Fanglong Zhu[1,2], QianQian Feng[1], Rangtong Liu[1], Baogang Yu[2], Yu Zhou[1]

[1)] **Zhongyuan University of Technology,**
Zhengzhou City, P. R. China
E-mail: Zhufanglong_168@163.com

[2)] **The Chinese People's Armed Police Forces Academy,**
Langfan City, P. R. China

Enhancing the Thermal Protective Performance of Firefighters' Protective Fabrics by Incorporating Phase Change Materials

Abstract

A composite fabric consisting of an outer shell, moisture barrier, thermal liner and comfort layer used for firefighters' protective clothing, was incorporated with shape-stabilised phase change material (PCM) powder in order to improve the thermal protection capability provided by thermal protective clothing. Then we conducted a series of FTP (fire testing protection) experiments to investigate the effects of PCM location and phase change temperature on the heat protection efficiency of firefighters' protective fabrics (FFPFs). Simultaneously the thermoregulation performance of the composite fabrics with PCMs was evaluated by using step-cooling experimental technology during the cooling process. Data from the FTP tests were also compared with those from the existing enthalpy formulation model of heat transfer through FFPFs embedded with PCMs. It was concluded that the use of PCMs could improve the heat buffering capacity. However, as PCM has a moderate melting temperature, it is better than the other two samples because they have a lower and higher melting temperature. Therefore PX 52 PCMs (melting temperature: 47 - 53 °C) could provide the maximum heat protection time compared with the other two kinds of PCMs.

Key words: *phase change material, fire protective clothing, thermal protective performance.*

Introduction

Clothing fabric containing phase change materials has the property of offering a suitable response to changes in external temperature or to external and environmental stimuli. Therefore it has been applied to firefighter protective clothing to improve thermal comfort or the heat protection effect, because of its high thermal storage capacities. Chou et al. [1] examined the effectiveness of ice-packs (ICE) and phase change material (PCM) cooling devices in reducing the physiological load based on the subjects' physiological and subjective responses while theyexercised on a bicycle ergometer when wearing firefighting protective clothing. Gao et al. [2] investigated the effects of the melting temperature of PCM used in a cooling vest on heat strain alleviation in an extremely hot environment. Carter et al. [3] compared the efficacy of the use of PCM vests during firefighting and that of 20 min cold water hand immersion following such activity.

The above-mentioned literatures described the application of PCM for the improvement of the thermal comfort of thermal protective clothing. However, structural firefighters can receive second or third-degree skin burns while working in thermal exposure, and firefighting protective clothing is designed to prevent the human body from getting burn injuries. The incorporation of PCM into firefighters' protective clothing for the improvement of heat protection is a new technology. Rossi and Bolli [4] studied the use of PCM to improve the thermal protection performance of firefighters' protective clothing and observed a heat buffering effect when the clothing was exposed to a thermal radiation source. Then Buhler et al. [5] compared different types of non-flammable PCMs such as saturated zeolites and salt hydrates for use in heat protective clothing. McCarthy and Marzo [6] conducted a series of bench-scale experiments involving FFPF both with PCMs and without to explore the effectiveness of PCM in improving the thermal protection of FFPF by comparing the data with a theoretical finite difference heat transfer model.

A wide spectrum of phase change material for textiles is available with different heat storage capacity and phase change temperature. Due to some of the problems, such as lack of segregation, supercooling or corrosion, inherent in inorganic PCMs, organic PCMs (paraffin waxes, PEGs, fatty acids and mixtures) are commonly chosen in textiles [7]. However, the direct addition of PCMs to fabrics presents leakage when they become liquid. In order to avoid this problem, PCMs should be confined to a container. One of the successful methods is the use of shape-stabilised composite PCMs which can be prepared through encapsulation of the PCM in a polymeric structure, such as high density polyethylene [8].

Another problem we are still facing is the high flammability of PCMs containing paraffin wax, which will limit its application in firefighter protective textiles. To avoid this problem, some possible solutions have been proposed. For example, Buher et al. [5] used non-flammable materials such as salt hydrates and zeolites as PCMs to investigate their heat buffering capacity. PCM composites with flame retardant treatment were also prepared as thermal storage materials [9]. Another flame retardant shape-stabilised composite PCMs were prepared using *n*-hexadecane as the phase change material and SiO_2 acting as the supporting material that is fire retardant [10].

Up to now, work on the influence of PCM location and phase change temperature has been scarce. The aim of this work was to improve the thermal protective performance of firefighter protective clothing to enhance the heat buffering capacity of fabric composites. This improvement was achieved by incorporating commercial form-stable PCM powders into FFPCs with the use of the PCM in a sandwich construction between two flame resistant fabrics which can avert burn or flame propagation.

Experimental details

Materials

Typical composite fabrics used in firefighter protective clothing containing PCMs were divided into four layers: the outer shell (OS), moisture barrier (MB), thermal liner (TL) and comfort layer (CL). Shape-stabilised PCM powder was incorporated into the composite fabric system in two ways: Position A and Position B, as shown in ***Figure 1***. The configurations were selected to compare various types of PCM to typical FFPF configurations.

For the composite fabric preparation, each layer of fabric was cut into 15 × 15 cm. Then the PX powder was added and evenly distributed over the entire fabric, with an area weight of 200 g/m^2. That is to say the amount of PCM powder was selected to be 4.5 g. Except for the outer shell, the other three layers containing PCM powder were quilted together. Lastly by placing the outer shell over the quilted layer, the composite fabric system was formed.

Rubittherm® PX 35, Rubittherm® PX 52, and Rubittherm® PX 82 (commercial grade supplied by Rubitherm Technologies GmbH, Germany) [11] were used as PCMs. The powder form of this bound PCM, which is also known as dry liquid, allows to fill containers (or textile covers) of any conceivable geometry without having to handle or store inconvenient liquids. The powder remains absolutely dry below and above the phase change temperature as the phase change occurs inside the material. Moreover Rubitherm® PCM powder is non-toxic and has the advantage of high PCM content and high heat storage capacity. The thermophysical parameters of these materials are listed in ***Table 1***.

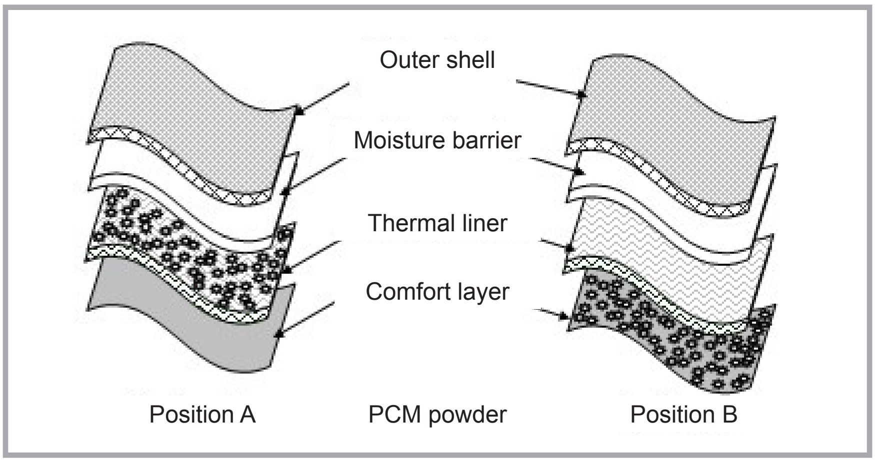

Figure 1. *PCM configuration within FFPF specimen assembly.*

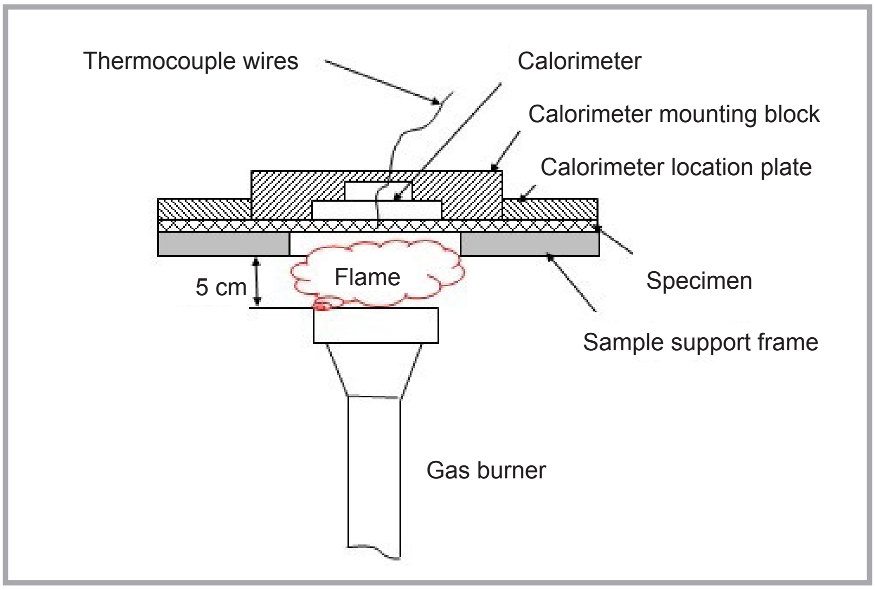

Figure 2. *Schematic diagram of heat transport in the firefighter protective fabrics and copper calorimeter.*

***Table 1**. Properties of the phase change materials used (PCM powders - series PX).*

PCM	Thermal conductivity, W/mK	Density, kg/m^3	Specific heat, kJ/kg K	Latent heat, kJ/kg	Melting temperature, °C
PX-35	0.1	694	0.6	118	29-35
PX-52	0.1	694	1.6	110	47-53
PX-82	0.1	690	1.6	105	77-85

Experimental set up and procedure for material behavior tests

Testing apparatus for evaluating the thermal protective performance of fire clothing is shown in ***Figure 2***, which is called Fire Testing Protection Apparatus (FTP30). The heat source was provided by a gas burner. Heat was transferred through the fabric specimen and air gap located between the fabric and copper calorimeter surface. Times for a temperature rise of 12 °C and 24 °C were recorder using a thermocouple mounted on the calorimeter. The mean result for three test specimens was calculated as the "heat transfer index" (HTRI12 and HTRI24) [12]. The time differences HTRI24-HTR12 gave a good indication of the skin pain alarm time. The heat sources corresponded to ISO 6942 (Protective clothing-protection against the heat and fire-method of the test: Evaluation of materials and material assemblies when exposed to a source of radiant heat) and ISO 91541(Protective clothing-Protection against heat and fire-determination of heat transmission on exposure to flame). The temperature rise versus time and heat flux was measured using a copper calorimeter located above the sample fabrics. The samples were exposed to the gas burner at a distance of 50 mm, where the heat flux was 84 kW/m^2.

Prior to testing, gas adjustment was conducted to calibrate the heat flux from a Meker burner in the desired range. This can be accomplished by comparing the copper sensor's temperature history with set values after a period of exposure time. A series of bench-scale experiments were conducted and compared to a theoretical

Table 2. Heat protection index for different configurations.

PCM	PCM position	PFFC Configuration	HTRI12, s	HTRI24, s	HTRI24 - HTRI12, s
Without	-	OS + MB + TL + CL	11.67	16.53	4.86
PX-35	A	OS + MB + PCM + TL + CL	15.13	22.07	6.94
	B	OS + MB + TL + PCM + CL	15.07	23.10	8.03
PX-52	A	OS + MB + PCM + TL + CL	15.67	22.03	6.36
	B	OS + MB + TL + PCM + CL	16.47	24.60	8.13
PX-82	A	OS + MB + PCM + TL + CL	15.47	22.67	7.20
	B	OS + MB + TL + PCM + CL	15.97	23.97	8.00

model to examine how PCM impacts the thermal protection provided by FTP-30. These experiments included FFPF samples both with and without the addition of phase change material. The overall uncertainty in the estimation of the thermal conductivity is no more than 7.1%, obtained by combining the precision and bias error using the root-square method.

Step-cooling experiments

Since there is no standard method for measuring the thermo-stabilised properties of thermal storage and stabilised textiles and clothing, we chose to use a step-cooling test procedure,described as follows. The specimen assembly was taken out from the FPA-30 once the heat protection tests were finished. Temperature profiles on the reverse side (close to the copper calorimeter) of the CL (cotton fabric) during the cooling period were evaluated by means of an infrared and visible - camera Fluke Ti32, Fluke Corporation, USA at a certain time interval. A cooling curve describing the temperature change with time can be derived. Simultaneously thermal and visual images in the temperature range from 20 to 250 °C with a precision of ± 2 °C at different times can be extracted by Fluke SmartView™ software.

Results and discussion

FTP experimental data

Table 2 lists the results of the heat protection index HTRI12, HTRI24 and the difference HTRI24 - HTRI12 (indication of the skin pain alarm time) for different configurations. The measurements were repeated three times for each kind of combination and the index estimated at average values from the three tests. The results shown in ***Table 2*** indicate that all the composite fabrics containing PCM had higher HTRI12, HTRI24 than that in the configuration without PCM. That is to say, PCM can contribute to the improvement of the heat protection of firefighter protective clothing. In our experiments, we also observed that the composite fabric containing PX 52 had the highest heat protection index HTRI compared to those with PX 35 and PX 82 when the PCM layer was located in Position A. This could be explained by two facts: One is that PX 35, whose melting temperature range is between 29 °C and 35 °C, had partly melted when the thermal exposure test began, thus resulting in the issue of a slow increase in the heat protection time. The other is that the PCMs need a minimum time to change their state, and if the phase change temperature of PCMs is too high, the PCMs may not completely melted when the heat protection time reached the condition in which temperature rise was 12 °C or 24 °C. Therefore PX 52 has a higher heat protection index HTRI than that of PX 82, though the values for specific heat are similar for the two kinds of PCMs (***Table 1***). The heat buffering capacity can be also characterised by temperature evolution on the copper calorimeter. ***Figure 3*** displays temperature variation versus time on the surface of the copper calorimeter for Position B without an air gap configuration. Compared to the parent fabrics, all the samples incorporating PCM had a reduced temperature increase on the copper calorimeter. In the latter phase, a higher temperature increase was experienced by composite fabrics containing PX 52 than that embedded with PX 82, as a result of the lower specific heat capacity of PCM PX 52. In other words, the PCM must melt prior to the fire fighter receiving burns. In general, a second-degree burn occurs when human skin reaches approximately 53 °C. The analysis indicated that the melting temperature of PCMs should be less than 53℃ when the PCM layer is close to human skin.

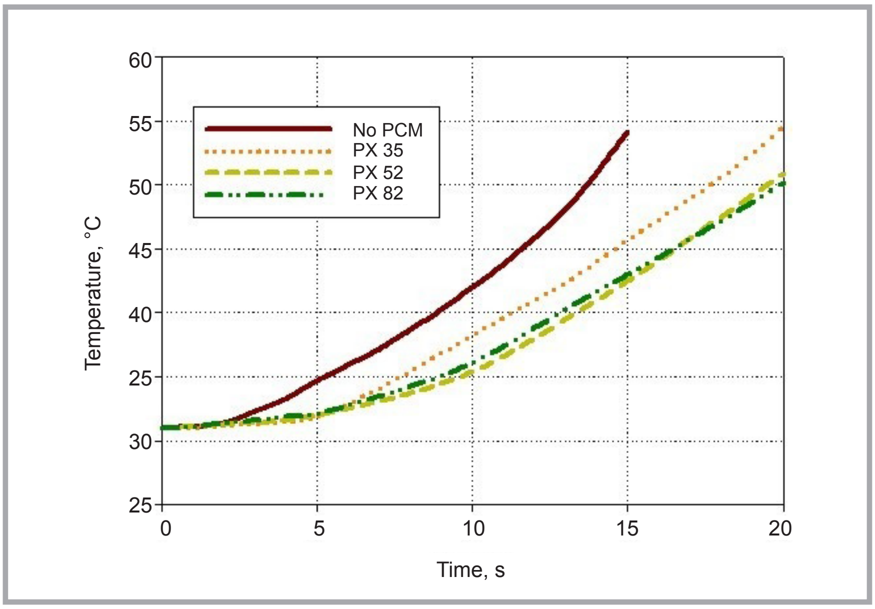

Figure 3. *Comparison of the temperature evolution on the surface of the copper calorimeter. (Configuration: Position B; Air gap: 0 mm).*

The heat buffering effect of PCM located in Position B can be compared with that in Position A. For all of the series PX PCMs used, the time difference of HTRI24-HTRI12 was higher when the PCM layer was coupled between the thermal liner and comfort layer (Position B). Heat transfer index HTRI24-HTRI12 is an indication of the skin pain alarm time. The higher the value of the index, the more excellent the thermal protective performance. Therefore the efficiency of the PCM was higher on condition that the PCM was placed in Position B under a high heat flux of 84 kW/m^2. In general, compared with low heat flux, under intense external heat flux conditions the temperature inside the clothing layer increased rapidly when the composite fabric's PCM layer was closer to the outer shell, which will have less time to completely undergo the phase change and the heat buffering efficiency offered by the

PCM will attenuate. Consequently the PCM located close to the innermost layer (Position A) can slow down the increase in temperature at the interface between the innermost layer and the copper calorimeter. The results were consistent with those reported in reference [15]. It can be also concluded that the addition of PCM powder caused a slight decrease in the copper calorimeter temperature for the composite fabric during fire exposure. Possibly experiments conducted under low heat flux conditions appear to a result, which is opposed to high heat flux. We will expand on this in the theoretical model study section.

Step-cooling experimental data

The heat buffering effect of PCMs can be also evaluated by the temperature variation approach, described by two contrastive curves (temperature vs. time), for the fabric containing PCM and the parent fabric under the same cooling conditions. Then the slope derived by the curve is able to estimate the effect of PCM on the thermal protective performance of FFPC. Here we called the approach 'the step-cooling test'.

Figure 4 gives comparisons of step-cooling curves observed by a thermal vision camera for the composite fabric containing PX 52 (Positions A & B) and the parent fabric. In all three cases, the surface temperature of CL decreased gradually with time and all the curves had a similar trend: varying fast and slow. During the cooling period, there was a temperature range when the temperature of the composite fabric with PCM was higher than that of the parent fabric. Therefore the presence of PX 52 affected the slope of the temperature curves, indicating that the PCMs were able to release part of the energy slowly when the surrounding temperature changed and that the composite fabric containing PCMs has excellent thermo-stabilised ability. It should be noted that the PCM location configuration exerted little influence on the shape of the temperature curves.

The regression curves (temperature *T* vs. time *t*) showed a good fit with the experimental data through Origin software analysis (***Figure 4***). Three regression equations can also be obtained and are shown in ***Table 3***.

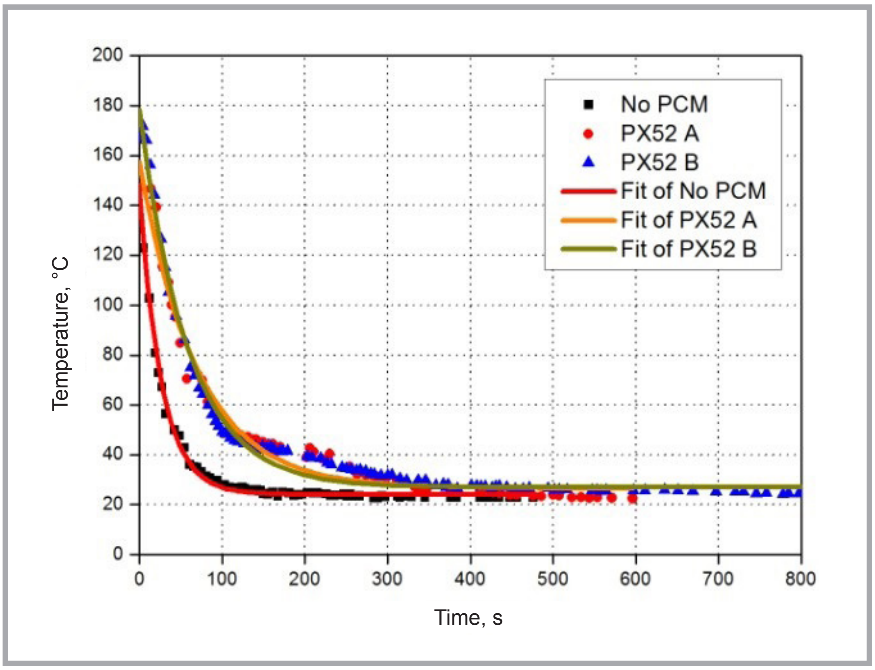

Figure 4. *Step-cooling curves and regression curves.*

Theoretical model

In order to characterise the heat protection effect of PCMs, a model for temperature history prediction was proposed. Very little additional work was conducted on modeling the heat transfer through thermal protective fabric layers containing PCMs or on investigating the heat protection ability [6, 13, 14]. In the paper the enthalpy formulation method was used in theoretically calculating the phase change process of the composite fabrics containing PCMs [15]. The governing heat transfer equation and boundary condition describing the behaviour of the composite fabrics, based on the conservation of energy, has the following form:

$$\rho C\frac{\partial T}{\partial t}=k\frac{\partial^2 T}{\partial^2 x}+Q_r+\rho h_m\frac{\partial Z}{\partial t} \quad (1)$$

$$-\lambda\frac{\partial T}{\partial x}=h_{fl}\left(T_g-T_{fab}\right) \quad (2)$$

where, ρ is the effect density, C the specific heat, k the thermal conductivity, h_m the melting heat of the PCM layer and Q_r is the radiation heat source term representing the internal heat generated by thermal radiation transferred to the internal region of the fabric. Q_r can be written in the form of $Q_r = \gamma q_{rad} e^{-gx}$ [16]. Here q_{rad} is the incident radiant heat flux from the thermal source, and γ the extinction coefficient of the fabric ($\gamma=-\frac{\ln\tau}{L_{fab}}$, τ - the transmissibility of the composite fabric, L_{fab} - the thickness of the composite fabric). We assumed that the incident radiant heat only penetrated into the outer shell. T_g and T_{fab} are the burn gas temperature and the fabric surface temperature, respectively. h_{fl} is the empirically estimated total heat transfer coefficient between the flame and surface of the composite fabric and can be determined by a series of experiments by means of the FTP-30 system without a fabric specimen. Z is the solid fraction presented in the PCM layer (Z = 1 is solid, Z = 0 is liquid), which can be described by the *erfc* smooth function $Z=\frac{1}{2}erfc\left(\frac{T-T_m}{T_0}\right)$ [14]. Here T_0 is the range over which the melting transition occurs (taken as ± 3°C) and T_m is the melting temperature of the PCM layer. It should be noted that the melting process (thermal conductivity, specific heat, latent heat *et.al*) from the bulk of PCM is mainly determined by the particle diameter distribution. The bulk of PCM is a loose particulate

Table 3. *Regression prediction equations.*

PCM configuration	Regression equation	Correlation coefficient, R^2
Without PCM	T = 121.6 exp(- t/26.7) + 24.0	0.9962
Position A	T = 130.9 exp(- t/69.3) + 26.5	0.9735
Position B	T = 151.2 exp(- t/58.5) + 26.9	0.9852

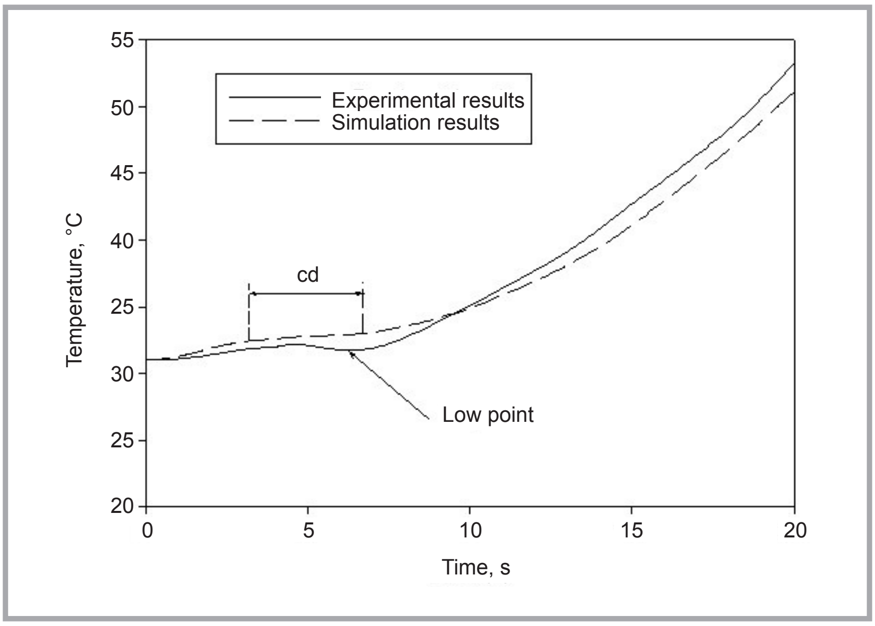

Figure 5. *Comparison of temperatures of copper calorimeter above composite fabric containing PX 52 using a numerical model and experiments.*

system with fractal geometrical characteristics. Here we applied the fractal analysis method to calculate the thermophysical parameters above [17, 18]. For simplification, the middle values from the melting temperature range (***Table 1***) were chosen for all the PCM layers.

The governing energy ***Equation 1*** was solved with the finite difference method. The differential equation can be transformed into a node equation for the temperature field by establishing a limited number of grids within the entire multilayered region, including the copper calorimeter. The Gauss-Seidel point-by-point iterative scheme was employed to eliminate nonlinearity due to the nonlinear radiation terms. The results were relatively irrespective of the grid size and the time step when using a grid size of 10^{-6} m and time step of 0.1 s.

Comparisons between experimental data and model predictions

The temperatures at the surface of the copper calorimeter under 84 kW/m^2 heat flux were calculated and compared with the experimental data for PX 52 PCM located at Position B. ***Figure 5*** clearly shows a substantial lowering of the temperature of the experimental profile (full line) at the early stage compared to ***Figure 3*** (cd phase). The phenomenon can be also observed for the other two PCMs. The temperature on the surface of the copper calorimeter will see no change or rise slowly according to the theoretical analysis prior to the completion of the phase change. However, there is a slope change in the temperature evolution history, where the temperature decreased suddenly and then increased quickly in a thermal exposure course of between 5 and 10 s.

In general, a phase change occurs when the temperature of the PCM layer reaches the phase change temperature for the configuration of Position B. When PX 52 changes its phase, the heat flux transfer from the flame through the TL layer to the PCM will be stored within the PCM and the temperature thereof will remain steady until the completion of the phase change. At the same time the cooling effect of the phase change is greater than the heating effect from the outside thermal source because the TL layer will insulate the heat flux transfer in copper calorimeter at the early intense heat flux exposure stage. Possibly it will give a different result under low heat flux conditions. We will extend the FTP experiments for low heat flux exposure in future research.

Moreover no flat plateau could be found in the experimental data contrasting with the results simulated. This can be explained by two facts: One is that the melting temperature of PX 52 fluctuates in the range of 47 to 53 °C. The other is that PCM needs a certain time for completion of the phase change. Therefore temperature distribution through the composite fabrics is heterogeneous and the PCM changes its phase in a slow manner [5]. However, these factors were not considered in the results calculated. These are also the limitations of the numerical model.

Conclusions

PCMs can be used to reduce heat stress and improve the heat protection effect for firefighters wearing thermal protective clothing under high flux exposure conditions. In this paper, shape-stabilised PCMs were incorporated into FFPFs with a weight value of 200 g/m^2 to investigate the effect of the PCM location and phase change temperature on the heat protection efficiency of FFPFs. It was found that all the composite fabrics containing PCMs had a higher heat protection time than the parent fabrics. The existing numerical heat transfer model gave the same results as the experimental data. It was also observed that the composite fabric containing PX 52, whose phase change temperature is in the range of 47 °C and 53 °C, had the highest heat protection index HTRI compared to those with PX 35 and PX 82. Finally the results of step-cooling tests showed that the addition of PCMs can cause a slow temperature decrease for the CL during the cooling process.

Acknowledgements

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A meeting to remember Professor Szosland

A meeting devoted to the memory of Professor Janusz Szosland Ph.D, D.Sc., Eng., Dr h.c. MGAT, Dr h.c. TUL was held on 13 February 2015 at Lodz University of Technology.

The meeting was organised by the Faculty of Material Technologies and Textile Design of Lodz University of Technology and the Polish Textile Association.

A great number of friends of Professor Szosland and representatives of the Textile Society, Government and University representatives, professors, directors of research centres and editors took part in this event.

The great lecture room of the Faculty was fully occupied with participants.

The meeting was inaugurated by Professor Józef Masajtis, Phd, D.Sc. Eng., the dean of the Faculty of Material Technologies and Textile Design, who presented comprehensively the scientific and social life as well as activity of Professor Szosland.

Elwira Zaręba, the current president of the Polish Textile Association, emphasised Professor Szosland's extraordinary dedication and energy with which he fulfilled his duties during the long years as President of the Association and next as Honorable President till the last days of his life.

The speech given by Mrs. Lidia Szosland was very moving.

The speakers were the following:

- Mr. Ryszard Bonisławski – senator of the Polish Parliament
- Mr. Tomasz Trela – The 1st V-ce President of the City of Łódź, who read a letter from President Zdanowska
- Professor Marian Mikołajczyk, Ph.D, D.Sc., Eng., – full member of the Polish Academy of Sciences, a long-time President of the Lódź Branch
- Professor Stanisław Liszewski, Ph.D, D.Sc. – President of the Lodz Scientific Society
- Mr. Julian Bąkowski, M.Sc. Eng – President of Association of Graduates from the Technical University of Łódź
- Jan Wojtysiak, Ph.D, D.Sc., Eng., – President of the General Board of the Polish Textile Association and Professor of the Institute for Sustainable Technologies – National Research Institute
- Professor Zbigniew Wrocławski – the oldest Polish Textile Scientist
- Elżbieta Paradowska, M.Sc, Eng. – President of the Wrocław Branch of the Polish Textile Association
- Mr. Antoni Smolarek – member of the Organisation Committee of "TEXTILCROSS" (a running event, since 2015 named "Professor Szosland TEXTILCROSS"), who highlighted the great interests of Professor Szosland in sports, especially long-distance runs.

After the official part, the participants of the meeting exchanged their impressions of their relations with Professor Szosland.