Supplemental Material

Table S1 Details of relevant fabrics used for thermal protective tests

Fabrics	Fiber content	Weave type	Weight /g·m^{-2}	Thickness/mm
Outer shell	93% Nomex 5% Kevlar 2% P140	Twill	200	0.414
Moisture barrier	80% Nomex 20% Kevlar PTFE	Hydroentanglement felt with PTFE	105	0.453
Thermal liner	80% Nomex 20% Kevlar	Needle-punched nonwoven	120	0.817
Commercial comfort layer	50% Nomex 50% Viscos	Plain	120	0.292
Nanofiber fabric (low density)	100% HPCMEs/PMIA nanofiber hollow yarns	Plain	136	0.695
Nanofiber fabric (high density)	100% HPCMEs/PMIA nanofiber hollow yarns	Plain	155	0.683

Table S2 Comparison of tensile strength between the prepared HPCMEs/PMIA nanofiber hollow yarns with several other reference materials.

NO.	Materials for testing	Tensile strength/MPa	Ref.
1	Cellulose acetate/PMIA and cellulose/PMIA composite nanofiber mats	16~18	20
2	PMIA nanofiber mats reinforced by multi-walled carbon nanotubes (MWNTs)	14~26	21
3	PMIA nanofiber mats treated by hot-stretching	21~33	22
4	PMIA nanofiber mats with spider-web-like structure	3.2~26.8	23
5	HPCMEs/PMIA nanofiber hollow yarns	20.3~36.7	This work

Table S3 Characteristic phase change parameters of the prepared nanofiber core-sheath and hollow yarns

Samples	Winding Speed	Twisting Speed	DSC Cycle	Heating Process				Cooling Process			
				$T_o/°C$	$T_p/°C$	$T_e/°C$	$\Delta H_m/kJ \cdot kg^{-1}$	$T_o/°C$	$T_p/°C$	$T_e/°C$	$\Delta H_c/kJ \cdot kg^{-1}$
HPCMEs/PMIA Fibers (1.5/1)	-	-	2nd	29.57	37.53	40.14	-30.26	30.71	26.58	16.20	30.35
Untreated Core-sheath Yarn	1.2	200	2nd	29.85	36.53	39.58	-15.18	29.50	25.21	20.59	17.60
Nanofiber Hollow Yarns	1.0	200	2nd	31.48	36.92	39.57	-22.54	29.59	25.84	19.65	24.41
	1.2	200	2nd	30.93	37.16	39.69	-21.77	29.94	26.20	18.21	24.27
	1.2	200	1st	31.93	35.27	40.17	-23.64	29.94	26.17	19.38	24.85
	1.4	200	2nd	31.61	36.75	39.44	-24.31	29.81	26.02	19.23	24.47
	1.6	200	2nd	30.91	36.84	39.52	-25.07	30.11	26.64	20.00	18.70
	1.8	200	2nd	31.67	37.68	40.40	-24.01	29.74	25.95	17.13	24.52
	2.0	200	2nd	30.78	37.15	39.68	-28.54	30.24	26.70	18.52	29.23
	1.2	150	2nd	33.15	37.25	39.71	-23.91	30.37	26.80	19.48	24.08
	1.2	230	2nd	32.60	37.05	39.87	-22.40	30.35	26.43	20.58	20.68
	1.2	260	2nd	30.78	37.21	39.64	-22.32	29.94	26.31	19.99	23.82
	1.2	300	2nd	29.88	37.33	39.85	-23.18	30.19	26.40	19.98	23.61

Table S4 Thermal storage properties of the prepared hollow yarns vs. several relevant samples.

NO.	PCMs	ΔH_m of PCMs /kJ·kg^{-1}	Supporting Materials	Useful Products	ΔH_m of the Products /kJ·kg^{-1}	Ref. (year)
1	Microcapsules	54.8	Polyester fabric	Coated fabrics	0.30~5.70	28 (2002)
2	Microcapsules	134.3	Polyester fabric	Impregnated fabrics	0.91~4.44	29 (2005)
3	Microcapsules	117.6	Nylon fabric	Coated fabrics	5.38~6.83	30 (2008)
4	Paraffin	115	PVA	Wet-spun fibers	15.35~25.01	31 (2008)
5	Paraffin	108	PVA	Wet-spun fibers	22.1~23.7	32 (2008)
6	Microcapsules	104.7	Cotton fabric	Coated fabrics	0.92~7.6	33 (2010)
7	Microcapsules	75.66	Several fabrics including: [82% Polyester, 18% Polyurethane] [11% Elastane, 35% Polyamide, 54% Polyester] [100% Polyamide] [100% Polyester coating with 100% PVC] [40% Polyester, 60% Cotton] [100% Polyamide] [100% Cotton]	Coated textiles	11.1~19.4	34 (2012)
8	Microcapsules	164.6	PA6	Electrospun yarns	0.46~4.29	35 (2016)
9	Microcapsules	**-**	Acrylic	Wet-spun fibers	4.6	36 (2013)
10	HPCMEs	76.56	PMIA/PVA	Electrospun yarns	15.18~28.54	Present study

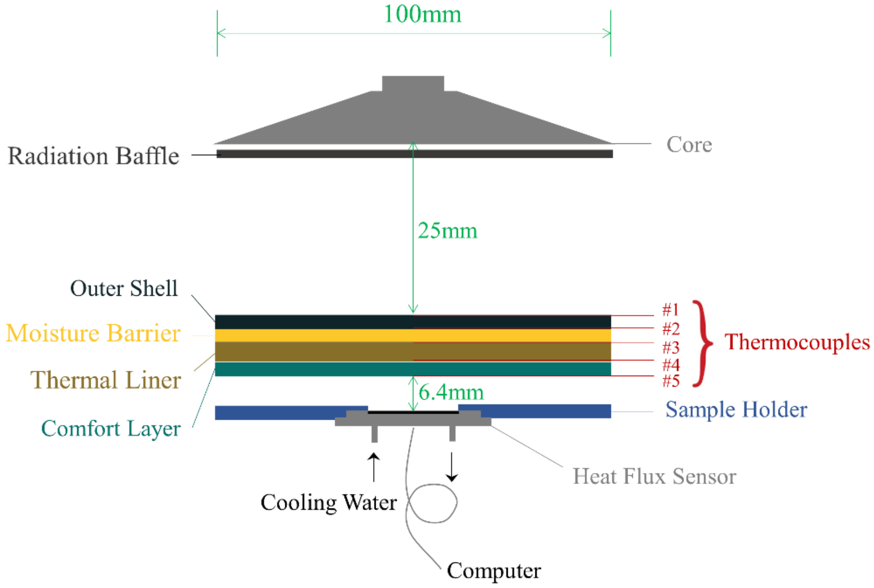

Fig. S1 Platform for thermal protective test.

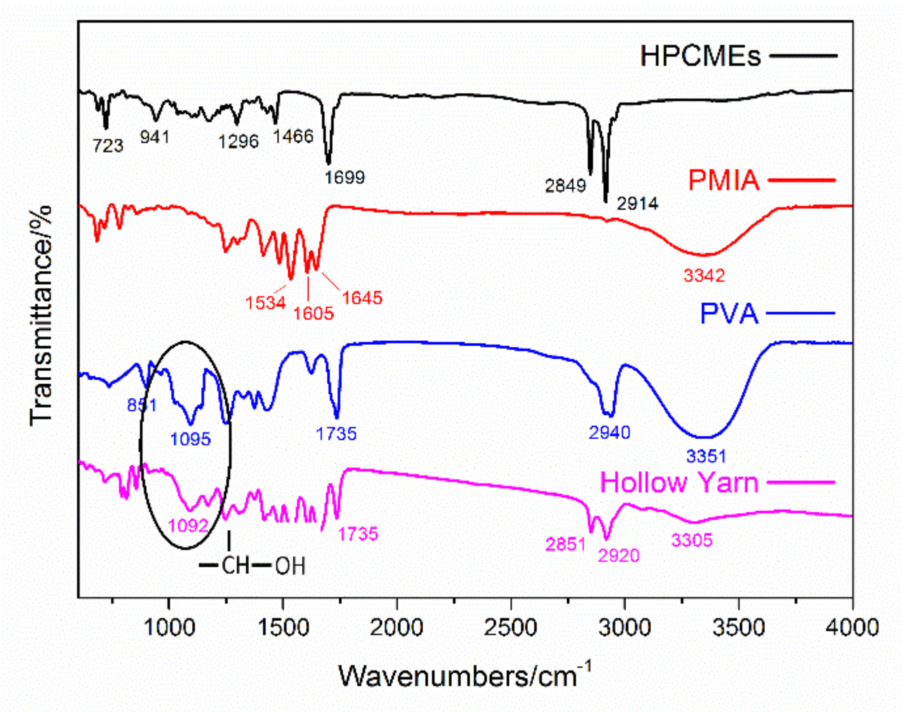

Fig. S2 FTIR spectra of HPCMEs, PMIA, PVA and the prepared hollow yarn.

For pure PMIA, PVA and the prepared hollow yarns, absorption peaks at ~3350 cm^{-1} result from the strong intermolecular and intramolecular bonds of hydroxyl groups. The peaks around 2900 cm^{-1} is assigned to C-H stretching vibrations from alkyl groups, while the strong absorbance centered at ~1700 cm^{-1} corresponding to the stretching vibration of carbonyl (C=O) groups. Another important absorption peak for PVA verified at the frequency of 1095 cm^{-1} is known to be the vibrational band of tertiary hydroxyl groups. In the present study, its appearance can be considered as the existence of PVA. As the obtained hollow yarns also show obvious characteristic peak at 1092 cm^{-1}, it can be concluded that there is still plenty of PVA remained even after the water treatment process.

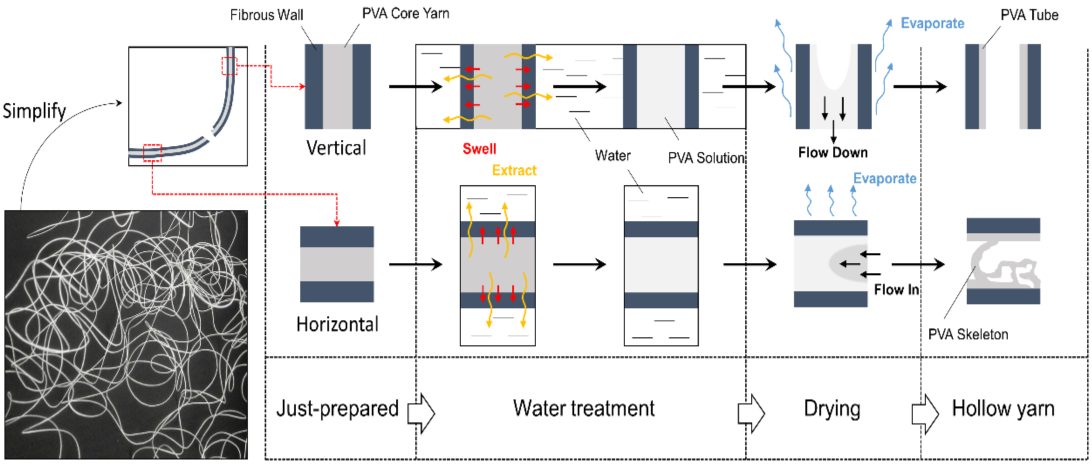

Fig. S3 Formation mechanism of uneven PVA distribution in one single hollow yarn.

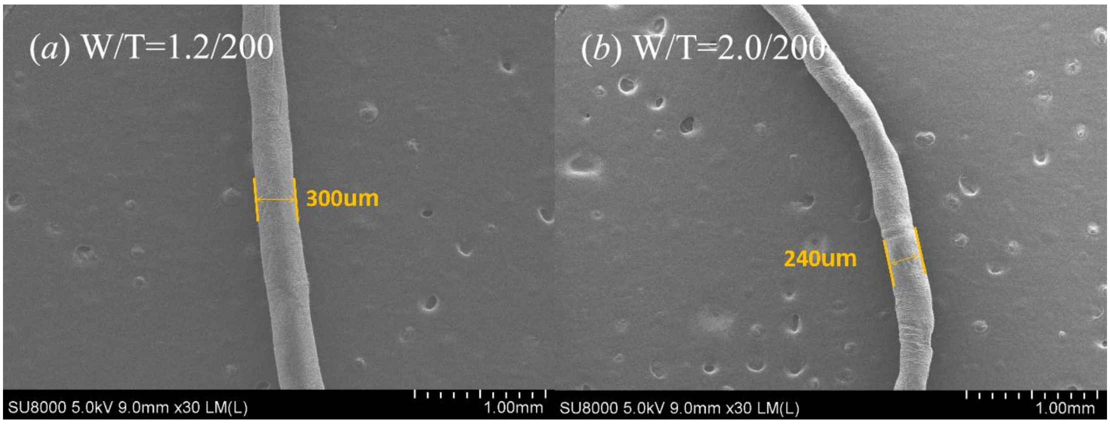

Fig. S4 SEM images of the nanofiber hollow yarns prepared under W/T of (a) 1.2/200 and (b) 2.0/200.

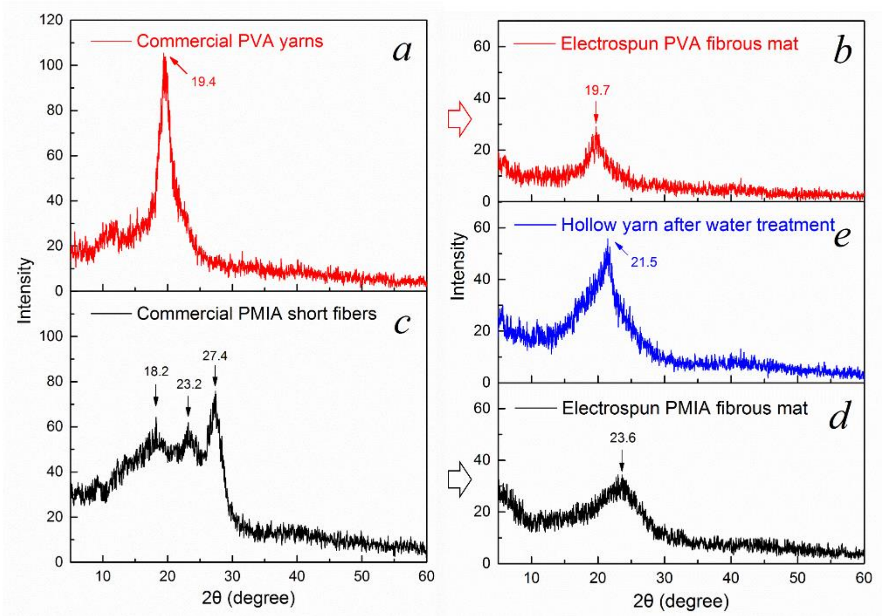

Fig. S5 XRD patterns of (a) commercial PVA yarns, (b) electrospun PVA fibrous mat, (c) commercial PMIA short fibers, (d) electrospun PMIA fibrous mat and (e) hollow yarns after water treatment.

It is apparent that the commercial PVA yarns are highly crystallized and show a sharp diffraction peak at the scattering angle of 19.4°. The PMIA short fibers prepared by intensive drawing at high temperatures also show three main diffraction peaks at 18.2°, 23.2° and 27.4°, respectively. By fabricating them into electrospun fibrous mats, however, their perfect crystal structure is destroyed. Their diffraction peaks therefore become flat, indicating amorphous structure or a phase between amorphous and highly crystallized structure.

Compared with above fibrous mats, the peak intensity of the prepared hollow yarns is a little bit stronger and sharper, which implies an increase of polymeric crystallinity. This may due to the stretching of PMIA ultrafine fibers during yarn fabrication. The stretching effect of ultrafine fibers resulting from the twister's rapid rotation is considered to be helpful for increasing the formation of some additional crystalline order and improving the degree of molecular orientation.

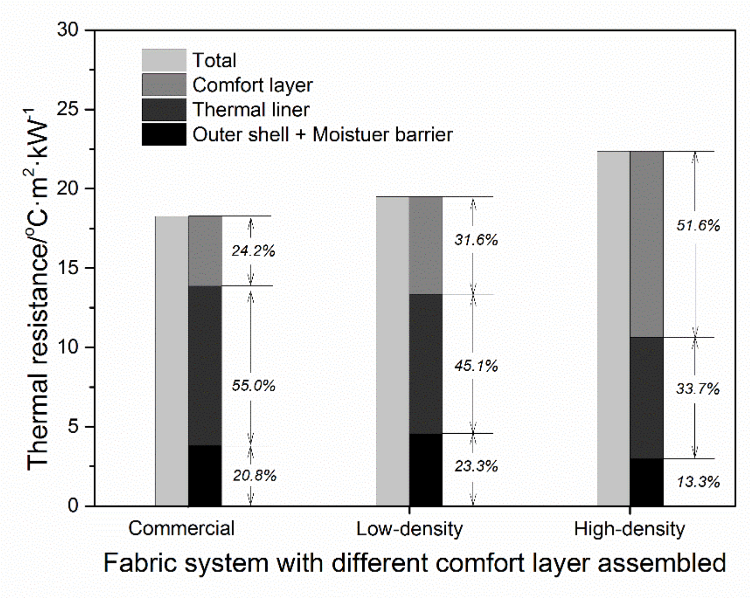

Fig. S6 Thermal resistance values for multilayered protective fabric systems with different comfort layer assembled.

“Commercial”, “Low-density” and “High-density” in this figure are short for corresponding fabric systems with commercial comfort layer, nanofiber fabric (low density) and nanofiber fabric (high density) assembled, respectively. It is obvious that the protective fabric systems with nanofiber hollow yarn fabrics assembled have larger resistance values, which means that these fabrics possess better thermal insulation performance. Take the High-density system for example, it is about 22.4% higher than that of the commercial one. The proportion of comfort layer in their total thermal insulation is also greatly improved. That is, the nanofiber comfort layer plays a more important role in thermal protection.