Shape memory poly (ether ether ketone)s with tunable chain stiffness, mechanical strength and high transition temperatures

Shuai Yang, Yang He and Jinsong Leng

Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin, P. R. China

ABSTRACT
Shape memory polymers, with intrinsic enhanced strength and high thermal stability, are highly demanded in aerospace, engineering manufacturing, and spatial structures. In this paper, we develop a series of thermoplastic shape memory poly(ether ether ketone)s (PEEKs) for the first time, achieving an excellent shape memory ability, high strength, and great thermal stability via a condensation polymerization. Through tuning the proportion of different bisphenol monomers, the flexibility of molecular main chains is adjusted, resulting in the regulation of transition temperature and mechanical performances. Synthesized PEEKs possess the tunable T$_g$ from 143.3°C to 178.6°C, the enhanced tensile strength from 48.4 to 65.1 MPa, and Young’s modulus from 0.45 to 1.8 GPa, in addition to the excellent heat-triggered shape memory effect, as indicated by high recovery ratio (94%–98.9%) and fixity ratio (over 99.5%). Furthermore, after incorporating the magnetocaloric Fe$_3$O$_4$ particles, the composites exhibit remotely noncontact magnetic-triggered shape memory behaviors (Fe$_3$O$_4$ content over 10 wt%). These synthesized T$_g$ tunable shape memory PEEKs and the composites have wide utilization potential in fields of engineering and aerospace structures, owing to the excellent mechanical properties, thermal stability, unique programmable deformation ability, and remote actuation.

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CONTACT Yang He yang.he@hit.edu.cn; Jinsong Leng lengjs@hit.edu.cn
Center for Composite Materials and Structures, Harbin Institute of Technology, Harbin 150080, P. R. China

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1. Introduction

Stimuli-responsive materials, which could make a corresponding response while receiving an external stimuli, possess wide utilizations in fields of flexible sensors, electronic devices, biomedical stands, aerospace structures, etc. [1,2]. Shape memory polymers (SMPs), as a kind of stimuli-responsive materials, are capable of memorizing the temporary shape after deformation and recovering the original shape upon the external stimuli, including heat [3], electric [4], magnetic [5], light [6], microwave [7], solvent [8], etc. Due to the unique deformable ability, SMPs have become the research hotspot, which are highly desirable for actuators, soft robots, biomedical stands, and aerospace structures [9–11]. Commonly, SMP systems contain the two parts of rigid regions and flexible regions in their internal structures, which are responsible for the operation of shape memory effect (SME). Rigid regions, including cross-linking nets, crystalline phases, and chain entanglements, are able to keep a stable permanent shape and recover to it. Flexible regions, including flexible chains and amorphous phases, mainly contribute to the deformation and maintaining of the temporary shape. When the temperature reaches the transition point, the SMPs deform from the permanent shape to the temporary shape by the external force, named as the shape fixity process. Afterward, while the temperature increases up to the transition point again, the SMPs of temporary shape could spontaneously recover to the permanent shape, and the shape recovery process is finished.

For thermoplastic SMPs, shape fixity and recovery ability are mostly related to the freezing and melting of the molecular chain segments, which concerns with the difference between the external temperature and the transition temperature of SMPs [12–15]. At present, the commonly used thermoplastic SMPs mainly contain shape memory poly(lactic acid) [16–18], shape memory poly(vinyl alcohol) [19,20], shape memory polyurethane [21–23], and so on, where the shape recovery ability originates from the flexible chains. Nevertheless, due to the flexible chain segments and low transition temperature, these kinds of SMPs exhibited poor mechanical performances and thermal stability, in addition to the low recovery force [24–26]. These intrinsic performance defects largely restrict the applications of thermoplastic SMPs in engineering structures, which require the enhanced mechanical performances and stability, in addition to the low recovery force [27,28]. Thus, it would be a great attempt to understand how to impart the enhanced mechanical performances and stability into thermoplastic SMPs for achieving the synthetic effect of flexible deformation ability and rigid stability. Poly(ether ether ketone) (PEEK) material, as a kind of engineering thermoplastics, exhibited the excellent mechanical properties, thermal stability, and resistance [29,30]. Besides, the great processability imparts a plenty of application patterns, such as films [31], plates [32], and 3D printing structures [33–35]. The excellent performances and diverse patterns endow PEEK with the wide utilization in fields of biomedical implants, engineering structures, and aerospace applications [36,37]. Nevertheless, at present, the research studies of shape memory PEEKs are focused on the investigation of shape memory properties of commercial PEEK or modified commercial PEEK [38–42]. How to endow PEEK materials with great SME
through designing molecular chains and conducting polymerizations has become meaningful and urgent, which could widely extend the utilization potential of PEEK materials.

In this paper, we put forward a facile method for the synthesis of PEEK with the excellent SME via a condensation polymerization for the first time. Besides, we tuned the flexibility of molecular chains via regulating the proportion of monomers, aiming to achieve the regulation of glass transition temperature ($T_g$) and mechanical performances. Through fabricating the alternating flexible and rigid main chains, these PEEKs exhibited the great shape memory behaviors. In addition, we integrated magnetic Fe$_3$O$_4$ particles into PEEK matrix for the fabrication of shape memory PEEK/Fe$_3$O$_4$ composites, which exhibited heat-triggered and exceptional remote magnetic-triggered shape memory behaviors.

2. Experimental section

The sections on Materials, Synthesis of shape memory PEEKs, Sample preparation, Characterization, and Shape memory test are described in detail in the Supporting Information.

3. Results and discussion

3.1. Structural and thermal properties

We synthesized various shape memory PEEKs via a condensation polymerization (Scheme 1) and signed those as P1, P2, P3, P4, and P5, corresponding to the proportion of methyl hydroquinone (MTHQ) and 4,4’-(9-fluorenylidene) diphenol (FNDP) of 1:0, 0.75:0.25, 0.5:0.5, 0.25:0.75, and 0:1, respectively.

$^1$H NMR analysis of synthesized PEEKs is shown in Figure 1a. The chemical shifts at 7.84, 7.06, and 6.99 ppm were concerned with the protons on benzene rings (a). The chemical shifts at 2.01–2.40 ppm were corresponded to the amino groups (b). For P2, as the integration of 4,4’-(9-fluorenylidene) diphenol, the chemical shifts at 7.24–7.44 ppm appeared, corresponding to the protons on fluorene groups (c). Besides, these chemical shifts became more significant with the increasing of 4,4’-(9-fluorenylidene) diphenol content, shown in P3, P4, and P5. For P5, the chemical shifts concerned with amino groups disappeared, due to the abandoning of methyl hydroquinone. FTIR spectra are shown in Figure 1b. The peaks at 3060 cm$^{-1}$ could be assigned to the fluorene groups. The characteristic peaks of methyl groups appeared at 2921 and 2850 cm$^{-1}$. The peaks at 1592 and 1228 cm$^{-1}$ were corresponded to the characteristic peaks of aryl carbonyl groups and aryl ether groups, respectively. According to the $^1$H NMR and FTIR spectra, we could conclude that the polymerization reaction has been regularly operated as expected. WAXD curves are shown in Figure 1c. Synthesized PEEKs exhibited a semi-crystalline characteristic, and the diffraction peaks were at $2\theta = 20.74^\circ$, 19.01$^\circ$, 19.48$^\circ$, 20.22$^\circ$, and
19.75°, corresponding to P1, P2, P3, P4, and P5, respectively. DSC curves of the synthesized PEEKs are shown in Figure 1d. For P1, as the binary copolymer, the $T_g$ was 143.3°C. With the increasing stiff 4,4’-(9-fluorenylidene) diphenol, the $T_g$ gradually increased, from 147.3°C to 157.1°C, 162.8°C, and 178.6°C, corresponding to P2, P3, P4, and P5, respectively. TGA curves are shown in Figure 1e. The weight loss at around 160–180°C was concerned with the internal nonvolatile solvent. The initial degradation temperature ($T_d$) of P1 was 434.4°C. Then, with the increasing

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**Scheme 1.** Synthetic pathway of shape memory PEEKs.

**Figure 1.** Characterization of various synthesized PEEKs (P1, P2, P3, P4, and P5): (a) $^1$H NMR spectra; (b) FTIR spectra; (c) WAXD curves; (d) DSC curves; and (e) TGA curves.
4,4’-(9-fluorenylidene) diphenol, the T, gradually decreased, from 448.1°C to 437.3°C, 419.7°C, and 414.6°C, corresponding to P2, P3, P4, and P5, respectively. While the temperature was increased up to 800°C, the residual mass ($\omega_m$) of PEEKs was 49.0%, 41.7%, 45.3%, 52.1%, and 56.6%, corresponding to P1, P2, P3, P4, and P5, respectively.

3.2. Successive infrared spectrum and solubility

We utilized P3 for instance and recorded the successive infrared spectrum during the reaction process, depicted in Figure 2a. With the operation of the polymerization reaction, the transmittance decreased first and subsequently remained relatively stable, as depicted in Figure 2b-e. While the temperature was increased to 120°C, all the monomers were dissolved in the solvent (TMSF). In Figure 2d, e, the decreasing ether bonds’ transmittance indicated the operation of polymerization reaction and formation of PEEK main chains.

The solubility of synthesized PEEKs in universal solvents is shown in Figure 3. In some polar solvents, including water, ethanol, methanol, and acetone, the synthesized PEEKs could not be dissolved. As for the nonpolar solvent, the synthesized PEEKs were readily soluble. As P2, P3, P4, and P5, they were soluble in DMAC, DMF, chloroform, THF, and NMP at room temperature and also soluble in DMSO while heating. Nevertheless, the solubility of P1 was relatively poor, which could be dissolved in such nonpolar solvent only while heating.

3.3. Mechanical performances

Figure 4 shows the static tensile test results of the prepared shape memory PEEK films. In Figure 4a, all the synthesized PEEK films exhibited brittle fracture, which was concerned with the intrinsic rigid molecular chains. In Figure 4b, the tensile strength of P1 was 48.4 MPa. After integrating 4,4’-(9-fluorenylidene) diphenol components, the tensile strength

![Figure 2](image-url) *Figure 2. (a) Successive infrared spectrum during the polymerization reaction of P3; the transmittance change at (b) 3598 cm$^{-1}$, (c) 1601 cm$^{-1}$, (d) 1295 cm$^{-1}$, and (e) 1107 cm$^{-1}$.***
increased to 51.4, 65.1, 58.2, and 56.1 MPa, corresponding to P2, P3, P4, and P5, respectively. The integration of stiff 4,4’-(9-fluorenylidene) diphenol components enhanced the molecular chains, improving the tensile strength. Nevertheless, with the increasing of stiff 4,4’-(9-fluorenylidene) diphenol components, the main chains became more rigid, resulting in the increasing brittleness of the PEEK material, which was adverse to the strength. Figure 4c exhibited an elongation at break, which of P1 was 5.1% and that of P2 was 11.4%. Compared with the binary copolymer of P1, the crystalline phase of P2 (terpolymer) was destructed, which was conducive to the toughness. As a result, the elongation at break increased. In addition, continuously increased the proportion of 4,4’-(9-fluorenylidene) diphenol components, the elongation at break decreased from 8.9% to 4.1% and 3.1%, corresponding to P3, P4, and P5, respectively. In Figure 4d, the Young’s modulus of P1 was 0.95 GPa. After integrating 4,4’-(9-fluorenylidene) diphenol components, the Young’s modulus decreased, to 0.45 and 0.73 GPa, corresponding to P2 and P3, respectively. The destruction of crystalline phase weakened the stiffness of polymers and decreased Young’s modulus. When the rigid 4,4’-(9-fluorenylidene) diphenol components continuously increased, the Young’s modulus increased, to 1.4 and 1.8 GPa, corresponding to P4 and P5, respectively.

**Figure 3.** Solubility of the synthesized PEEKs in diverse solvents (concentration: 10 wt%. +: soluble at room temperature; ±: soluble upon heating; −: insoluble. DMAc: N,N-dimethylacetamide; DMF: N, N-dimethylformamide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran; NMP: N-methyl-2-pyrrolidone).
DMA curves are shown in Figure 5. Figure 5a shows that the storage modulus of PEEKs increased gradually from P2 to P5, which was attributed to the increasing of stiff 4,4’-(9-fluorenylidene) diphenol components. In Figure 5b, with the increasing of 4,4’-(9-fluorenylidene) diphenol components, the $T_g$ exhibited an increasing trend, which was consistent with the testing results of DSC. However, the $T_g$ values were not the same, concerning with the different testing mechanisms.

**Figure 4.** Static tensile test results of the prepared PEEKs specimens: (a) stress–strain curves, (b) tensile strength, (c) elongation at break, and (d) Young’s modulus.

**Figure 5.** DMA curves of synthesized PEEKs: (a) storage modulus and loss modulus and (b) Tan δ.
3.4. Heat-triggered shape memory behaviors

Heat-triggered shape memory behaviors of the various synthesized PEEKs were characterized through the corresponding heat-triggered shape memory test, shown in Figure 6. The shape recovery ratio and fixity ratio of the synthesized PEEKs by ‘U’ shape testing are recorded in Figure 6a, b. In Figure 6a, with the increasing of 4,4’-(9-fluorenylidene) diphenol content, the flexibility of main chains weakened, which is adverse to the shape recovery ability. Thus, the recovery ratio gradually decreased, from 94.9% to 94.3%, 93.6%, 92.6%, and 91%, corresponding to P1, P2, P3, P4, and P5, respectively. Besides, these PEEKs exhibited the excellent shape fixity ability, which was reflected by the high fixity ratio (over 99%), shown in Figure 6b. Figure 6c shows the change trend of the recovery ratio of P3 during the whole shape memory process. The P3 sample could recover to the original shape within 25s, and the recovery ratio was up to 93.6%. Figure 6d shows the change of P3’s recovery ratio during the five round shape memory processes. After five times of consecutive shape recovery and refixation processes, the recovery ratio decreased from 93.6% to 92.8%, 92.7%, 92.4%, and 92.3%, respectively. Due to the rigid molecular chains of P3 and the poor movement ability, the shape memory behaviors might be slightly weakened during the round shape memory processes. The stable and high recovery ratio indicated the excellent reproducibility of shape memory.

![Figure 6](image-url)
behaviors. In addition, we used DMA to perform the stretchable shape memory cycles of P3, depicted in Figure S1. Initially, the shape recovery ratio was relatively low. Afterward, the recovery ratio was increased and relatively stable.

3.5. Structures and performances of P1/Fe₃O₄ composites

P1 was utilized as PEEK matrix, and magnetic Fe₃O₄ particles were integrated into P1 matrix to fabricate P1/Fe₃O₄ composites for the achievement of remotely magnetic-triggered shape memory behaviors and enhanced mechanical performances. Figure 7a shows FTIR spectra of synthesized P1 and P1/Fe₃O₄ composites. For P1, the peak at 2922 cm⁻¹ was attributed to the stretching vibration of phenol methyl groups. The aryl ether groups and aryl carbonyl groups in main chains were corresponded to the characteristic peaks at 1221 and 1593 cm⁻¹, respectively. After adding Fe₃O₄ particles, there

![Figure 7](image-url)

**Figure 7.** Characterization of prepared P1/Fe₃O₄ composites (Fe₃O₄ content of 0 wt%, 5 wt%, 10 wt%, 15 wt%, and 20 wt%): (a) FTIR spectra of P1 and 20 wt% Fe₃O₄/P1 composite; (b) WAXD curves; (c) 2D SAXS patterns of P1; (d) 1D SAXS curves; and (e) the long period as a function of temperature during the heating process (from 25°C to 130°C).
was not any change for peak positions, indicating that the integration of Fe₂O₄ particles into PEEK matrix was just the physical padding and blending procedure, and there was no occurrence of the cross-linking reaction between P1 and Fe₂O₄ fillers. Meanwhile, after the addition of Fe₂O₄ particles, the spectra transmittance decreased, which was concerned with the light absorption and hindrance of the dark-color Fe₂O₄ particles. WAXD curves of P1/Fe₂O₄ composites and Fe₂O₄ nanoparticles are shown in Figure 7b. Synthesized P1 exhibited semi-crystalline characteristic, and the diffraction peak was at 20.7°. After integrating Fe₂O₄ nanoparticles, the characteristic peaks of Fe₂O₄ (30.2°, 35.6°, 43.0°, 53.5°, 57.1°, and 62.7°) occurred in P1/Fe₂O₄ composites. Besides, with the increasing of Fe₂O₄ content, the intensity ratio of Fe₂O₄ to P1 in the curves of composites intended to increase. In addition, the integration of Fe₂O₄ nanoparticles might exert an effect on the intrinsic crystalline structures of P1. SAXS patterns of P1 during the heating process from 25°C to 130°C are shown in Figure 7c. Initially, the PEEK sample exhibited round scattered signals. When the temperature was increased to 105°C, scattering fringes occurred in the vertical direction. In addition, they became intense with the increasing of temperature. Nevertheless, when heating to 120°C, the scattered signals weakened, and several slight scattering fringes occurred in different directions. The state was retained with the increasing of temperature. In Figure 7d, with the increasing of temperature, the peak slightly shifted to the higher q value. Correspondingly, the long period decreased with the increasing of temperature, as shown in Figure 7e. During the phase transformation, the distance among the internal crystalline lamellae decreased, and the long period decreased.

Figure 8 shows static tensile test results of P1/Fe₂O₄ composites with different Fe₂O₄ content, in addition to the SAXS patterns during the tensile tests. Figure 8a shows the conventional stress–strain curves. The fracture mode of P1 and the composites was brittle fracture. Figure 8b shows the tensile strength. With the increasing of Fe₂O₄ content, the tensile strength increased gradually, from 50.3 MPa to 52.15, 58.57, and 68.57 MPa, corresponding to the Fe₂O₄ content of 0, 5, 10, and 15 wt%, respectively. When the Fe₂O₄ content was increased up to 20 wt%, the tensile strength decreased, of 59.65 MPa. The excess Fe₂O₄ particles might disperse badly or gather, detrimental to the mechanical performances. Similarly, the Young’s modulus of the composites increased from 0.91 GPa to 0.95, 1, and 1.42 GPa, corresponding to the Fe₂O₄ content of 0, 5, 10, and 15 wt%, respectively. While the Fe₂O₄ content was 20 wt%, the Young’s modulus decreased, to 1.33 GPa, as shown in Figure 8d. In Figure 8c, the elongation at break of the composite with 5 wt% Fe₂O₄ content was 5.82%, higher than that of P1. Then, with continuously increased Fe₂O₄ content, the elongation at break decreased gradually, from 5.82% to 5.8%, 5.05%, and 4.62%, corresponding to the Fe₂O₄ content of 5, 10, 15, and 20 wt%, respectively. Figure 8e shows the SAXS patterns during the tensile tests (horizontal tensile direction). It could be observed that during the stretching process, the horizontal scattered fringes occurred, which was concerned with the orientation of molecular chains and occurrence of vertical microstacks, in addition to the fact that the accumulation of microstacks resulted in the fracture of samples. The q max value and long period are shown in Figure 8f. During the stretching process, the q max value slightly decreased and the long period increased.
DSC curves of P1/Fe₃O₄ composites are shown in Figure 9a. The T_g of P1 was 143.3°C, which did not change a lot after the integration of Fe₃O₄. The T_g was 141.3°C, 142.3°C, 142.8°C, and 141.3°C, corresponding to the Fe₃O₄ content of 5, 10, 15, and 20 wt%, respectively. The relatively constant T_g indicated that the integration of Fe₃O₄ into P1 matrix was just physical blending. Figure 9b shows the TGA curves. The initial degradation temperature (T_d) of composites was 434.3°C to 422.4°C, 412.8°C, 425.4°C, and 431.8°C, corresponding to the Fe₃O₄ content of 0, 5, 10, 15, and 20 wt%, respectively. Meanwhile, the residual mass (ω_m) of composites at 800°C gradually increased from 49.0% to 52.3%, 53.1%, 60.0%, and 58.3%, corresponding to the Fe₃O₄ content of 0, 5, 10, 15, and 20 wt%, respectively. DMA curves of P1/Fe₃O₄ composites are shown in Figure 9c, d. In Figure 9c, after adding Fe₃O₄ particles, the storage modulus gradually increased. The highest storage modulus was of 10 wt% Fe₃O₄ content, and then, this decreased with the
increasing of Fe$_3$O$_4$. In Figure 9d, the T$_g$ of composites did not change a lot after the integration of Fe$_3$O$_4$, which was consistent with the results of DSC curves; nevertheless, the values were not the same, which could be attributed to the different measurement mechanisms.

3.6. Remotely magnetic-triggered shape memory behaviors

The magnetic-triggered shape memory behaviors of P1/Fe$_3$O$_4$ composites were investigated, shown in Figure 10. Figure 10a shows the whole shape recovery process of the composite with 15 wt% content of Fe$_3$O$_4$. The sample approximately recovered to the original shape within 45s, indicating the desirable magnetic-triggered shape memory ability. Figure 10b shows the thermal infrared images of the composite during the recovery process. The temperature gradually increased under the magnetic fields, and the shape recovery behaviors were triggered while the temperature reached up to T$_g$. The specimens were fabricated via the superposition of multiple films (four layers), avoiding the excessive heat dissipation. The surface temperature of specimens was relatively lower, and the internal temperature was higher, inducing the shape recovery behaviors. Figure 10c shows the shape recovery ratio. When the Fe$_3$O$_4$ content was 5 wt%, the recovery behaviors could not be triggered. With the increasing of Fe$_3$O$_4$ content, the shape recovery behaviors were triggered, and the recovery ratio gradually increased from 65.2% to 85.3% and 90.0%, corresponding to the Fe$_3$O$_4$ content of 10,
4. Conclusion

In this paper, we synthesized a series of shape memory PEEKs through a condensation polymerization and regulated the transition temperature and mechanical performances by tuning the proportion of MTHQ and FNDP monomers. The synthesized PEEKs exhibited the tunable $T_g$ from 143.3°C to 178.6°C, high thermal stability, and enhanced mechanical performances (tensile strength of 48.4–65.1 MPa and Young’s modulus of 0.45–1.8 GPa), indicating the excellent thermal and mechanical performances. Besides, synthesized PEEKs exhibited excellent heat-triggered SME, including high recovery ratio (91%–94.9%), fixity ratio (over 99%), and reproducibility of shape memory behaviors (from 93.6% to 92.3% after five times of round shape memory processes). Additionally, we integrated magnetic Fe$_3$O$_4$ particles into P1 matrix to fabricate P1/Fe$_3$O$_4$ composites, which exhibited the enhanced mechanical performances. Due to the magnetocaloric...
effect of Fe$_3$O$_4$ particles, the composites exhibited remotely noncontact magnetic-triggered shape memory behaviors (Fe$_3$O$_4$ content over 10 wt%). With the increasing of Fe$_3$O$_4$ content, the recovery ratio gradually increased from 65.2% to 85.3% and 90%, corresponding to the Fe$_3$O$_4$ content of 10, 15, and 20 wt%, respectively. These synthesized T$_g$ tunable shape memory PEEKs and PEEK/Fe$_3$O$_4$ composites have wide utilization potential in fields of engineering and aerospace structures, owing to the excellent mechanical properties, thermal stability, unique programmable deformation ability, and remote actuation.

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**ORCID**

Jinsong Leng [http://orcid.org/0000-0001-5098-9871](http://orcid.org/0000-0001-5098-9871)

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