Multi-Layer Phase Change Materials System for Thermal Energy Storage

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SUMMARY OF THE THESIS

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Abstract

The aim of the dissertation work is to prepare and characterize a multi-layer fabric for buffering thermal shocks from the environment using a phase change material (PCM) and protection against leakage of PCM in the liquid state (above and in the phase change region)

Although there have been various PCM contained textiles, there are still some problems with their practical use. The amount of PCM in fibers or fabric is limited when they significantly deteriorate other properties (e.g., mechanical property, breathability etc.).

The multi-layer fabric is composed from PCM-loaded layer, barrier layer and protective layer. By controlling the interfacial adhesion of melting PCMs on barrier layer or protection layer, the leakage phenomena were totally avoided. The PEG and paraffin wax were selected as PCMs in such multi-layer fabric. The maximum loading amount of PCMs in the multi-layer fabric was 45 wt%. Correspondingly, the overall enthalpy value of the multi-layer fabric was high as 78 J/g, which supported thermal buffering effects

Besides, the introduction of metal microparticles in the PCM-loaded layer was able to enhance heat transfer through the whole multi-layer fabric.

Furthermore, the breathability of the multi-layer fabric was also realized by modifying PCM-loaded layer. The PCM-loaded layer was split to system of air pockets and PCM pockets. However, the heat transfer through the breathable multi-layer fabric became complicated. The size of air pockets was strongly connected to the mutual heat transfer between PCM pockets and air pockets.

The research work not only provided an alternative to have a textile containing PCM, but also extended the application of nanofibrous membranes in smart textiles. It has been verified that the nanofibrous PUR membrane incorporated into the multilayer textiles meets the requirements of preventing PCM leakage during phase changes and ensures their practical use.

Keywords: *PCM, PUR nanofibrous membrane, PCM leakage, interfacial adhesion, thermal energy storage, thermal buffering effect, metal particles, breathability*

Abstrakt

Cílem disertační práce je připravit a charakterizovat vícevrstvou tkaninu pro tlumení tepelných šoků z okolí s využitím materiálu s fázovou změnou (PCM) a ochranu před únikem PCM v kapalném stavu (nad a v oblasti změny fáze). Ačkoli jsou známy textilie obsahující PCM v různé formě (obvykle zapouzdřených v mikro kapsulích), existují stále problémy s jejich praktickým použitím. Množství PCM ve vláknech nebo tkaninách je omezené, protože se významně zhoršují jiné vlastnosti (např. mechanické vlastnosti, prodyšnost atd.). Navržená vícevrstvá textilie se skládá z vrstvy plněné PCM, bariérové vrstvy a ochranné vrstvy. Řízením mezifázové adheze roztavených PCM na bariérové vrstvě nebo ochranné vrstvě bylo zcela zabráněno jevu úniku. PEG a parafínový vosk byly vybrány jako vhodné PCM v připravené vícevrstvé textilii. Maximální množství PCM v připravené vícevrstvé tkanině bylo 45 % hmotnostních procent, což výrazně převyšuje množství kapsulí PCM na textiliích. Celková hodnota entalpie vícevrstvé tkaniny byla také vysoká, tj. 78 J/g, což podporovalo tepelné tlumící efekty.

Kromě toho zavedení kovových mikročástic do vrstvy plněné PCM o zvýšilo přenos tepla celou vícevrstvou textilii.

Zlepšení prodyšnosti připravené vícevrstvé tkaniny byl také realizováno úpravou vrstvy plněné PCM. Vrstva plněná PCM byla rozdělena na vzduchové kapsy a kapsy obsahující PCM. Zkomplikoval se však přenos tepla prodyšnější vícevrstvou textilií. Optimální velikost vzduchových kapes byla silně ovlivněna vzájemným přenosem tepla mezi PCM obsahující kapsami a vzduchovými kapsami.

Výzkumná práce poskytla nejen novou alternativu k přípravě textilií obsahující PCM, ale také rozšířila aplikaci speciálních nanovlákenných membrán v inteligentních textiliích. Bylo ověřeno, že nanovlákenná PUR membrána začleněná do vícevrstvé textilie splňuje požadavky zabránění úniku PCM při fázových změnách a zajištuje jejich praktické použití.

Klíčová slova: *PCM, PUR nanovlákenná membrána, únik PCM, mezifázová adheze, akumulace tepelné energie, tepelný tlumicí efekt, kovové částice, prodyšnost*

摘要

本论文成功提出一种纤维多层相变材料（PCM）系统, 并用于缓冲环境中的热冲击及熔融 PCM 的泄漏。尽管已经出现了多种载有 PCM 的纺织品，但在实际使用过程中仍存在一些问题，尤其是纤维或织物中的 PCM 负载量受到限制。当 PCM 负载量增加时，负载 PCM 的纺织品的其他性能会受到影响（例如机械性能、透气性等）。该论文所提出的纤维多层 PCM 系统由 PCM 负载层、阻隔层和保护层组成。通过控制熔融相变材料在阻挡层或保护层上的界面粘附行为，PCM 的泄漏得以控制。在这种纤维多层 PCM 系统中，选择聚乙二醇和石蜡作为相变材料。纤维多层 PCM 系统中 PCM 的最大负载量为 45 wt%，且纤维多层 PCM 系统的总焓值高达 78 J/g，足以支撑热缓冲效应。通过使用不同分子量的 PCM，可以调节纤维多层 PCM 系统的工作温度。另外，在 PCM 负载层中引入金属微粒能够增强整个纤维多层 PCM 系统的传热。 此外，通过改进 PCM 负载层的结构，将 PCM 负载层被分成气穴和 PCM 穴，从而使得纤维多层 PCM 系统的透气性得以改善。但是，该透气纤维多层 PCM 系统的热传递行为比较复杂，并与气穴及 PCM 穴的大小相关。

该研究工作不仅为含有 PCM 的纺织品提供了替代方案，而且扩展了纳米纤维膜在智能纺织品中的应用。尤其是，含有纳米纤维 PUR 膜的多层纺织品中的满足相变过程中防止 PCM 泄漏的要求，保证了其实际使用。

关键词：PCM， PUR 纳米纤维膜，渗漏，界面粘附，热能储存，热缓冲效应，金属颗粒，透气性

Content

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List of abbreviation

BN: boron nitride
CA: capric acid
CNF: cellulose nanofiber
CS: chitosan
EG: expanded graphite
FSPCM: form-stable PCM
H-SiC-modified MF: hydrophobic-silicon carbide modified melamine-formaldehyde
GO: graphene oxide
LA: lauric acid
MA: myristic acid
MES: methyl stearate
MF: melamine-formaldehyde resin
MP: metal particle
MPF: melamine-paraformaldehyde
MPCM: PCM capsule
MUF: melamine-urea-formaldehyde
MWCNT: multi-walled carbon nanotube
MP: methyl palmitate
PAN: polyacrylonitrile
PCM: phase change material
PDMS: polydimethylsiloxane
PEG: polyethylene glycol
PET: polyester
PMMA: poly(methyl methacrylate)
PP: polypropylene
PU: polyurethane
PVA: polyvinyl alcohol
PVDF: polyvinylidene fluoride
PVP: polyvinylpyrrolidone
PW: paraffin wax
SA: stearic acid
SWCNT: single-wall carbon nanotube
TD: tetradecyl alcohol
UF: urea formaldehyde

List of Symbols

Bi: Biot number

D_0: length of PCM pocket before heating/cooling cycles (mm)

D_1: length of PCM pocket after heating/cooling cycles (mm)

h: free convection coefficient (W m^{-2} K^{-1})

I: thermal insulation value

k: thermal conductivity (W m^{-1} K^{-1})

L: thickness of the sample (mm)

L_0: thickness of PCM pocket before heating/cooling cycles(mm)

L_1: thickness of PCM pocket after heating/cooling cycles (mm)

p: PCM loading amount (wt%)

$p_{overall}$: overall PCM loading amount in fibrous multi-layer PCM system (wt%)

R_{PEG}: mass ratio of PEG to viscose fabric

t: time (s)

$t_{h,65}$: time to reach 65 ^{o}C during heating process (s)

$t_{c,40}$: time to reach 40 ^{o}C during cooling process (s)

t_{phase}: time for phase transition (s)

T: temperature (^{o}C)

T_f: the final temperature of sample (^{o}C)

T_i: the initial temperature of sample (^{o}C)

T_s: is the sample temperature with time t (^{o}C)

T_{phase}: temperature for phase transition (^{o}C)

τ: is the cooling (heating) rate constant (^{o}C/s)

χ_0: predicted relative crystalline degree according to database (%)

χ: experimental relative crystalline degree according to measurement (%)

$\Delta H_{m,sample}$: measured melting enthalpy value of sample (J/g)

$\Delta H_{m,PCM}^{T}$: theoretical melting enthalpy value of PCM (J/g)

$\Delta H_{m,PCM}$: measured melting enthalpy value of the measured PCM (J/g)

$\Delta H_{m,overall}$: overall enthalpy value of sample (J/g)

η: PCM encapsulation efficiency (%)

1. *Introduction*

Phase change materials (PCM) are a group of materials that adsorb/release thermal energy during their phase transition. The PCM could be applied in various fields, including building materials, solar energy storage, the thermal management of the electronic system, food storage, smart textiles, and so on [1–6]. The discussions of the PCM related to the PCMs classification, the preparation of PCMs, the application of PCM have been reviewed in various published works [2,7–14]. Besides, the toxicity, health hazards, and commercialization of PCMs are reviewed by S.S. Chandel et al [15]. It is also reported that the market revenue of the PCMs is increasing with rate of 19 % and can reaches 5.1 billion dollars, which is shown in **Figure 1 (A)**.

Especially, the PCM-incorporated textiles have attracted more and more attention even from academics (**Figure 1 (B)**) (PCMs publications are determined by search ‘phase change material’ for ‘abstract’ or ‘title’ or ‘keyword’, and PCM-incorporated textile publications are determined by search ‘phase change material’ and ‘textile’ or ‘fabric’ or ‘yarn’ or ‘fiber’ for ‘abstract’ or ‘title’ or ‘keyword’). It is well known that the first introduction of PCM into textiles was realized from NASA in the early 1980s, which was aimed to improve the thermal protection against the extreme temperature fluctuation in the outer space. The basic working principal of PCM-incorporated textiles is the realization of thermal energy storage when the phase transition of PCM between the solid and liquid phase while the temperature of PCM during the phase transition is little altered. Besides, the thermal resistance of the PCM-incorporated textiles is enhanced when there is the phase transition of PCM. Now, there are various commercial PCM-incorporated textile products over the globe (e.g., air condition thermal fiber from Outlast company, Smartskin fabric, Triangle R&D and so on), which is shown in **Figure 1 (C)**. The main function of the PCM-incorporated textiles includes thermal regulation, heat protection, thermal energy harvesting and so on (**Figure 1 (D)**). The main reasons for the rapid development of the PCM textiles could be two aspects:

1) The first aspect is based on the various functional applications of textiles. It is indicated that the concept of ‘textile structures’ include fiber, yarn, and fabric [16]. Since the successful fabrication of the ultrafine fibers via the advanced technologies, the flexibility of the ultrafine fibers supports the high compatibility with various other materials. Besides, the yarns are considered a special structure where the twist enhances the mechanical property. The release/store of the mechanical property in the yarns could be realized. In addition, the fabric is a stable porous structure. By modifying the fabric, various applications are proposed, including the antibacterial property, oil/water separation, particle filtration, thermal regulation, Joule heating property, optical property, EMI shielding etc. [17–26].
2) The second aspect is based on the usage of the PCM. The usage of the PCM is proposed to enhance the thermal regulation and thermal energy storage, and also supports the light radiation-thermal energy conversion, solar-thermal energy conversion, and so on [27].

Although there has been a great achievement in PCM-incorporated textiles, there are still some challenges. The limited thermal energy storage of PCM-incorporated textiles is found, which is caused by limited mass of PCMs in the textiles and confined crystallization of PCMs in the textiles. So, how to effectively increase thermal energy storage and thermal buffering effect of PCM-incorporated textiles should be focused on. Besides, the thermal energy storage efficiency of PCM-incorporated textiles is low. Enhancing the thermal energy storage efficiency of PCM textiles can support other applications, which is also necessary to be solved.

This dissertation work is in the form of commented set of published scientific papers dealing with preparation, characterization and testing of multi-layer fabric for buffering thermal shocks from the environment by using of PCM. In total, the set of scientific paper contains 20 research works published in impact factor journals and 17 conference paper. There were 5 published chapters in scientific books.

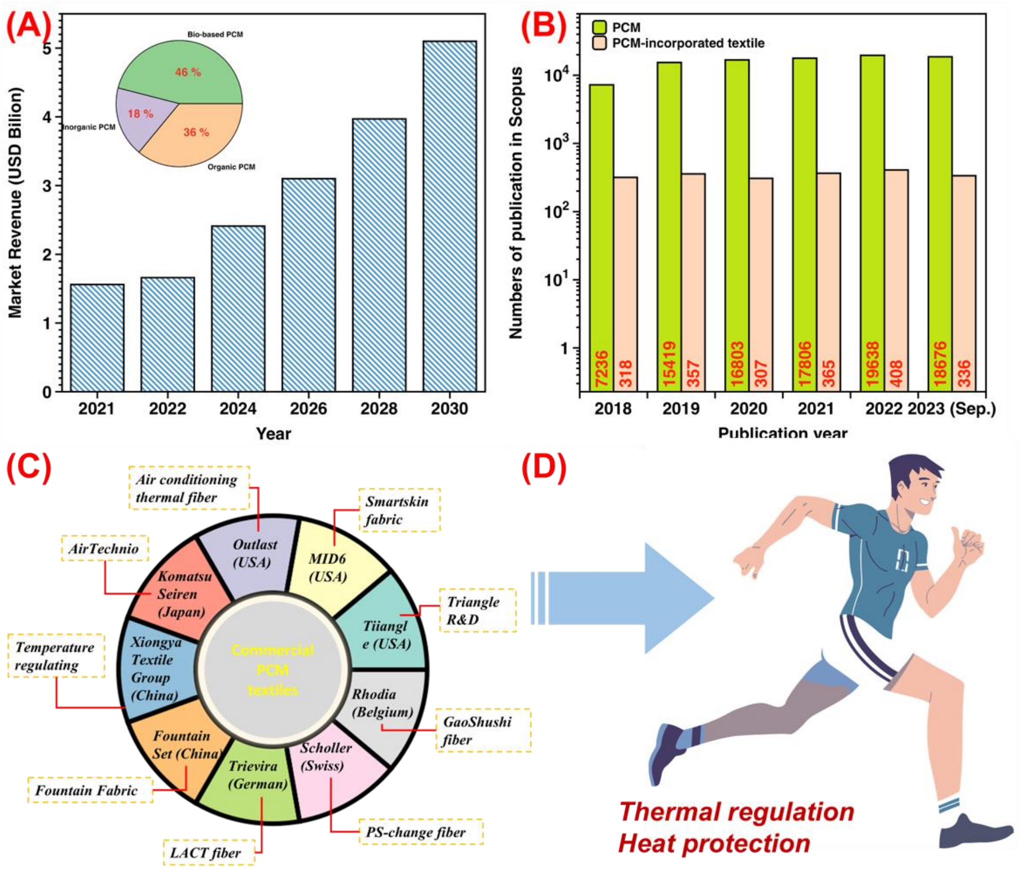

Figure 1 Necessity to develop PCM-incorporated textiles (A: Current market revenue of PCMs and their podcast, B: publications related to PCMs and PCM-incorporated textiles from Scopus, C: famous commercial products, and D: function of PCM-incorporated textiles for human

2. State of the Art

2.1 Suitable PCM for textiles

It is well known that the PCM is classified into two types: inorganic PCM and organic PCM [28]. However, the phase separation and corrosion property of inorganic PCM are found, which make inorganic PCMs unsuitable for textiles. So, the organic PCM are used for textiles, which includes paraffin wax, fatty acid, polyethylene glycol and so on. However, the leakage and low thermal conductivity of the organic PCM are the main problems for the practical applications. To avoid leakage, microencapsulated PCMs (MPCM) and form-stable PCMs (FSPCM) have been proposed [29–31].

- PCM capsules (MPCM)

MPCM has been the most industrial technology and its application in textiles has been studied for decades [32,33]. The summary for the MPCM is shown in **Figure 2 (A)**. The MPCM consists of supporting materials as shell and PCM as core, where stability of thermal energy storage and phase transition of MPCM is enhanced [34]. The biggest advantage of MPCM is the good encapsulation of PCMs. Besides, there are various preparation methods for development of MPCM, such as suspension-like polymerization, photo-induced microencapsulation, interfacial polymerization etc. According to the shell type of MPCM, there are three MPCM, including organic MPCM, ceramic MPCM and metallic MPCM. Among three MPCM, the organic MPCM are usually for textiles since they have no corrosion and easy control. However, the poor mechanical property of the organic MPCM is found, which results in unexpected destroy of MPCM during their coating on fabrics. Besides, the overall thermal conductivity of the MPCM reduces the heat transfer efficiency. In addition, the encapsulation efficiency of MPCM requires modification and the reproducibility of the MPCM is difficult [33].

- Form-stable PCM (FSPCM)

FSPCM is an alternative to avoid leakage of PCM and realize thermal energy storage, which is shown in **Figure 2 (B)**. FSPCM is usually prepared by filling PCM into porous materials (e.g., zeolite, aerogel, foam etc.) [29,35–38]. Although the leakage of molten PCMs can be avoided, the self-crystalline behavior of the encapsulated PCM in the FSPCM is significantly confined and thermal energy storage and phase transition behavior of the FSPCM is different from pure PCM [39,40]. Besides, the environment could have a side effect on the phase transition behavior and thermal energy storage of FSPCM. For example, our recent work revealed that a significant side effect of hot and humid environment resulted in a reduced overall thermal energy storage of PCM/expanded graphite composites [41].

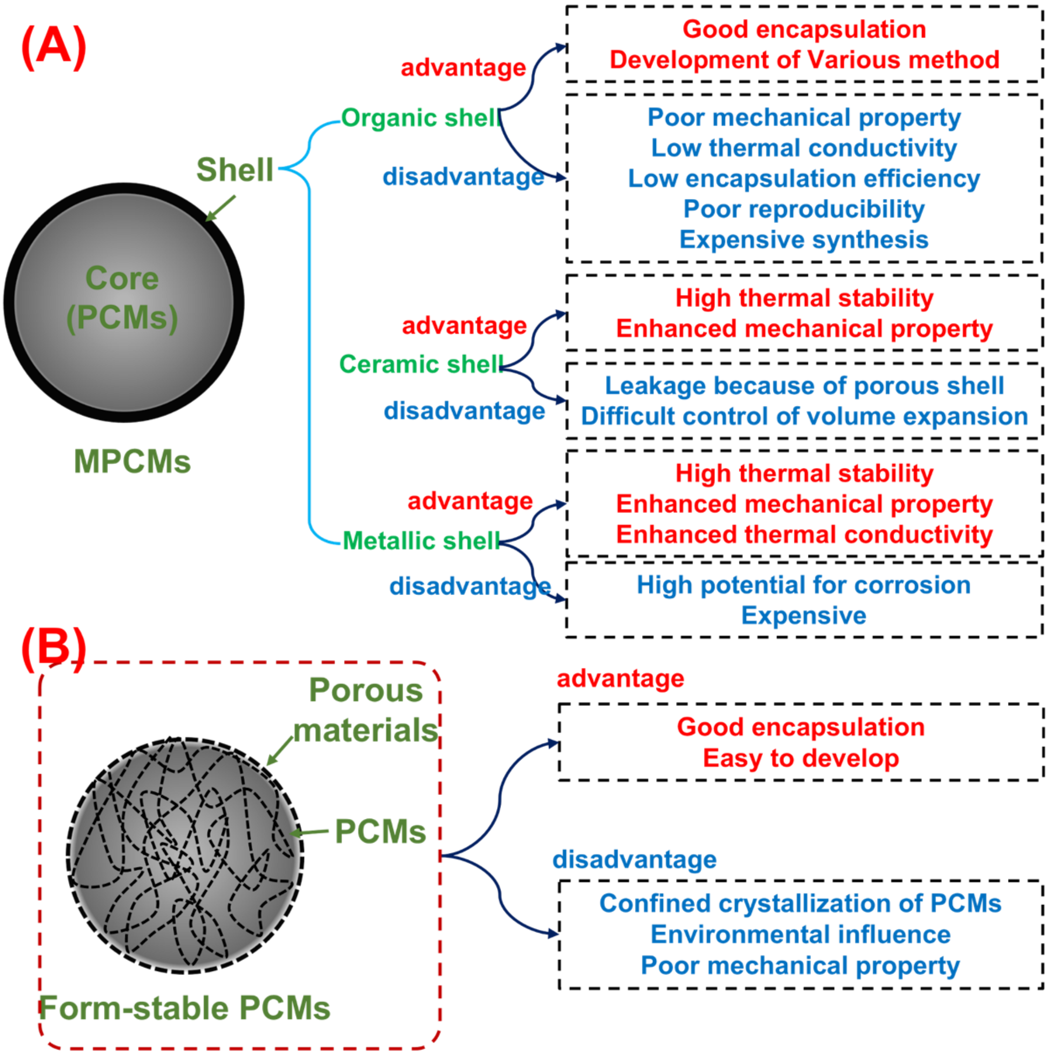

Figure 2 Current problems of PCM (A: MPCM, and B: FSPCM)

2.2 Incorporation of PCMs into textiles

2.2.1 PCM containing fibers

For PCM containing fibers, the PCM are trapped in the fiber matrix. Various technologies are used to prepare the PCM containing fibers, including electrospinning, centrifugal spinning, molten spinning, solution spinning, dry-jet quenching spinning, interfacial polyelectrolyte complex spinning, vacuum impregnation, and injection spinning [44]. Then, the various polymers have been successfully used as the supporting materials for the storage of the different PCMs, including polyester (PET), polyvinyl alcohol (PVA), polyurethane (PUR), and etc. Although there is a great achievement in PCM incorporated fibers, some drawbacks or problems remain to be solved.

As shown in **Figure 3 (A)**, two key factors are taken into consideration for the PCM containing fibers. Firstly, the PCM loading amount of the PCM containing fibers is limited, which is related to the mechanical property. Higher PCM loading amount reduces the mechanical property of

PCM containing fibers although increase the thermal energy storage. Especial for MPCM containing fibers, the recommended maximum MPCM loading amount is 10 wt% [28]. Secondly, there is a strong confinement of PCM inside the PCM containing fibers, which results in reduced thermal energy storage. Besides, it is reported that the PCM containing fibers have a stable phase transition behavior after heating/cooling cycles. However, the mechanical property of the PCM containing fibers after heating/cooling cycles should be different from the one without heating/cooling cycles since the crystalline structure of the PCM inside the PCM containing fibers is altered, although there are no research works to report.

The PCM containing fibers are also for fabrication of PCM containing yarns or PCM containing fabrics. In this case, the similar problems are found as described.

Apart from such PCM containing fibers, the coating of PCM on the fibers is an alternative. However, it is not standard as PCM containing fibers and there are few works related to such topic.

2.2.2 PCM containing fabrics

For PCM containing fabrics, the pad-dry-cure coating method is the most popular to have a coating of MPCM (or FSPCM) on the fabric [5,42,43]. To enhance the ability of MPCM (or FSPCM) on the fabric, the binder is necessary to be used. Then, such MPCM (or FSPCM)-coated fabrics have thermal regulation behavior. Although there are some achievements in the MPCM-coated fabrics, some problems remain to be solved, which is shown in **Figure 3 (B)**.

Firstly, the MPCM loading amount on the fabric is limited and shorter thermal buffering effect is suggested. Secondly, the surface chemistry and mechanical property of PCM containing fabrics are changed since there is a coating by using binders. The type of binders significantly affects thermal comfort (e.g., moisture management etc.). Thirdly, the breathability (e.g., air permeability, water vapor permeability) is reduced since there is a MPCM (or FSPCM) coating layer on the fabric surface. Fourthly, loss or damage of MPCM possibly happens because of external mechanical damage (e.g., due to washing, abrasion). The leakage of the MPCM also possibly happens during the coating process.

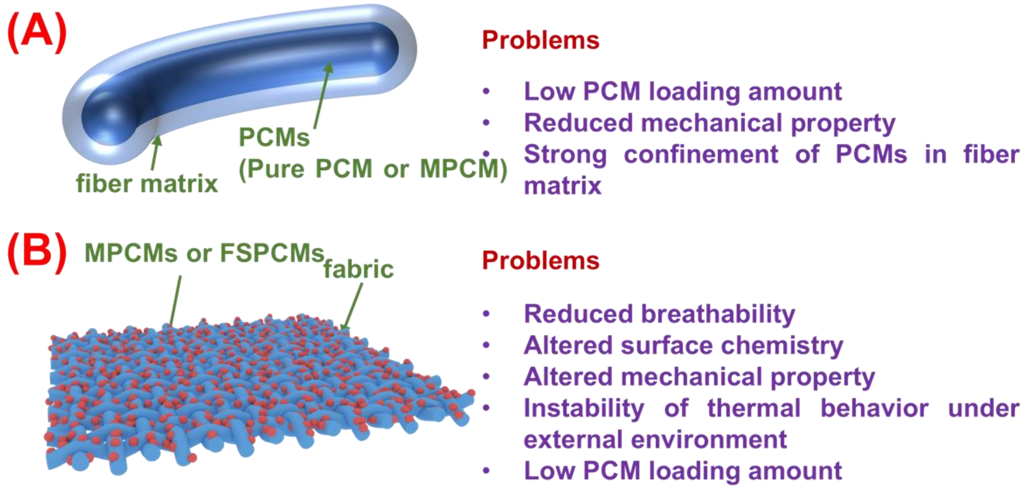

Figure 3 Current problems of PCM-incorporated textiles (A: PCM containing fibers, and B: PCM containing fabrics)

2.2.3 Characterization of PCM-incorporated textiles

There are various methods to characterize thermal buffering effect of PCM-incorporated textiles. Among all the methods, the temperature-time curve (T-history) is the most convenient one to characterize thermal buffering effect. The whole T-history or selected points only can be used for characterization of thermal buffering effect of PCM [42,45]. Besides, the protection time of the PCM-incorporated textiles has been proposed. This time is determined by the time corresponding to half of difference of final and initial temperature [46]. However, such characterization of T-history cannot provide the exact thermal buffering effect range of the PCM-incorporated textiles.

Kinetics of temperature changes are formally expressed as rate equation of first order is equivalent to so-called Newton's cooling law (used of course for both cooling and heating), which is expressed by **equation (1)**.

$$\frac{dT}{dt} = -(T - T_i)/\tau \tag{1}$$

Where, T_f is the final temperature of sample (for $t\rightarrow\infty$), T_i is the initial temperature of sample, T is the sample temperature in time t and τ is the cooling (heating) rate constant.

By integrating of this differential equation in suitable limits (from t=0 where $T= T_i$ till time t where temperature is T), the integral form is expressed in **equation (2)**.

$$T_f - T = (T_f - T_i)e^{-t/\tau} \tag{2}$$

Formal linearization of **equation (2)** is expressed by **equation (3)**:

$$\ln[(T_f - T)] = \ln[(T_f - T_i)] - t/\tau \tag{3}$$

The τ can be therefore approximately related to slope of dependence y = ln (T -T_f) on $x = t$ by linear least squares method.

Figure 4 (A) and **(A')** present one example for standard application of Newton's cooling law. For the common fabric, the temperature-time curve (T-history) is classic, and the parameters of Newton's cooling law are interpretated with physical meaning, and the relevant thermal property of fabric (e.g., thermal conductivity, thermal resistance etc.) can be estimated [27]. To extend the application of this model for better fitting of complex T-history curves with different parts, the different models are proposed for individual parts [28]. As a result, the calculated heating or cooling constants corresponds to different parts of T-history. For PCM-incorporated textiles, the T-history curve consists of three parts, including first sensitive heat storage part with solid PCM, latent heat storage part with solid-liquid PCM and second sensitive heat storage part with liquid PCM. By formal splitting of kinetic **equation (2)** into the three parts of T-history of PCM-incorporated textiles can be estimated. More precise is to integrate rate **equation (1)** for different parts of T history in different limits.

For *Part I,* obviously the lower limit is $t = 0$ and $T = T_i$. This part is bounded by end point (t_1. T_1) which is constraint. Then, the modified **equation (4)** is obtained.

$$\frac{T-T_f}{T_i-T_f} = e^{-(t)/\tau} \tag{4}$$

For *Part II*, the lower limit starts from the point of $t = t_1$ and $T = T_i$ and ends at the point of $t = t_2$ and $T = T_2$. Then, the modified **equation (5)** is obtained.

$$\frac{T-T_f}{T_2-T_f} = e^{-(t-t_2)/\tau} \tag{5}$$

For *Part III*, the lower limit is at point of $t = t_2$ and $T = T_2$ and higher limit could be at point of $t = t_3$ and $T = T_f$. Then, the modified **equation (6)** is obtained.

$$\frac{T-T_f}{T_3-T_f} = e^{-(t-t_3)/\tau} \tag{6}$$

It should be noticed that the use of **equation (1)** assumes here that for all parts have an equilibrium temperature (e.g., T_f). To having the turning points for three parts, the plot of $\ln[(T - T_f)]$ against t can be used. By observing the three linear segments in this plot, the three parts corresponding to solid phase state of textile and PCM, phase transition state of PCM and liquid phase state of PCM are suggested. A pure empirical model based on exponential model expressed in **equation (7)** is proposed. The A is the factor, and the parameter with subscript *1, 2, 3* in **equation (7)** represents three parts of PCMs (solid phase state, phase transition state and liquid phase state).

$$T_f = \begin{cases} T_i + A_1 e^{-\frac{t_1}{\tau_1}} \\ T_2 + A_2 e^{-\frac{t_2}{\tau_2}} \\ T_3 + A_3 e^{-\frac{t_3}{\tau_3}} \end{cases} \tag{7}$$

However, it is hard to obtain the turning points for three parts from T-history curve. By having logarithm for **equation (7),** the three linear parts can be obtained. By observing the linear segments in the plot of $\ln[(T_f - T)]$ aganist *t*, the three parts corresponding to solid phase state, phase transition state and liquid phase state are suggested. After having linear fitting for each part of $\ln[(T_f - T)]$ aganist t, the parameters including A and τ can be found. By having intersection points of adjacent linear equations, the turning points at time *t* are found. Then, the nonlinear fitting models according to **equation (7)** for full heating T history is used. By taking errors into consideration, the theoretical turning points (time and temperature) for phase transition are estimated by having the intersection points of adjacent nonlinear model in **equation (7)**. **Figure 4 (B)** and **(B')** present one example for standard application of modified Newton's cooling law.

Besides, the thermal insulation (*I*) can provide the potential overheat injury of PCM-incorporated textiles when the PCM-incorporated textiles reach heat balance during heating process, which is expressed in **equation (8)**. The T_h is the temperature of the heater and T_r is the environmental temperature.

$$I = (T_h - T_f)/(T_h - T_r) \tag{8}$$

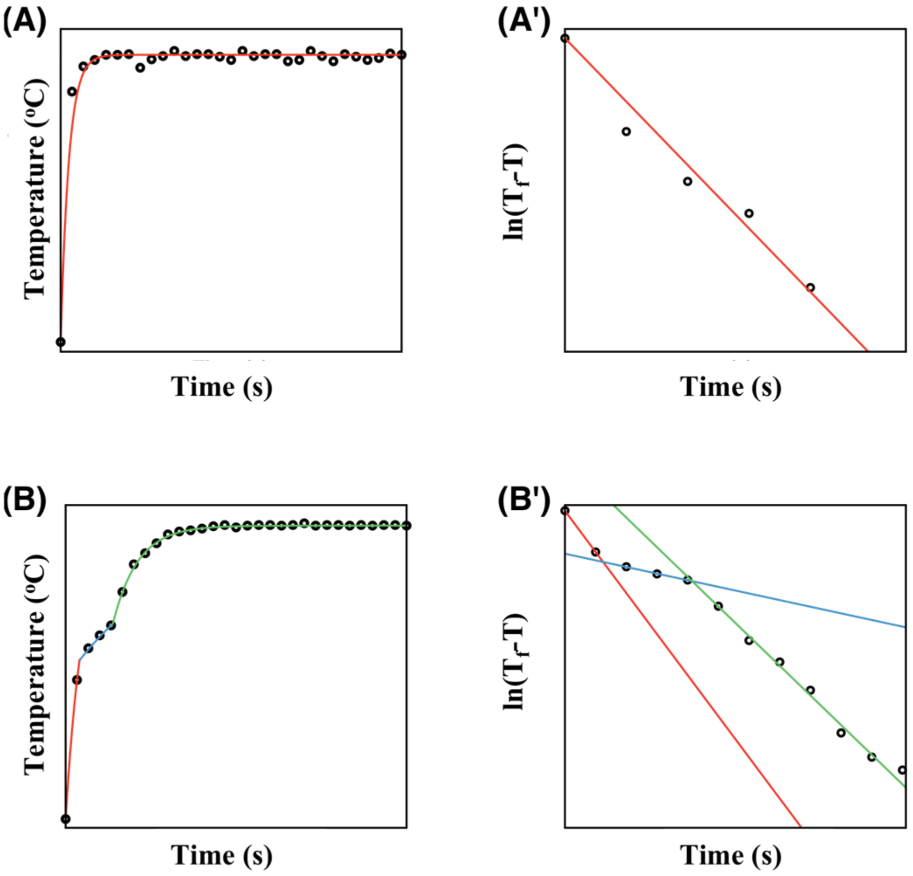

Figure 4 Example for application of Newton's cooling law (A: heating curve with standard Newton's cooling law, A': standard plot of $\ln[(T_f - T)]$ against *t*, B: heating curve with modified Newton's cooling law, and B': nonlinear regression model for $\ln[(T_f - T)]$ against *t*)

3. *Motivation and aims*

It is well known that the leakage of PCM during heating/cooling cycles is governed by viscosity of molten PCMs and interfacial adhesion between molten PCMs and fabrics if the pure PCMs are coated on fabrics directly. From this point of view, the multi-layer fabric structure with barrier layers covering the PCM-loaded layer (pure PCM-coated fabrics) is promising to avoid leakage [47]. For the selection of the barrier layers, the nanofibrous membranes are advantageous. There are two reasons:

1) By controlling porosity and surface chemistry, various nanofibrous membranes have been applied for oil/water separation, air filtration etc. [48–52].
2) The high resistance against mass transfer of nanofibrous membrane-coated fabrics have been proposed [53,54].

From this point of view, the nanofibrous membranes can be used as barrier layer to resist against the penetration of molten PCMs.

In this work, we first tried to use nanofibrous membranes in the fibrous multi-layer PCM system. As shown in **Figure 5**, the fibrous multi-layer PCM system consists of PCM-loaded layer, barrier layer and protection layer. The PCM-loaded layer is PCM-coated fabric. The viscose nonwoven fabric was selected as substrate for coating of various organic PCM (e.g., PEG, PW, myristic acid etc.) since the viscose nonwoven fabric is porous and has a good interfacial adhesion with organic PCM. The PCM-coated fabrics have a mass percentage of PCMs ranging from 80 wt% to 90 wt%. The nanofibrous membrane is used for barrier layer as described. Because of weak mechanical property of barrier layer (nanofibrous membrane), the protection layer was used to avoid damage of barrier layer under external environment. The commercial PET knitted fabric was selected for protection layer. Still, it is necessary to avoid the effect of liquid on the PCM inside the fibrous multi-layer PCM system. Although net PET film has a low surface energy and hydrophobic property, the fibrous structure of PET fabric would result in wicking of solution. Then, the alternatively commercial PET fabric with hydrophobic coating (5 μL water contact angle of 122^{o}) is also selected as protection layer. The details about used fibrous materials are given in **Table 1**, and their structure and morphology are shown in **Figure 6**.

The main objectives of this work include four aims by following strategy as shown in **Figure 5**:

- The first objective is to find suitable multi-layer fabric structures to contain PCM. The multi-layer fabric structure is composed of PCM-loaded layer, barrier layer and protection layer and stabilized by using commercial fibrous tape to connect each layer. Firstly, three different organic PCMs with similar melting/solidifying points are used, including PEG 6000, paraffin wax (PW) and myristic acid (MA) (**Table 2**). Besides, the different fibrous multi-layer PCM systems with different structures are prepared, which is given in **Table 4**. After investigating leakage phenomena of PCM from the fibrous multi-layer PCM system, the selected fibrous materials in the multi-layer fabric containing PCM will be proven. The wetting behavior of molten PCM on various fibrous materials will be also estimated, which are considered for leakage phenomena.
- The second objective is complex characterization of thermal property of the prepared fibrous multi-layer PCM system. The thermal energy storage and phase transition behavior of the suitable fibrous multi-layer PCM system will be investigated by using differential scanning calorimetry (DSC). In addition, the thermal buffering effect will be evaluated by recording heating/cooling T-history curves. Especially, the application of Newton's cooling law is to characterize heating T-history of the fibrous multi-layer PCM system.
- The third objective is to improve the thermal energy storage efficiency of the suitable fibrous multi-layer PCM system. Different metal particles (MP) including copper (Cu), aluminum (Al), silver (Ag), iron (Fe), and zinc (Zn) will be introduced in PCM-loaded layer to increase thermal conductivity supporting energy storage efficiency (Details of MP are given in **Table 3**). Correspondingly, thermal energy storage, phase transition behavior

and thermal buffering effect of the MP-incorporated fibrous multi-layer PCM system will be investigated.

- The fourth objective is to improve the breathability of the fibrous multi-layer PCM system. The PCM-loaded layer of the fibrous multi-layer PCM system will be modified and consists of PCM pocket and air pocket. The breathability, thermal energy storage, phase transition behavior and thermal buffering effect of the multi-layer PCM fabrics will be investigated.

This dissertation thesis represents a set of published scientific papers accompanied by a detailed discussion of current state of knowledge about preparation and characterization of fibrous multi-layer phase change material (PCM) system with enhanced thermal conductivity and protection against leakage of PCM in the liquid state. Full results can be found in published work (**[1]**, **[2]**, **[3]**, **[4]** and **[6]** in **Sec. 9.1**).

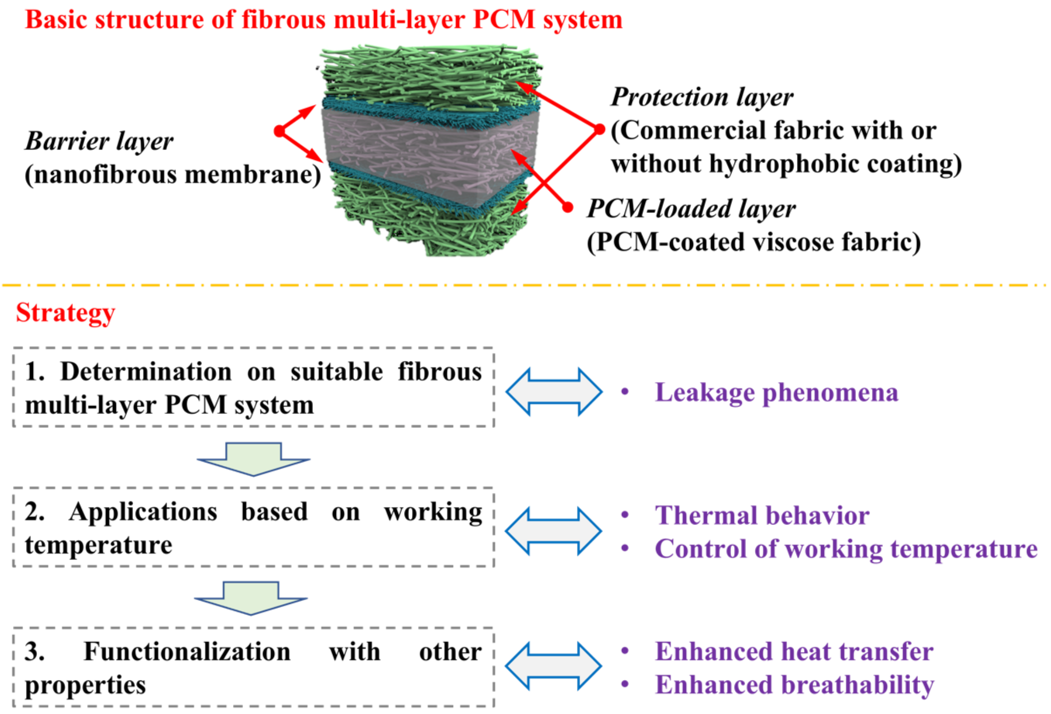

Figure 5 Basic structure of a fibrous multi-layer PCM system and development strategy

Table 1 Details for fibrous materials (mean±standard error)

Fibrous materials	Areal density	Thickness	Diameter of fiber	Water contact angle*	Surface porosity (%)
Viscose nonwoven fabric	47±1.21g/m^2	0.33±0.02mm	13.8±4.79μm	0°	15.5±1.3

PET knitted fabric	200±2.35g/m^2	0.57±0.01mm	12.5±1.49m	0^o	4.1±1.2
PET knitted fabric with hydrophobic coating	212±2.51g/m^2	0.54±0.01mm	13.57±1.05μm	122±2.1^o	6.3±1.1
PU nanofibrous membrane	6.0±1.02g/m^2	0.1±0.01mm	292±132nm	131±2.1^o	3.5±1.2

*: water contact angle values were measured after 5 min deposition

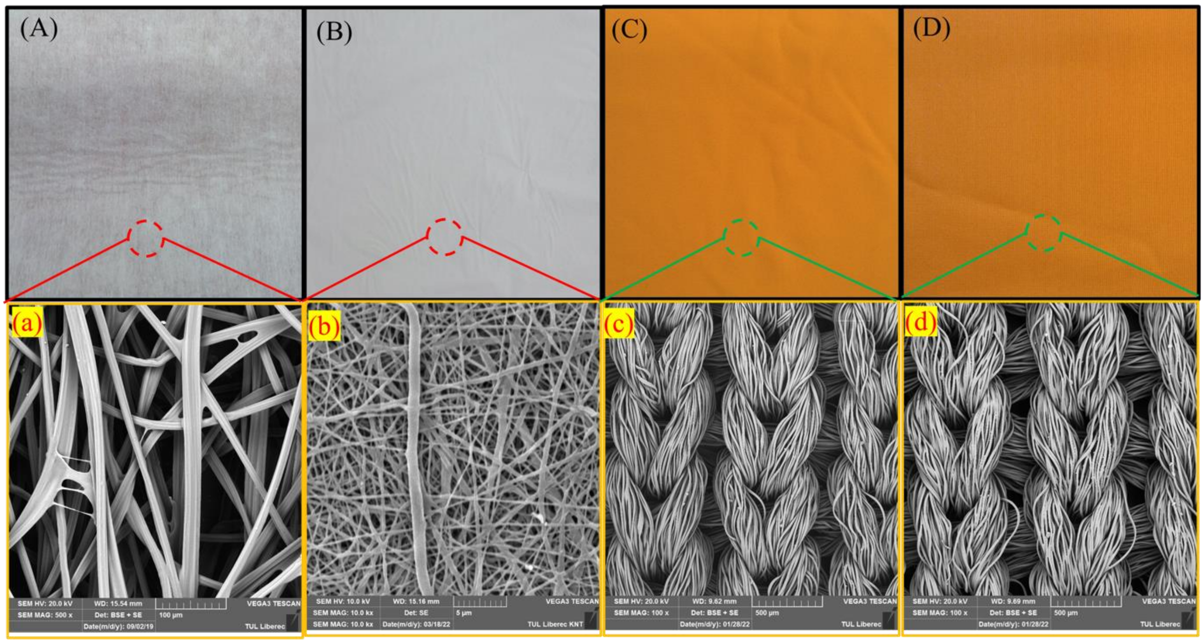

Figure 6 Structure and morphology of used fibrous materials (A, B, C, D: macroscopical images of viscose nonwoven fabric, PU nanofibrous membrane, PET fabric and PET fabric with hydrophobic coating; a, b, c, and d: SEM images of viscose nonwoven fabric, PU nanofibrous membrane, PET fabric and PET fabric with hydrophobic coating)

Table 2 Details of used organic PCMs from Sigma Aldrich datasheet

Label	Materials	Melting point (^{o}C)
PEG 600	Polyethylene glycol with molecular weight of 600 g/mol	17-22
PEG 1000	Polyethylene glycol with molecular weight of 1000 g/mol	33-40
PEG 1500	Polyethylene glycol with molecular weight of 1500 g/mol	43-49
PEG 4000	Polyethylene glycol with molecular weight of 4000 g/mol	53-58
PEG 6000	Polyethylene glycol with molecular weight of 6000 g/mol	58-63

PW	Paraffin wax	58-62
MA	Myristic acid	52-54

Table 3 Details of metal particles (MP) from company

MP type	Diameter (D50) (μm)
Cu	35.00
Al	51.47
Ag	23.00
Fe	25.00
Zn	3.60

Table 4 Description of multi-layer PCM fabrics

Sample code	Protection layer	Barrier layer	PCM-loaded layer
$C1_{MA}$	PET fabric	-	MA-coated viscose fabric
$C2_{MA}$	PET fabric	PU nanofibrous membrane	
$C3_{MA}$	PEG fabric with hydrophobic coating	-	
$C4_{MA}$	PEG fabric with hydrophobic coating	PU nanofibrous membrane	
$C1_{PW}$	PET fabric	-	PW-coated viscose fabric
$C2_{PW}$	PET fabric	PU nanofibrous membrane	
$C3_{PW}$	PEG fabric with hydrophobic coating	-	
$C4_{PW}$	PEG fabric with hydrophobic coating	PU nanofibrous membrane	
$C1_{PEG}$	PET fabric	-	PEG-coated viscose fabric
$C2_{PEG}$	PET fabric	PU nanofibrous membrane	
$C3_{PEG}$	PEG fabric with hydrophobic coating	-	
$C4_{PEG}$	PEG fabric with hydrophobic coating	PU nanofibrous membrane	

4. Construction of A Fibrous Multi-layer PCM System

Various fibrous multi-layer PCM systems have been developed according to **Table 4**. At first, the leakage of PCM textiles should be solved. After checking leakage phenomena of different combinations of fibrous multi-layer PCM system, two structure of the fibrous multi-layer PCM systems without leakage were successfully obtained. The first one ($C4_{(PW)}$) was the sample consisting of polyester fabric with hydrophobic coating as protection layer, PU nanofibrous membrane as barrier layer and PEG-coated viscose fabric as PCM-loaded layer. The second one ($C4_{(PEG)}$) was the sample consisting of polyester fabric with hydrophobic coating as protection layer, PU nanofibrous membrane as barrier layer and PEG-coated viscose fabric as PCM-loaded layer.

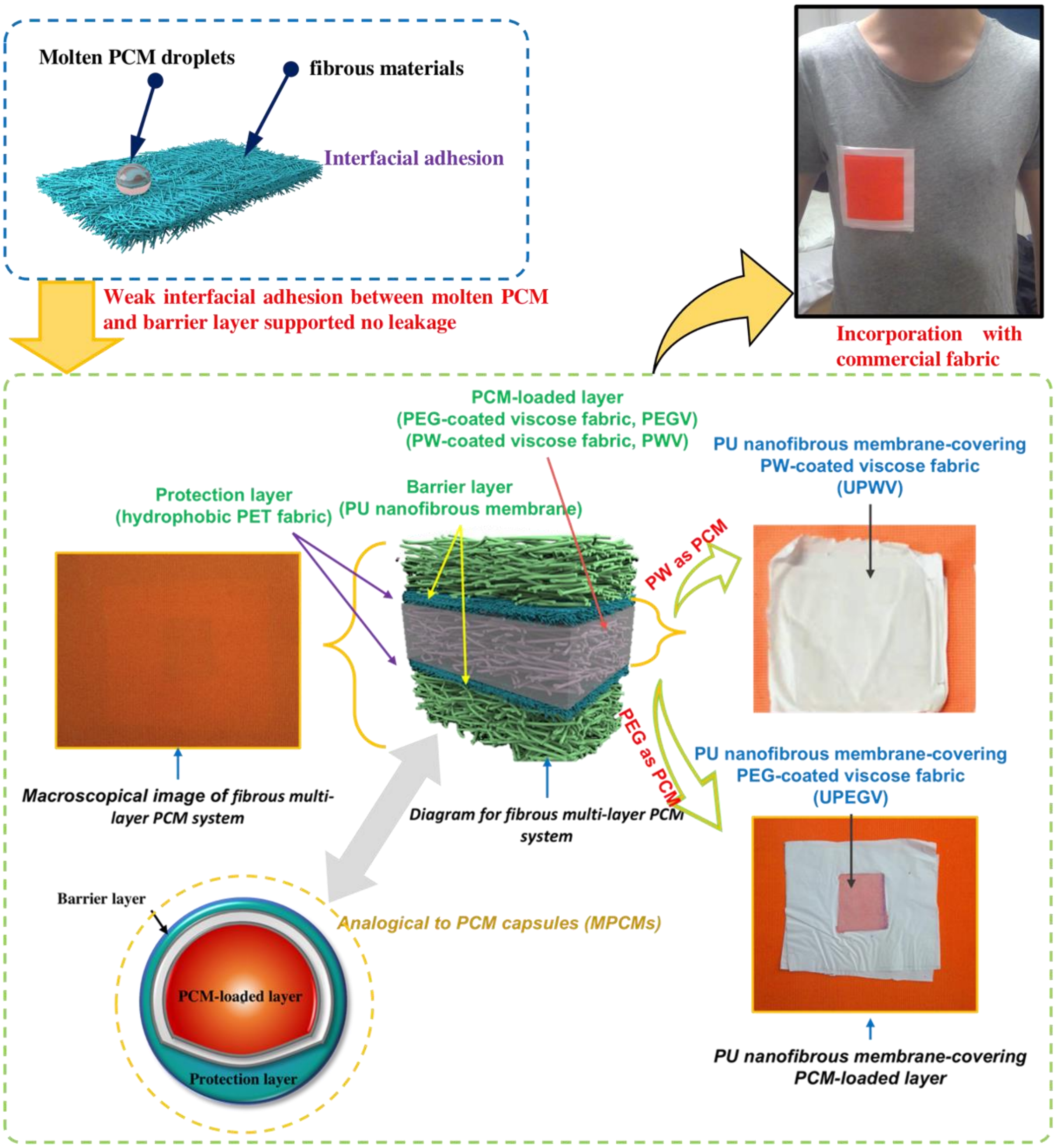

Figure 7 PCM loading situation inside the fibrous multi-layer PCM system and analogy of fibrous multi-layer PCM system to MPCMs

4.1 Mechanism to avoid leakage

It is noticed that the leakage phenomena could be a result of interfacial adhesion between molten PCMs and fibrous materials. The contact angle of molten PCM droplets on the fibrous membrane were investigated. As a result, molten PW droplets can be only on the PU nanofibrous membrane and have a stable contact angle of 110°. Molten PEG droplets can be only on the PU nanofibrous membrane and have a stable contact angle of 130°. The weak interfacial adhesion between molten PW and PU nanofibrous membrane was found, and the weak interfacial adhesion between molten PEG and PET fabric with hydrophobic coating was found (**Figure 7Figure 7**). Especially for C4$_{(PEG)}$, the successful barrier for resistance of molten PEG was realized by both PET knitted fabric with hydrophobic coating as protection layer and PU nanofibrous membrane as barrier layers. So, a combination of weak interfacial adhesion of molten PCMs and fibrous materials and the use of nanofibrous membrane in fibrous multi-layer system accounted for no leakage phenomena.

Besides, the PCM (including PEG and PW) were well kept inside the sample C4 fibrous multi-layer PCM system containing PET fabric with hydrophobic coating as protection layer. So, the fibrous multi-layer PCM system can resist the side effects from external environment (e.g., rubbing, water pouring etc.).

For MPCM-coated fabrics, we have reported that the MPCMs are possibly destroyed during padding-coating-drying method. For example, the phase transition and enthalpy values are changed when compared with net MPCMs. It is proposed that the leakage of MPCMs happens because of unexpected mechanical property of their shells. However, the fibrous multi-layer PCM system should be a relatively better control of phase transition and enthalpy values under different external environments because of PET fabric with hydrophobic coating as protection layer.

4.2 High PCM loading performance in the fibrous multi-layer PCM system

The PCM loading performance is essential for thermal behavior of the PCM-incorporated materials, including encapsulation efficiency, PCM loading amount, relative crystalline degree and working temperature range.

The PCM loading amount (p) is directly related to the thermal energy storage, and higher PCM loading amount supports the higher thermal energy storage. Besides, the self-crystalline behavior of the PCM inside the PCM-incorporated materials is altered because of the confined space for crystallization (e.g., MPCMs, PCM containing fibers, form-stable PCM etc.). The higher predicted relative crystalline degree (χ_0) of the PCM in the PCM-incorporated materials also supports the higher thermal energy storage. The DSC method is usually for the relative crystalline degree by using **equation (9)**, where $\Delta H_{m,sample}$ is the measured melting enthalpy value of sample (J/g), p is the PCM loading amount and $\Delta H_{m,PCM}^{T}$ is the theoretical melting enthalpy value of PCM. The calculation of the relative crystalline degree is based on the PCM loading amount. It is noticed that paraffin wax has a solid-solid phase transition and solid-liquid phase transition. So, the **equation (10)** modified from **equation (9)** could be used to reveal characterize the experimental relative crystalline degree (χ), where $\Delta H_{m,PCM}$ is the measured melting enthalpy value of the PCM. The experimental relative crystalline degree obtained from **equation (10)** only reveals the effect of PCM-incorporated textile on the self-crystalline behavior of PCM. Indeed, it is difficult to determine the practical PCM loading amount in PCM-containing fibers, MPCMs and other PCM-incorporated composites. Instead of the PCM loading amount, the encapsulation efficiency (η) is proposed as a result of PCM loading amount and relative crystalline degree of encapsulated PCMs, which is the ratio of the measured enthalpy value (ΔH_{sample}) of the PCM-incorporated materials to the measured enthalpy value (ΔH_{PCM}) of net PCMs (**equation (11)**). Besides, the overall enthalpy value ($\Delta H_{m,overall}$) of the fibrous multi-layer PCM system is calculated according to **equation (12)**. The $p_{overall}$ is the PCM loading amount of the whole fibrous multi-layer PCM system.

$$\chi_0 = \frac{\Delta H_{m,sample}}{\Delta H^{T}_{m,PCM} \times p} \tag{9}$$

$$\chi = \frac{\Delta H_{m,sample}}{\Delta H_{m,PCM} \times p} \tag{10}$$

$$\eta = \frac{\Delta H_{sample}}{\Delta H_{PCM}} \times 100\% \tag{11}$$

$$\Delta H_{m,overall} = \frac{\Delta H_{m,sample}}{p} \times p_{overall} \tag{12}$$

Especially, there were several characterizations of the fibrous multi-layer PCM system. The first one was that the fibrous multi-layer PCM system had a similar structure as MPCMs and was analogical to the MPCMs as shown in Chyba! Nenalezen zdroj odkazů.. From this point, the fibrous multi-layer PCM system was in fact the 'big' PCM encapsulations. The second one was that the fibrous multi-layer PCM system was already a composite fabric and can be incorporated into commercial textiles. So, the overall PCM performance of the fibrous multi-layer PCM system was presented and compared with current reported PCM products (including MPCMs, PCM containing fibers, and PCM containing fabrics) for the advantages.

4.2.1 Encapsulation efficiency of the fibrous multi-layer PCM system and current PCM products

The encapsulation efficiency and molten enthalpy values of the fibrous multi-layer PCM system ($C4_{(PW)}$ and $C4_{(PEG,6000)}$) was 55 % and 73 J/g, and 44 % and 78 J/g, respectively. As shown in **Figure 8 (A)**, the fibrous multi-layer PCM system had a relative low encapsulation efficiency and molten enthalpy values when compared with MPCMs [55–70]. According to **equation (11)**, the encapsulation efficiency is strongly influenced by $\Delta H_{m,sample}$ and $\Delta H_{m,sample}$ is significantly affected by PCM loading amount. So, the encapsulation efficiency can be increased by having relatively higher PCM loading amount in the fibrous multi-layer PCM system containing protection layers with small areal density. The ideal maximum encapsulation efficiency of the fibrous multi-layer PCM system was infinitely close to the fibrous multi-layer PCM system without protection layer (e.g., UPWV) with encapsulation efficiency of 78.9 %, which is comparable with reported MPCMs. The ideal maximum molten enthalpy value of the fibrous multi-layer PCM system (C4$_{(\mathrm{PW})}$) can reach 105 J/g and have a medium center in the **Figure 8 (A)**.

The fibrous multi-layer PCM system also has a comparable encapsulation efficiency with PCM containing fibers. As shown in **Figure 8 (B)**, the encapsulation efficiency of the fibrous multi-layer PCM system (C4$_{(\mathrm{PEG,6000})}$ and C4$_{(\mathrm{PW})}$) is higher than most reported PCM-reported fibers [71–82]. The encapsulation efficiency can be increased by using thin fibrous materials (e.g., ultrafine nonwoven fabric) as protection layers. The ideal maximum encapsulation efficiency of the fibrous multi-layer PCM system (C4$_{(\mathrm{PW})}$) is close to UPWV and the highest among the samples in **Figure 8 (B)**.

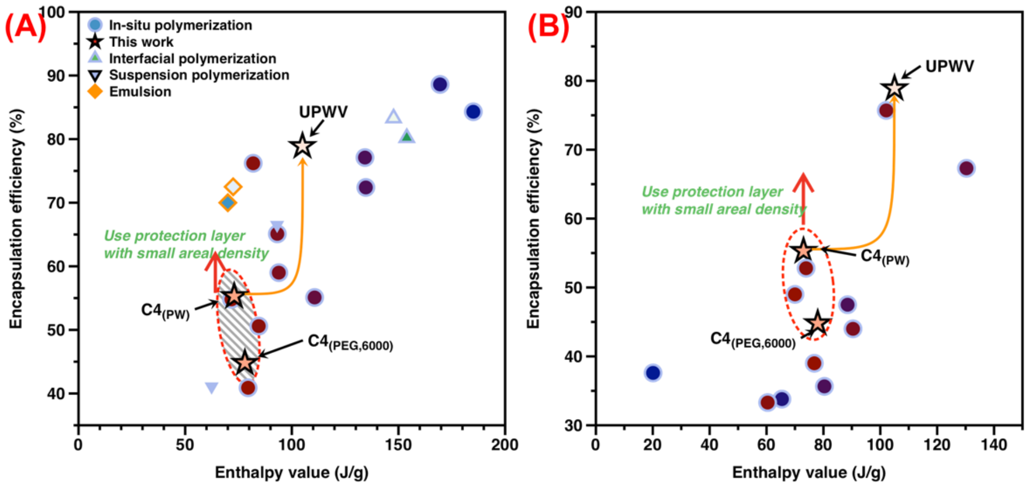

Figure 8 Comparison of this work with MPCM (A) and PCM containing fibers (B) in PCM encapsulation efficiency

4.2.2 PCM loading amount of the fibrous multi-layer PCM system and current PCM products

As described in published work (**[3]** in **Sec. 9.1**), the optimal maximum loading amount of PW and PEG in the PCM-loaded layer is around 90 wt%. By taking the mass of nanofibrous membranes and PET fabrics with hydrophobic coating, the optimal maximum loading amount of PW and PEG in the fibrous multi-layer PCM system reached 46 wt%.

As shown in **Figure 9 (A)**, the PCM loading amount in the fibrous multi-layer PCM system is very close to most of PCM containing fibers [72,78,81–84]. Besides, the PCM loading amount in the fibrous multi-layer PCM system is much higher than PCM containing fabrics as shown in **Figure 9 (B)**. So, the high PCM loading amount in the fibrous multi-layer PCM system was found.

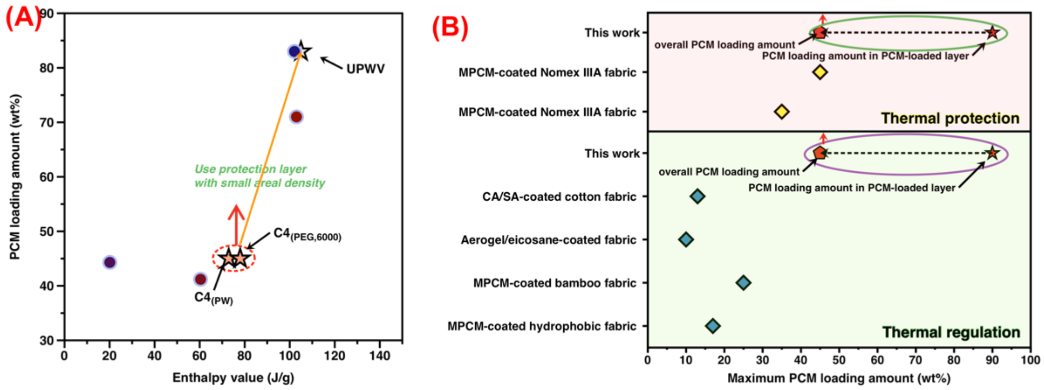

Figure 9 Comparison of this work with PCM containing fibers in PCM loading amount (A) and with PCM containing fabric for potential applications (B)

4.2.3 Experimental relative crystalline degree of PCM in the fibrous multi-layer PCM system and current PCM products

The experimental relative crystalline degree ratios of PCM in the fibrous multi-layer PCM system and current PCM products are shown in **Figure 10** [73,78,80,82,85–88]. Obviously, the PCMs in the fibrous multi-layer PCM system have highest relative crystalline degree ratio (>95%). The little confinement of the fibrous multi-layer PCM system on the self-crystalline behavior was found.

The reason is that the PCM-loaded layer is the PCM-coated viscose nonwoven fabric and PU nanofibrous membrane just slightly affected the self-crystalline behavior of PCM. In contrast, the supporting materials for other PCM products resulted in a strong confinement. For PCM containing fibers, the self-crystalline behavior of the PCM in the fiber matrix was affected by the fiber diameter and interfacial adhesion between PCMs and fiber materials. The similar reason was also for MPCMs and other form-stable PCMs (e.g., PCM/aerogel composites).

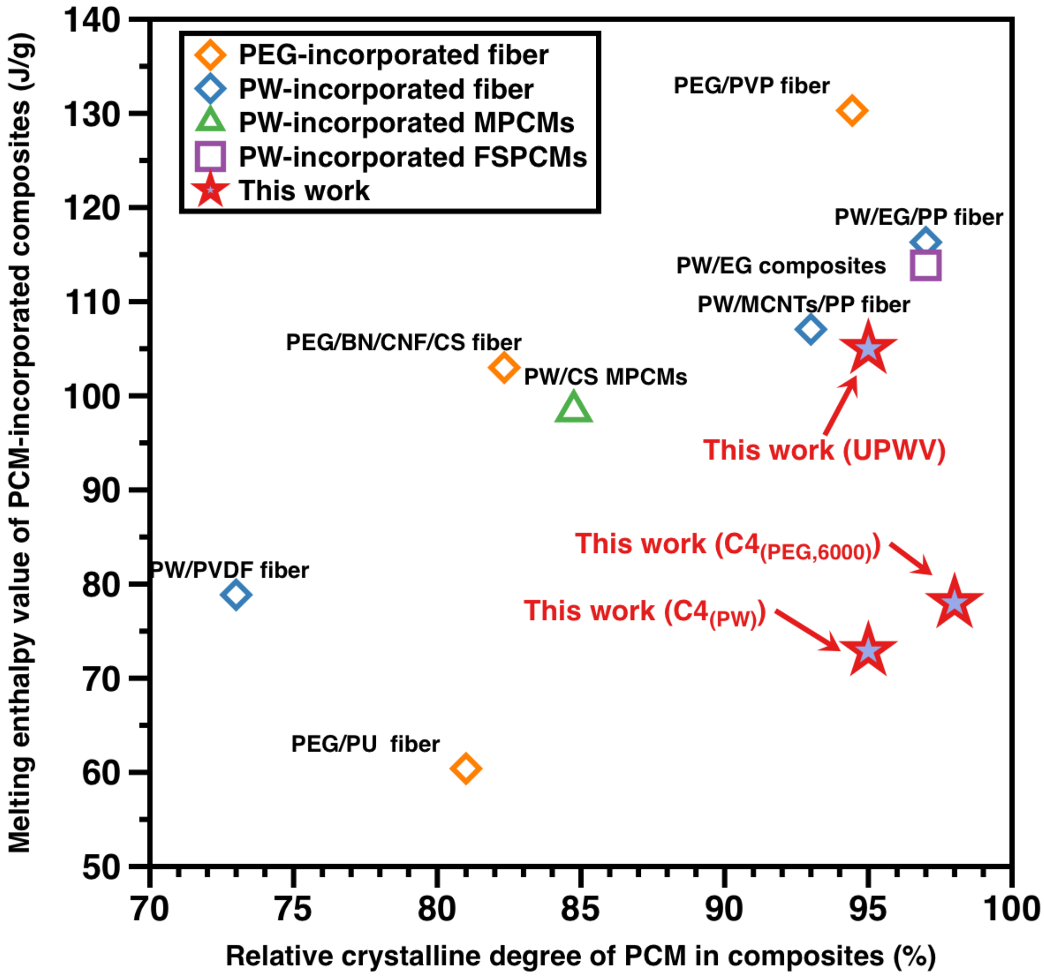

Figure 10 Comparison of this work with other reported work in crystallinity of PCM

4.2.4 Controlled working temperature range and selected applications

It had been proved that the PEG and PW were suitable in the proposed fibrous multi-layer PCM system. The thermal behavior (including phase transition and enthalpy value) of PEG was up to the molecular weight and the thermal behavior of PW was up to the carbon numbers. In this case, various PEGs with different molecular weights were used as PCMs in the fibrous multi-layer PCM system.

As shown in **Figure 11**, the working temperature ranges of the fibrous multi-layer PCM system was successfully controlled by using different PEGs while the enthalpy values were very close although there was a slight increase when the PEG with higher molecular weight was used.

The enthalpy values of the fibrous multi-layer PCM system were higher than the PCM products from famous Outlast company while the working temperature range of the fibrous multi-layer PCM system were easier to be controlled.

Besides, enthalpy values of the fibrous multi-layer PCM system were smaller than the PCM-incorporated materials from literature. However, the overall thermal energy storage of the fibrous multi-layer PCM system can be increased by having relatively higher PCM loading amount in the fibrous multi-layer PCM system containing protection layers with small areal density.

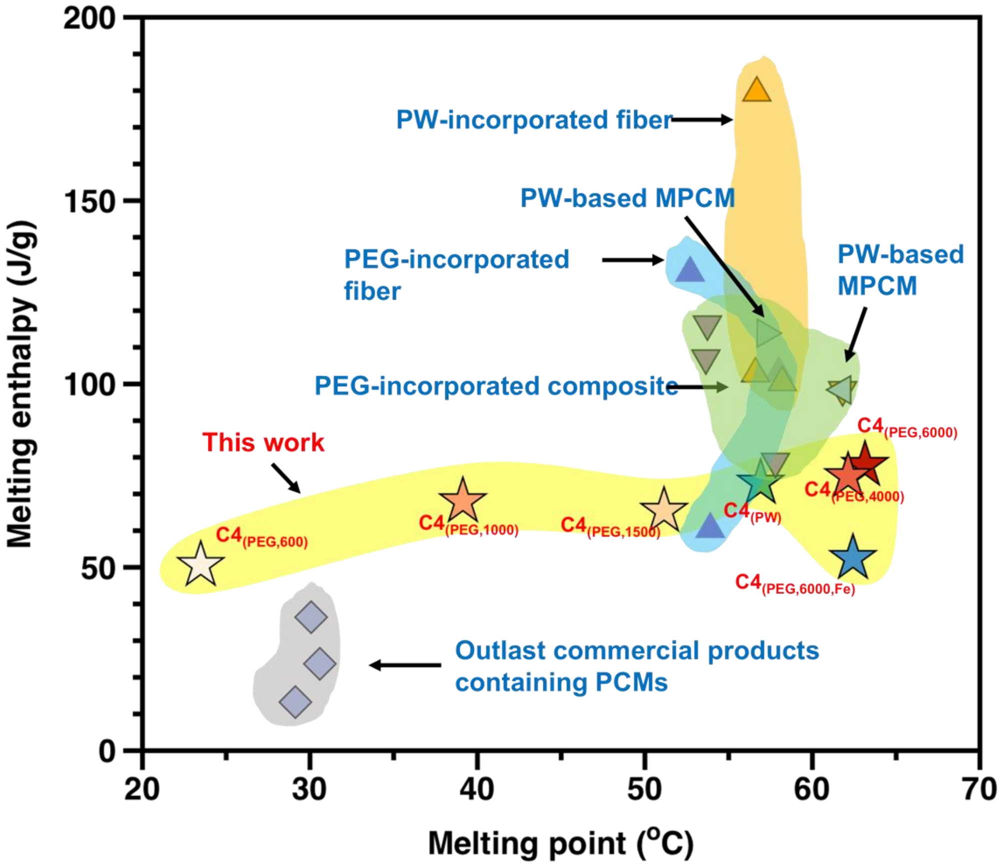

Figure 11 Comparison of this work with current PCM-incorporated products in the field of working temperature range and enthalpy values

4.2.5 Thermal buffering effect of the fibrous multi-layer PCM system

To reveal thermal buffering effect of the fibrous multi-layer PCM system, PEG 6000 and PW were selected as PCM, respectively. The higher melting point of PEG 6000 and PW than room temperature could provide an understanding of thermal buffering effect.

Figure 12 (A) presents full T-history of multi-layer fabric without PCM (reference sample), multi-layer fabric with PEG 6000 ($C4_{PEG,6000}$) and multi-layer fabric with PW ($C4_{PW}$). Obviously, the thermal buffering effect was found in the $C4_{(PEG,6000)}$ and $C4_{PW}$ samples when compared with $C4_{reference}$ sample without PCMs. Generally, the time for each sample to reach selected temperature during T-history was available to characterize thermal buffering effect.

By taking phase transition of PCM into consideration, both the time to reach 65 ^{o}C during heating process ($t_{h,65}$), and the time to reach 40 ^{o}C during cooling process were selected ($t_{c,40}$). The $t_{c,40}$ value of reference sample, C4$_{(PEG,6000)}$, and C4$_{PW}$ was 4s, 207s and 108s, respectively. From this point of view, the sample C4$_{(PEG,6000)}$ had the better thermal buffering effect than C4$_{(PW)}$.

To further reveal the temperature increasing rate in each part in the heating T-history curves of all the samples, the modified Newton's cooling law was used to characterize by referring **equation (4)-(7)**.

Especially, the application of modified Newton's cooling of to characterize the heating T-history was valid only when Biot number (Bi) of the sample should be smaller than 0.1. Since T-history for the samples was measured under room temperature, the free convection was taken into consideration. Then, the free convection coefficient (h) was chosen as 8 W m^{-2} K^{-1}. According to **equation (13)**, Bi number was calculated. The L (mm) was the thickness of the sample, and the k (W m^{-1} K^{-1}) was the thermal conductivity of the sample. Both L and k were measured by using ALAMBETA setup a [41]. As a result, the calculated Bi number value of C4$_{(reference)}$, C4$_{(PEG,6000)}$, and C4$_{(PW)}$ ranged from 0.1 to 0.2. So, the modified Newton's cooling las could roughly evaluate the heating T-history [42].

$$Bi = \frac{hL}{k} \tag{13}$$

As shown in **Figure 12 (B)**, good fittings for three linear parts including solid phase, phase transition phase and liquid phase were found. After having the intersection points of estimated x and y values from **Figure 12 (B)**, the fittings for heating T-history curves were found and shown in **Figure 12 (C)**. By calculating the intersection points of estimated t and T values, the time (t_{phase}) and temperature (T_{phase}) for phase transition range of multi-layer PCM fabrics were determined.

As shown in **Figure 12 (D)**, the sample C4$_{(PEG,6000)}$ had higher t_{phase} and T_{phase} values than the sample C4$_{PW}$, which also supported that C4$_{PEG}$ sample had better thermal buffering effect than C4$_{PW}$.

In addition, the thermal insulation values (I) of all the samples were calculated according to **equation (8)**, and were schemed in **Figure 12 (E)**. The T_h was the heating temperature of 80 ^{o}C and T_r was the room temperature. As a result, both sample C4$_{(PEG,6000)}$ and C4$_{PW}$ had lower I values than C4$_{reference}$ from heating T-history, which was caused by large amount of still air in C4$_{reference}$ sample.

By comparing with other methods of reported work, the application of Newton's cooling law can not only exactly determine the thermal buffering effect but also predict the T-history.

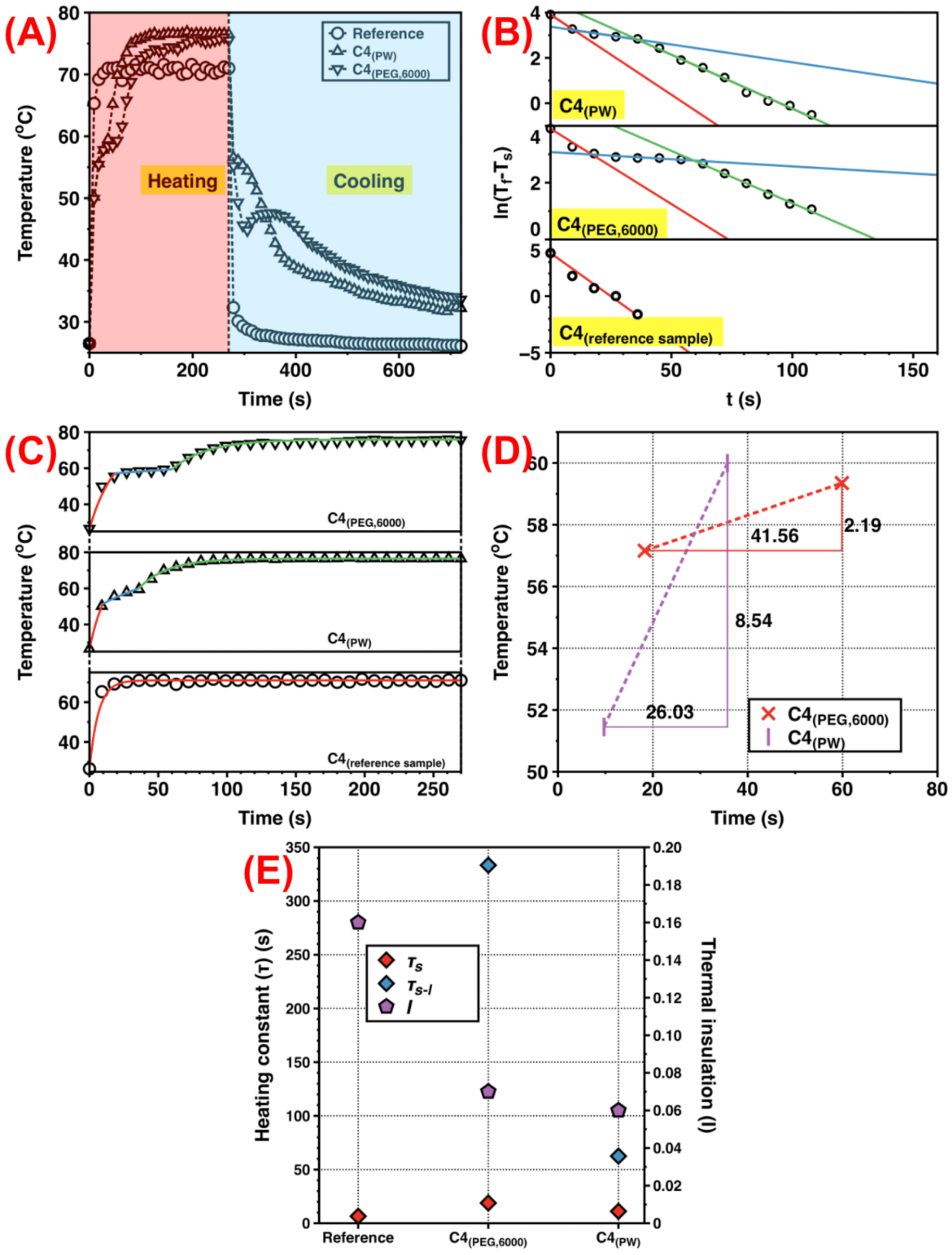

Figure 12 T-history of multi-layer fabrics containing PW and PEG (A), plots of ln [T_f-T_s] against *t* (B), heating T-history with fitting models (C), estimated phase transition range (D) and evaluation of thermal buffering (E)

5. *Enhanced heat transfer efficiency*

Different metal microparticles (Cu, Al, Ag, Fe and Zn) are introduced in the PCM-loaded layer to enhance the heat transfer efficiency according to published work (**[3]** in **Sec. 9.1**). The Fe microparticles are the best one of six different microparticles to be introduced in PCM-loaded layer.

The thermal conductivity values of the Fe-incorporated fibrous multi-layer PCM system ($C4_{(PEG,6000,Fe)}$) are smaller than 0.1 W K^{-1} m^{-1}, which is schemed in **Figure 13 (A)**. Especially, the thermal conductivity of the Fe-incorporated fibrous multi-layer PCM fabrics ($C4_{(PEG,6000,Fe)}$) is 0.0573 W K^{-1} m^{-1}, which is just slightly higher than the fibrous multi-layer PCM fabrics ($C4_{(PEG,6000)}$) with thermal conductivity of 0.0543 W K^{-1} m^{-1}. Besides, the comparison of the Fe-incorporated fibrous multi-layer PCM fabrics with neat PCMs or other PCM-incorporated materials (including PCM containing fibers, MPCMs, carbon-based PCM composites and metal-based PCM composites) is also shown in **Figure 13 (A)** [74,82,89–105], and the Fe-incorporated fibrous multi-layer PCM fabrics have lowest thermal conductivity. The main reason is that the fibrous multi-layer PCM system contains five layers and fours layers are fibrous materials with small thermal conductivity. The used viscose nonwoven fabric has a thermal conductivity of 0.0298 W K^{-1} m^{-1}, and PET fabric with hydrophobic coating has a thermal conductivity of 0.0693 W K^{-1} m^{-1}. Besides, the PCM-loaded layer has a small thermal conductivity. The PEG-coated viscose fabric ($UPEGV_{6000}$) has a small thermal conductivity of 0.0395 W K^{-1} m^{-1}, and the PEG/Fe-coated viscose fabric ($UPEGV_{6000,Fe}$) has a small thermal conductivity of 0.0654 W K^{-1} m^{-1}.

Although the overall thermal conductivity of the Fe-incorporated fibrous multi-layer PCM system is small, some characters are observed:

- The thermal conductivity of the Fe-incorporated fibrous multi-layer PCM system is very close to common fabric (e.g., viscose nonwoven fabric with a thermal conductivity of 0.0298 W K^{-1} m^{-1}). In this case, the Fe-incorporated fibrous multi-layer PCM system has a similar thermal comfort as common fabric, which is totally different from other reported thermal enhanced PCM products. It validates the suitable application of Fe-incorporated fibrous multi-layer PCM systém in the textile.
- The incorporation of Fe microparticles in the PCM-loaded layer still enhances the heat transfer efficiency. The thermal conductivity of the PCM-loaded layer ($UPEGV_{6000,Fe}$) is increased 65.6%.
- The temperature of $C4_{(PEG,6000,Fe)}$ increases faster than $C4_{(PEG,6000)}$, as shown in **Figure 13 (B)**. **Figure 13 (C)** presented the estimated phase transition range in detail. However, the phase transition range of $C4_{(PEG,6000,Fe)}$ started later and lasted longer than than $C4_{(PEG,6000)}$. The $C4_{(PEG,6000,Fe)}$ has a phase transition for 47.06 s while the temperature is increased 6.52 ^{o}C. The reason is that the heat transfer through the whole fibrous multi-layer PCM system with or without Fe microparticles is indeed non-uniform during phase transition. The surface temperature of the fibrous multi-layer PCM system with or without Fe microparticles is affected by the thermal conductivity, thickness, molten points etc. Besides, more precise control of thermal buffering effect in the limited temperature was observed for the $C4_{(PEG,6000,Fe)}$.

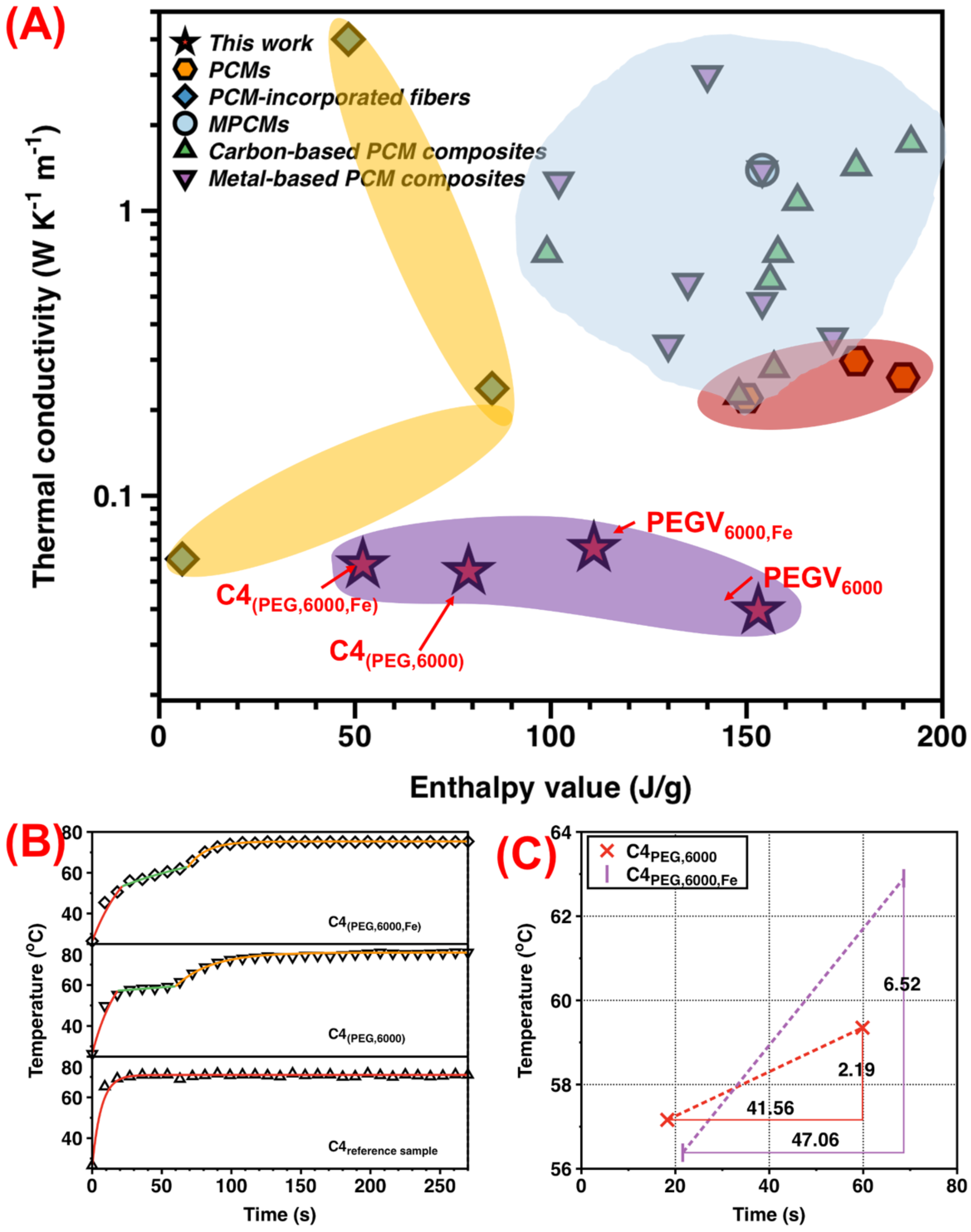

Figure 13 Estimation of thermal conductivity enhancement of Fe-incorporated fibrous multi-layer PCM system (A: comparison with PCM products, B: T-history of Fe-incorporated fibrous multi-layer PCM system, and C: thermal buffering range of Fe-incorporated fibrous multi-layer PCM system)

6. Controlled breathability by modifying PCM-loaded Layer

There is no breathability since PCM-loaded layer is a composite where there is no path for air or water vapor to penetrate. For the fibrous multi-layer PCM system, introduction of air pocket is an alternative to enhance mass transfer and incorporate other materials for functions [106]. To realize breathability, the PCM-loaded layer is modified and consists of air pocket and PCM pocket (PEG-coated viscose fabric). The PCM pockets are uniformly distributed between two barrier layers with certain air gaps.

Since the PCM-loaded layer comprises of PCM pockets and air pockets, as shown in the **Figure 14 (A)**, the possibility of PEG leakage within the PCM-loaded layer must be considered. At first, there was no PEG leakage observed through the fibrous multi-layer PCM system after heating/cooling cycles, either from the vertical or planar direction. As explained in the **Sec. '4'**, The combination of the weak interfacial adhesion between molten PEG and the protection layer (PET fabric with hydrophobic coating) and the use of a PU nanofibrous membrane in the fibrous multi-layer PCM system were responsible for this outcome.

However, it was observed that the diffusion of molten PEG within the PCM pocket inside the fibrous multi-layer PCM system was strongly linked to the amount of loaded PEG. For instance, **Figure 14 (B-i)** displays the leakage phenomena of sample $UPEGV_{10-1}$ with mass ratio (R_{PEG}) of PEG to viscose fabric of 10:1, where the PEG has dispersed throughout the PCM pocket and air pocket, resulting in obvious leakage. However, when the mass ratio of PEG to viscose fabric in the PCM-loaded layer was reduced to 5:1, the sample $UPEGV_{5-1}$ exhibited a clear boundary between the PCM pocket and air pocket, and minimal diffusion of molten PEG was detected (**Figure 14 (B-ii)**). The following reasons are found:

- When there was a higher loading amount of PEG in the PCM pocket as shown in **Figure 14 (B-iv)**, some PEGs were located outside of the viscose fabric. Before heating process with pressure, the PCM pocket ideally had a width of D_0 and thickness of L_0. During the heating process with pressure, the PEG outside of the viscose fabric was forced to move along the fabric surface direction because molten PEG was movable. Then after heating process with pressure, the dimension of the PCM pocket was changed and D_0 became D_1 and L_0 became L_1. The D_0 was smaller than D_1 and L_0 was higher than L_1. Consequently, during heating and cooling cycles with pressure, the PEG outside the viscose fabric melted and began to move along the fabric surface direction, leading to leakage phenomena. For example, the $UPEGV_{10-1}$ had a PEG diffusion and instability of PEG encapsulation.
- However, when the PEG loading amount was limited as shown in **Figure 14 (B-iii)**, the majority of PEG was efficiently adsorbed by the viscose fabric, despite of a very small amount being outside the fabric. It was supposed that the movement of molten PEG inside the viscose fabric was not affected and dimensions including thickness and length were not significantly changed. In details, D_0 and L_0 values were almost same as D_1 and L_1. After undergoing heating and cooling cycles under pressure, the PEG located outside of the viscose fabric is completely melted, while still remaining within the coverage of the PCM pocket.

Therefore, the optimal PCM-loaded layer for creating a breathable fibrous multi-layer PCM system is the $PEGV_{5-1}$ with a R_{PEG} ratio of 5:1.

By modifying the size of the PCM pocket and the breathability of the fibrous multi-layer PCM system was modified. When the size of the PCM pocket was decreased from 3 mm to 2 mm, the air permeability of the breathable fibrous multi-layer PCM system was increased from 4.6 mm/s to 9 mm/s under 100 Pa, and water vapor permeability of the breathable fibrous multi-layer PCM system was increased from 31.4 m^2 Pa W^{-1} to 43.4 m^2 Pa W^{-1}. Although the breathability was realized, there is no comparability of the breathable fibrous multi-layer PCM system with other work [107–112], which was shown in **Figure 15 (A)**. This is attributed to the presence of two layers of PU nanofibrous membranes. However, the overall air permeability could be enhanced by having non-uniform placement and form of the PCM pocket inside the fibrous multi-layer PCM system.

Besides, the overall enthalpy value of the breathable fibrous multi-layer PCM system was 7.8 J/g, which was higher than majority of the MPCM-coated fabrics (**Figure 15 (B)**). By combining with breathability and use of nanofibrous membrane, the breathable fibrous multi-layer PCM system has a potential in special applications (e.g., mask etc.).

Since there were air pockets and PCM pockets in the breathable fibrous multi-layer PCM system, there was a heterogenous heat transfer through the whole breathable fibrous multi-layer PCM system. As shown in **Figure 14 (C)**, the air pocket faster reached the final stable temperature while it took a longer time for PCM pocket to reach the final stable temperature. Besides, it was found that the phase transition of the PCM pocket always started from the boarder between PCM pocket and air pocket and diffused to the center of PCM pocket from FLIR video. Such phenomena were caused by heterogenous heat transfer through air pocket and PCM pocket. There was only thermal convection for air pocket while there was ideally the thermal conduction for PCM pocket. However, the temperature change rate was higher than PCM pocket when the phase transition starts. Then, the heat transfer from the air pocket to the PCM pocket happened. As a result, the phase transition of PEG at the perimeter of the PCM pocket commenced earlier and exhibited a quicker rate of change due to the coupling of thermal conduction and thermal convection. In contrast, the phase transition of PEG at the center of the PCM pocket was solely impacted by thermal conduction.

Additionally, the comparative analysis with previous research highlighted the adaptable nature of the permeable fibrous multi-layer PCM system, depicted in **Figure 16 (A-i)**, **(A-ii)** and **(A-iii)**. Therefore, it is recommended that breathable fibrous multi-layer PCM system are suitable for various human body parts (e.g. safeguarding the chest, arms and legs) with optimal compatibility with textiles.

In addition, a PET fabric with hydrophobic coating was utilized as a protective layer, proposing waterproof and self-cleaning capabilities for the breathable fibrous multi-layer PCM system. The majority of dyes were simply drop out as depicted in **Figure 16 (B-i)**, **(B-ii)** and **(B-iii)**, whilst water droplets were efficiently deposited on the fibrous multi-layer PCM system surface as presented in **Figure 16 (C)**. Therefore, in practical application, PEG as phase change material (PCM) could be well safeguarded.

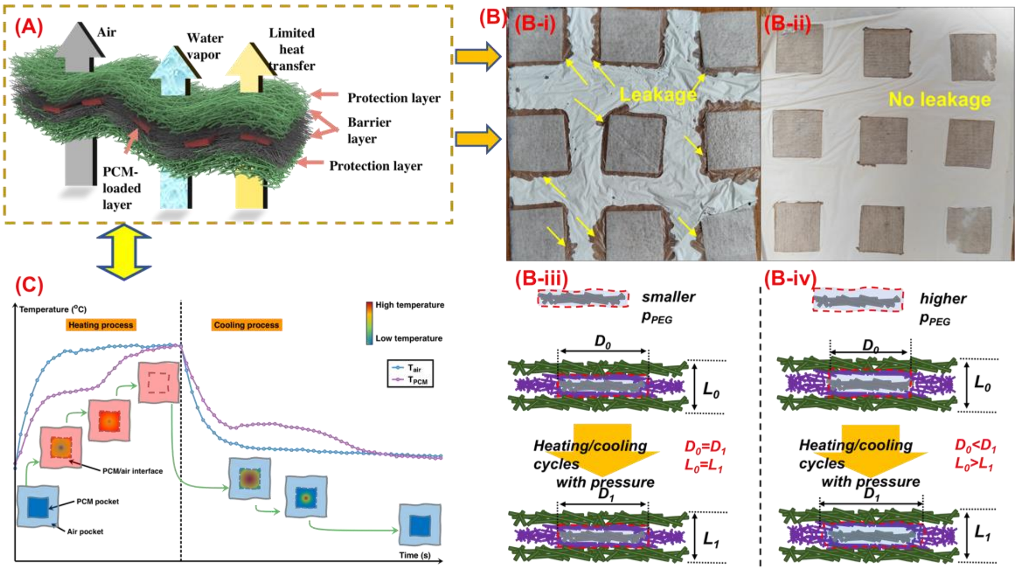

Figure 14 Diagram for breathable fibrous multi-layer PCM system (A), control of leakage phenomena (B), diagram for T-history curves of air pocket and PCM pocket (C)

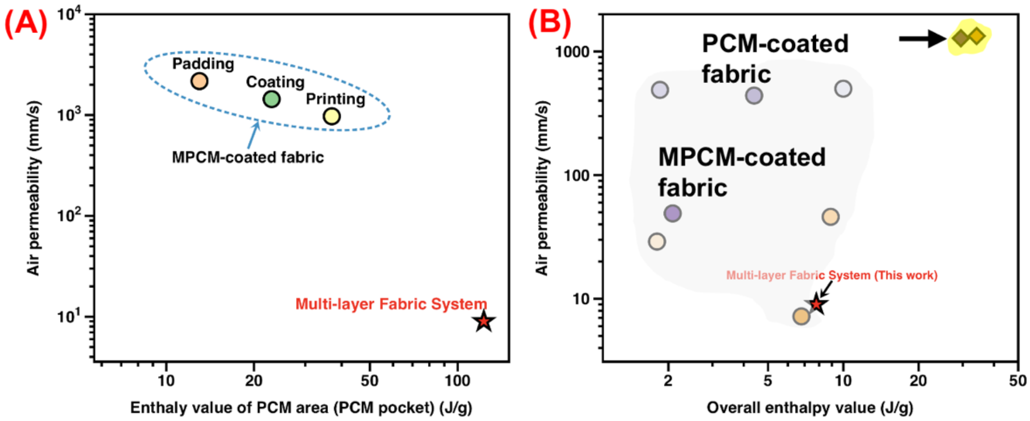

Figure 15 Comparison of this work with air pocket-introduced MPCM-coated fabric (A) and MPCM-coated fabrics without air pocket (B)

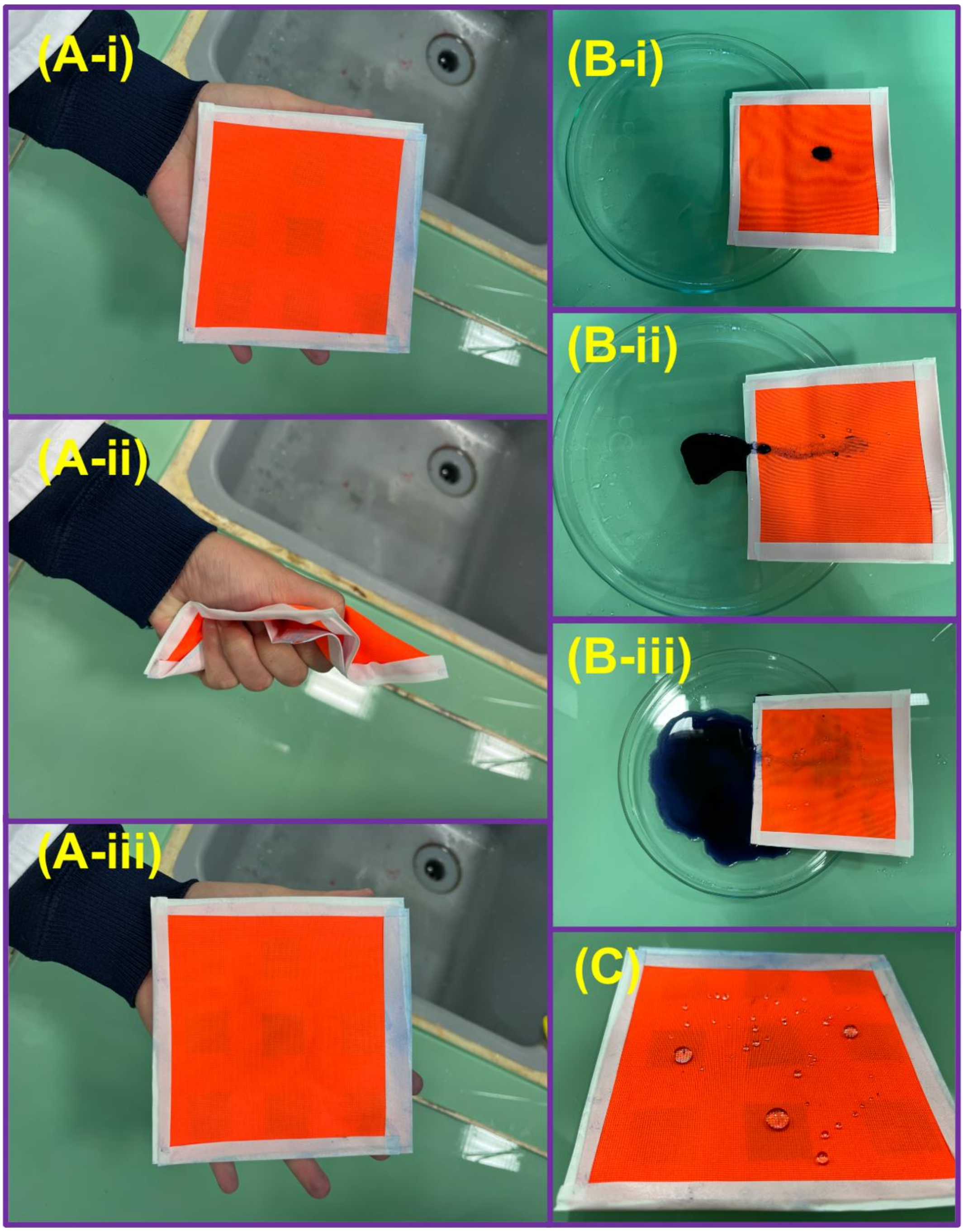

Figure 16 Flexibility (A), self-cleaning property (B) and hydrophobicity (C) of the fibrous multi-layer PCM system

7. Conclusion

This dissertation is conceived as a summary of published scientific and professional works, where the author of this thesis the the first author. In order to emphasize the topicality of the studies topic, the novelty and author motivation to research activities, the work is supplemented with citations of other research works published in the given area.

The present work established a fibrous multi-layer PCM system. The fibrous multi-layer PCM system consisted of PCM-loaded layer, barrier layer and protection layer. The fibrous multi-layer PCM system could meet various applications and practical situations. The following conclusion have been drawn:

- By controlling the interfacial adhesion of molten PCMs on barrier layer or protection layer, the leakage phenomena were totally avoided. The PEG and paraffin wax were suitable as PCMs in such fibrous multi-layer PCM system. The advantage of the fibrous multi-layer PCM system over other PCM textiles was the PCM loading amount. The maximum loading amount of PCMs in the multi-layer PCM fabric was 45 wt%. The overall enthalpy value of the multi-layer PCM fabric is high as 78 J/g. Besides, the working temperature of the fibrous multi-layer PCM system is easily adjusted by using different PCMs. In addition, the PCM performance of the fibrous multi-layer PCM system could be improved by using the protection layer with small areal density.
- The Newton's cooling law was successfully modified to characterize the heating T-history of the fibrous multi-layer PCM system. Especially, the thermal buffering effect was exactly determined by applying Newton's cooling law. The mathematical prediction of the T-history of fibrous multi-layer PCM system was also realized.
- The thermal enhancement of the fibrous multi-layer PCM system was realized by introducing metal microparticles in the PCM-loaded layer. The overall enthalpy value of the fibrous multi-layer PCM system containing metal microparticles was higher than 50 J/g.
- The breathability of the fibrous multi-layer PCM system was realized by modifying PCM-loaded layer, and the PCM-loaded layer was separated into PCM pocket and air pocket. There was a limitation of PCM loading amount in the PCM pocket of the breathable fibrous multi-layer PCM system. Besides, higher air pocket inside the fibrous multi-layer PCM system resulted in better breathability. However, the breathability was small since there were two layers of nanofibrous membranes inside the fibrous multi-layer PCM system. Still, the introduction of the air pocket provided an alternative to enhance breathability. Besides, the PCM pocket and air pocket had different T-history behaviors because of their different thermal resistances. It was found that the size of air pocket was strongly connected to the mutual heat transfer between PCM pocket and air pocket.

8. References

[1] N. Zhang, Y. Yuan, X. Cao, Y. Du, Z. Zhang, Y. Gui, Latent Heat Thermal Energy Storage Systems with Solid–Liquid Phase Change Materials: A Review, Adv Eng Mater. 20 (2018) 1700753. https://doi.org/10.1002/adem.201700753.

[2] G. Alva, Y. Lin, L. Liu, G. Fang, Synthesis, characterization and applications of microencapsulated phase change materials in thermal energy storage: A review, Energ Buildings. 144 (2017) 276–294. https://doi.org/10.1016/j.enbuild.2017.03.063.

[3] W. Chalco-Sandoval, M.J. Fabra, A. López-Rubio, J.M. Lagaron, Use of phase change materials to develop electrospun coatings of interest in food packaging applications, J Food Eng. 192 (2017) 122–128. https://doi.org/10.1016/j.jfoodeng.2015.01.019.

[4] C. Zhu, Y. Chen, R. Cong, F. Ran, G. Fang, Improved thermal properties of stearic acid/high density polyethylene/carbon fiber composite heat storage materials, Sol Energ Mat Sol C. 219 (2021). https://doi.org/10.1016/j.solmat.2020.110782.

[5] K. Iqbal, A. Khan, D. Sun, M. Ashraf, A. Rehman, F. Safdar, A. Basit, H.S. Maqsood, Phase change materials, their synthesis and application in textiles—a review, J Text Inst. 110 (2019) 625–638. https://doi.org/10.1080/00405000.2018.1548088.

[6] K. Yang, J. Wiener, M. Venkataraman, Y. Wang, T. Yang, G. Zhang, G. Zhu, J. Yao, J. Militky, Thermal analysis of PEG/Metal particle-coated viscose fabric, Polym Test. 100 (2021) 107231. https://doi.org/10.1016/j.polymertesting.2021.107231.

[7] H. Peng, J. Wang, X. Zhang, J. Ma, T. Shen, S. Li, B. Dong, A review on synthesis, characterization and application of nanoencapsulated phase change materials for thermal energy storage systems, Appl Therm Eng. 185 (2021). https://doi.org/10.1016/j.applthermaleng.2020.116326.

[8] Z.A. Qureshi, H.M. Ali, S. Khushnood, Recent advances on thermal conductivity enhancement of phase change materials for energy storage system: A review, Int J Heat Mass Tran. 127 (2018) 838–856. https://doi.org/10.1016/j.ijheatmasstransfer.2018.08.049.

[9] F. Ran, Y. Chen, R. Cong, G. Fang, Flow and heat transfer characteristics of microencapsulated phase change slurry in thermal energy systems: A review, Renew Sustain Energy Rev. 134 (2020). https://doi.org/10.1016/j.rser.2020.110101.

[10] T. Rehman, H.M. Ali, M.M. Janjua, U. Sajjad, W.-M. Yan, A critical review on heat transfer augmentation of phase change materials embedded with porous materials/foams, Int J Heat Mass Tran. 135 (2019) 649–673. https://doi.org/10.1016/j.ijheatmasstransfer.2019.02.001.

[11] P. Gadhave, F. Pathan, S. Kore, C. Prabhune, Comprehensive review of phase change material based latent heat thermal energy storage system, Int J Ambient Energy. (2021). https://doi.org/10.1080/01430750.2021.1873848.

[12] A. Safari, R. Saidur, F.A. Sulaiman, Y. Xu, J. Dong, A review on supercooling of Phase Change Materials in thermal energy storage systems, Renew Sustain Energy Rev. 70 (2017) 905–919. https://doi.org/10.1016/j.rser.2016.11.272.

[13] D.G. Prajapati, B. Kandasubramanian, A Review on Polymeric-Based Phase Change Material for Thermo-Regulating Fabric Application, Polym Rev. 60 (2020) 389–419. https://doi.org/10.1080/15583724.2019.1677709.

[14] H. Liu, Z. Wei, W. He, J. Zhao, Thermal issues about Li-ion batteries and recent progress in battery thermal management systems: A review, Energ Convers Manage. 150 (2017) 304–330. https://doi.org/10.1016/j.enconman.2017.08.016.

[15] S.S. Chandel, T. Agarwal, Review of current state of research on energy storage, toxicity, health hazards and commercialization of phase changing materials, Renew Sustain Energy Rev. 67 (2017) 581–596. https://doi.org/10.1016/j.rser.2016.09.070.

[16] N.PAN, P.Gibson, Thermal and moisture transport in fibrous materials, 1st ed., Woodhead Publishing, 2006.

[17] J. Militky, O. Novak, D. Kremenakova, J. Wiener, M. Venkataraman, G. Zhu, J. Yao, A. Aneja, A Review of Impact of Textile Research on Protective Face Masks, Materials. 14 (2021) 1937. https://doi.org/10.3390/ma14081937.

[18] S. Faheem, V. Baheti, M. Tunak, J. Wiener, J. Militky, Flame resistance behavior of cotton fabrics coated with bilayer assemblies of ammonium polyphosphate and casein, Cellulose. 26 (2019) 3557–3574. https://doi.org/10.1007/s10570-019-02296-1.

[19] M. Venkataraman, R. Mishra, J. Militky, X. Xiong, J. Marek, J. Yao, G. Zhu, Electrospun nanofibrous membranes embedded with aerogel for advanced thermal and transport properties, Polym Advan Technol. 29 (2018) 2583–2592. https://doi.org/10.1002/pat.4369.

[20] M.Z. Khan, V. Baheti, J. Militky, A. Ali, M. Vikova, Superhydrophobicity, UV protection and oil/water separation properties of fly ash/Trimethoxy(octadecyl)silane coated cotton fabrics, Carbohyd Polym. 202 (2018) 571–580. https://doi.org/10.1016/j.carbpol.2018.08.145.

[21] T. Yang, X. Xiong, R. Mishra, J. Novák, J. Militký, Sound absorption and compression properties of perpendicular-laid nonwovens, Text Res J. 89 (2019) 612–624. https://doi.org/10.1177/0040517517753634.

[22] K. Yang, A.P. Periyasamy, M. Venkataraman, J. Militky, D. Kremenakova, J. Vecernik, R. Pulíček, Resistance against penetration of electromagnetic radiation for ultra-light Cu/Ni-coated polyester fibrous materials, Polymers-Basel. 12 (2020). https://doi.org/10.3390/polym12092029.

[23] X. Zhang, Z. Jin, L. Hu, X. Zhou, K. Yang, D. Kremenakova, J. Militky, A Silver Yarn-Incorporated Song Brocade Fabric with Enhanced Electromagnetic Shielding, Materials. 14 (2021) 3779. https://doi.org/10.3390/ma14143779.

[24] X. Zhang, Z. Jin, A Kind of Song Brocade Fabric with NFC Data Masking Function Used for Making Purse, Iop Conf Ser Mater Sci Eng. 389 (2018) 012037. https://doi.org/10.1088/1757-899x/389/1/012037.

[25] Y. Wang, V. Baheti, K. Yang, T. Yang, J. Wiener, J. Militký, Utility of whiskerized carbon fabric surfaces in resistive heating of composites, Polym Composite. (2021). https://doi.org/10.1002/pc.26012.

[26] A.P. Periyasamy, K. Yang, X. Xiong, M. Venkataraman, J. Militky, R. Mishra, D. Kremenakova, Effect of silanization on copper coated milife fabric with improved EMI shielding effectiveness, Mater Chem Phys. 239 (2020). https://doi.org/10.1016/j.matchemphys.2019.122008.

[27] C. Wani, P.K. Loharkar, A Review of Phase Change Materials as an Alternative for Solar Thermal Energy Storage, Mater Today Proc. 4 (2017) 10264–10267. https://doi.org/10.1016/j.matpr.2017.06.361.

[28] S.A. Mohamed, F.A. Al-Sulaiman, N.I. Ibrahim, Md.H. Zahir, A. Al-Ahmed, R. Saidur, B.S. Yılbaş, A.Z. Sahin, A review on current status and challenges of inorganic phase change materials for thermal energy storage systems, Renew Sustain Energy Rev. 70 (2017) 1072–1089. https://doi.org/10.1016/j.rser.2016.12.012.

[29] K. Yang, M. Venkataraman, J. Karpiskova, Y. Suzuki, S. Ullah, I.-S. Kim, J. Militky, Y. Wang, T. Yang, J. Wiener, G. Zhu, J. Yao, Structural analysis of embedding polyethylene glycol in silica aerogel, Micropor Mesopor Mat. 310 (2021) 110636. https://doi.org/10.1016/j.micromeso.2020.110636.

[30] L. Pathak, G.V.N. Trivedi, R. Parameshwaran, S.S. Deshmukh, Microencapsulated phase change materials as slurries for thermal energy storage: A review, Mater Today Proc. 44 (2021) 1960–1963. https://doi.org/10.1016/j.matpr.2020.12.101.

[31] S. Sundararajan, A.B. Samui, P.S. Kulkarni, Versatility of polyethylene glycol (PEG) in designing solid–solid phase change materials (PCMs) for thermal management and their application to innovative technologies, J Mater Chem A. 5 (2017) 18379–18396. https://doi.org/10.1039/c7ta04968d.

[32] J.L. Reyez-Araiza, J. Pineda-Piñón, J.M. López-Romero, J.R. Gasca-Tirado, M.A. Contreras, J.C.J. Correa, L.M. Apátiga-Castro, E.M. Rivera-Muñoz, R.R. Velazquez-Castillo, J. de J.P. Bueno, A. Manzano-Ramirez, Thermal Energy Storage by the Encapsulation of Phase Change Materials in Building Elements—A Review, Materials. 14 (2021) 1420. https://doi.org/10.3390/ma14061420.

[33] H. Liu, X. Wang, D. Wu, Innovative design of microencapsulated phase change materials for thermal energy storage and versatile applications: a review, Sustain Energy Fuels. 3 (2019) 1091–1149. https://doi.org/10.1039/c9se00019d.

[34] L. Zhang, W. Yang, Z. Jiang, F. He, K. Zhang, J. Fan, J. Wu, Graphene oxide-modified microencapsulated phase change materials with high encapsulation capacity and enhanced leakage-prevention performance, Appl Energ. 197 (2017) 354–363. https://doi.org/10.1016/j.apenergy.2017.04.041.

[35] A. Shaid, L. Wang, S. Islam, J.Y. Cai, R. Padhye, Preparation of aerogel-eicosane microparticles for thermoregulatory coating on textile, Appl Therm Eng. 107 (2016) 602–611. https://doi.org/10.1016/j.applthermaleng.2016.06.187.

[36] C.E. Tas, O. Karaoglu, B.A. Tas, E. Ertas, H. Unal, H. Bildirir, Improved latent heat storage properties through mesopore enrichment of a zeolitic shape stabilizer, Sol Energ Mat Sol C. 216 (2020) 110677. https://doi.org/10.1016/j.solmat.2020.110677.

[37] J.S. Baruah, V. Athawale, P. Rath, A. Bhattacharya, Melting and energy storage characteristics of macro-encapsulated PCM-metal foam system, Int J Heat Mass Tran. 182 (2022) 121993. https://doi.org/10.1016/j.ijheatmasstransfer.2021.121993.

[38] H. Su, P. Lin, H. Lu, X. Zhao, X. Sheng, Y. Chen, Janus-Type Hydroxyapatite-Incorporated Kevlar Aerogel@Kevlar Aerogel Supported Phase-Change Material Gel toward Wearable Personal Thermal Management, Acs Appl Mater Inter. 14 (2022) 12617–12629. https://doi.org/10.1021/acsami.1c23774.

[39] H. Gao, J. Wang, X. Chen, G. Wang, X. Huang, A. Li, W. Dong, Nanoconfinement effects on thermal properties of nanoporous shape-stabilized composite PCMs: A review, Nano Energy. 53 (2018) 769–797. https://doi.org/10.1016/j.nanoen.2018.09.007.

[40] W. Aftab, X. Huang, W. Wu, Z. Liang, A. Mahmood, R. Zou, Nanoconfined phase change materials for thermal energy applications, Energ Environ Sci. 11 (2018) 1392–1424. https://doi.org/10.1039/c7ee03587j.

[41] K. Yang, X. Zhang, M. Venkataraman, J. Wiener, S. Palanisamy, S. Sozcu, X. Tan, D. Kremenakova, G. Zhu, J. Yao, J. Militky, Structural Analysis of Phase Change Materials (PCMs)/Expanded Graphite (EG) Composites and Their Thermal Behavior under Hot and Humid Conditions, Chempluschem. (2023). https://doi.org/10.1002/cplu.202300081.

[42] K. Yang, M. Venkataraman, X. Zhang, J. Wiener, G. Zhu, J. Yao, J. Militky, Review: incorporation of organic PCMs into textiles, J Mater Sci. 57 (2022) 798–847. https://doi.org/10.1007/s10853-021-06641-3.

[43] A. Karaszewska, I. Kamińska, A. Nejman, B. Gajdzicki, W. Fortuniak, J. Chojnowski, S. Slomkowski, P. Sowinski, Thermal-regulation of nonwoven fabrics by microcapsules of n-eicosane coated with a polysiloxane elastomer, Mater Chem Phys. 226 (2019) 204–213. https://doi.org/10.1016/j.matchemphys.2019.01.029.

[44] Y. Wu, C. Chen, Y. Jia, J. Wu, Y. Huang, L. Wang, Review on electrospun ultrafine phase change fibers (PCFs) for thermal energy storage, Appl Energ. 210 (2018) 167–181. https://doi.org/10.1016/j.apenergy.2017.11.001.

[45] F. Haghighat, S.A.H. Ravandi, M.N. Esfahany, A. Valipouri, Z. Zarezade, Thermal performance of electrospun core-shell phase change fibrous layers at simulated body conditions, Appl Therm Eng. 161 (2019) 113924. https://doi.org/10.1016/j.applthermaleng.2019.113924.

[46] L. Hes, luboshes@vslib.cz, B.I. Lu, Using a Thermal Simulator to Determine the Amount of Time that Humans are Thermally Protected by Fabrics Containing Phase Change

Materials, Res J Text Appar. Volume 8 (2004) 51–56. https://doi.org/10.1108/rjta-08-02-2004-b007.

[47] K. Yang, M. Venkataraman, Y.-F. Wang, X.-M. Xiong, T. Yang, J. Wiener, J. Militky, R. Mishra, J. Marek, G.-C. Zhu, J.-M. Yao, Thermal behaviour of multi-layer composite containing PEG and laponite as PCM, in: 2019: pp. 671–676. https://www.scopus.com/inward/record.uri?eid=2-s2.0-85073789344&partnerID=40&md5=b022b850ae171de76f4b12525e6cf9a0.

[48] N. Wang, M. Cai, X. Yang, Y. Yang, Electret nanofibrous membrane with enhanced filtration performance and wearing comfortability for face mask, J Colloid Interf Sci. 530 (2018) 695–703. https://doi.org/10.1016/j.jcis.2018.07.021.

[49] W. Ma, Z. Jiang, T. Lu, R. Xiong, C. Huang, Lightweight, elastic and superhydrophobic multifunctional nanofibrous aerogel for self-cleaning, oil/water separation and pressure sensing, Chem Eng J. 430 (2022) 132989. https://doi.org/10.1016/j.cej.2021.132989.

[50] B. Xiang, G. Shi, P. Mu, J. Li, Eco-friendly WBF/PAN nanofiber composite membrane for efficient separation various surfactant-stabilized oil-in-water emulsions, Colloids Surfaces Physicochem Eng Aspects. 645 (2022) 128917. https://doi.org/10.1016/j.colsurfa.2022.128917.

[51] M. Cao, Y. Hu, W. Cheng, S. Huan, T. Bai, Z. Niu, Y. Zhao, G. Yue, Y. Zhao, G. Han, Lignin-based multi-scale cellular aerogels assembled from co-electrospun nanofibers for oil/water separation and energy storage, Chem Eng J. 436 (2022) 135233. https://doi.org/10.1016/j.cej.2022.135233.

[52] Z. Chu, Y. Li, A. Zhou, L. Zhang, X. Zhang, Y. Yang, Z. Yang, Polydimethylsiloxane-decorated magnetic cellulose nanofiber composite for highly efficient oil-water separation, Carbohyd Polym. 277 (2022) 118787. https://doi.org/10.1016/j.carbpol.2021.118787.

[53] R. Knížek, D. Karhánková, V. Bajzík, O. Jirsák, Lamination of Nanofibre Layers for Clothing Applications, Fibres Text East Europe. 27 (2019) 16–22. https://doi.org/10.5604/01.3001.0012.7503.

[54] R. Bagherzadeh, M. Latifi, S.S. Najar, M.A. Tehran, M. Gorji, L. Kong, Transport properties of multi-layer fabric based on electrospun nanofiber mats as a breathable barrier textile material, Text Res J. 82 (2012) 70–76. https://doi.org/10.1177/0040517511420766.

[55] S. Han, Y. Chen, S. Lyu, Z. Chen, S. Wang, F. Fu, Effects of processing conditions on the properties of paraffin/melamine-urea-formaldehyde microcapsules prepared by in situ polymerization, Colloids Surf. A: Physicochem. Eng. Asp. 585 (2020) 124046. https://doi.org/10.1016/j.colsurfa.2019.124046.

[56] Z. Zhang, Z. Zhang, T. Chang, J. Wang, X. Wang, G. Zhou, Phase change material microcapsules with melamine resin shell via cellulose nanocrystal stabilized Pickering emulsion in-situ polymerization, Chem. Eng. J. 428 (2022) 131164. https://doi.org/10.1016/j.cej.2021.131164.

[57] Y. Konuklu, F. Erzin, Preparation of pentadecane/poly(melamine-urea-formaldehyde) microcapsules for thermal energy storage applications, Int. J. Energy Res. 43 (2019) 6322–6326. https://doi.org/10.1002/er.4346.

[58] A.T. Naikwadi, A.B. Samui, P.A. Mahanwar, Melamine-formaldehyde microencapsulated n-Tetracosane phase change material for solar thermal energy storage in coating, Sol. Energy Mater. Sol. Cells. 215 (2020) 110676. https://doi.org/10.1016/j.solmat.2020.110676.

[59] B. Zhang, S. Li, X. Fei, H. Zhao, X. Lou, Enhanced mechanical properties and thermal conductivity of paraffin microcapsules shelled by hydrophobic-silicon carbide modified melamine-formaldehyde resin, Colloids Surf. A: Physicochem. Eng. Asp. 603 (2020) 125219. https://doi.org/10.1016/j.colsurfa.2020.125219.

[60] J. Singh, S. Parvate, J.R. Vennapusa, T.K. Maiti, P. Dixit, S. Chattopadhyay, Facile method to prepare 1-dodecanol@poly(melamine-paraformaldehyde) phase change energy storage microcapsules via surfactant-free method, J. Energy Storage. 49 (2022) 104089. https://doi.org/10.1016/j.est.2022.104089.

[61] S.I. Hussain, S. Kalaiselvam, Nanoencapsulation of oleic acid phase change material with Ag2O nanoparticles-based urea formaldehyde shell for building thermal energy storage, J. Therm. Anal. Calorim. 140 (2020) 133–147. https://doi.org/10.1007/s10973-019-08732-5.

[62] E.G. Saraç, E. Öner, M.V. Kahraman, Microencapsulated organic coconut oil as a natural phase change material for thermo-regulating cellulosic fabrics, Cellulose. 26 (2019) 8939–8950. https://doi.org/10.1007/s10570-019-02701-9.

[63] G.N. Kumar, B. Al-Aifan, R. Parameshwaran, V.V. Ram, Facile synthesis of microencapsulated 1-dodecanol/melamine-formaldehyde phase change material using in-situ polymerization for thermal energy storage, Colloids Surf. A: Physicochem. Eng. Asp. 610 (2021) 125698. https://doi.org/10.1016/j.colsurfa.2020.125698.

[64] B. Praveen, S. Suresh, V. Pethurajan, Heat transfer performance of graphene nano-platelets laden micro-encapsulated PCM with polymer shell for thermal energy storage based heat sink, Appl. Therm. Eng. 156 (2019) 237–249. https://doi.org/10.1016/j.applthermaleng.2019.04.072.

[65] X. Wang, C. Zhang, K. Wang, Y. Huang, Z. Chen, Highly efficient photothermal conversion capric acid phase change microcapsule: Silicon carbide modified melamine urea formaldehyde, J. Colloid Interface Sci. 582 (2021) 30–40. https://doi.org/10.1016/j.jcis.2020.08.014.

[66] S. Lu, T. Shen, J. Xing, Q. Song, J. Shao, J. Zhang, C. Xin, Preparation and characterization of cross-linked polyurethane shell microencapsulated phase change materials by interfacial polymerization, Mater. Lett. 211 (2018) 36–39. https://doi.org/10.1016/j.matlet.2017.09.074.

[67] H. Nikpourian, A.R. Bahramian, M. Abdollahi, On the thermal performance of a novel PCM nanocapsule: The effect of core/shell, Renew. Energy. 151 (2020) 322–331. https://doi.org/10.1016/j.renene.2019.11.027.

[68] J.A. Ansari, R. Al-Shannaq, J. Kurdi, S.A. Al-Muhtaseb, C.A. Ikutegbe, M.M. Farid, A Rapid Method for Low Temperature Microencapsulation of Phase Change Materials (PCMs) Using a Coiled Tube Ultraviolet Reactor, Energies. 14 (2021) 7867. https://doi.org/10.3390/en14237867.

[69] R. Pradhan, A.P. Ramaswamy, Encapsulation of paraffin wax by rigid cross-linked poly (styrene divinylbenzene-acrylic acid) and its thermal characterization, SN Appl. Sci. 1 (2019) 859. https://doi.org/10.1007/s42452-019-0891-8.

[70] D. Xu, R. Yang, Efficient preparation and characterization of paraffin-based microcapsules by emulsion polymerization, J. Appl. Polym. Sci. 136 (2019) 47552. https://doi.org/10.1002/app.47552.

[71] F. Haghighat, S.A.H. Ravandi, M.N. Esfahany, A. Valipouri, A comprehensive study on optimizing and thermoregulating properties of core–shell fibrous structures through coaxial electrospinning, J Mater Sci. 53 (2018) 4665–4682. https://doi.org/10.1007/s10853-017-1856-1.

[72] L. Zhao, J. Luo, Y. Li, H. Wang, G. Song, G. Tang, Emulsion-electrospinning n-octadecane/silk composite fiber as environmental-friendly form-stable phase change materials, J Appl Polym Sci. 134 (2017). https://doi.org/10.1002/app.45538.

[73] D. Luo, F. Wei, H. Shao, L. Xiang, J. Yang, Z. Cui, S. Qin, J. Yu, Shape stabilization, thermal energy storage behavior and thermal conductivity enhancement of flexible paraffin/MWCNTs/PP hollow fiber membrane composite phase change materials, J Mater Sci. 53 (2018) 15500–15513. https://doi.org/10.1007/s10853-018-2722-5.

[74] N. Xie, J. Niu, X. Gao, Y. Fang, Z. Zhang, Fabrication and characterization of electrospun fatty acid form-stable phase change materials in the presence of copper nanoparticles, Int J Energ Res. 44 (2020) 8567–8577. https://doi.org/10.1002/er.5543.

[75] H. Ke, Electrospun methyl stearate/PET form-stable phase change composite nanofibres for storage and retrieval of thermal energy, Mater Res Innov. 22 (2018) 150–158. https://doi.org/10.1080/14328917.2016.1266203.

[76] L. Zhou, F. Shi, G. Liu, J. Ye, P. Han, G. Zhang, Fabrication and characterization of in situ cross-linked electrospun Poly(vinyl alcohol)/phase change material nanofibers, Sol Energy. 213 (2021) 339–349. https://doi.org/10.1016/j.solener.2020.11.039.

[77] T. Dong, W. jiang, Y. liu, Y. Wu, Y. Qi, J. Li, Y. Ma, H. Ben, G. Han, A phase change material embedded composite consisting of kapok and hollow PET fibers for dynamic thermal comfort regulation, Ind Crop Prod. 158 (2020). https://doi.org/10.1016/j.indcrop.2020.112945.

[78] W. Feng, Y.-S. Zhang, Y.-W. Shao, T. Huang, N. Zhang, J.-H. Yang, X.-D. Qi, Y. Wang, Coaxial electrospun membranes with thermal energy storage and shape memory functions for simultaneous thermal/moisture management in personal cooling textiles, Eur Polym J. 145 (2021). https://doi.org/10.1016/j.eurpolymj.2020.110245.

[79] E.C.B. Noyan, E. Onder, N. Sarier, R. Arat, Development of heat storing poly(acrylonitrile) nanofibers by coaxial electrospinning, Thermochim Acta. 662 (2018) 135–148. https://doi.org/10.1016/j.tca.2018.02.008.

[80] X. Zhang, J. Qiao, H. Zhao, Z. Huang, Y. Liu, M. Fang, X. Wu, X. Min, Preparation and performance of novel polyvinylpyrrolidone/polyethylene glycol phase change materials composite fibers by centrifugal spinning, Chem Phys Lett. 691 (2018) 314–318. https://doi.org/10.1016/j.cplett.2017.11.041.

[81] Y. Yan, W. Li, R. Zhu, C. Lin, R. Hufenus, Flexible phase change material fiber: A simple route to thermal energy control textiles, Materials. 14 (2021) 1–18. https://doi.org/10.3390/ma14020401.

[82] H. Fang, J. Lin, L. Zhang, A. Chen, F. Wu, L. Geng, X. Peng, Fibrous form-stable phase change materials with high thermal conductivity fabricated by interfacial polyelectrolyte complex spinning, Carbohyd Polym. 249 (2020). https://doi.org/10.1016/j.carbpol.2020.116836.

[83] J. Wu, R. Hu, S. Zeng, W. Xi, S. Huang, J. Deng, G. Tao, Flexible and Robust Biomaterial Microstructured Colored Textiles for Personal Thermoregulation, Acs Appl Mater Inter. 12 (2020) 19015–19022. https://doi.org/10.1021/acsami.0c02300.

[84] Y.-H. Ahn, S.J.A. DeWitt, S. McGuire, R.P. Lively, Incorporation of phase change materials into fibers for sustainable thermal energy storage, Ind Eng Chem Res. (2021). https://doi.org/10.1021/acs.iecr.0c06140.

[85] L. Xiang, D. Luo, J. Yang, X. Sun, J. Jin, S. Qin, Construction and Design of Paraffin/PVDF Hollow Fiber Linear-Phase Change Energy Storage Materials, Energ Fuel. 33 (2019) 11584–11591. https://doi.org/10.1021/acs.energyfuels.9b02852.

[86] H. Qi, T. Zhang, D. Zhang, K. Wang, Y. Wang, Paraffin/chitosan composite phase change materials fabricated by piercing-solidifying method for thermal energy storage, Aip Adv. 10 (2020) 035218. https://doi.org/10.1063/1.5140582.

[87] M. Kenisarin, K. Mahkamov, F. Kahwash, I. Makhkamova, Enhancing thermal conductivity of paraffin wax 53–57 °C using expanded graphite, Sol Energ Mat Sol C. 200 (2019) 110026. https://doi.org/10.1016/j.solmat.2019.110026.

[88] D. Luo, L. Xiang, X. Sun, L. Xie, D. Zhou, S. Qin, Phase-change smart lines based on paraffin-expanded graphite/polypropylene hollow fiber membrane composite phase change materials for heat storage, Energy. 197 (2020). https://doi.org/10.1016/j.energy.2020.117252.

[89] B. Tang, M. Qiu, S. Zhang, Thermal conductivity enhancement of PEG/SiO2 composite PCM by in situ Cu doping, Sol Energ Mat Sol C. 105 (2012) 242–248. https://doi.org/10.1016/j.solmat.2012.06.012.

[90] A.W. Kuziel, G. Dzido, R. Turczyn, R.G. Jędrysiak, A. Kolanowska, A. Tracz, W. Zięba, A. Cyganiuk, A.P. Terzyk, S. Boncel, Ultra-long carbon nanotube-paraffin composites of record thermal conductivity and high phase change enthalpy among paraffin-based heat

storage materials, J. Energy Storage. 36 (2021) 102396. https://doi.org/10.1016/j.est.2021.102396.

[91] C. Li, B. Zhang, B. Xie, X. Zhao, J. Chen, Z. Chen, Y. Long, Stearic acid/expanded graphite as a composite phase change thermal energy storage material for tankless solar water heater, Sustain. Cities Soc. 44 (2019) 458–464. https://doi.org/10.1016/j.scs.2018.10.041.

[92] N. Sheng, Z. Rao, C. Zhu, H. Habazaki, Honeycomb carbon fibers strengthened composite phase change materials for superior thermal energy storage, Appl Therm Eng. 164 (2020). https://doi.org/10.1016/j.applthermaleng.2019.114493.

[93] Y. Tang, G. Alva, X. Huang, D. Su, L. Liu, G. Fang, Thermal properties and morphologies of MA–SA eutectics/CNTs as composite PCMs in thermal energy storage, Energy Build. 127 (2016) 603–610. https://doi.org/10.1016/j.enbuild.2016.06.031.

[94] A. Karaipekli, A. Biçer, A. Sarı, V.V. Tyagi, Thermal characteristics of expanded perlite/paraffin composite phase change material with enhanced thermal conductivity using carbon nanotubes, Energy Convers. Manag. 134 (2017) 373–381. https://doi.org/10.1016/j.enconman.2016.12.053.

[95] W. Jin, L. Jiang, L. Chen, T. Yin, Y. Gu, M. Guo, X. Yan, X. Ben, Enhancement of thermal conductivity by graphene as additive in lauric-stearic acid/treated diatomite composite phase change materials for heat storage in building envelope, Energy Build. 246 (2021) 111087. https://doi.org/10.1016/j.enbuild.2021.111087.

[96] J.-L. Zeng, S.-H. Zheng, S.-B. Yu, F.-R. Zhu, J. Gan, L. Zhu, Z.-L. Xiao, X.-Y. Zhu, Z. Zhu, L.-X. Sun, Z. Cao, Preparation and thermal properties of palmitic acid/polyaniline/exfoliated graphite nanoplatelets form-stable phase change materials, Appl. Energy. 115 (2014) 603–609. https://doi.org/10.1016/j.apenergy.2013.10.061.

[97] D.G. Atinafu, C. Wang, W. Dong, X. Chen, M. Du, H. Gao, G. Wang, In-situ derived graphene from solid sodium acetate for enhanced photothermal conversion, thermal conductivity, and energy storage capacity of phase change materials, Sol. Energy Mater. Sol. Cells. 205 (2020) 110269. https://doi.org/10.1016/j.solmat.2019.110269.

[98] X. Zheng, X. Gao, Z. Huang, Z. Li, Y. Fang, Z. Zhang, Form-stable paraffin/graphene aerogel/copper foam composite phase change material for solar energy conversion and storage, Sol. Energy Mater. Sol. Cells. 226 (2021) 111083. https://doi.org/10.1016/j.solmat.2021.111083.

[99] X. Huang, Y. Lin, G. Alva, G. Fang, Thermal properties and thermal conductivity enhancement of composite phase change materials using myristyl alcohol/metal foam for solar thermal storage, Sol. Energy Mater. Sol. Cells. 170 (2017) 68–76. https://doi.org/10.1016/j.solmat.2017.05.059.

[100] J.Y. Do, N. Son, J. Shin, R.K. Chava, S.W. Joo, M. Kang, n-Eicosane-Fe3O4@SiO2@Cu microcapsule phase change material and its improved thermal conductivity and heat transfer performance, Mater. Des. 198 (2021) 109357. https://doi.org/10.1016/j.matdes.2020.109357.

[101] R. Wen, X. Zhu, C. Yang, Z. Sun, L. Zhang, Y. Xu, J. Qiao, X. Wu, X. Min, Z. Huang, A novel composite phase change material from lauric acid, nano-Cu and attapulgite: Preparation, characterization and thermal conductivity enhancement, J. Energy Storage. 46 (2022) 103921. https://doi.org/10.1016/j.est.2021.103921.

[102] B. Zhao, Y. Wang, C. Wang, R. Zhu, N. Sheng, C. Zhu, Z. Rao, Thermal conductivity enhancement and shape stabilization of phase change thermal storage material reinforced by combustion synthesized porous Al2O3, J. Energy Storage. 42 (2021) 103028. https://doi.org/10.1016/j.est.2021.103028.

[103] S. Fan, H. Gao, W. Dong, J. Tang, J. Wang, M. Yang, G. Wang, Shape-Stabilized Phase Change Materials Based on Stearic Acid and Mesoporous Hollow SiO2 Microspheres (SA/SiO2) for Thermal Energy Storage, Eur. J. Inorg. Chem. 2017 (2017) 2138–2143. https://doi.org/10.1002/ejic.201601380.

[104] B. Tang, H. Wei, D. Zhao, S. Zhang, Light-heat conversion and thermal conductivity enhancement of PEG/SiO2 composite PCM by in situ Ti4O7 doping, Sol. Energy Mater. Sol. Cells. 161 (2017) 183–189. https://doi.org/10.1016/j.solmat.2016.12.003.

[105] W. Xia, X. Fei, Q. Wang, Y. Lu, M.T. Innocent, J. Zhou, S. Yu, H. Xiang, M. Zhu, Nano-hybridized form-stable ester@F-SiO<inf>2</inf> phase change materials for melt-spun PA6 fibers engineered towards smart thermal management fabrics, Chem Eng J. 403 (2021). https://doi.org/10.1016/j.cej.2020.126369.

[106] X. Xiong, M. Venkataraman, D. Jašíková, T. Yang, R. Mishra, J. Militký, M. Petrů, An experimental evaluation of convective heat transfer in multi-layered fibrous materials composed by different middle layer structures, J Ind Text. (2019) 152808371987884. https://doi.org/10.1177/1528083719878845.

[107] A. Nejman, M. Cieślak, B. Gajdzicki, B. Goetzendorf-Grabowska, A. Karaszewska, Methods of PCM microcapsules application and the thermal properties of modified knitted fabric, Thermochim Acta. 589 (2014) 158–163. https://doi.org/10.1016/j.tca.2014.05.037.

[108] A. Shahid, S. Miah, A. Rahim, Thermal and breathability management of microencapsulated phase change material (MPCM) incorporated jute fabric, J Eng Fiber Fabr. 16 (2021) 155892502110295. https://doi.org/10.1177/15589250211029564.

[109] T.R. Kar, A.K. Samanta, H.D. Sinnur, M. Kumar, Studies on Effect of Application of Capric Acid and Stearic Acid based Reactive Phase Change Materials (rPCM) with PHAMS Binder on Thermal Comfort of Cotton Khadi Fabric as Thermo-tropic Smart Textiles., J Nat Fibers. (2021). https://doi.org/10.1080/15440478.2021.1880517.

[110] Y. Shin, D. Yoo, K. Son, Development of thermoregulating textile materials with microencapsulated phase change materials (PCM). IV. Performance properties and hand of fabrics treated with PCM microcapsules, J. Appl. Polym. Sci. 97 (2005) 910–915. https://doi.org/10.1002/app.21846.

[111] K. Choi, G. Cho, Physical and mechanical properties of thermostatic fabrics treated with nanoencapsulated phase change materials, J Appl Polym Sci. 121 (2011) 3238–3245. https://doi.org/10.1002/app.33870.

[112] K. Yang, L. Martinkova, O. Ctibor, X. Zhang, M. Venkataraman, J. Wiener, G. Zhu, G. Zhang, J. Yao, J. Militky, Mass transfer and thermal buffering effect of hydrophobic fabrics with single-side coating of MPCMs, Prog Org Coat. 172 (2022) 107151. https://doi.org/10.1016/j.porgcoat.2022.107151.

9. List of publications by author

9.1 Journal articles

[1] **K. Yang**, X. Zhang, M. Venkataraman, J. Wiener, X. Tan, G. Zhu, J. Yao, J. Militky, Sandwich Fibrous PEG Encapsulations for Thermal Energy Storage, **ChemPhysChem**. (2023). https://doi.org/10.1002/cphc.202300234. **(Q2, IF: 2.9) (cited by 1)**

[2] **K. Yang**, X. Zhang, J. Wiener, M. Venkataraman, Y. Wang, G. Zhu, J. Yao, J. Militky, Nanofibrous Membranes in Multilayer Fabrics to Avoid PCM Leakages, **ChemNanoMat**. (2022). https://doi.org/10.1002/cnma.202200352. **(Q2, IF: 3.8) (cited by 3)**

[3] **K. Yang**, J. Wiener, M. Venkataraman, Y. Wang, T. Yang, G. Zhang, G. Zhu, J. Yao, J. Militky, Thermal Analysis of PEG/Metal Particle-coated Viscose Fabric, **Polym Test**. (2021) 107231. https://doi.org/10.1016/j.polymertesting.2021.107231. (**Q1, IF: 5.1**) **(cited by 20)**

[4] **K. Yang**, L. Martinkova, O. Ctibor, X. Zhang, M. Venkataraman, J. Wiener, G. Zhu, G. Zhang, J. Yao, J. Militky, Mass transfer and thermal buffering effect of hydrophobic fabrics with single-side coating of MPCMs, **Prog Org Coat.** 172 (2022) 107151. https://doi.org/10.1016/j.porgcoat.2022.107151. (**Q1, IF: 6.6**) **(cited by 4)**

[5] **K. Yang**, Q. Peng, M. Venkataraman, J. Novotna, J. Karpiskova, J. Mullerova, J. Wiener, M. Vikova, G. Zhu, J. Yao, J. Militky, Hydrophobicity, water moisture transfer and breathability of PTFE-coated viscose fabrics prepared by electrospraying technology and sintering process, **Prog Org Coat**. 165 (2022) 106775. https://doi.org/10.1016/j.porgcoat.2022.106775. (**Q1, IF: 6.6**) **(cited by 10)**

[6] **K. Yang**, M. Venkataraman, X. Zhang, J. Wiener, G. Zhu, J. Yao, J. Militky., Review: incorporation of organic PCMs into textiles, **Journal of Materials Science** (2021). doi: https://doi.org/10.1007/s10853-021-06641-3. **(Q2, IF: 4.5) (cited by 28)**

[7] **K. Yang**, M. Venkataraman, J. Karpiskova, Y. Suzuki, S. Ullah, I.-S. Kim, J. Militky, Y. Wang, T. Yang, J. Wiener, G. Zhu, J. Yao, Structural analysis of embedding polyethylene glycol in silica aerogel, **Micropor Mesopor Mat**. 310 (2021). https://doi.org/10.1016/j.micromeso.2020.110636. **(Q1, IF: 5.2) (cited by 22)**

[8] **K. Yang**, X. Zhang, M. Venkataraman, J. Wiener, S. Palanisamy, S. Sebnem, X. Tan, D. Kremenakova, G. Zhu, J. Yao, J. Militky, Structural Analysis of Phase Change Materials (PCMs)/Expanded Graphite (EG) Composites and Their Thermal Behavior under Hot and Humid Conditions, **ChemPlusChem**. (2023). https://doi.org/10.1002/cplu.202300081. **(Q2, IF: 3.4) (cited by 4)**

[9] **K. Yang**, M. Venkataraman, J. Wiener, X. Zhang, M. Stuchlik, G. Zhu, J. Yao, J. Militky, Crystallization Mechanism of Micro Flake Cu Particle-filled Poly(ethylene glycol) Composites, **Thermochim Acta**. (2022) 179172. https://doi.org/10.1016/j.tca.2022.179172. **(Q2, IF: 3.5) (cited by 7)**

[10] **K. Yang**, A.P. Periyasamy, M. Venkataraman, J. Militky, D. Kremenakova, J. Vecernik, R. Pulíček, Resistance against penetration of electromagnetic radiation for ultra-light Cu/Ni-coated polyester fibrous materials, **Polymers-Basel**. 12 (2020).

https://doi.org/10.3390/polym12092029. **(Q1, IF: 5) (cited by 12)**

[11] X. Zhang, **K. Yang**, D. Kremenakova, J. Militky, Luminance bahavior and tensile property of twisted side-emitting polymer optical fibers bundles, polymer testing. (2023) 108016. https://doi.org/10.1016/j.polymertesting.2023.108016. **(Q1, IF: 5.1**) **(cited by 0)**

[12] Y. Wang, V. Baheti, **K. Yang**, T. Yang, J. Wiener, J. Militký, Utility of whiskerized carbon fabric surfaces in resistive heating of composites, Polym Composite. (2021). https://doi.org/10.1002/pc.26012. **(Q1, IF: 5.2) (cited by 7)**

[13] X. Tan, Q. Peng, **K. Yang**, T. Yang, J. Saskova, J. Wiener, M. Venkataraman, J. Militky, W. Xiong, J. Xu, Preparation and Characterization of corn husk nanocellulose coating on electrospun polyamide 6, Alexandria Eng J. (2021). https://doi.org/10.1016/j.aej.2021.10.011. **(Q1, IF: 6.8) (cited by 10)**

[14] A.P. Periyasamy, **K. Yang**, X. Xiong, M. Venkataraman, J. Militky, R. Mishra, D. Kremenakova, Effect of silanization on copper coated milife fabric with improved EMI shielding effectiveness, Mater Chem Phys. 239 (2020). https://doi.org/10.1016/j.matchemphys.2019.122008. **(Q2, IF: 4.6) (cited by 32)**

[15] Y. Wang, V. Baheti, M.Z. Khan, M. Vikova, **K. Yang**, T. Yang, J. Militky, A facile approach to develop multifunctional cotton fabrics with hydrophobic self cleaning and UV protection properties using ZnO particles and.pdf, The Journal of The Textile Institue. (2021). https://doi.org/10.1080/00405000.2021.1975905. **(Q2, IF: 1.7) (cited by 8)**

[16] X. Zhang, Z. Jin, L. Hu, X. Zhou, **K. Yang**, D. Kremenakova, J. Militky, A Silver Yarn-Incorporated Song Brocade Fabric with Enhanced Electromagnetic Shielding, Materials. 14 (2021) 3779. https://doi.org/10.3390/ma14143779. **(Q1, IF: 3.4) (cited by 3)**

[17] T. Yang, F. Saati, K.V. Horoshenkov, X. Xiong, **K. Yang**, R. Mishra, S. Marburg, J. Militký, Study on the sound absorption behavior of multi-component polyester nonwovens: experimental and numerical methods, Text Res J. 89 (2019) 3342–3361. https://doi.org/10.1177/0040517518811940. **(Q2, IF: 2.3) (cited by 44)**

[18] X. Xiong, M. Venkataraman, T. Yang, K. Kucerova, J. Militký, **K. Yang**, G. Zhu, J. Yao, Transport properties of electro-sprayed polytetrafluoroethylene fibrous layer filled with aerogels/phase change materials, Nanomaterials-Basel. 10 (2020) 1–14. https://doi.org/10.3390/nano10102042. **(Q1, IF: 5.3) (cited by 7)**

[19] Y.F. Wang, V. Baheti, **K. Yang**, M. Venkataraman, T. Yang, J. Militky, Study on ohmic heating behavior of fly ash filledarbon woven/epoxy resin composite?, J Fiber Bioeng Informatics. 13 (2020) 1–11. https://doi.org/10.3993/jfbim00329.

[20] Q. Peng, **K. Yang**, M. Venkataraman, X. Tan, X. Xiong, J. Novotna, J. Karpiskova, J. Hruza, M. Stuchlík, J. Militky, Preparation of electrosprayed composite coated microporous filter for particulate matter capture, Nano Sel. (2021). https://doi.org/10.1002/nano.202100186.

[21] **K. Yang**, X. Zhang, M. Venkataraman, K. Chen, Y. Wang, J. Wiener, G. Zhu, J. Yao, J. Militky, Thermal Behavior of Flexible and Breathable Sandwich Fibrous Polyethylene

Glycol (PEG) Encapsulations, **Textile Research Journal**. (2023) **(Submitted) (Q2, IF: 2.3)**

9.2 Conference paper

[1] **K. Yang**, Q. Peng, M. Venkataraman, J. Novotna, X. Xiong, J. Wiener, Y. Wang, X. Tan, G. Zhu, J. Yao, J. Militky, Hydrophobic Breathable Fabric via Electrospraying Technology. **Autex Conference 2021**.

[2] **K. Yang,** M. Venkataraman, Y. Wang, J. Wiener, J. Milikty. Preparation of Polyamide 6 Nanofibrous Membranes Coated with Polyethylene Glycol. **47th Textile Research Symposium 2019**.

[3] **K. Yang**, M. Venkataraman, Y.-F. Wang, X.-M. Xiong, T. Yang, J. Wiener, J. Militky, R. Mishra, J. Marek, G.-C. Zhu, J.-M. Yao, Thermal behaviour of multi-layer composite containing PEG and laponite as PCM, in: 2019: pp. 671–676.

[4] S. Hu, D. Wang, **K. Yang**, Y.-F. Wang, T. Yang, Q.-Y. Peng, X.-D. Tan, D. Kremenakova, J. Militky, M. Venkataraman, A.P. Periyasamy, Copper coated textiles for inhibition of virus spread, in: 2020: pp. 84–91.

[5] Q.-Y. Peng, S.-L. Xiao, X.-D. Tan, **K. Yang**, Y.-F. Wang, T. Yang, D. Wang, S. Hu, X.-M. Xiong, M. Venkataraman, J. Militky, Dendrimer-grafted PLGA nanofibrous matrix-mediated gene delivery systems, in: 2020: pp. 152–158.

[6] Y.-F. Wang, J. Militky, A.P. Periyasamy, M. Venkataraman, V. Baheti, **K. Yang**, S. Hu, D. Wang, X.-D. Tan, T. Yang, Q.-Y. Peng, Disinfection mechanisms of UV light and ozonization, in: 2020: pp. 173–180.

[7] Y.-F. Wang, D. Karthik, **K. Yang**, T. Yang, X.-M. Xiong, V. Baheti, J. Militký, Electrical heating properties of carbon fabric/green epoxy composites filled with fly ash, in: 2019: pp. 44–51.

[8] Y.-F. Wang, V. Baheti, **K. Yang**, S. Hu, D. Wang, X.-D. Tan, T. Yang, J. Militký, Electrical heating properties of various carbonized textile structures, in: 2020: pp. 99–106.

[9] A.P. Periyasamy, **K. Yang**, X. Xiong, M. Venkatraman, J. Militky, R. Mishra, D. Kremenakova, Influence of EMI Shielding on Silane-coated Conductive Fabric, in: 2019: pp. 67–71.

[10] X.-D. Tan, Q.-Y. Peng, **K. Yang**, J. Saskova, A.P. Periyasamy, J. Militky, J. Wiener, Influence of UV light and ozonization on microbes, in: 2020: pp. 159–166.

[11] Q.-Y. Peng, M. Venkataraman, **K. Yang**, J. Militky, Kinetic model for disinfection with photo-oxidation, in: 2020: pp. 68–75.

[12] M. Venkataraman, **K. Yang**, A.P. Periyasamy, X. Xiong, J. Militky, R. Mishra, Modification of electromagnetic property of copper coated milife fabrics, in: 2019: pp. 694–700.

[13] T. Yang, F. Saati, X.-M. Xiong, Y.-F. Wang, **K. Yang**, R. Mishra, J. Militký, M. Petrů, Numerical modelling of the acoustic properties of polyester non-woven, in: 2019: pp. 767–776.

[14] M. Venkataraman, R. Mishra, K. Yang, J. Militky, D. Kremenakova, G. Zhu, J. Yao, Preparation of Electrosprayed Microporous Membranes, in: 2018. https://doi.org/10.1088/1757-899x/460/1/012017.

[15] X.-D. Tan, Q.-Y. Peng, **K. Yang**, Y.-F. Wang, T. Yang, D. Wang, S. Hu, X.-M. Xiong, J. Saskova, J. Wiener, M. Venkataraman, J. Militky, The effect of electrode materials and ultrasound on electrochemical reduction, in: 2020: pp. 554–560.

[16] D. Wang, S. Hu, D. Kremenakova, J. Militky, M. Venkataraman, Y.-F. Wang, **K. Yang**, Q. Peng, X.-D. Tan, Virology of SARS-CoV-2, in: 2020: pp. 49–55.

[17] M. Venkataraman, X.-M. Xiong, T. Yang, **K. Yang,** Y.-F. Wang, R. Mishra, J. Militký, Thermal performance of Kevlar woven fabrics coated with silica aerogel, in: 2019: pp. 687–693.

9.3 Book chapters

[1] **K. Yang**, X. Zhang, M. Venkataraman, J. Wiener, J. Militky. Phase Change Materials in Textiles for Thermal Regulation, in Advanced Multifunctional Materials from Fibrous Structure. Springer, 2023: 27-47. https://doi.org/10.1007/978-981-99-6002-6_2.

[2] **K. Yang**, M. Venkataraman, J. Wiener, J. Militký, Photoluminescence PCMs and their potential for thermal adaptive textiles, in multifunctional Phase Change Materials. Elsevier, 2023: pp. 255-277. https://doi.org/10.1016/B978-0-323-85719-2.00006-7.

[3] **K. Yang**, X. Zhang, M. Venkataraman, J. Militký, Characterization of Polymer Crystallization by Using Thermal Analsys, in: Polymer Crystallization: Methods, Characterization and Applications, Wiley, 2023: 13-31. https://onlinelibrary.wiley.com/doi/10.1002/9783527839247.ch2.

[4] **K. Yang**, M. Venkataraman, J. Militký, Textiles and Their Use in Microbial Protection, in: Fundamental Principles for Moisture Harvesting System and Its Design of Fabric, 1st ed., CRC Press, 2021: pp. 283–298. https://doi.org/10.1201/9781003140436-17.

[5] **K. Yang**, M. Venkataraman, J. Militky, J. Wiener. A review of PCM and their application in textile, in: Recent trends in fibrous material science. 2020.

10. Curriculum vitate

Mr. Kai Yang, M.Eng

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Phone: number:	(+086) 13554273589 (China) (+420) 776147273 (Czech Republic)
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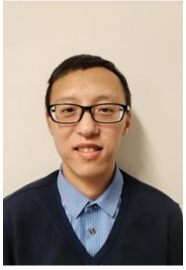
H index (WOS)	8

Kai Yang (KMI, TUL)

ResearchGate



Research area

- Application of phase change material in textile
- Confined polymer crystallization via thermal analysis

Education

Degree	Time	University	Subject	Topic
Ph.D Study	2018.01.19-now	Technical University of Liberec (Czech Republic)	Textile Engineering	● ***Application of phase change material in textile.*** ● ***Modification of fabric surface via eletrospraying.***
Master of Engineering	2014.09-2017.06	Wuhan Textile University (China)	Textile Engineering	***Design of a centrifugal spinning setup for polymer fibers.***
Bachelor	2010.09-2014.06	Wuhan Textile University (China)	Textile Engineering	***Ultrasonic dyeing for fabrics.***
Internship Study	2022.06-2022.09	INOTEX company (Czech Republic)	Textile Engineering	***Thermal behavior of MPCM-coated fabrics.***
Internship Study	2019.10-2019.11	Shinshu University (Japan)	Textile Engineering	***Structural analysis of confined polymer in aerogel.***

Projects

SGS-2021-6023 (leader)	**Heat transfer of a nanofibrous membrane-incorporated multi-layer fabric system containing PCM**
SGS-2020-6036 (leader)	**Preparation of PTFE membranes with tuned porosity via electro-spraying method**
SGS-2019-6047 (leader)	**Investigation on thermal properties of multi-layer composites containing PEG/aerogel**

Awards

Best presentation during SGC conference 2021

11. Recommendation of Supervisor

Recommendation of the supervisor on Ph.D. thesis of Kai Yang M.Eng.

Date: 10.01.2024

Thesis title: **Multi-Layer Phase Change Materials System for Thermal Energy Storage**

The PhD thesis of Kai Yang is concerned with the preparation and characterization of a fibrous multi-layer phase change material (PCM) system for buffering thermal shocks from the environment. The fibrous multi-layer PCM system composed from PCM-loaded layer, barrier layer and protective layer was developed. By controlling the interfacial adhesion of melting PCMs on barrier layer or protection layer, the leakage phenomena were avoided. The PEG and paraffin wax were selected as PCM. The maximum loading amount of these PCMs in the fibrous multi-layer PCM system was 45 wt.% which was ensuring the good overall enthalpy 78 J/g supporting thermal buffering effects. The introduction of metal microparticles into PCM-loaded layer was able to enhance heat transfer through the whole system.

The breathability of the fibrous multi-layer PCM system was ensured by splitting of PCM-loaded layer to system of air pockets and PCM pockets. The size of air pockets tuning the mutual heat transfer between PCM pockets and air pockets was selected.

The thesis adheres to the specified format and successfully achieves all of its intended objectives. The candidate has demonstrated a high level of systematicity over the course of his research, thus achieving outstanding results through the pursuit of specific aims. He employed advanced scientific methods to evaluate and examine data. The discussions pertaining to the outcomes are coherent and include comparisons of the attained results with those of other published works. The language proficiency exhibited in the thesis is commendable and satisfies the standards expected at the doctoral level. Majority of his findings exhibit novelty and have already been published by him in high-impacted academic journals. His exceptional abilities are evidenced by his publication record in journals with high-impact factors. Throughout his research tenure at TUL, he has promoted his findings through the publication of 21 papers in journals with high-impact factors, 5 book chapters, and 17 articles in conference proceedings. Throughout his academic pursuits, he demonstrated a high level of diligence and competency. The findings of the dissertation are valuable, innovative, and readily applicable in practical settings. Thus, it is highly recommended that the thesis be presented for the final doctoral defense.

When searching for plagiarism, a match of 1 percent only was found. Reason is the form of a dissertation thesis as an annotated overview of published articles.

Prof. Ing. Jiří Militký, CSc. EURING

Supervisor

12. Reviews of the Opponents

Opponent report on doctoral dissertation – Mr. Kai Yang, M.Eng

Opponent: Jan Marek MSc., PhD. – InoTEX, technical and sales director

The importance of thermo-regulating barrier properties is increasing. As working and living conditions shift to more extreme environments, as demands on living comfort are increasing, but also as a result of the steep increase in energy prices and the costs associated with regulating the quality of the environment in buildings through air conditioning. It can be expected that the importance of thermal regulatory properties will also increase as a result of ongoing climate change.

A tool for achieving thermoregulatory properties is the application of PCM. As an extensive introductory literature review has shown, it is possible to use textile substrates as their carriers. However, with regard to the need to achieve optimal efficiency and stability of the effect, it is necessary to look for a suitable way of incorporation of PCMs systems exhibiting the thermal energy storage into the textiles.

The development of textile products leading to new functional and multifunctional properties was therefore the impetus for the focus of the dissertation of Kai Yang, M.Eng. *"Multi-Layer Phase Change Materials Systems for Thermal Energy Storage"*.

Informed by the limitations, especially the risk of deterioration of the necessary mechanical - physical properties of the fabric when using PCM fibers and the negative effect of film-forming polymer binder on stiffness, breathability (air and moisture vapour permeability) affecting the thermal comfort management, author focused on the multi-layer fabric structure in which the PCM coated layer (Vis NW) is covered with barrier layers to avoid leakage. Due to the extensive experience of the training faculty of textile engineering he focused on the suitability of using PU based nanomembranes as a barrier against the undesirable PCM leakage that would prevent the loss of thermo-regulatory ability of functional textiles and prevent the deterioration of their thermo-regulatory barrier properties. De to the weak mechanical durability of nanomembranes the commercial PET knitted surface fabric was used at the same time as a protection of nanomembranes. Alternatively, the hydrophobized PET fabric as surface protection layer was used (parameters of used knits summarized in the table 1). Melting points of selected organic PCMs were defined (PEGs 600-6000, paraffin wax, myristic acid). Multilayer constructions containing PCMs (PW, PEG 6000) loaded Vis NW fabric both sides covered by PU barrier nanomembranes and hydrophobized PET knit surface layers were used as standards in minimizing PCM leakage, achieving thermal control and control of working temperatures, and finally providing other utility functions (increasing heat transfer and breathability). Various characteristics of fibre multilayer PCM systems were analysed towards the construction of a fibrous multi-layer PCM system (mechanism to avoid leakage, PCM loading performance - including encapsulation efficiency, PCM loading amount, relative crystalline degree and range of working temperature. An extensive set of figures presents comparisons of PCM incorporated products used in the dissertation and commercial products su ch as Outlast. Figures were also used to display estimated phase transition range and evaluation of thermal buffering. The possibility of next increasing the heat transfer efficiency by the addition of Fe microparticles presented in the dissertation was also demonstrated using other metal microparticles (listed in the attached author's publication 9.3 Appendix 1).

In order to achieve the stability of the thermal-regulatory effect and the necessary wearing comfort of the multi-layer construction used for the application of PCM, where their compact application on Vis NT reduces the permeability of air and water vapour, a unique solution was designed by using air "pockets"; in the sandwich layer containing PCM, free spaces (air) and areas with PCM deposition alternate. Measurements have shown that by choosing an optimized mass ratio of PCM (PEG) and carrier Vis textile, it is possible to minimize its diffusion of the molten PEG from the places of its deposition into the space of the air pockets during heating/cooling cycles. The rationale for this phenomenon is given and supported in more detail by figures contained in the Full Text Appendix of the publication of the team led by aspirant (9.2-Appendix1).

The conclusions presented by the author at the end of the dissertation describe the established properties of the proposed fibrous multi-layer PCM system, which give a prerequisite for its application in practice.

The extent of the literature search (113 references), as well as his publication activity (10 Journal publications as corresponding author of team + 11 as co-author, partly presented in the quite unique Appendix 1 with Full text reprints of 5 Research Journal Articles – Kai Yang as corresponding representative of the team), 5 cited book chapters and 17 team presentation on conferences proves that he devotes adequate attention to this inseparable work associated with scientific activities.

The doctoral student has demonstrated the ability of independent scientific research work. From the experience with his work on the development of PCM functional textiles, which he carried out partly in the InoTEX technological laboratory as part of his cooperation on an international project (CZ-PRC), it is possible to confirm his thoroughness and systematic approach to experiment planning. In addition, during the period of restrictions related with the Covid 19 pandemic, his involvement in the project overcame limitations that would otherwise have significantly jeopardize the fulfilment of the joint project assignment of TUL/InoTEX with Zheijang Sci-Tech Uni.

The dissertation thesis describes the scope of work carried out and a clear summary of the results with factually and clearly formulated conclusions (supplemented by Appendix 2 – with 7 tabular Details for comparison). The thesis ends with a proposal of further activities P 11- Future prospects).

Questions to be answered during thesis defence:

1. Air pocket/PCM pocket structure – presented as a solution to achieve the thermo-barrier effect and breathability comfort of multi-layer fabric with embedded PCM – what is the idea of the method of its industrial production?
2. Is it possible to compare the final user properties of multilayer textile PCM structures with other known alternatives (advantages/disadvantages)?

I recommend the Kai Yang´s, M.Eng. dissertation thesis for defense.

Jan Marek MSc., PhD.　　　　　　　　Dvůr Králové nad Labem, 10.03.2024

Referee's report on PhD. thesis of

Kai Yang

"Multi-Layer Phase Change Materials System for Thermal Energy Storage "

Professor Miroslav Černík

The presented thesis comprises 155 pages, with about one hundred pages of reprints of the author's papers. The thesis deals with decreasing the leakage of PCM during heating/cooling by applying nanofibrous membranes, thermal enhancement and increasing the breathability of the fabrics.

Chapter 1 (Introduction) introduces the subject and defines the function of PCM-incorporated textiles. The second aspect is to enhance thermal regulation and energy storage and support the light radiation-thermal energy conversion. This topic is solved by presenting scientific papers. The papers deal with preparing, characterizing, and testing multi-layer fabric. In total, the author published 20 research papers on this topic, and four of them, where he is the first author, are presented in the appendix. The author's contribution to the subject of the thesis is sufficient.

Chapter 2 (State of the Art) discusses two types of PCM – microcapsulated organic PCM and form-stable PCM. The PCM-containing fibres are prepared using various technologies, including electrospinning, centrifugal spinning, solution spinning, etc. The primary characteristic of the PCM fabrics is the measurement of kinetics of the temperature changes. A pure empirical model was proposed based on observing three parts of ln(T) vs t plot. On the other hand, the parts correspond to the solid phase state, phase transition state and liquid PCM state. Then, the model is not empirical because it describes the natural physical forms of PCM material on the fabrics, but in this case, it should be confirmed by measurement.

Chapter 3 (Motivation and aims). The motivation and aims of the work are defined and logical. According to the author, this is the first work where nanofibrous membranes are used in the fibrous multi-layer PCM system. The work's main objective is to find a suitable multi-layer fabric structure to contain PCM, make its complex characteristics and improve its thermal energy storage efficiency. Also, the breathability of the fabrics was optimized.

Chapter 4 (Construction of A Fibrous Multi-layer PCM System). After various fibrous multi-layer systems were prepared, two structures without leakage were obtained and used for other testing. The chapter presented the performance of the system compared to other similar systems. The methods used in the thesis are relevant for fulfilling the thesis aim.

Chapter 5 (Enhanced heat transfer efficiency) and 6 (Controlled breathability by modifying PCM-loaded Layer) describe results taken from provided publications.

Chapter 6 (Conclusions). The author came to the following conclusions: The leakage was avoided by controlling the interfacial adhesion of the layers, and the maximum loading amount of PCMs was 45%. Metal microparticles enhanced the enthalpy of the system. The question is whether the enthalpy of the multi-layer PCM fabric is 78 J/g and that of the PCM containing metal microparticles is 50 J/g. It is strange.

Referee remarks, question and conclusions

The thesis is logically divided into chapters, the content is illustrated, and all determined results are simply described.

QUESTIONS

1. The author said that phase change materials (PCM) adsorb/release thermal energy during phase transition. Do you know some material which does not absorb/release thermal energy during its phase transition? And why did you write adsorb? Is it not absorption? Did you not mention the material that absorbs/releases thermal energy to provide desired heating or cooling?
2. In calculating Bi number, there are different units – h and K in meters L in mm. Could you show the details of the calculation?
3. Why is the enthalpy of the multi-layer PCM fabric 78 J/g, and why for the PCM containing metal microparticles it is only 50 J/g?

Imperfections and recommendations

The language of the thesis is good, and the thesis is nicely written. I did not find many errors and mistypes. Some examples:

1. Equation 1 has an error: index f is missing
2. Table 1: Areal density is expressed in g/m^2. The numbers are not statistically correct, e.g. 200±2.35.
3. *Figure15Figure15* on page 28,
4. Some of the figures are very small and unreadable, e.g. Fig.14,

Referee's conclusion

The presented thesis is based on four scientific papers selected from a significantly broader set of his publications. The publications have 4, 1, 18 and 5 citations till now. So, the referees independently checked the papers during publication, and the scientific community was interested in the author´s results. The student is the first author of these publications, and his contribution was substantial. The thesis's text is logical, has all the necessary parts, and shows that the author understands the problem. The thesis has a significant influence on the field of study.

The recommendations mentioned above and the questions are not so significant that they decrease the scientific merit of the thesis.

The thesis is good and meets all criteria to be taken to the defence. I, therefore, recommend the thesis be taken for defence in front of the committee.

In Liberec (Czech R.) on May 30, 2024 **Prof. Dr. Ing. Miroslav Černík, CSc.**