

Shape-stabilized phase change materials with high phase change enthalpy based on synthetic comb-like poly(acrylonitrile-co-ethylene glycol) for thermal management

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Shape-stabilized poly(acrylonitrile-co-ethylene glycol) (PANEG) copolymer with comb-like structure was prepared via simple free-radical solution polymerization, where acrylic acid poly(ethylene glycol) methyl ether ester (MPEGA) and acrylonitrile (AN) were employed as monomers. Fourier transform infrared spectroscopy (FTIR), ^1H and ^{13}C nuclear magnetic resonance spectroscopy (^1H and ^{13}C NMR), wide-angle X-ray diffraction (WXAD) were used to characterize the chemical structure of resultant PANEG. In addition, the influences of MPEGA contents on energy storage performance, thermal reliability and thermal stability of PANEG materials were evaluated based on differential scanning calorimetry (DSC), polarizing optical microscopy (POM), thermal infrared imager and thermogravimetry analyzer (TG). The comb-like PANEG demonstrated a favorable temperature regulation performance and thermal reliability. With the increase of MPEGA contents, the enthalpy of PANEG increased, and when the content of MPEGA was 80 wt%, the phase change enthalpy of synthesized PANEG-80 reached to 106.70 J/g with a stable heat storage performance after 100 thermal cycling. Thermal infrared images and cooling curves revealed that synthetic PANEG could sustain a temperature in ranges of 22–31 °C for continuous 25 min, presenting excellent temperature regulation performance. Also, comb-like PANEG could be uniformly dissolved in dimethyl sulfoxide (DMSO), indicating that PANEG phase change fibers with potential applications in fields of intelligent thermoregulating textile and heat energy management could be obtained via one-step wet spinning.

phase change material, acrylonitrile, poly(ethylene glycol) derivative, thermal management

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1 Introduction

Phase change material (PCM) is a type of material with a special ability for phase changing by variation of the temperature of surrounding media, associated with heat release or storage [1–3]. PCM has a high application value in fields of heat storage thermoregulating fibers, intelligent thermostat textile, building insulation, solar energy storage and waste heat recovery [4–6]. However, conventional phase change materi-

als (such as inorganic and organic phase change materials) are generally under modification via encapsulation or chemical bonding instead of utilizing directly so as to achieve stability without leakage when in use [7,8]. In terms of encapsulation, adsorption in PCM with three-dimensional materials and package in PCM with microcapsules are most common means [9,10]. Feng *et al.* [11] prepared shape-stabilized graphene oxide aerogel (GOxA)/paraffin PCM by infiltrating GOxA with paraffin, where GOxA component provided good mechanical support for composite PCM via interfacial bonding and no melt leakage phenomenon appeared

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even if the temperature exceeded the melting point of paraffin. Zhang *et al.* [12] adopted copper foam to load phase change material and then analyzed the influences of foam on thermal conductivity of phase change media via three-dimensional mathematical model. Although foam composite could favorably absorb the phase change materials, the application in field of flexible materials was limited due to its intrinsic morphological structure. Microcapsule method was applied to immobilize the phase change materials in micropheres and then to disperse into the polymer matrix in order to load phase change materials into polymer fibers without leakage. Fang *et al.* [13] used sol-gel method to encapsulate the phase change medium-octadecane into silica microcapsules with the particle size of 500 nm to 2 μm , and its enthalpy could reach up to 226.26 J/g as there was no chemical reaction between silica and octadecane while its heat resistance temperature (initial degradation temperature) was only around 120 °C. Fang *et al.* [14] synthesized nanoencapsulated phase change material with a uniform distribution of 151.3 nm and a melting enthalpy of 83.38 J/g, where polystyrene and silica were used as shell and *n*-tetradecane served as core material. However, it was regretful that its degradation temperature was only 85 °C. Therefore, heat resistance was a main challenging issue existed in preparation of phase change materials via microcapsule method. Additionally, the size of microcapsule, the strength of capsule, the dispersibility of microcapsule in the polymer should be considered [15].

In aspect of chemical modification, functional macromonomers are usually used to synthesize phase change material with cross-linking or comb-like structure [16]. Shape-stabilized phase change materials can be directly obtained via chemical cross-linking process. Nevertheless, the resultant material has a poor plasticity and a difficult forming process under the impact of cross-linking structure [17,18]. Chen *et al.* [19] adopted 4,4'-diphenylmethane diisocyanate to synthesize solid-solid phase change materials (SSPCMs) with different cross-linking degrees where β -cyclodextrin and polyethylene glycol were used as rigid and flexible chain respectively. It was revealed that phase change enthalpy of SSPCM could reach to 111.60 J/g under a low crosslinking degree. Three-dimensional polymer network was also used to adjust the morphological stability of phase change materials so as to reduce the influences of chemical crosslinking on phase change enthalpy. Guo *et al.* [20,21] blended cross-linking poly(acrylonitrile-coitaconate) (P(AN-co-IA)) copolymer with PEG to prepare a composite phase change material with an enthalpy of 118.5 J/g. Tang *et al.* [22] dispersed paraffin into three-dimensional network material with cross-linking phase-change structure (CPCS) that was synthesized *in situ* by tris(4-isocyanatophenyl) methane (TTI) and PEG, and the enthalpy of obtained composite phase change material reached up to 210.6 J/g at a paraffin weight content of 74%. Compared to material

with cross-linking network structure, phase change material with comb-like molecular chain was more attractive. Shi *et al.* [23] prepared shape-stabilized poly(ethylene-*g*-maleic anhydride)-*g*-alkyl alcohol copolymer with comb-like structure via transesterification method, where poly(ethylene-*g*-maleic anhydride) (EMA) and *n*-alkyl alcohols ($n=14, 16, 18, 26$) were used as monomers. It was found that phase change enthalpy raised from 125.7 J/g to 146.2 J/g with the increase of length in side chains, and graphene oxide (GO) nanoplatelets also increased the heat resistance temperature of above mentioned materials obviously where the degradation temperature was improved by 77 °C. Moreover, comb-like phase change materials were considered to be more attractive in fields of fiber preparation due to its advantage of being able to melt or dissolve [24].

Herein, a series of comb-like poly(acrylonitrile-*co*-ethylene glycol) (PANEG) copolymers were prepared via free-radical solution polymerization where acrylonitrile (AN) was chosen as matrix and acrylic acid poly(ethylene glycol) methyl ether ester (MPEGA) as phase change media. As we all know, polyacrylonitrile (PAN) fiber was mainly synthesized from AN monomer with similar properties as wool. Based on different monomer ratios, the synthesized PANEG in this paper were expected to spun directly or after blending with PAN to improve the thermostat performances of PAN fiber. In this paper, the energy storage performance and thermal reliability of PANEG were synthetically evaluated by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and thermal infrared imager to investigate the relations between MPEGA contents and temperature regulation performance of PANEG, which was proper to fabricate phase change materials with high enthalpy via solution processing.

2 Experimental

2.1 Materials

Acrylonitrile (AR), azobisisobutyronitrile (AR), dimethyl sulfoxide (DMSO, AR) and ethanol (AR) were purchased from Sinopharm Group Chemical Reagent Co., Ltd. (China). Wherein the polymerization inhibitor was removed from acrylonitrile via atmospheric distillation, and azobisisobutyronitrile was placed in refrigerator after secondary recrystallization of purification treatment with ethanol. Polyethylene glycol methyl ether methacrylate ($M_n \approx 2000$, 50 wt% in H_2O) was purchased from SIGMA company (USA) and was untreated prior to use.

2.2 Preparation of comb-like poly(acrylonitrile-*co*-ethylene glycol) copolymers

As schematically shown in Figure 1, nitrogen was first injected to remove the air in the three-necked flask. Then the

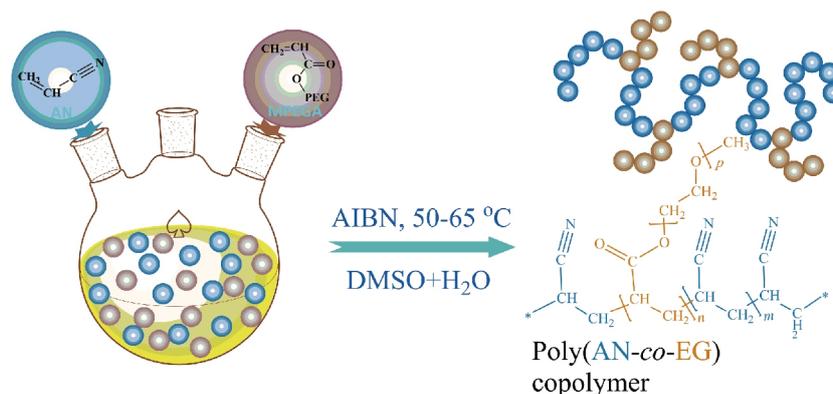


Figure 1 Synthetic route of PANEG phase change materials (color online).

solvent DMSO and H₂O, the reaction monomers of acrylonitrile and MPEGA, the initiator AIBN were added orderly into flask according to the composition in Table 1. After thorough mixture of reaction solution for 30 min, the reaction temperature was raised to 55 °C and a series of resultant PANEG-*n* copolymers were obtained after 5 h. In this paper, *n* represented the mass fraction of MPEGA in synthesized PANEG. Finally, the synthesized PANEG series were stored for further use after washed, filtered and dried.

2.3 Characterization

2.3.1 Structure characterization of PANEG copolymers

Fourier transform infrared spectroscopy (FTIR, Thermo Fisher, USA), nuclear magnetic resonance spectroscopy (¹³C and ¹H NMR, Bruke Avance 400, Switzerland), RIGAKU/Max-2550 PC wide-angle X-ray diffraction (WXAD, Rigaku, Japan) were used to characterize the chemical structure of PANEG copolymers. The attenuated total reflection (ATR) attachment with a resolution of 4 cm⁻¹ and a scanning frequency of 32 times was adapted during FTIR test. NMR spectroscopy used deuterated DMSO as solvent and tetramethylsiloxane (TMS) as calibration object with a sample concentration of 1.0 mg/mL. The Cu K α target (voltage: 40 kV, current: 40 mA) was utilized in wide-angle X-ray diffraction (WXRD). The spectral wavelength was 1.54056 Å, the scanning angle was 5°–60° and the scanning

step was 0.02°. All samples were placed in the laboratory for one week before testing.

2.3.2 Thermal and temperature regulation performance of PANEG copolymers

The melting crystalline enthalpy of synthesized PANEG copolymer was determined by DSC (Q20, TA company, USA). Firstly, about 10 mg of samples were heated from room temperature to 100 °C, after 2 min of isothermality to eliminate thermal history, the temperature was gradually cooled to -20 °C and then heated to 100 °C. The entire testing process was under nitrogen atmosphere. The melting rate and freezing rate were both 10 °C/min.

Polarizing optical microscopy (POM, BX51-P, OLYMPUS Company, Japan) was used to observe the crystal morphological changes of PANEG during isothermal crystallization under room temperature. At first, the temperature was heated to 100 °C at a melting rate of 10 °C/min, after 2 min of isothermality to eliminate thermal history, the temperature was cooled to the set temperature at a freezing rate of 10 °C/min and then the crystal morphology changes during the entire process were observed and recorded.

FLIR300 thermal infrared imager was adopted to collect the thermal imagery patterns and the heat release curves of samples. First, the test sample with round sheet shape (diameter: 25 mm, thickness: 3.5 mm) was placed in a thermal environment of 80 °C for 10 min, and then it was transferred quickly to an isothermal environment of 20 °C to collect images of samples via thermal infrared imager. Meanwhile, the insulation properties series of PANEG under 20 °C temperature were analyzed by transferring image changes into heat release curves with software.

2.3.3 Thermal reliability and stability of PANEG

DSC (Q20, TA Company, USA) was used to evaluate the thermal reliability of samples after several thermal cycles. Firstly, about 10 mg of samples were heated from room temperature to 80 °C, after 2 min of isothermality to eliminate thermal history, the temperature was cooled to -20 °C and then heated to 80 °C. The enthalpy changes after 100 heat cycles was evalu-

Table 1 Composition of various PANEG copolymers

| Samples | AN (mL) | MPEGA (mL) | DMSO (mL) | H ₂ O (mL) | AIBN (g) |
|--------------------|---------|------------|-----------|-----------------------|----------|
| PAN | 25.0 | 0 | 40 | 40.0 | 0.1 |
| PANEG-20 | 19.8 | 7.4 | 40 | 36.3 | 0.1 |
| PANEG-40 | 14.8 | 14.8 | 40 | 32.6 | 0.1 |
| PANEG-60 | 10.0 | 22.0 | 40 | 29.0 | 0.1 |
| PANEG-80 | 5.0 | 29.6 | 40 | 25.2 | 0.1 |
| PANEG-90 | 2.5 | 33.4 | 40 | 23.3 | 0.1 |
| PMEG ^{a)} | 0 | 37.0 | 40 | 21.8 | 0.1 |

a) PMEg is a homopolymer of polyethylene glycol methyl ether methacrylate (MPEGA).

ated. The entire characterization process was performed under nitrogen atmosphere. The melting rate and freezing rate were both 10 °C/min.

To characterize the thermal stability of PANEG copolymers, TG 209 F1 Iris thermogravimetric analyzer (TG, NETZSCH, Germany) was applied to analyze the heat-resistance curves of samples under nitrogen atmosphere with a heating rate of 10 °C/min in a temperature range of 30–600 °C.

3 Results and discussion

3.1 Chemical characterization of PANEG copolymers

FTIR spectra of synthesized PANEG copolymers with different monomer contents were shown in Figure 2. From FTIR of polyacrylonitrile (PAN) in Figure 2(a), it could be concluded that C–H stretching vibration absorption peaks in –CH₂ and –CH– were at 2937 cm⁻¹ and characteristic absorption peaks of –C≡N appeared at 2243 cm⁻¹ [25,26], while absorption peaks at 2937 and 2937 cm⁻¹ belonged to the variable angle vibration absorption peaks of C–H [27]. Based on spectrum of PMEG in Figure 2(f), the vibration absorption peak of methylene could be obviously observed at 2857 cm⁻¹. Peaks at 1723 and 1110 cm⁻¹ represented characteristic absorption peaks of C=O group and polyethylene glycol ether oxygen bond (–C–O–C–) respectively [28]. It could also be seen from spectra of PANEG in Figure 2(b–e) that all series of PANEG copolymers presented characteristic absorption peaks of C=O group at 1723 cm⁻¹. With the increase of MPEGA contents, the strength of characteristic absorption peak of cyano group (–C≡N) at 2243 cm⁻¹ and vibration absorption peak of –CH– at around 2937–2857 cm⁻¹ band were weakened while the vibration absorption peak of methylene group was strengthened, indicating that the expected PANEG copolymers were successfully synthesized via random copolymerization of acrylonitrile monomer and MPEGA monomer.

To support the results obtained from FTIR, ¹H NMR and

¹³C NMR were further used to characterize the molecular chain structure of synthesized PANEG. ¹H NMR and ¹³C NMR spectra of PAN, PMEG and PANEG were shown in Figure 3(A, B). From Figure 3(A), the chemical shift peaks of methylene hydrogen atoms and tertiary hydrogen in PAN main chain appeared at δ=2.0–2.2 ppm and δ=3.05–3.25 ppm respectively, while the absorption peak of deuterated DMSO solvent was at δ=2.5 ppm and among deuterated solvent, the characteristic absorption peak of H in H₂O appeared at δ=3.3 ppm. Compared with spectra of PAN, PMEG and PANEG, the synthesized PANEG contained both PAN and PMEG segments, and an obvious chemical shift peak of methylene group in PMEG segment appeared at δ=3.51 ppm. Similarly, in ¹³C NMR spectra of Figure 3(B), the chemical shift peaks of cyano carbon atom, methylene carbon atom and tertiary hydrogen atom of PAN component in PANEG appeared at δ 120, 33.3 and 27.8 ppm respectively [29]. The chemical shift peaks of methylene carbon atom and methyl carbon atom of PMEG component were at δ 70.4 and 58.6 ppm respectively. Therefore, the NMR results

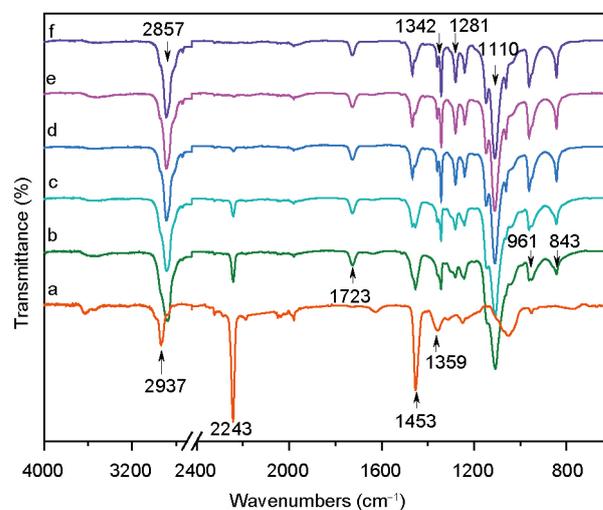


Figure 2 FTIR of PAN and series of PANEG. (a) PAN; (b) PANEG-20; (c) PANEG-40; (d) PANEG-60; (e) PANEG-80; (f) PMEG (color online).

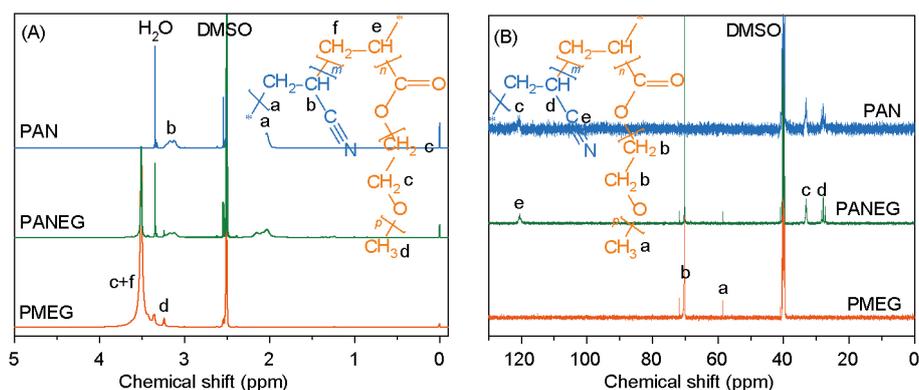


Figure 3 ¹H NMR (A) and ¹³C NMR (B) of PAN, PANEG and PMEG (color online).

favorably confirmed that MPEGA was successfully introduced into monomer AN polymerization system and PANEG materials were synthesized.

WXRd could not only analyze the composition of copolymer material, but could also reflect the crystalline structure of polymer material. WXRd spectra of PAN and series of PANEG were shown in Figure 4. It could be observed that when PAN content was less than 40 wt%, two obvious and sharp diffraction peaks at 19.0° and 23.2° belonging to (120) and (032) crystal faces of polyethylene glycol (PEG) both existed in the synthesized PMEG and PANEG copolymers. The results indicated that on the one hand the synthesized PANEG showed good crystallization abilities, and on the other hand, the chemical structure composition of synthesized PANEG was verified with the support of FTIR and NMR. With the decrease of MPEGA contents, it could be seen from curves of PANEG-40 and PANEG-20 that the peak intensity of (120) and (032) crystal faces in PANEG decreased and half width of the peaks increased. This was mainly due to the limitations of comb-like chemical structure in PEG molecular chain segment which resulted in a decreased crystalline ability of PEG molecular chain and a smaller crystalline microdomain [30]. It was then indicated that the crystallization behavior of materials could be better adjusted by controlling the ratio of monomer acrylonitrile and MPEGA.

3.2 Thermoregulatory behaviors of PANEG

DSC curves of PAN, PEG2000 and PANEG copolymers were shown in Figure 5. The thermal properties of PANEG phase change materials could be directly evaluated according to the changes in melting crystallization enthalpy. It could be observed from Figure 5(a) that the initial and the peak melting crystallization temperatures of synthesized PMEG homopolymer were 29.10 and 17.60 °C respectively with a melting crystallization enthalpy of 117.70 J/g. The enthalpy

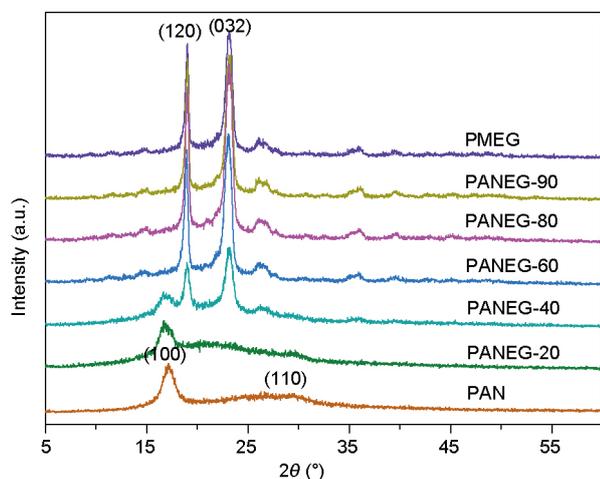


Figure 4 WXRd spectra of PAN and series of PANEG (color online).

and the crystallization temperature of PMEG were obviously lower than those of neat PEG2000 (Figure 5(h)). It was because that the comb-like molecular chain structure of PMEG restricted the movement of PEG branches, lowering its enthalpy and crystallization temperature [31]. The neat PAN copolymer in Figure 5(g) showed no melting and crystalline peaks. Compared with homopolymers of PMEG and PAN, it could be observed from DSC curves of PANEG copolymers in Figure 5 (b–f) that with the increase of acrylonitrile monomer contents, the crystallization enthalpy decreased and the temperature of melting crystallization peak shifted to a lower temperature. This was mainly resulted from no obvious phase change in -20 – 100 °C and no contribution of neat PAN molecular chain during phase change process. Also, a small content of PAN component in PANEG molecular chain could ease the limitations of branching points in comb-like molecular chains on the crystallization abilities of PEG segments which could then facilitate the crystallization of copolymers. This acceleration effect of PAN components on the crystallization of PANEG copolymers was weak, so the melting crystallization enthalpy decreased slightly with the increase of PAN contents. In addition, the PAN segment in PANEG molecular chain belonged to a kind of rigid segment and the crystallization abilities of PEG component were limited via the chemical bond of molecular chain, leading to the melting crystallization peak in PANEG shifted to a lower temperature. Interestingly, when the content of PAN was less than 40 wt%, PANEG could maintain a crystallization heat release at 2–24 °C with a crystallization enthalpy of 98.20–117.70 J/g, which resulted in a more suitable phase change temperature range and a greater thermoregulating ability compared with phase change material with cross-linking structure [21,32]. Isothermal polarizing optical microscopy (POM) images in Figure 6 and Figure S1 (Supporting Information online) showed the crystalline abilities of series of PANEG copolymers when the PAN content was below 40 wt%. From Figure 6 and Figure S1, it could be concluded that the nucleation quantity of PANEG increased and the spherical size decreased when PAN content increased. Based on DSC analysis, it was indicated that comb-like molecular chain and rigid PAN unit had a restrict effect on the crystalline behavior of PEG molecular chain, and also the crystalline enthalpy from DSC decreased with the increase of PAN contents. Therefore, the enhanced effect of nucleation quantity on crystallization was obviously weaker than the restrict effect of rigid groups and comb-like structure, leading to a decrease in the total crystalline ability of PANEG copolymer which was consistent with DSC analysis in Figure 5.

In order to intuitively illustrate the insulation effect of synthesized phase change materials, Figure 7 presented the infrared insulation imaging patterns and the heat release curves of PAN and series of PANEG. It could be seen from

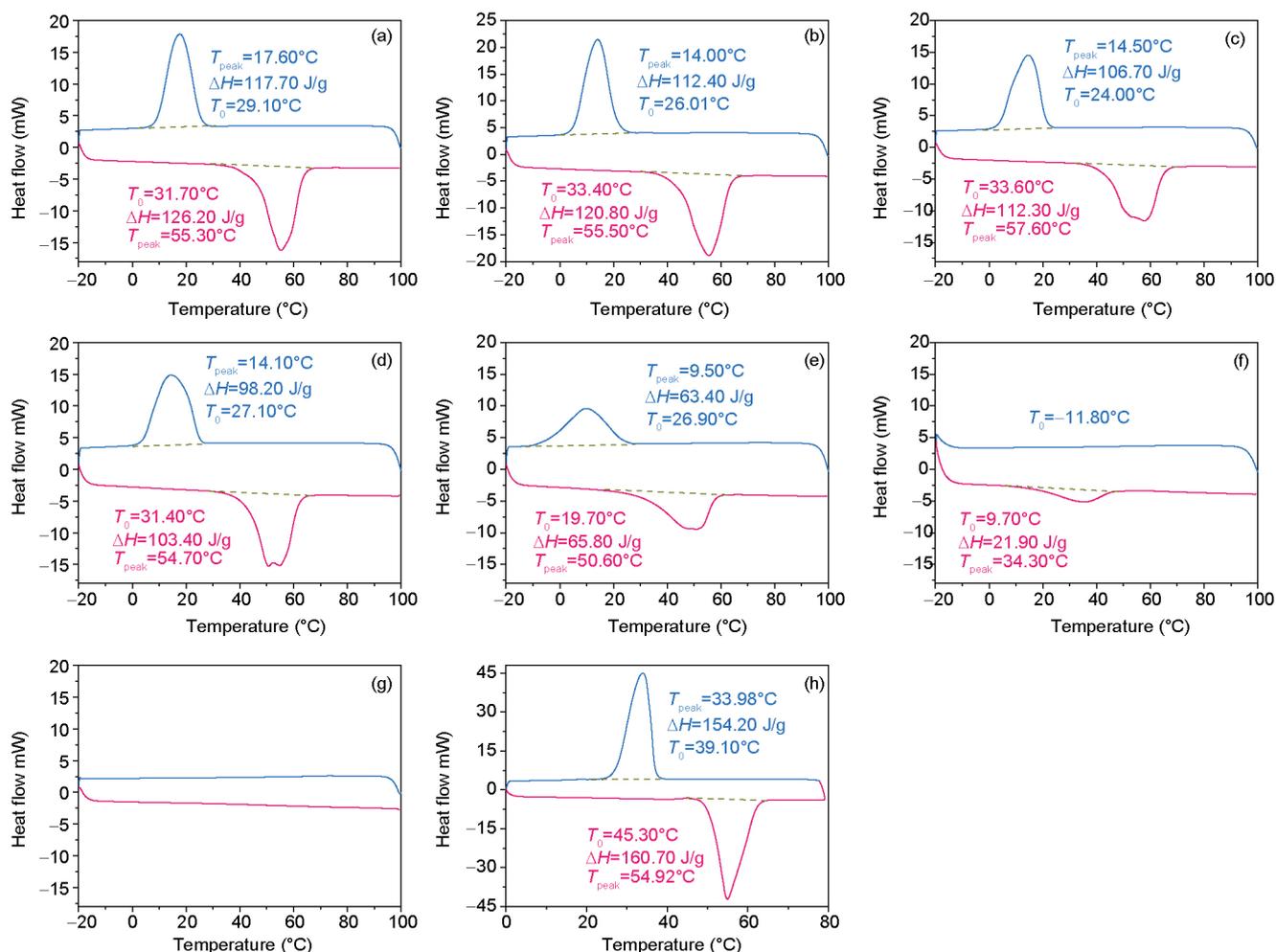


Figure 5 DSC curves of PAN and series of PANEG. (a) PMEG; (b) PANEG-90; (c) PANEG-80; (d) PANEG-60; (e) PANEG-40; (f) PANEG-20; (g) PAN; (h) PEG2000 (color online).

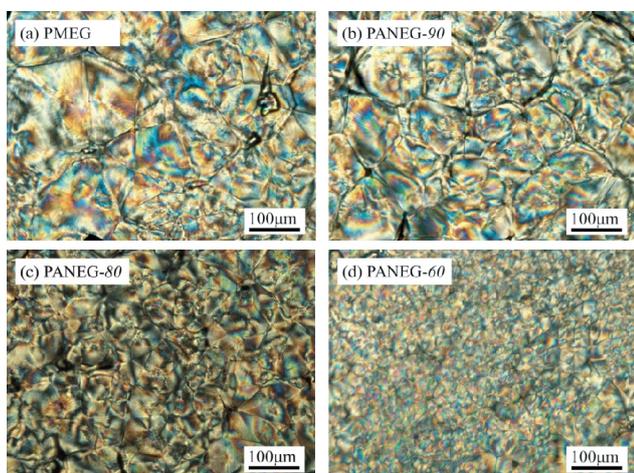


Figure 6 POM images of series of PANEG at 15 °C (color online).

Figure 7 that PMEG, PANEG-90, PANEG-80 and PANEG-60 samples always maintained good insulation effect when the sample was transferred rapidly from constant temperature of 80 °C to 20 °C. Based on heat release curves in left

Figure 7, PANEG proved to obtain the best insulation effect which showed the insulation platform starting at 30.4 °C with an insulation time of more than 27 min. In contrast, neat PAN homopolymer showed almost no insulation effect. For synthesized PANEG copolymers, PANEG-60 showed an insulation platform at 28.5–29.6 °C for 25 min compared to that of neat PAN when content of PAN was less than 40 wt%. These results were in agreement with DSC analysis. In addition, when content of PAN was more than 40 wt%, the synthesized PANEG showed an existing and a relatively low insulation effect compared to that of PAN.

3.3 Thermal reliability and stability of PANEG

The thermal reliability and thermal stability were two main indicators to evaluate phase change materials. In order to illustrate the thermal reliability of PANEG, thermal performance indicators of samples under simulated circulation condition were firstly tested. Taking PANEG-80 for example, as shown in **Figure 8**, the initial crystallization temperature, the crystallization peak temperature and the crystallization

enthalpy of PANEG-80 sample under 100 endothermic and exothermic cycling were barely changed (Table S1, Supporting Information online), indicating that PANEG-80 had a good thermal reliability. According to above data, it could be predicted that PANEG phase change materials had a great potential application in fields of textile fibers (Figure S2).

The TG and DTG curves of PAN and series of PANEG copolymers under nitrogen atmosphere were exhibited in Figure 9. The corresponding thermogravimetric parameters such as the initial degradation temperature (T_0), the 5% weight loss temperature ($T_{5\%}$), the maximum weight loss temperature (T_{max}) and the complete decomposition temperature (T_f) were listed in Table 2. It could be found from Table 2 and Figure 9 that T_0 of PAN was 273.20 °C and T_{max}

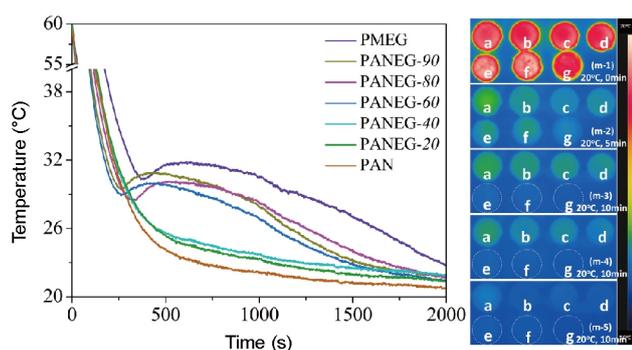


Figure 7 Heat release curves and infrared imaging photos of PAN and series of PANEG at constant temperature of 20 °C. (a) PMEG; (b) PANEG-90; (c) PANEG-80; (d) PANEG-60; (e) PANEG-40; (f) PANEG-20; (g) PAN (color online).

was 281.95 °C. It was worth noting that the heat resistance increased after PMEG unit was introduced into PAN molecular chain, especially when the content of MPEGA was 20 wt%–40 wt%, its initial degradation temperature (335.80–336.81 °C) and maximum degradation temperature (403.78–406.34 °C) were both higher than that of PAN and PMEG homopolymer. Therefore, it was indicated that the synthesized PANEG had a good thermal stability and its initial degradation temperature could be increased by 65 °C from 273.20 °C of PAN to 336.81 °C of PANEG-60 [33–35].

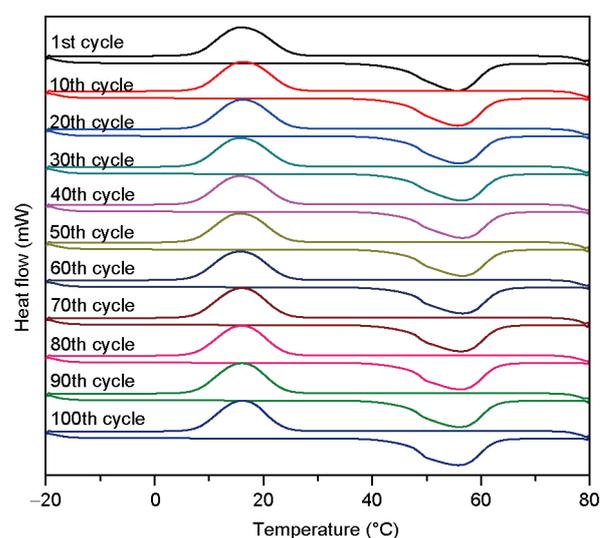


Figure 8 DSC curves of PANEG-80 under heat cycling (color online).

Table 2 The parameters of thermal stability of PAN and PANEG copolymers

| Samples | T_0 (°C) | $T_{5\%}$ (°C) | T_{max-1} (°C) | T_{max-2} (°C) | T_f (°C) |
|----------|------------|----------------|------------------|------------------|------------|
| PMEG | 288.22 | 324.73 | – | 394.73 | 426.73 |
| PANEG-80 | 335.80 | 358.30 | – | 403.78 | 436.30 |
| PANEG-60 | 336.81 | 359.31 | – | 406.34 | 444.81 |
| PANEG-40 | 301.34 | 312.34 | 313.34 | 415.34 | 452.84 |
| PANEG-20 | 289.40 | 296.05 | 298.35 | 414.46 | 502.40 |
| PAN | 273.20 | 278.07 | 281.95 | – | 592.40 |

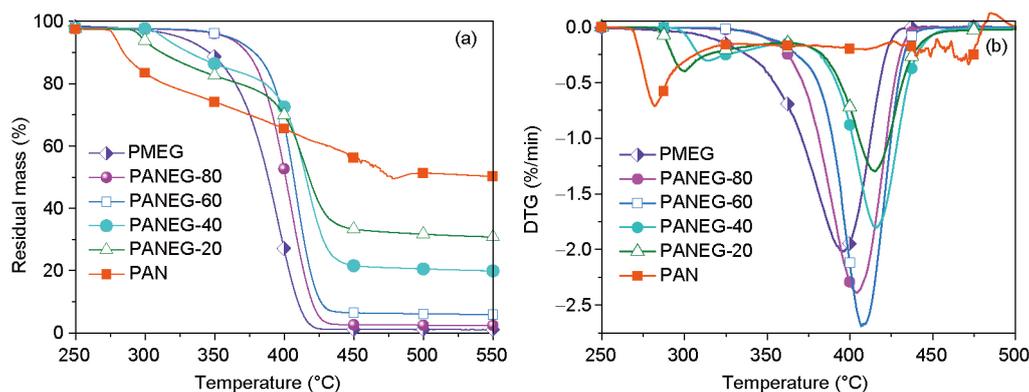


Figure 9 The TG (a) and DTG (b) curves of PAN and series of PANEG (color online).

4 Conclusions

In this paper, a series of shape-stabilized poly(acrylonitrile-co-ethylene glycol) (PANEG) copolymers with comb-like structure were successfully prepared. Interestingly, when the content of acrylonitrile monomer was less than 40 wt%, PANEG copolymers could achieve the crystallization exotherm at 2–24 °C with a phase change enthalpy of 98.20–117.70 J/g which had a more suitable phase change thermoregulating temperature and a higher phase change enthalpy compared to that of phase change materials with cross-linking structure. PAN showed almost no insulation effect while PANEG-90, PANEG-80 and PANEG-60 all presented a temperature insulation platform at 28.5–29.6 °C and a insulation time of 25 min, demonstrating an excellent temperature regulation performance. The synthesized PANEG copolymers not only had an excellent insulation property, but also presented a good thermal reliability. The initial crystallization temperature, the crystallization peak temperature and the crystallization enthalpy of PANEG-80 sample under 15 endothermic and exothermic cycles were barely changed. In addition, the heat resistance of PANEG was enhanced significantly, and when the contents of MPEGAs was 20 wt%–40 wt%, its initial degradation temperature could be increased by 65 °C from 273.20 °C of PAN to 336.81 °C of PANEG-60.

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Conflict of interest The authors declare that they have no conflict of interest.

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