Supporting information

Dual Heating Mode Fluffy Phase Change Fibers for Personal Thermal Management

Chengwei Xu[1,3 *], Xiaojie Shen[1], Yuan Yao[1], Lu Liu[2], Haotian Qi[1], Feng Wang[1], Lirong Li[1, *]

[1] College of Electrical, Energy and Power Engineering, Yangzhou University, Yangzhou, 225127, China

[2] State Key Laboratory of Disaster Prevention & Mitigtion of Explosion & Impact, Army Engineering University of PLA, Nanjing 210007, China

[3] School of Materials Science and Engineering, Jiangsu University, Zhenjiang, 212013, China

Corresponding author Email: xu_cw@yzu.edu.cn (C.W. Xu); llr_320@163.com (L.R. Li).

Note S1. Materials and Methods

Materials

Polyethylene glycol (PEG, Mn=1000) was purchased from Shanghai Meryer Chemical Technology Co., Ltd., China. polystyrene was purchased from Alfa Aesar Chemical Co., Ltd., China. polyurethane (P4394) was purchased from Huntsman Co., Ltd., China. N, N-dimethylformamide (DMF, 99.5%) was obtained from Energy Chemical Co., Ltd., China. Trimethylolpropane tris (2-methyl-1-aziridine propionate) (TTMA) was purchased from Aladdin chemical Co., Ltd., China. Hydrazine hydrate ($N_2H_4 \cdot H_2O$, 85%) and copper acetate monohydrate ($Cu\text{-}(CH_3COO)_2 \cdot H_2O$, 99%) were supplied by Sinopharm Chemical Reagents Co., Ltd., China.

Preparation of the FPCW

First, PS and PU were dissolved in DMF at a mass ratio of 4:2 to obtain a precursor shell solution at a concentration of 20 wt% by magnetic stirring for 10 h at room temperature. Then TTMA was mixed into the PS/PU precursor solution at a concentration of 20 wt% relative to the total polymer weight and stirred for 2 h. Similarly, PEG was dissolved in DMF and stirred continuously for 6 h to prepare a core solution at a concentration of 20 wt%. The injection rate of the shell and core solutions was 3 ml/h, the supply voltage was 25 kV, the speed of the reciprocating platform was 300 cm/min, the rotating speed of the cylinder collector was 17 rpm, and the distance from the spinneret to the cylinder was 18 cm. The relative humidity was controlled at 80%±5% during the spinning process. When finished, the fiber wadding was peeled off from cylinder collector and dried at 20°C for 1 hour to remove the residual solvent. Then, the as-prepared the fiber wadding was heated at 60°C for 1 hour to obtain FPCW.

Preparation of the Cu-FPCW

At room temperature, 0.8 g of copper acetate monohydrate was dissolved in 40 mL of distilled water under magnetic stirring. Subsequently, 1.5 mL of hydrazine hydrate was added dropwise to the copper acetate solution to obtain uniformly dispersed nano-copper particles. Afterward, the as-prepared FPCW was immersed in the mixed solution for 24 h, and then repeatedly rinsed with distilled water to completely remove the reducing agent. Finally, the sample was dried in a vacuum oven at 60°C to obtain Cu-FPCW.

Characterizations

The surface morphology of the samples were observed by a scanning electron microscope (S-4800Ⅱ, Hitachi, Japan). The TEM images of samples were obtained by a transmission electron microscopy (Tecnai 12, Philips, Netherlands). Surface functional groups was performed by Fourier transformed infrared spectro-photometer (FTIR, iS20, Thermo Scientific Nicolet, USA) in the range of 400-4000cm-1. The mechanical properties were tested by a dynamic thermomechanical analyzer (DMA-Q800, TA, USA). The sample has a width of 5.5 mm, a length of 7 mm, a thickness of 1 mm, a strain rate of 0.05 N/min, and a preload force of 0.1 N. The compression test was measured at a rate of 0.5 %/min. A contact angle goniometer (JC2000D, China) was used to test the hydrophilicity of the sample. A FT-IR spectrometer (iS50, Thermo Scientific Nicolet, USA) equipped with a diffuse integrating sphere was used to measure the IR reflectance (R) and transmittance (T) of the sample. The phase change enthalpies of samples were investigated by a differential scanning calorimeter (DSC8500, PerkinElmer, USA). The porosity of FPCW was defined as:

$$Porosity = \frac{\rho_0 - \rho_1}{\rho_0} \quad (1)$$

Where, ρ_0 is the density of polymer; mg/cm^3 and ρ_1 is the density of wadding, mg/cm^3.

Thermal measurements

The infrared images of samples were taken with an infrared camera (X160A, Yoseen Infrared, China) after irradiating by IR lamp. The cycle tests were conducted by a thermostatic oven. The heating and cooling were set at 10 °C/min and the sample was kept at 60 °C for 10 min for PEG melting completely. The heated and cooled process were conducted consecutively 100 times. Different supply voltages were supplied by a transformer (MS-3010DS, China) to conduct electric heating test.

Other tests

Water vapor transmission rate was measured by the wet cup method. Briefly, a test cups (YM-11) were filled with 34 ml distilled water and sealed with samples. The sealed cups were then placed in an environment with a temperature of 38%±2 °C and a relative humidity of 50%±2%. The cups were weighed every 12 h. The water vapor transmission (WVT, g/cm^2) of samples is calculated by the following:

$$WVT = \frac{\Delta m}{A} \quad (2)$$

where, Δm is the reductions in mass of distilled water; A is the mouth area of cup.

Approximately 100 mg of FPCW and Cu-FPCW (both containing 50 wt % PEG) were placed on a 60 °C hot-stage. A piece of quantitative filter paper was positioned beneath each specimen. After 100 melt-freeze cycles, both the specimens and the filter papers were weighed. In addition, the same specimens were subjected to 100 compression-recovery cycles (described in Fig. 2G) to simulate wear conditions, followed by a second weighing of the specimens and filter papers. A Cu-FPCW sample was immersed in a beaker filled with 25 °C water and agitated with a magnetic stirrer. Each washing cycle lasted 20 min and was repeated 20 times.

Note S2. Mie scattering calculation model

According to Mie scattering theory, assuming that the direction of radiant heat flow is perpendicular to the fiber layer, the spectral extinction coefficient Q_{ext} of infinitely fibers can be calculated according to the following formula[1]:

$$Q_{ext} = \frac{2}{\alpha^2}\sum_{n=1}^{\infty}(2n+1)\operatorname{Re}(a_n + b_n) \tag{3}$$

where, α is the scale parameter; a_n and b_n are an and bn are functions related to Bessel functions, which are calculated as follows:

$$a_n = \frac{\psi_n(\alpha)\psi_n^{'}(m\alpha) - m\psi_n^{'}(\alpha)\psi_n(m\alpha)}{\xi_n(\alpha)\psi_n^{'}(m\alpha) - m\xi_n^{'}(\alpha)\psi_n(m\alpha)} \tag{4}$$

$$b_n = \frac{m\psi_n(\alpha)\psi_n^{'}(m\alpha) - \psi_n^{'}(\alpha)\psi_n(m\alpha)}{m\xi_n(\alpha)\psi_n^{'}(m\alpha) - \xi_n^{'}(\alpha)\psi_n(m\alpha)} \tag{5}$$

where, ψ_n and is the complex high-order Bessel function of the first kind and ξ_n is the Hankel function of the first kind; m is complex refractive index. The Rosseland extinction coefficient β_λ and average extinction coefficient β_A:

$$\beta_\lambda = \frac{4Q_{ext}a}{\pi d} \tag{6}$$

$$\beta_A = \left(\int_3^{15}\frac{E_{b\lambda}}{\beta_\lambda E_b}d\lambda\right)^{-1} \tag{7}$$

where, a is the volume fraction of the fiber, %; d is the fiber diameter, m; $E_{b\lambda}$ is the spectral radiation, W/m^3; E_b is the blackbody radiation, W/m^2.

Radiative thermal conductivity K_r of samples is defined as [2]:

$$K_r = \frac{16\sigma T^3}{3\beta_a} \tag{8}$$

where, is the Stefan-Boltzmann constant, $W/(m^2 \cdot K^4)$; T is the temperature of human skin, K.

Supporting Figures

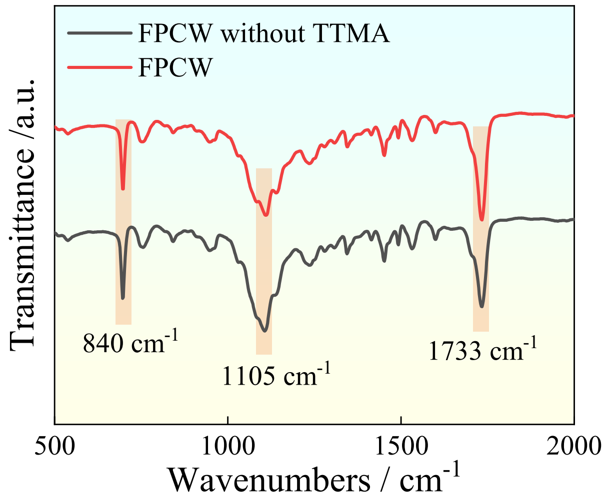

Fig. S1 FTIR spectra of the FPCW and FPCW without TTMA.

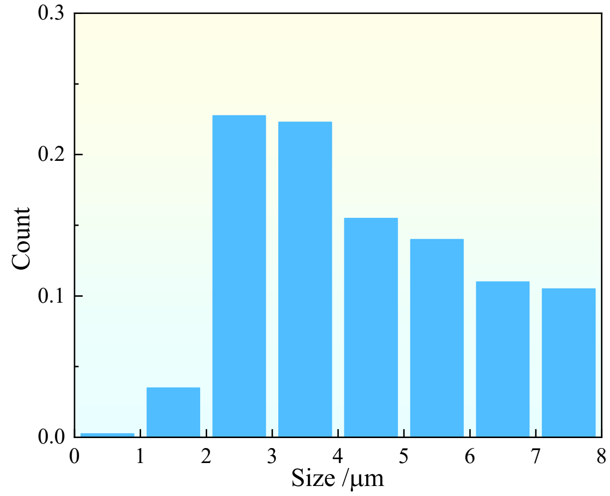

Fig. S2 Fiber diameter distribution of FPCW.

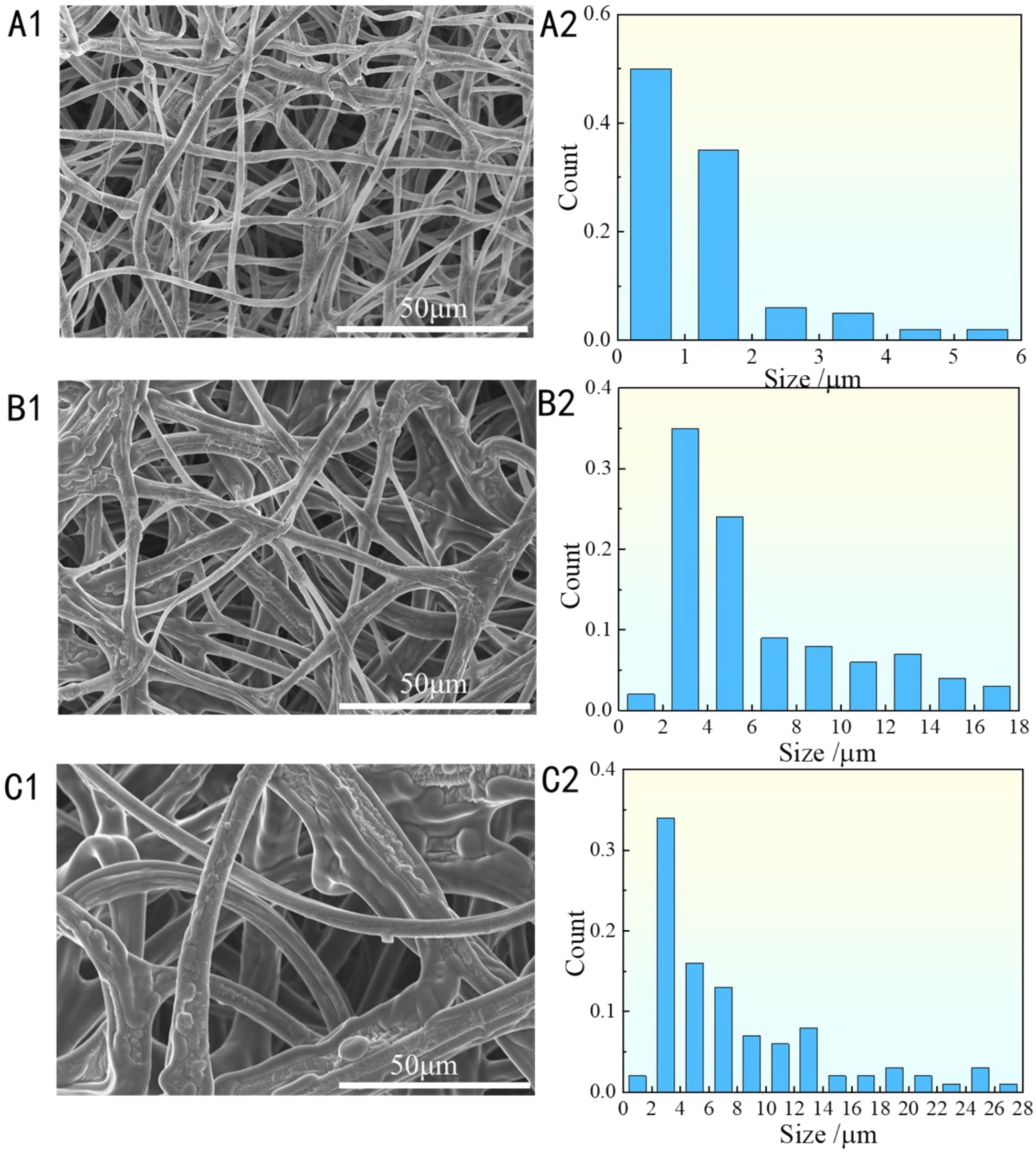

Fig. S3 SEM images of FPCW and Fiber diameter distribution with different PEG content, A) and D) 0.3; B) and E) 0.6; C) and F) 0.7.

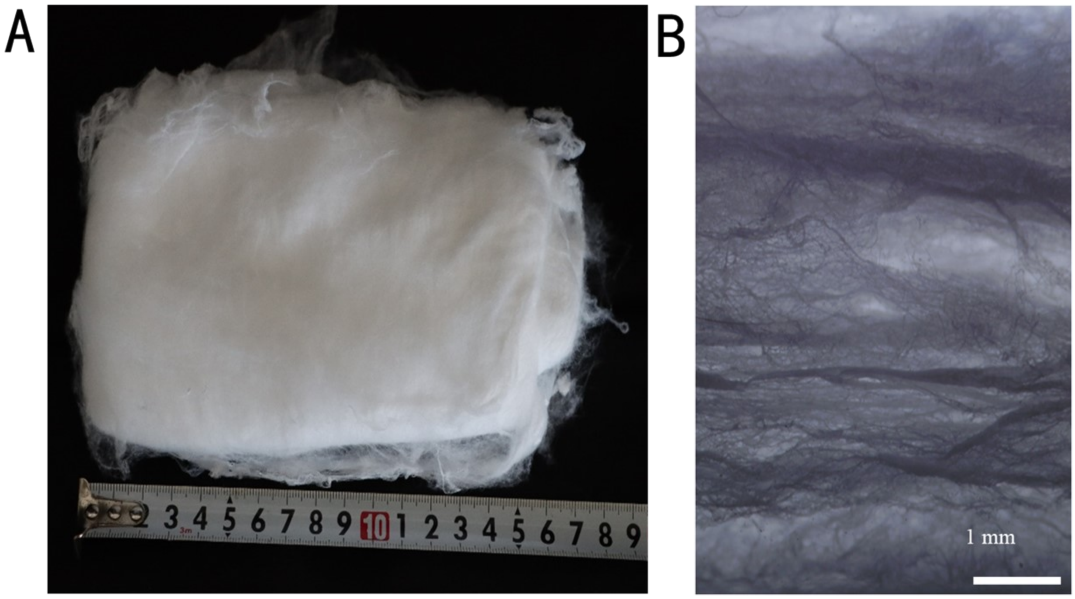

Fig. S4 A) Optical image of as-prepared FPCW after 30 minutes of electrospinning; B) Optical images of interior structure of FPCW.

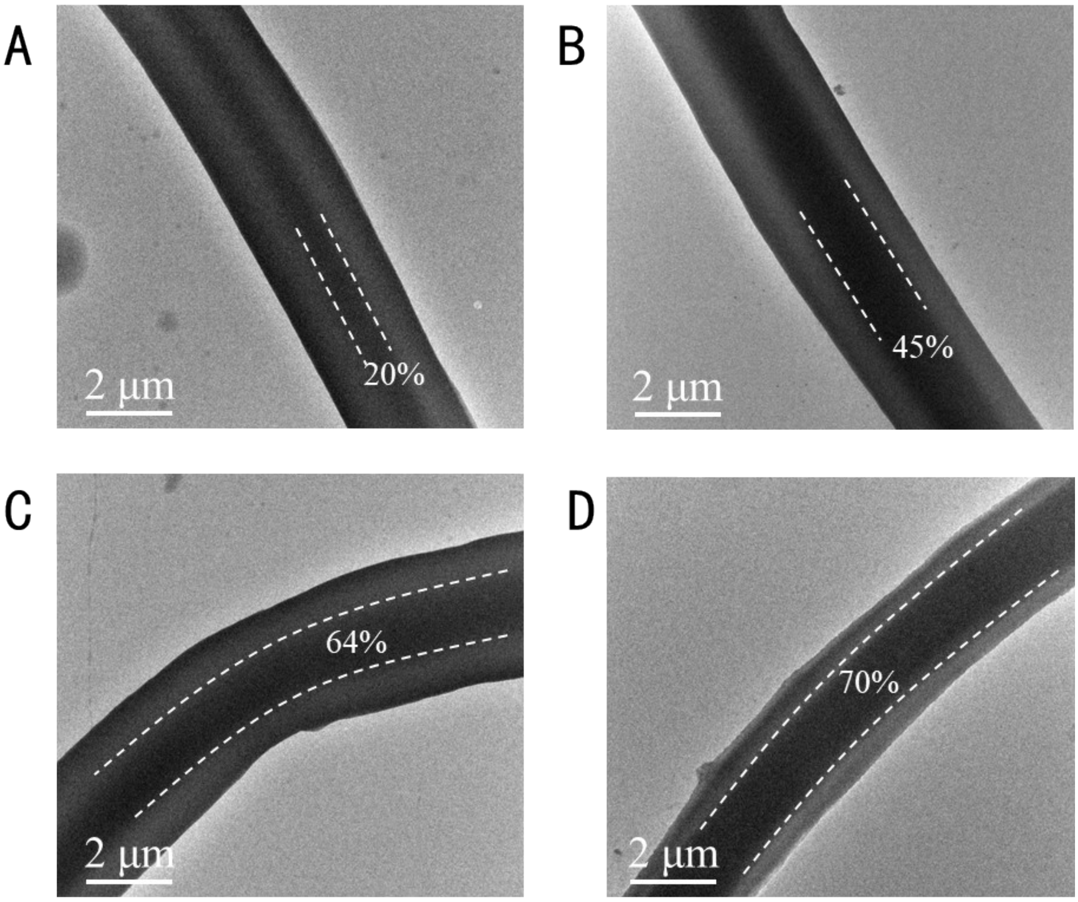

Fig. S5 TEM image of FPCW with different PEG content, A) 0.3; B) 0.5; C) 0.6; D) 0.7.

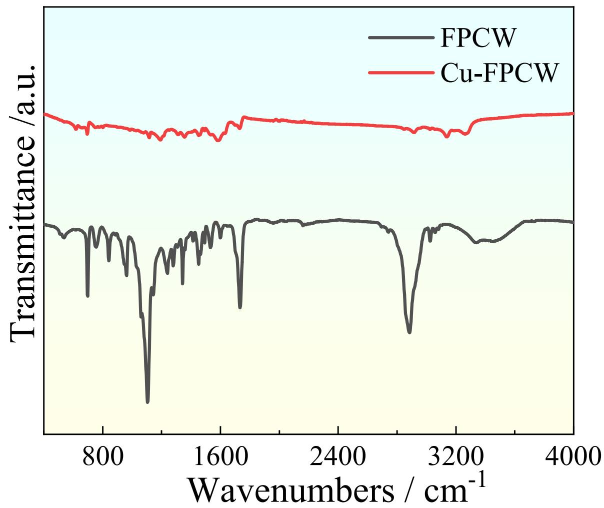

Fig. S6 FTIR spectra of the Cu-FPCW and FPCW.

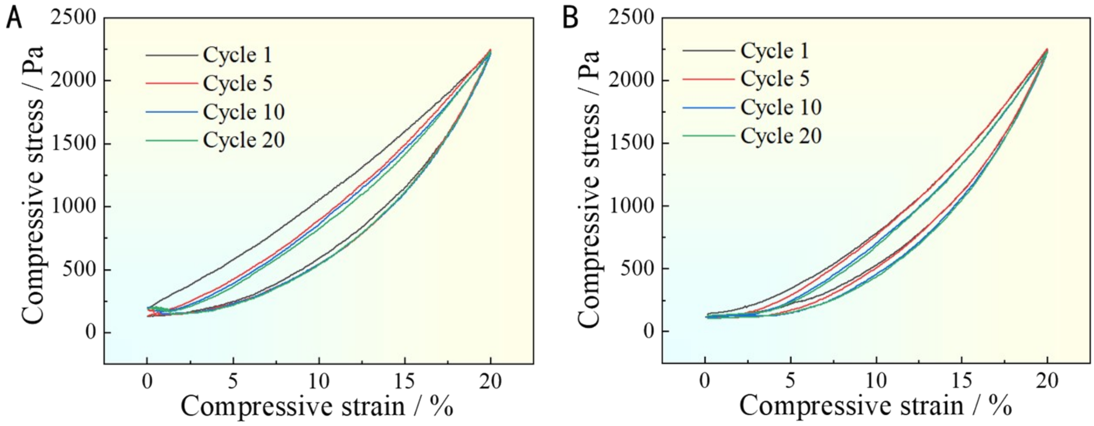

Fig. S7 A 20-cycle fatigue compression test of A) FPCW and B) Cu-FPCW with ε= 20%.

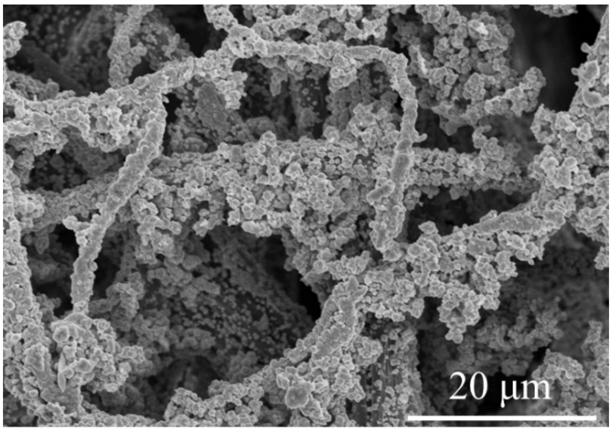

Fig. S8 SEM images of Cu-FPCW after 20 compression cycles (ε = 20%).

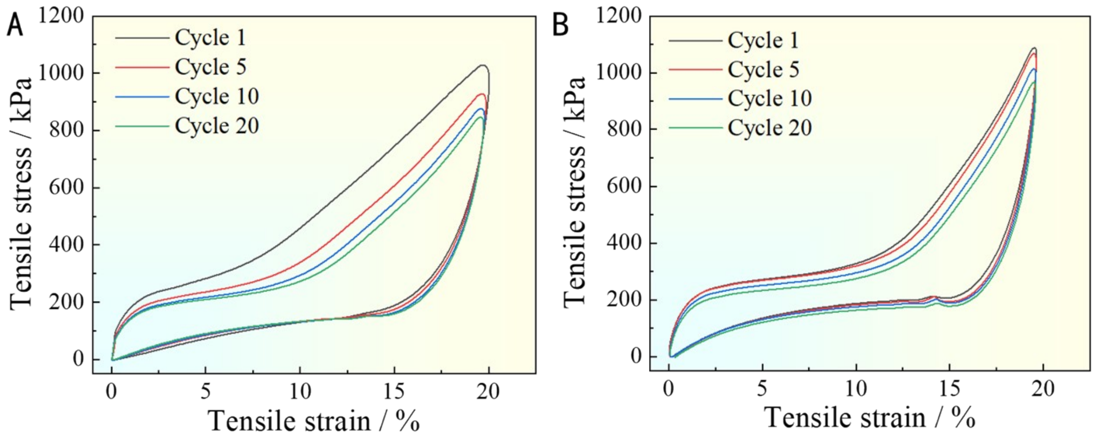

Fig. S9 A 20-cycle fatigue tensile test of A) FPCW and B) Cu-FPCW with ε = 20%.

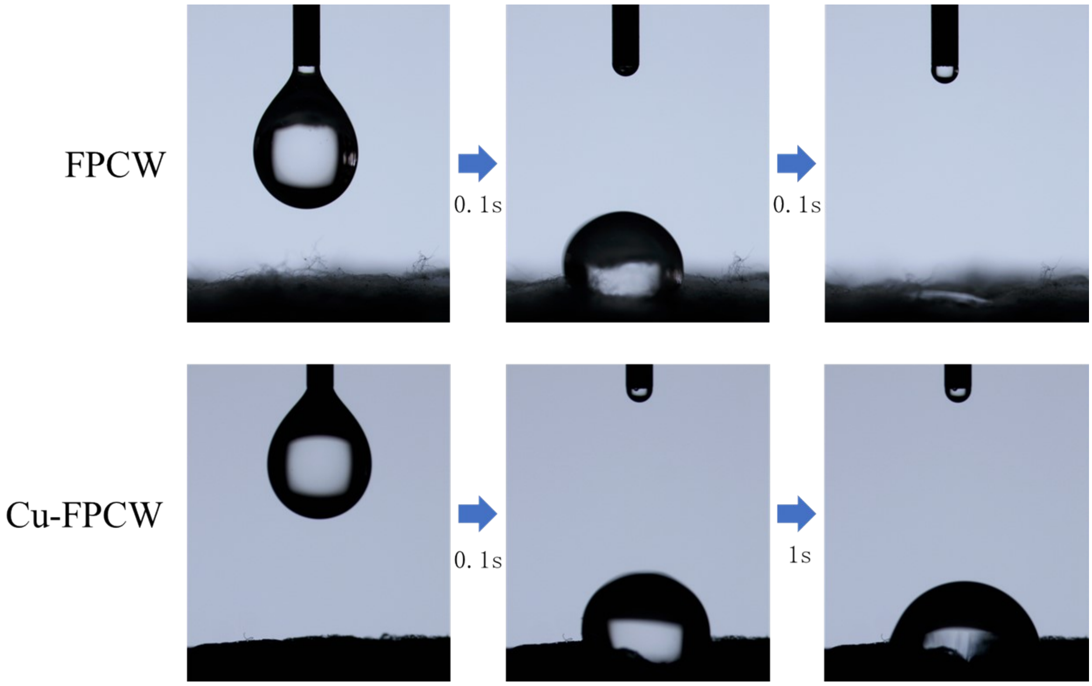

Fig. S10 Optical images showing static contact angle of FPCW and Cu-FPCW.

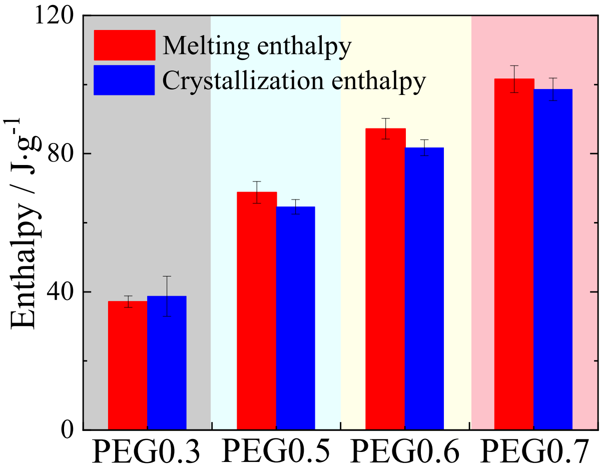

Fig. S11 Enthalpy variation of FPCW with different PEG content.

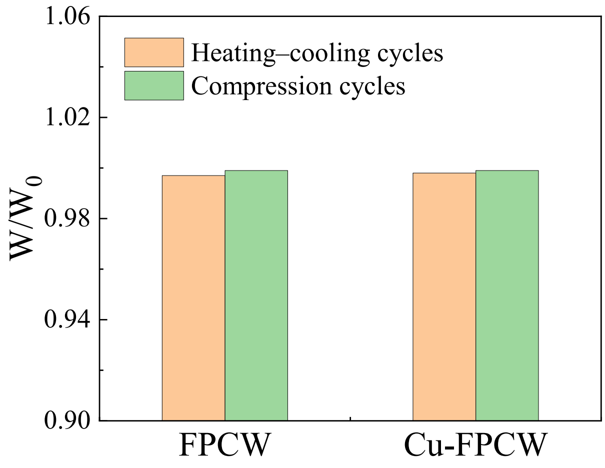

Fig. S12 Weight comparison after 100 heating-cooling cycles and 100 compression cycles.

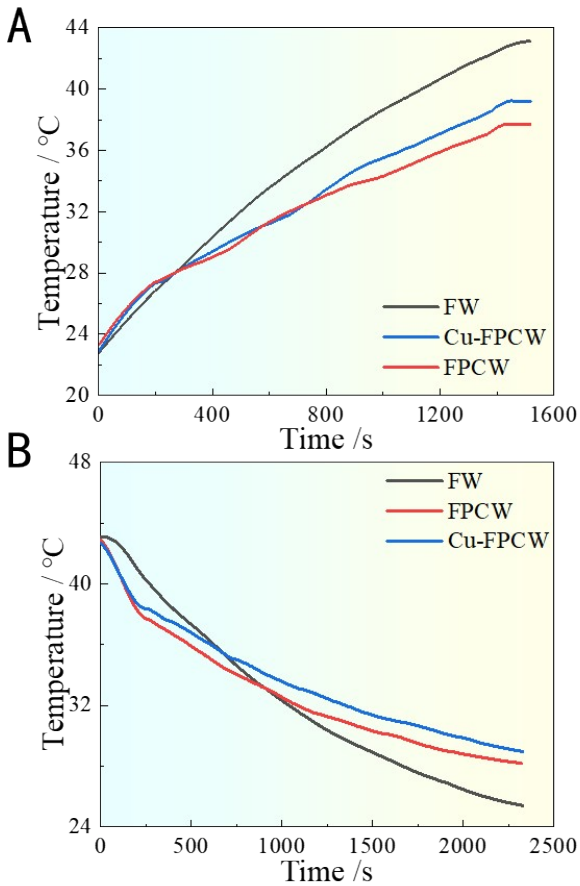

Fig. S13 The temperature curves of FW, FPCW and Cu-FPCW in heating A) and cooling B) process.

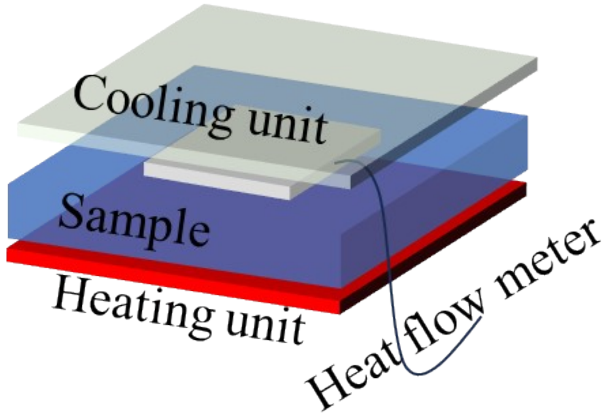

Fig. S14 Schematic of thermal conductivity measurement setup.

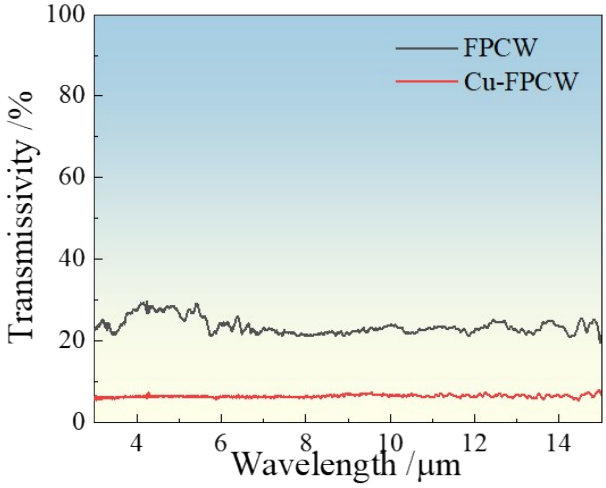

Fig. S15 Transmissivity of Cu-FPCW and FPCW.

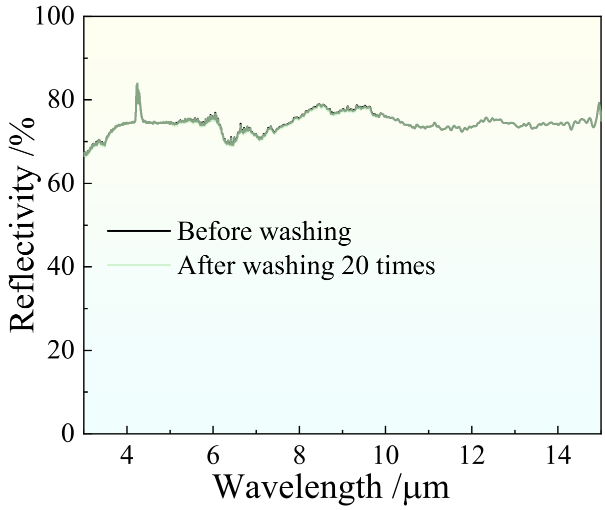

Fig. S16 Reflectivity spectral comparison of Cu-FPCW before and after 20 wash cycles.

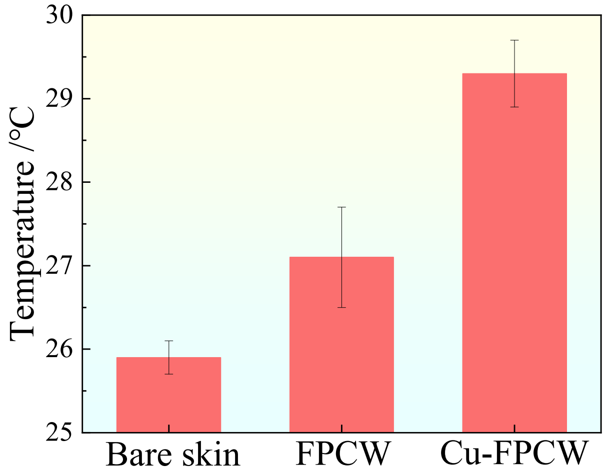

Fig. S17 The final temperature of bare skin, and simulated skin covered with FPCW and Cu-FPCW during the radiative heating.

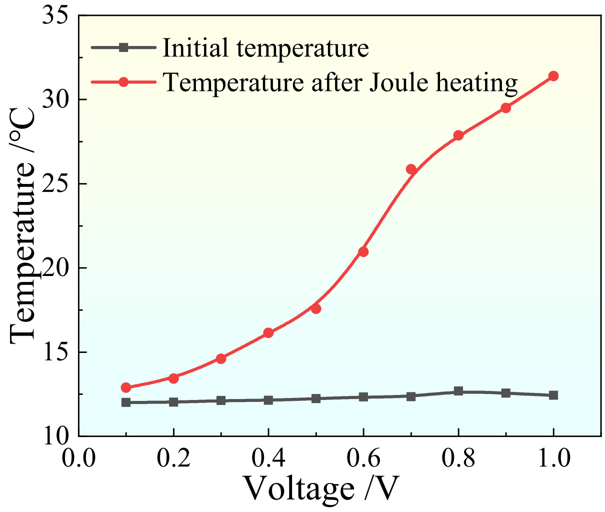

Fig. S18 The stable temperature of Cu-FPCW under different driving voltages.

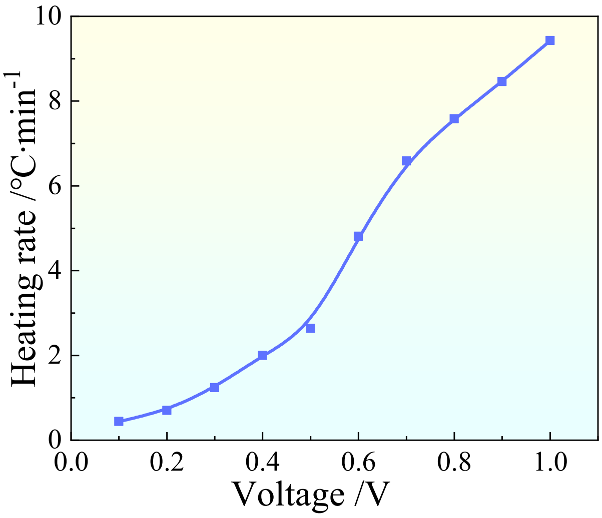

Fig. S19 The heating rate of Cu-FPCW under different driving voltages.

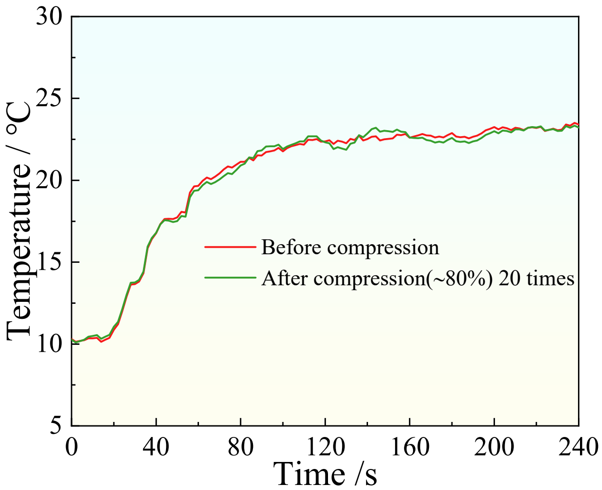

Fig. S20 Internal temperature curves of the Cu-FPCW under 0.7 V before and after 20 compressions.

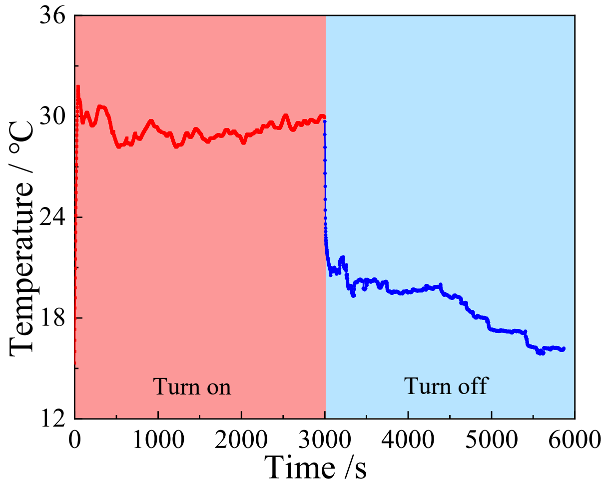

Fig. S21 Continuous electric heating stability of Cu-FPCW under a supply voltage of 1.0 V.

Reference:

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