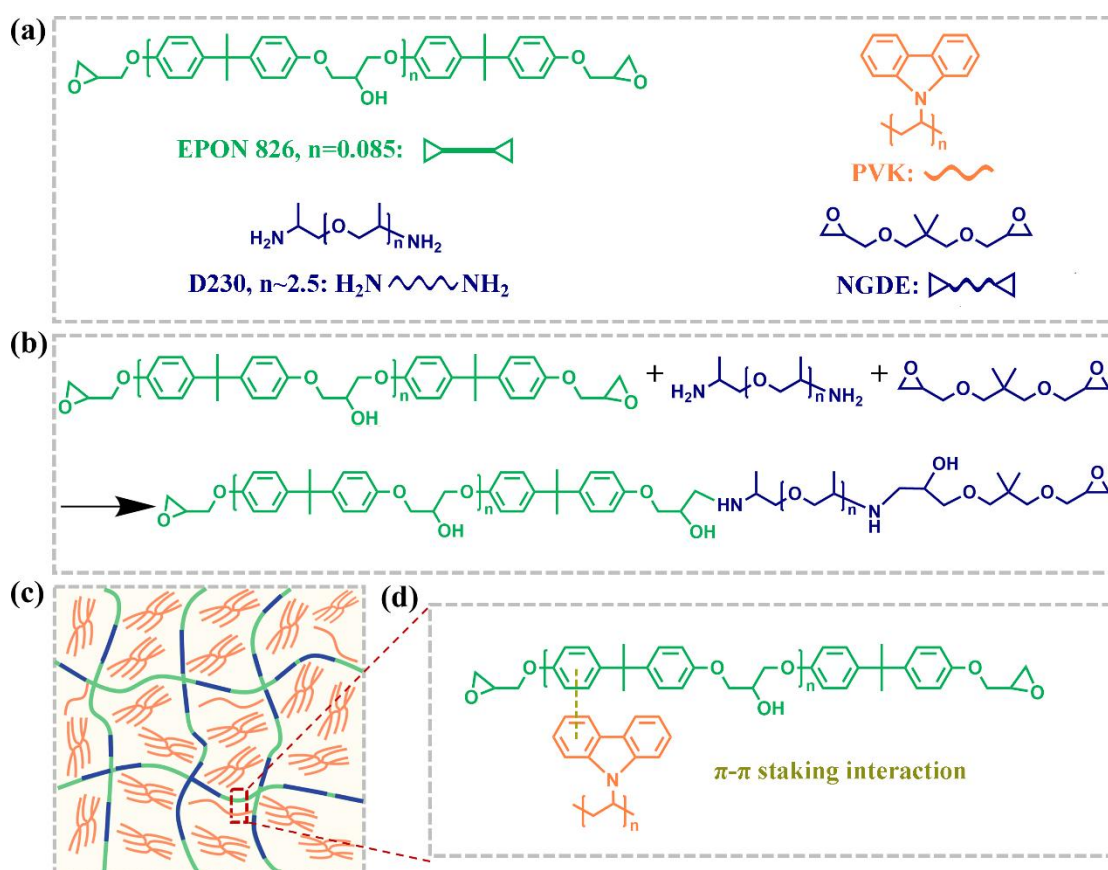


Figure 1 (a) Chemical structures of EPON 826, PVK, NGDE, and D230 that are used to prepare PVK/epoxy SMP composites. (b) A schematic diagram of the epoxy–amine curing reaction of epoxy SMPs. (c) Schematic diagram of a fully cured cross-linked network. (d) Possible π - π stacking interaction of PVK and EPON826.

The dispersion of PVK molecules in the matrix greatly may affect the composite properties. The molecular weight of PVK, cosolvent type, and mixing temperature can modulate the chain entanglement and dispersion of PVK in epoxy resin, as well as the

π - π stacking interactions between PVK and epoxy molecular chains, which directly determine the reinforcing effect of the filler in the matrix. Accordingly, we optimized the preparation conditions by adjusting the PVK molecular weight, mixing temperature, cosolvent, and solvent evaporation process. Figure 2a and 2b displayed photographs of PVK/epoxy SMP composites, in which the molecular weights of PVK were 25 kDa and 90 kDa, respectively. Evidently, PVK with a molecular weight of 25 kDa yielded less flocculent precipitate than PVK with a molecular weight of 90 kDa. This suggested that higher molecular weight led to stronger chain entanglement, which hindered the penetration and diffusion of PVK into the crosslinked epoxy resin network.

Although low-molecular-weight PVK exhibited less flocculent precipitate compared with high-molecular-weight PVK, it still failed to produce homogeneous composites. To address this issue, we employed THF to dissolve PVK and tuned the mixing temperature to facilitate PVK dispersion in the mixture before curing. THF pretreatment slightly improved PVK dispersion in the SMP composite (Figure 2c), yet flocculent precipitate could still be observed. Upon raising the mixing temperature from 25 °C to 40 °C, small aggregates appeared instead of obvious flocculent precipitate (Figure 2d).

Additionally, the solvent evaporation process during sample preparation may also influence the uniformity of the composite materials. After solvent removal via rotary evaporation, PVK disperse better than the previous samples (Figure 2e). However, it still failed to achieve monodispersion within the PVK/epoxy SMP composite. Interparticle interactions induce small flocculent aggregates. Distinct boundaries

between filler-enriched domains and bare matrix regions were observed, indicating insufficient dispersion uniformity. Figure 2f presented composites prepared using a three-stage progressive heating-evaporation-curing strategy. This method involved slowly evaporating the solvent at 55°C for 2 hours, followed by gradual temperature elevation for staged curing. Treated via this segmented process, PVK achieved homogeneous distribution within the matrix. This approach likely reduced the solvent evaporation rate, prevented boiling overflow or local precipitation, and thus maintained the structural integrity and performance stability of the final material. Based on these findings, this study employed the three-stage progressive heating-evaporation-curing strategy to prepare a series of composite material films with PVK contents of 0.3%, 0.5%, 0.8%, 1%, and 1.2%.

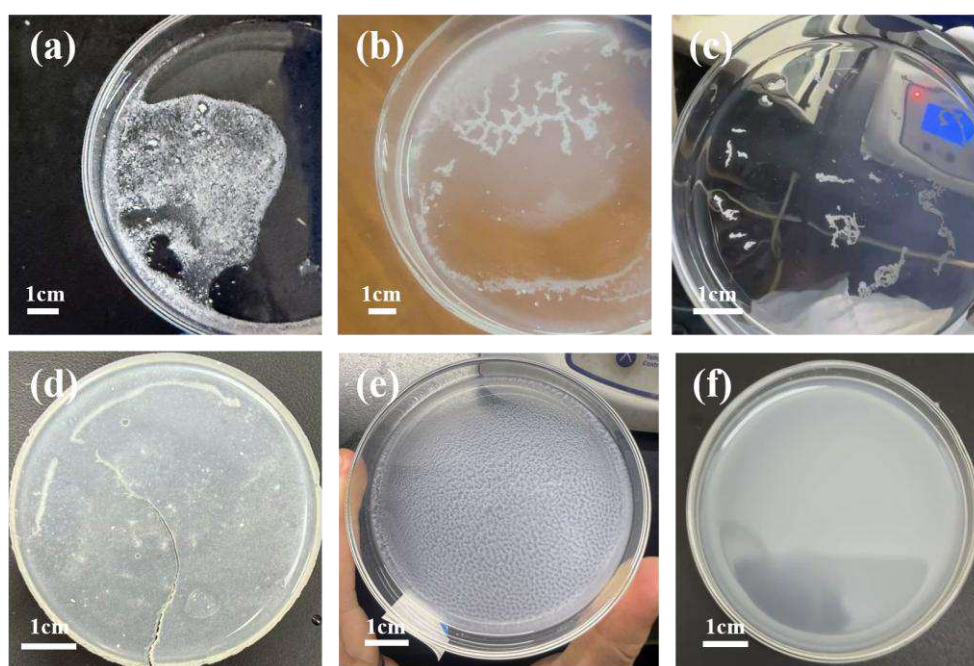


Figure 2 Optimizing the preparation conditions of PVK/Epoxy SMP composites by adjusting the PVK molecular weight, mixing temperature, cosolvent, and solvent evaporation process. The molecular weights of PVK are (a) 25 kDa and (b) 90 kDa. (c) Introducing THF as cosolvent. (d) Raising the mixing temperature from 25 °C to 40 °C. (e) THF was removed via rotary evaporation. (f) PVK/Epoxy SMP composites prepared using a three-stage progressive heating-evaporation-curing strategy

3.2 Micromorphology and Microstructure of PVK/Epoxy SMP Composites with Varying PVK contents

Scanning electron microscopy (SEM) was employed to characterize the internal microstructure of SMP containing different PVK loadings. The cross-sectional morphology was presented in Figure 3. Distinct layered features can be observed in all SEM images. The neat epoxy-based SMP (REF) exhibited a relatively smooth surface (Figure 3a). As the PVK content increases from 0.3% to 1.2% (Figure 3b-3f), PVK particles were dispersed throughout the polymer matrix, and the most prominent PVK particles appeared at 1.2% content (Figure 3f). These results confirmed that the crosslinked epoxy network can encapsulate and immobilize PVK effectively.

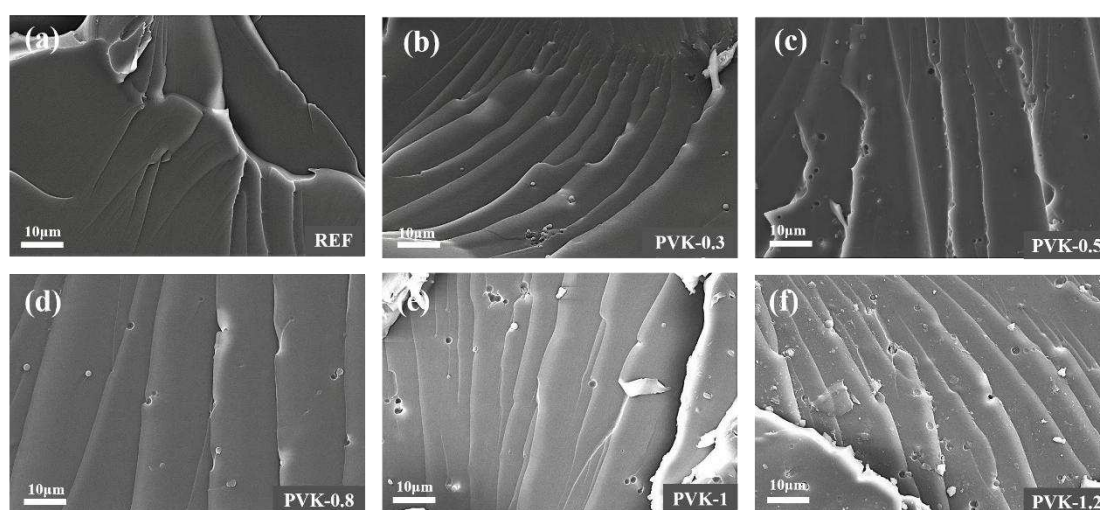


Figure 3 SEM images of composites with varying PVK contents: (a) REF (PVK-0); (b) PVK-0.3; (c) PVK-0.5; (d) PVK-0.8; (e) PVK-1; (f) PVK-1.2.

Figure 4a showed the gel content of PVK/epoxy SMP composites. There was no significant reduction in gel content across all samples, indicating that PVK encapsulated within the epoxy resin exhibits excellent solvent resistance. Figure 4b showed the DSC heating curves of REF and PVK-modified samples. A clear glass-transition step was observed for all samples, while no obvious crystallization or

melting peaks could be detected in the temperature range of 20-160 °C, indicating the amorphous nature of these blends. Notably, the T_g values of the PVK-containing composites are located in the range of approximately 37-45 °C (Table 2), which is highly relevant for biomedical shape-memory applications. A T_g slightly above body temperature ensures excellent shape fixation under physiological conditions while allowing rapid shape recovery under mild external heating, making the composites promising candidates for controllable thermally triggered biomedical devices.

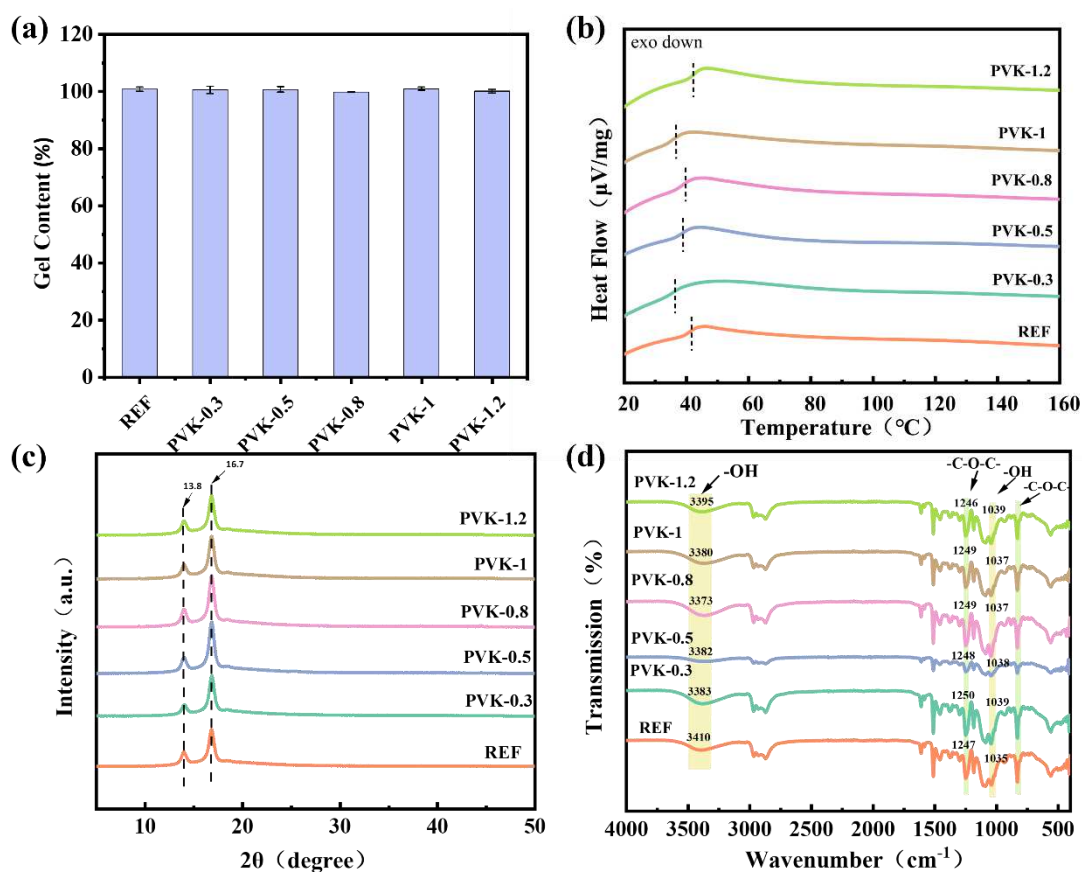


Figure 4 (a) The gel content of composites with different PVK concentrations. (b) DSC curve of PVK/epoxy SMP composites series. (c) XRD patterns of different samples. (d) FTIR spectra of composites with different PVK contents.

Figure 4c illustrated the molecular arrangement in the crystalline regions and microcrystalline structures of the composites based on X-ray diffraction (XRD) results.

All samples exhibited two characteristic peaks at $2\theta \approx 13.8^\circ$ and 16.7° , indicating that

the introduction of PVK can not alter the overall crystallinity. The positions of the diffraction peaks remained unchanged, suggesting that PVK and the epoxy system were physically blended without chemical cross-linking. Although epoxy curing systems were amorphous polymers, the epoxy molecular segments and the cured cross-linked network still exhibited localized short-range ordered arrangements. The stacking of molecular chains formed a weakly ordered structure. As PVK content increased, the intensity of the diffraction peak at 16.8° slightly increased, possibly due to an increase in the ordered structure formed by the stacking of PVK segments with the epoxy resin.

Table 2 Glass transition temperatures of PVK/epoxy SMP Composites series.

Glass transition temperature (T_g , °C)	
REF (PVK-0)	41.6
PVK-0.3	35.8
PVK-0.5	39.3
PVK-0.8	39.5
PVK-1	36.9
PVK-1.2	42.5

Figure 4d showed the Fourier transform infrared (FTIR) spectra of various composites with different PVK contents. The FTIR spectra of PVK/epoxy SMP samples showed high similarity to that of the neat epoxy reference. No new characteristic peaks appeared after PVK incorporation, which indicated the absence of newly formed chemical bonds. Furthermore, a noticeable red shift was observed in the O-H stretching vibration from 3410 cm^{-1} to approximately 3373 cm^{-1} , implying

strengthened intermolecular interactions, particularly hydrogen bonding. These results indicate that the carbazole groups of PVK interact strongly with the epoxy network through π - π interactions and hydrogen-bonding effects, restricting chain mobility and promoting a more ordered molecular packing structure. Consequently, the synergistic enhancement of intermolecular interactions and chain ordering contributes to the improved thermal and shape-memory properties of the EP/PVK composites.

3.3 The mechanical properties of PVK/epoxy SMP Composites with different PVK contents

Figure 5 showed the quasi-static tensile stress-strain curves for each group of specimens tested at room temperature. All specimens exhibited typical ductile polymer tensile behavior, which can be divided into four sequential stages: elastic deformation, yielding, strain hardening, and fracture. During the elastic deformation stage, stress and strain showed a linear positive correlation, indicating the material's reversible deformation behavior. When the strain reached 10% to 15%, a distinct yield peak appeared on the curve, signifying the onset of plastic deformation. After yielding, the stress initially decreased slightly (strain softening), then entered a strain hardening phase where stress gradually increased with strain until ultimate fracture occurred. At room temperature, the yield strength of all PVK-doped specimens exceeded that of the REF group. Among the samples, the one with 0.3% PVK content exhibited the highest yield strength, reaching 43 MPa. However, it fractured when stretched to about 20%, indicating poor flexibility. In contrast, the sample with 0.5% PVK content maintained toughness comparable to the control group while demonstrating superior strength

performance. As the PVK content increased further, the yield strength of the samples showed a slight decline, though it remained higher than that of the undoped sample. The toughness at higher PVK contents was similar to that of the 0.3% sample, both being poor. These results indicated that doping with PVK can effectively enhance the load-bearing capacity and stiffness of the epoxy resin matrix. However, only at an optimal content (0.5%) can both rigidity and flexibility be improved simultaneously. Excessive or insufficient PVK content reduced the fracture strain of the material, causing it to exhibit brittle behavior.

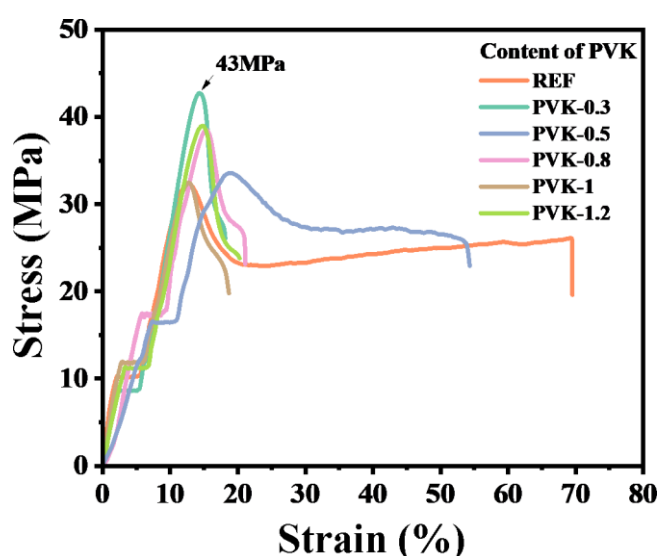


Figure 5 Stress-strain curve of PVK/epoxy composites with different PVK contents

3.4 Electrochemical impedance characteristics of PVK/epoxy SMP composites

As a side-chain conjugated polymer, PVK exhibits inherent charge-transport capability. Figure 6 displayed high-frequency Nyquist plots of composites with different PVK loadings. All curves featured a complete capacitive arc and a 45° diffusion slope at low frequencies. The REF sample exhibited the maximum arc resistance across the measured frequency range, indicating the highest charge transfer

resistance of the neat crosslinked epoxy network. After PVK incorporation, the capacitive arc radius of all composite samples decreased significantly, revealing that PVK lowered the overall charge transfer resistance and enhanced ionic conductivity. For low doping levels (PVK-0.3 to PVK-0.8), the capacitive arc radius continuously declined with increased PVK loading. This confirmed uniform dispersion of low-concentration PVK in epoxy. As the content of PVK increased, phase separation induced more phase interfaces and reduced charge transfer resistance. At high doping concentrations (PVK-1.0 to PVK-1.2), the capacitive arc radius raised slightly along with charge transfer resistance. Excessive PVK triggered particle aggregation in the matrix, partially blocking interfacial ionic channels, while the rigid conjugated segments of PVK restricted molecular chain mobility. Even so, all doped composites maintained lower charge transfer resistance than the reference sample. Detailed resistance data were listed in Table 3.

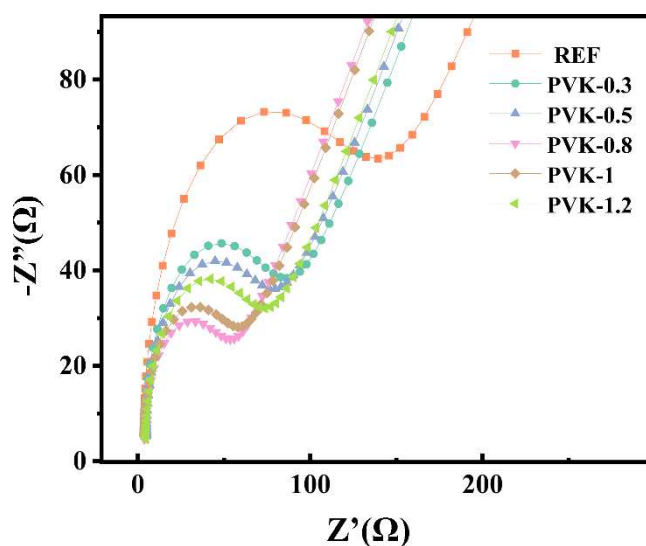


Figure 6 High-frequency Nyquist plots of composites with different PVK contents

Table 3 R_{ct} values of composites with different PVK contents

	REF	PVK-0.3	PVK-0.5	PVK-0.8	PVK-1	PVK-1.2
R_{ct} (Ω)	118.6	70.21	64.82	43.85	47.83	60.09

3.5 Shape memory property of PVK/epoxy SMP Composites

According to electrochemical impedance results, PVK-0.8 exhibits the best charge-transport capability. Therefore, a sample containing 0.8% PVK was selected to investigate the shape memory properties of the composites. Its thermally induced shape memory behavior was characterized, and the results are presented in Figure 7. The material's original permanent shape was rectangular, but it can be manipulated to assume various temporary shapes under external force. After softening in a 60 °C hot water bath, force was applied to deform the film. It was then immediately transferred to a 10 °C cold water bath and held for 5 seconds to stabilize and fix the temporary shape (e.g., circular, spiral, wavy). When reintroduced to the 60 °C hot water bath, the film spontaneously reverted to its original rectangular form within 5–6 seconds. These results confirmed that the composite with 0.8% PVK exhibited excellent shape retention and recovery under thermal stimulation, demonstrating a favorable thermally induced shape memory effect. This behavior occurred because the epoxy shape-memory polymer used in this study was an amorphous system composed of a fixed phase and a reversible phase. The chemical crosslinking points formed the stationary phase that maintained the material's original shape, while the amorphous-to-glass transition of the cured polymer segments served as the core mechanism for the reversible phase to retain its temporary shape. Heating above the glass transition

temperature of the reversible phase allowed the segments to gain mobility and be reshaped. Upon cooling, the molecular chains vitrified, enabling fixation of the reversible phase and formation of the temporary shape. Reheating beyond this temperature induced entropy-driven segmental motion, allowing the polymer chains to return to their free conformations and restore the material's original shape.

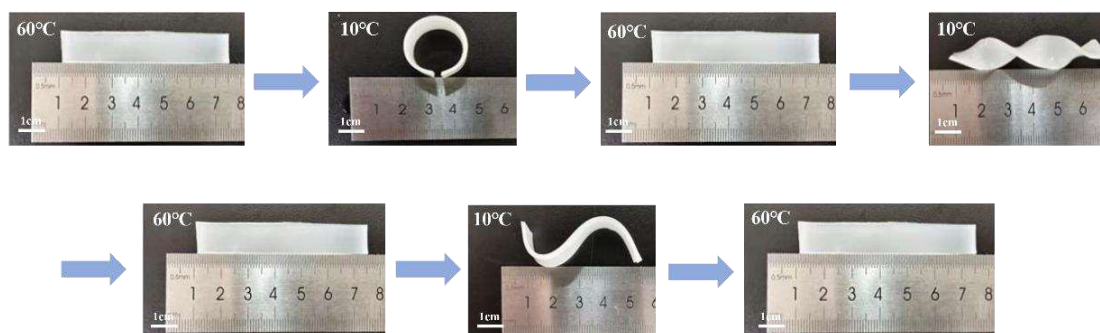


Figure 7 The shape memory properties of PVK/epoxy SMP composites with PVK content of 0.8%. Starting from its original rectangular shape (permanent shape), the film can be twisted into various forms when immersed in hot water and then fixed in cold water. Upon reheating in hot water, it naturally returned to its original rectangular shape.

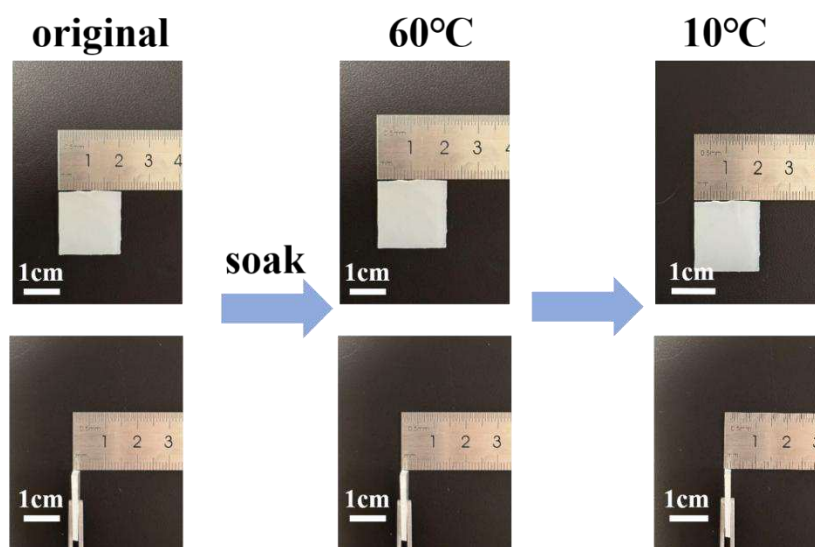


Figure 8 The length and thickness of film before and after immersion in hot and cold water

Additionally, the swelling behavior of the sample with 0.8% PVK in water was shown in Figure 8. After immersing the sample (2×20×20 mm) in water at 60°C and 10°C for 10 minutes each, measurements of length and thickness showed no dimensional changes. This indicated that the material does not swell in water,

demonstrating excellent volume stability and no significant expansion or contraction due to temperature changes.

3.6 Hemocompatibility properties of PVK/epoxy SMP Composites

Benefiting from favorable shape memory properties, PVK/epoxy SMP may allow facile implantation during surgical procedures. Moreover, PVK doping renders this composite promising for diverse biomedical applications including organic bioelectronic interfaces. To evaluate the biocompatibility of the PVK/epoxy resin SMP composite, we examined its impact on red blood cells through hemolysis tests (Figure 9). In the positive control group, the supernatant was uniformly red without red blood cell sediment at the tube's bottom, whereas the negative control group's supernatant was clear, with noticeable red blood cell sedimentation at the bottom. As shown in Figure 9a, after adding samples with different PVK contents, the PVK-0% and PVK-0.3% samples exhibited minimal hemolysis. However, the PVK-0.5%, PVK-0.8%, PVK-1%, and PVK-1.2% samples all induced hemolysis, with the hemolysis rate of PVK-1.2% exceeding 10%. Notably, the molecular structure of these SMP materials lacked functional groups that directly harm red blood cells. Therefore, we hypothesized that hemolysis arised from red blood cell membrane damage triggered by trace unreacted polymer monomers. To address this, we washed the SMP samples with PBS to remove residual unreacted monomers and repeated the hemolysis tests. As shown in Figure 9b, the results indicated that the hemolysis rates significantly decreased after washing with PBS, with almost no hemolysis observed. This confirmed that the samples exhibit excellent blood compatibility. Comparison of the two sets of hemolysis

experiments clearly showed that residual monomers in the samples were the primary cause of red blood cell membrane damage. We speculated that this effect may stem from residual amino groups in the D230 or PVK components that were not fully encapsulated within the epoxy crosslinked network. These groups may form hydrogen bonds with the red blood cell surface, leading to membrane rupture and triggering hemolysis.

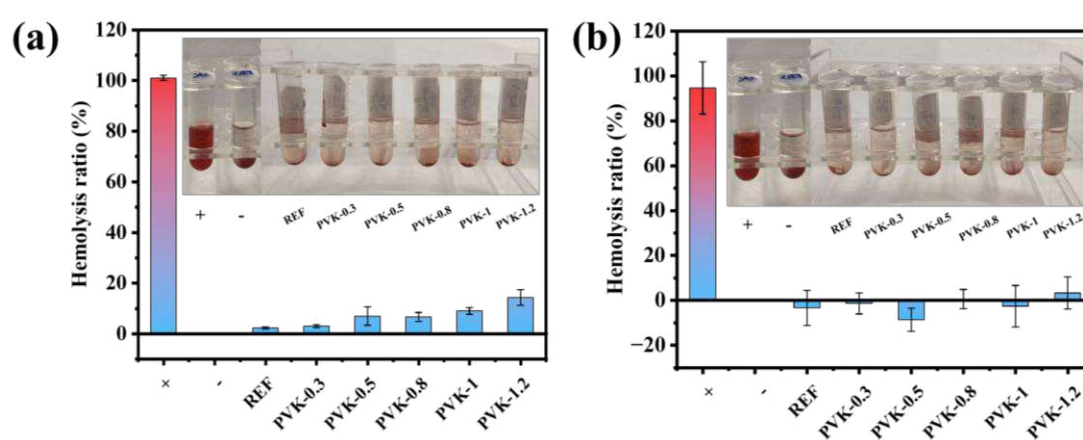


Figure 9 (a) Blood compatibility of unpurified samples from various groups. (b) Blood compatibility of each group of samples after washing with PBS. “+” and “-” represent positive and negative control respectively. The data represent the mean $\pm$ SD (n=3).

3.7 Cytocompatibility properties of PVK/epoxy SMP Composites

Cytocompatibility constitutes another critical consideration for PVK/epoxy SMP when deployed as a biomedical material. Hence, we evaluated cell viability to assess the biological safety of the composite. Figure 10 showed the results of cell viability tests conducted using the MTT assay across various experimental groups. The CELL group served as the blank control, and its cell viability was normalized to 100%, representing the normal survival rate of cells without material exposure. The REF group showed the lowest cell activity at about 60%, indicating that this reference material significantly suppressed cellular activity. The cell viability of materials in the PVK-0.3

to PVK-1.2 series displayed a general upward trend, increasing steadily from around 70% in PVK-0.3 to nearly 100% in PVK-1.2, which was essentially comparable to the cell viability of the CELL group. The cell viability rates of both PVK-0.8 and PVK-1 exceed 85%, indicating good cell compatibility. PVK-1.2 demonstrated the best cell compatibility, with no significant negative impact on cell growth and survival. The results indicated that the biocompatibility of the PVK series materials improved with component regulation.

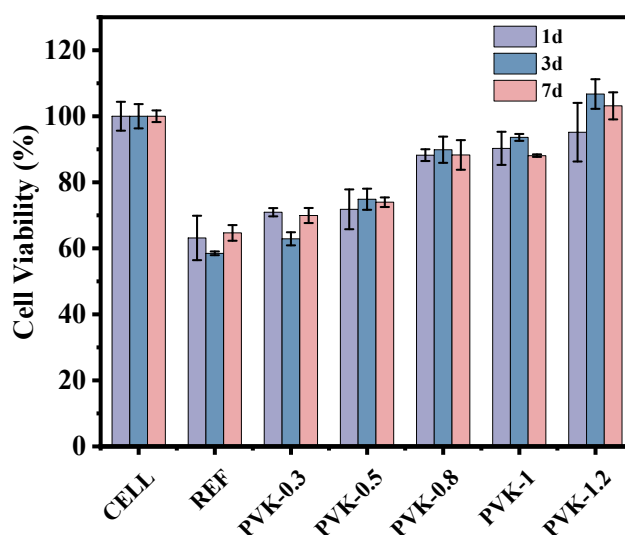


Figure 10 Cell viability of MSCs after treating with the growth media extracts of the SMPs. (Each sample group, from left to right, represents cell viability after 1 day, 3 days, and 7 days of culture.)

The cellular compatibility of SMP was further evaluated using a live/dead staining assay. The results were shown in Figure 11. The green fluorescence in the upper section indicated viable cells, while the red fluorescence in the lower section corresponded to dead cells. Figure 11a represented the control group without any sample doping. Figure 11b showed the treatment group with neat epoxy SMP extract, where two dead cells were visible. Figures 11c-g depicted groups treated with composites doped with varying contents of PVK. Cell viability remained relatively high across all samples. These findings confirmed that PVK-doped SMP exhibited excellent biocompatibility. This

provided experimental support for the practical application of this material in biomedical fields.

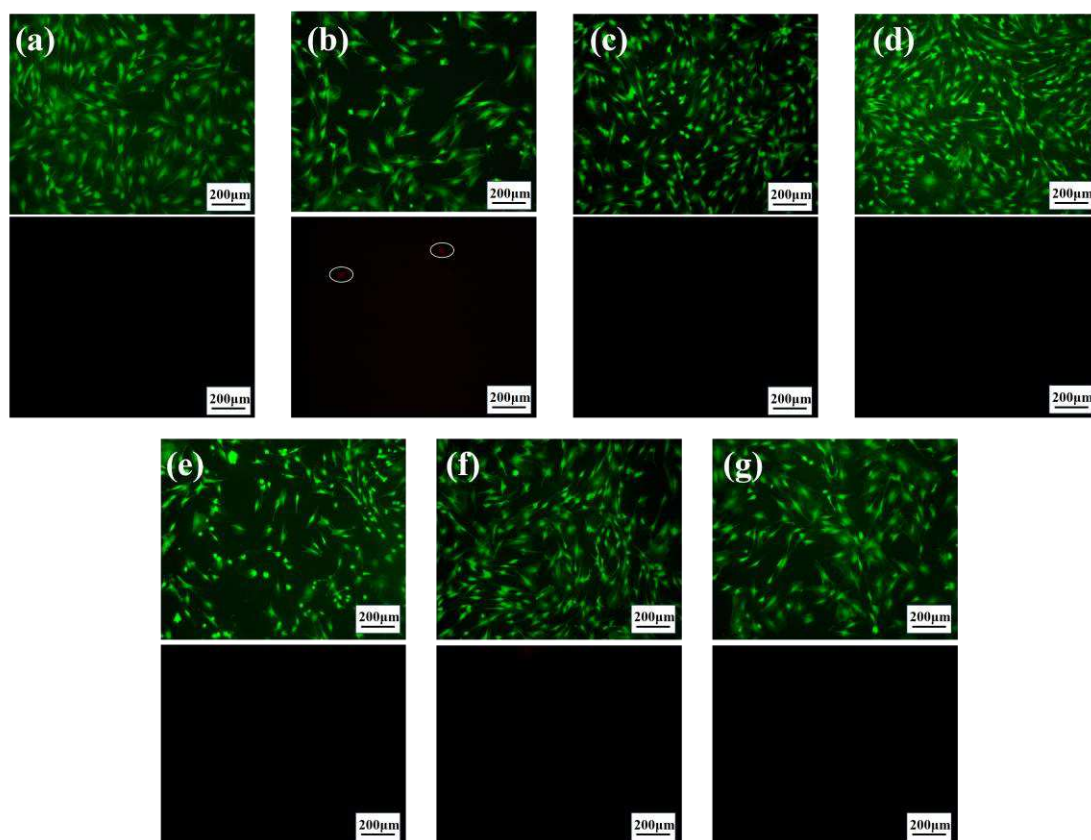


Figure 11 (a) Cells cultured in complete medium as the control group. And the live/dead fluorescent staining images of MSCs after being treated with the growth media extracts of the (b) REF, (c) PVK-0.3, (d) PVK-0.5, (e) PVK-0.8, (f) PVK-1, and (g) PVK-1.2 for 24h.

4. Conclusions

In conclusion, we developed a shape memory polymer system exhibiting excellent mechanical properties, reduced charge transfer resistance, desirable shape memory characteristics, and biocompatibility. This system primarily utilized D230 as a “bridge” to introduce the flexible NGDE into EPON826, thereby forming a cross-linked network. The study successfully integrated PVK into the epoxy-based shape memory polymer, resulting in a uniform composite film with excellent shape memory performance and volume stability. When the PVK content was optimized at a 0.5% content, the rigid

carbazole structure in PVK significantly enhanced the mechanical strength of the shape memory polymer without compromising the inherent shape memory properties of the matrix. Moreover, PVK-doped composites maintained lower charge transfer resistance than the reference sample. Additionally, PVK doping further improved the biocompatibility of the material. This work opens new avenues for the development of intelligent materials and their practical applications in biological settings, providing innovative technical solutions.

Declarations

Ethics approval and consent to participate

This study strictly complied with and implements international and national ethical requirements for biomedical research and was approved by the Medical Ethics Committee of Henan Polytechnic University.

Consent for publication

Not applicable.

Availability of data and materials

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

Competing interests

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.

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Authors' contributions

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Yue Yang: Investigation.

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Jiajie Yu: Investigation.

Binbin Wang: Investigation

Jianguo Liao: Investigation

Yijia Guan: Funding acquisition, Methodology, Investigation, Supervision.

Yanru Zhang: Methodology, Investigation, Project administration.

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