

Energy Release Studies of Human Feet for Mapping μ PCM Quantity in Socks for Thermoregulation

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Abstract

Pure PCM and microencapsulated PCM (μ PCM) were analysed for heat capacity and core content using DSC analysis and were tested for stability against heat and solvent. The energy release rate of human feet was quantified through a novel in-house tester using a water and air medium. The energy release rate from various experiments were compared and ranges of the quantity of μ PCM recommended for a definite period of thermoregulation with and without a factor of safety. Based on theoretical predictions, socks were treated with μ PCM at add-on values of 0.2 g to 5 g corresponding to 1% and 25% per weight of the socks, respectively. The socks treated were subjected to wear trials and evaluated against the untreated one. It was found that the thermoregulation period of the μ PCM treated socks were proportional to their add-on weight and were in close agreement with the theoretical predictions proposed. The presence of μ PCM on the treated socks was observed through a scanning electron microscope.

Key words: microencapsulated PCM, μ PCM, thermoregulation, energy, stability, socks.

Introduction

As a result of metabolic actions, the human body produces heat, sweat and other metabolic by-products which must be released/dissipated into the atmosphere mapping with their rate of production [1]. Such a release ensures the comfort of the body and is controlled by various factors which can be broadly classified into two categories, the first one being natural environmental factors such as the temperature, humidity and wind flow of the environment, and the second one artificial factors like the clothing used to cover the body [2]. Clothes are designed based on the first factors in order to have proper control over the loss of heat and sweat from the human body [3, 4]. Hence as clothing becomes the integral part of the human being, it significantly influences the comfort of the wearer [5]. Like clothing, in the present scenario the use of shoes has become mandatory in everyday professional activities, which would last roughly 8 hours. Because of such prolonged use of shoes, feet experience discomfort caused by the localised accumulation of heat and moisture [6]. Works on the incorporation of antimicrobial agents in shoes and socks are reported [7].

The use of phase change materials (PCMs) appears to be promising as it has the capacity to absorb heat and maintain the feet temperature, thus providing comfort to the wearer [8]. The commonly preferred PCM is n-octadecane due to its suitability in terms of its melting and crystallising temperature being close to

the human body temperature [9]. Such microencapsulated PCMs (μ PCMs) have been widely studied for the purpose of the thermoregulation function of textile materials for various special end applications, of which using μ PCMs in shoes and socks is one area [10]. An important factor to be considered when PCM is used for thermoregulation upon absorbing heat is the quantity of thermal energy released by the system [11]. Such released energy from the system should be absorbed by the PCM, which would depend on the heat capacity of the PCM [12, 13]. This decides the total thermoregulation of the system for a given quantity of μ PCM. Therefore the application of μ PCM for the thermoregulation of any system would require study of the energy release by the system and the quantity of μ PCM required for a definite period of thermoregulation [14]. The incorporation of PCM in textile materials enhances the thermoregulation and comfort to the wearer [15]. There is a need to study the energy release by human feet, the system in this case, and then to map it with the heat capacity of μ PCM (for a given core content) for the purpose of establishing the quantity for μ PCM required for such a long time period of thermoregulation. Although there are a number of research works reported on the use of μ PCMs in various textiles as well as in shoes and socks, studies focusing with an exclusive insight into the energy release of human feet and its corresponding mapping with the heat capacity of μ PCM are very limited. Therefore, in this research work, first the energy release rate of hu-

Nomenclature

g	grams
g/cc	grams per cubic centimeter
g/m ²	grams per square meter
h	hour
ΔH	heat of melting
J/g	joules per grams
J/min	joules per minutes
J/h	joules per hour
J/g-K	joules per gram kelvin
kg/m ³	kilogram per cube metre
L	litres
ml	millilitre
m/min	metre per minute
mJ	milli-joules
μ PCM	microencapsulated PCM
rpm	revaluation per minute
T_C	crystallisation temperature
T_M	melting temperature
W/m-K	watts per meter kelvin

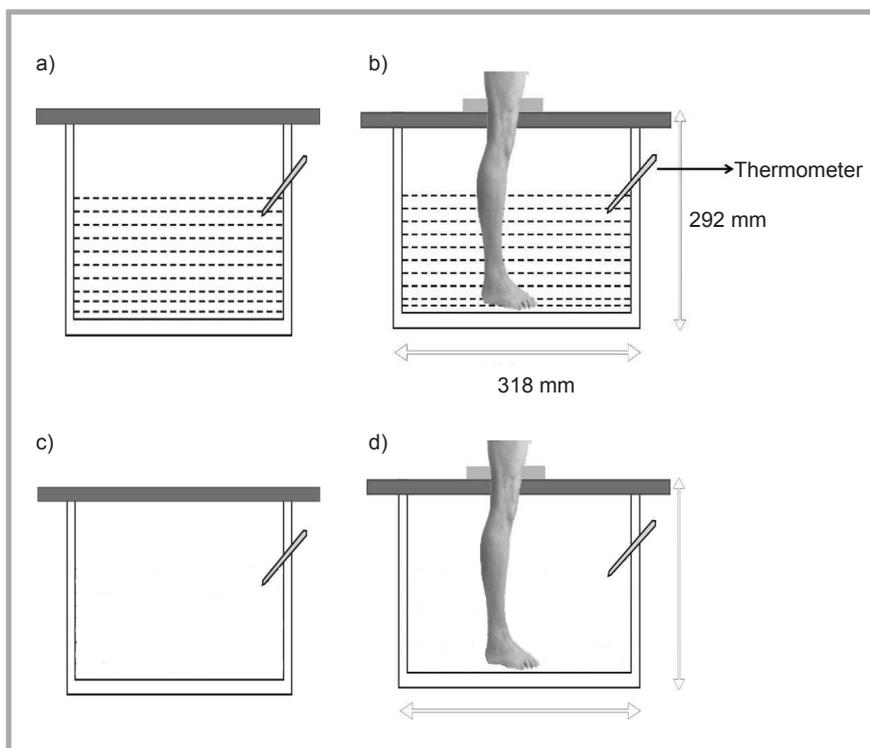


Figure 1. Isolated chamber containing: a) water medium without feet, b) water medium with feet, c) air medium without feet, and d) air medium with feet.

man feet was studied systematically, using which the quantity of μ PCM required for a definite period of thermoregulations was established.

Materials and methods

Materials

Cotton/Lycra socks of 80% cotton, 20% lycra and 30 courses per inch (CPI), 42 wales per inch (WPI) and 256 g/m² areal density were used for the study. Microencapsulated phase change materials (μ PCMs) were purchased from Microtek laboratories, Inc., USA. Polyurethane binder was purchased from Bionic Chemicals, Salem, Tamilnadu (India). Cyclohexane and benzene were purchased from Nice Chemicals, Cochin, Kerala (India).

DSC analysis

DSC measurements of the μ PCM were carried out using NETZSCH DSC 200 (the Netherlands). In this technique, a sample is placed inside a crucible, which is then placed inside the measurement cell (furnace) of the DSC system along with a reference pan, which is normally empty. The heating and cooling cycle of N-Octadecane, the PCM and μ PCM were maintained at 5 °C/min. Energy associated with melting and crystallisation was measured in J/g.

Temperature stability test

The stability of the capsule in heating was tested at 80 °C, 100 °C, 150 °C and 200 °C for 15 minutes to 90 minutes. The μ PCM was kept inside an oven on tissue paper. Leakage of PCM on the tissue paper and the change in colour of the μ PCM were observed at 15 min intervals.

Solvent stability test

The μ PCM selected were washed with cyclohexane [9] and benzene at room temperature to study the stability of the μ PCM in solvent washing. A known weight of the μ PCM was washed and stirred with 10 ml of cyclohexane and benzene for 1 min, 5 min and 10 min, then poured on filter paper after filtering, and the μ PCM was removed from the filter paper. Again the was μ PCM rinsed with 10 ml of cyclohexane and benzene for 30 seconds and filtered on other filter paper. Then 5 ml of cyclohexane and benzene was poured over the capsules being filtered through the second filter paper, which were then removed and dried in open atmosphere, and the weight loss and core content percentage were measured.

Energy release testing chamber

A separate isolated system was designed wherein the quantity of water taken is isolated from the atmospheric conditions

with a well insulated container using a suitable insulating material. The container has a hole through which feet can be inserted and again closed with necessary air proofing and insulation. In another small hole a thermometer is inserted to measure the rise in temperature of the water. The test was carried out with and without feet in two different mediums i.e. water (**Figure 1.a** and **b**) and air (**Figure 1.c** and **d**). Of the two, water at two different temperatures was tested separately to study the effect of the medium temperature upon the heat release rate of average human feet. The change in temperature inside the chamber was tested. An average adult aged 35 with a body weight of 78 kg and height of 165 cm was involved in the experiment to use his feet inside the chamber for the purpose of establishing the average energy released by human feet.

Application of μ PCM on socks

Cotton/Lycra (80/20) socks were used for this experiment. Coating materials were prepared by mixing phase change materials, binding agents and water with a proportion of 3:3 (PCM: binding agents). The coating compositions were stirred at 800 rpm for 1 h. The socks were cut to a size of 12 cm x 12 cm and soaked in coating materials for 10 min and then passed through a padding mangle at a speed of 20 m/min. A pressure of 5 kgf/min was maintained to remove excess solution. The socks were padded with 80% wet pickup, dried at 80 °C at a speed of 25 m/min and cured at 120 °C at a speed of 35 m/min for 3 min [16].

SEM analysis

The surface morphology of the micro encapsulated (μ PCM) treated and untreated sock samples was observed by a Scanning Electron Microscope (Carl Zesis, EVO 18).

Subjective wear trial

The socks were given for wear trial and the heat accumulated inside the shoe was compared by the wearer against the other untreated socks on the another leg. The weights of μ PCM were from 0.2 to 5 g, ranging from the weight of the socks. The heat sensation was calculated at different time intervals. The time intervals were from 30 min to 600 min (10 h). Subjective measurements were taken from 20 people. The measurement recorded the heat sensation of 11 or more people.

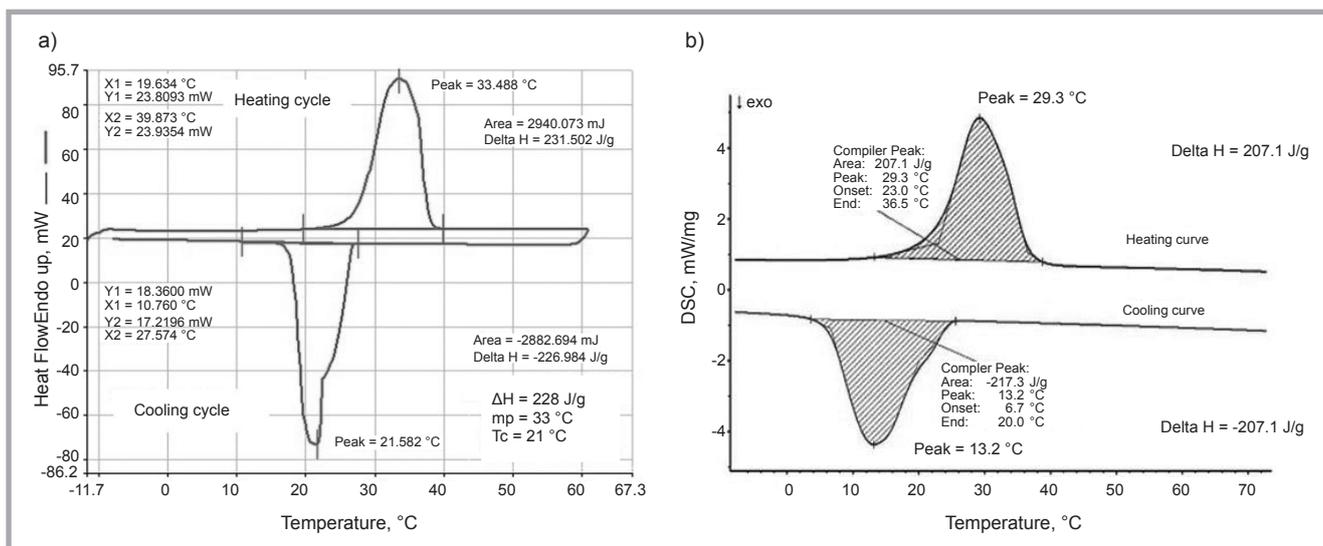


Figure 2. DSC thermogram: a) *n*-Octadecane, PCM, b) Microencapsulated PCM, μ PCM.

Results and discussion

Core content and heat capacity

Pure PCM (*n*-octadecane) and microencapsulated PCM (μ PCM) were subjected to DSC analysis to characterise its melting (T_M), crystallising (T_C), and heat of melting (ΔH), and hence to calculate the core content of the μ PCM. The results of DSC thermograms of the PCM and μ PCM are presented in *Figure 1.a* and *Figure 1.b*, respectively.

It can be observed from *Figure 2.a* that PCM has a melting peak at 33.48 °C, while the crystallisation peak is at 21.58 °C. The area under the curve of the melting peak is found to be, as observed in *Figure 2.a*, 2940 mJ and the ΔH value is 231.50 J/g. Similar values can be observed at the crystallisation peak, where ΔH is -226.98 J/g, corresponding to exothermic reactions, as crystallisation is an exothermic reaction, while melting is an endothermic reaction. Observing both the melting and crystallisation traces of PCM, the ΔH value can be averaged as 228 J/g, with the melting peak corresponding to 33 °C, and the temperature of crystallisation being 21 °C. This indicates that *n*-octadecane can be used as a thermo regulating substance for the human body as the crystallisation and melting temperature range is within a narrow temperature limit of the human body temperature i.e. 32 °C. Periyasamy et al. [9] also similarly reported in their paper that *n*-octadecane can be used for thermoregulation of the human body because of its suitable characteristics. Furthermore it can be observed in *Figure 2.b*

that the ΔH value, as well as the melting and crystallisation point of μ PCM are close to those of the PCM; however, with slightly different values i.e. the melting peak and ΔH value are found to be 29.3 °C and 207.1 J/g, respectively, for the heating trace, and the crystallisation peak and ΔH value are found to be 13.2 °C and 217.3 J/g, respectively, for the cooling trace. One important point to note is that the ΔH value of the μ PCM decreases compared with the ΔH value of PCM, which may be because of the presence of dead polymers in the μ PCM. This gives an idea about the presence of the dead polymer content in μ PCM and prompts calculation of the core content of μ PCM with the relative heat of fusions (ΔH) of the μ PCM and PCM, as shown in *Equation (1)*. Accordingly a core content value of 89.46% is obtained, meaning that micro encapsulated PCM (μ PCM) has 89.46% of pure PCM and 10.54% of dead polymer. This finding is the basis for calculation of the energy absorbing capacity of the μ PCM treated socks and accordingly to calculate the quantity of μ PCM required for the thermal regulation of socks for shoes. Prior to that, in

the subsequent section, the stability of the micro encapsulated PCM is discussed.

$$\begin{aligned} \text{Core content} &= (\Delta H \text{ of } \mu\text{PCM} / \Delta H \\ &\quad \text{of PCM}) \times 100 \\ &= (207.1 \text{ J/g} / 231.5 \text{ J/g}) \times 100 \\ &= 89.46\% \end{aligned} \quad (1)$$

Temperature stability of μ PCM

Table 1 presents the test results of the μ PCM exposed to various temperatures i.e. 80 °C, 100 °C, 150 °C and 200 °C for 15 minutes to 90 minutes. The leakage of PCM on tissue paper and the change in colour of the μ PCM were observed at 15 min intervals.

It can be observed from *Table 1* that there was no leakage for all these temperature ranges. The temperature limit was stopped at 200 °C after a time period of 90 minutes, because mostly the textile-like socks would not undergo more than this temperature. The general utilisation temperature may be close to the human body temperature, and the PCM also responds only in that limit. But during utilisation, the fabric would undergo

Table 1. Leakage study of μ PCM. Note: Y – yes; N – no.

Time, min	Leakage observation, Y/N				Colour change			
	80 °C	100 °C	150 °C	200 °C	80 °C	100 °C	150 °C	200 °C
15	N	N	N	N	N	N	N	N
30	N	N	N	N	N	N	N	Brown
45	N	N	N	N	N	N	N	Dark Brown
60	N	N	N	N	N	N	N	–
75	N	N	N	N	N	N	N	–
90	N	N	N	N	N	N	N	–

Table 2. Stability of μ PCM to cyclohexane and benzene.

Solvent	Treatment time, min	Weight of μ PCM in g		% Weight loss [(W1 - W2)/W1]*100	Core content, %
		Before treatment, W1	After treatment, W2		
Cyclohexane	1	1.04	0.87	16.34	74.84
	5	1.09	0.92	15.59	75.51
	10	1.08	0.88	18.52	72.89
Benzene	1	1.03	0.88	14.56	76.43
	5	1.12	0.87	22.32	69.49
	10	1.01	0.74	26.73	65.55

Table 3. Time of the rise in temperature of cold and ambient water.

Cold water, temperature	Time of temperature rise 1 °C, min					Average time, min	Standard deviation	Coefficient of variance	Error in the mean
17 °C	0	0	0	0	0	0	0	0	0
18 °C	43	47	44	46	45	44.6	1.64	3.68	0.74
19 °C	104	103	106	105	105	104.6	1.68	1.60	0.75
Ambient water, temperature	Time of temperature rise 1 °C, min					Average time, min	Standard deviation	Coefficient of variance	Error in the mean
27 °C	0	0	0	0	0	0	0	0	0
28 °C	117	118	121	122	121	119.8	2.17	1.81	0.97
29 °C	192	193	195	197	196	194.6	2.07	1.06	0.93

high extreme temperature conditions, as in the case of ironing. Hence the capsule should have stability at those temperatures. When observed for colour change, there was a notable change in colour at 200 °C after 30 minutes of exposure, which indicates that the polymer starts to degrade at that particular point; however even here there was no leakage observed up to 90 minutes at 200 °C. The exposure of the μ PCM treated socks to less than 200 °C for a short exposure time period i.e. 15 minutes can be safe, which is the first inference of the stability to temperature.

Solvent stability of μ PCM

Subsequent to the temperature stability, the μ PCM were subjected to solvent stability using good solvents for PCM – n-octadecane i.e. if pure PCM is dissolved in cyclohexane and benzene, then it would spontaneously get dissolved. This would give an idea of the polymeric porous nature and stability of the μ PCM towards the chemicals and other reagents.

It can be observed from **Table 2** that for a treatment time of 1 min, 5 min, and 10 min the weight loss calculated% is found to be 16.34%, 15.59% and 18.52%, respectively, for cyclohexane. Therefore we can say that there is a notable weight loss for treatment times of 1 to 10 minutes. The presence of the corresponding core content is found to be 74.84%,

75.51% and 72.89% for a treatment time of 1 min, 5 min and 10 min, respectively. It can be safely concluded that the stability of micro encapsulated PCM in the solvents is very good because the loss of core content was around 10% only. Most of the time the washing conditions would use water and a combination of soap chemicals which would not have the similar effect as cyclohexane. Cyclohexane is a very powerful solvent for n – octadecane. It was tested for the next solvent – benzene and the weight loss was found to be 14.56%, 22.32% and 26.73% for 1 min, 5 min, and 10 min, respectively. And the core content after the loss of PCM due to the solvent treatment is found to be 76.43%, 66.49% and 65.55% for 1 min, 5 min and 10 min respectively. In this case the maximum loss of the PCM after treatment with benzene for 10 min was observed and the core content is found to be 65.55%. But that did not yield a very big loss, only about 20% of the actual core content even after treatment of 10 min with benzene, as it can be clearly observed that there still remains a 65.55% core content. Again it can be inferred that these tests are just to give an indication of the stability of PCM inside the microcapsule towards the worst solubilising conditions. However, in actual situations, as has been stated above, it would not actually have these two powerful solvents of PCM, rather there will be other organic and inorganic chemicals

which would not have such a solubilising effect, and thus it can be safely inferred that the μ PCM used for the application of sock treatment would have good stability throughout washing and other chemical exposure conditions.

Quantity of μ PCM for thermal regulation of PCM

In this section the quantity of μ PCM required for treating socks is discussed based on the calculation of the total thermo regulation time required by the socks. For example, if the socks are treated with an unknown% of concentration, which is normally done with a 1-2% add on, as in the case of regular chemical processing, it does not indicate how long the μ PCM treated socks would perform the thermo regulation operation. For this purpose, an in-house experiment was carried out to first measure the energy released by human feet. Such tests are conducted in two modes, the first of which uses water and the second – air inside the chamber. Results of the studies are discussed in the following sections.

Energy release study with cold water and ambient water inside the chamber

In an isolated chamber, a test was carried out without feet to ensure if there is any influence of the atmosphere on the addition of energy to the isolated water. Tests were also carried out with feet in cold and ambient water. Results of the time required to increase the temperature of cold (17 °C) and ambient water (27 °C) are shown in **Table 3**.

From **Table 3** the average time required to raise the temperature of cold and ambient water in the chamber with feet can be observed. The temperature profile of isolated water with and without feet is shown in **Figure 3**.

Figures 3.a, 3.b and **3.c** represent the results of isolated water without feet, with feet in cold and ambient water, respectively.

It can be observed from **Figure 3.a** that the temperature of the isolated water remains the same over a period up to 105 min, indicating that the insulation provided is sufficiently enough to protect the isolated water from outside atmospheric temperature diffusion. Furthermore the temperature in the presence of feet increases with time i.e. the initial water temperature is 17 °C, and after 45 and

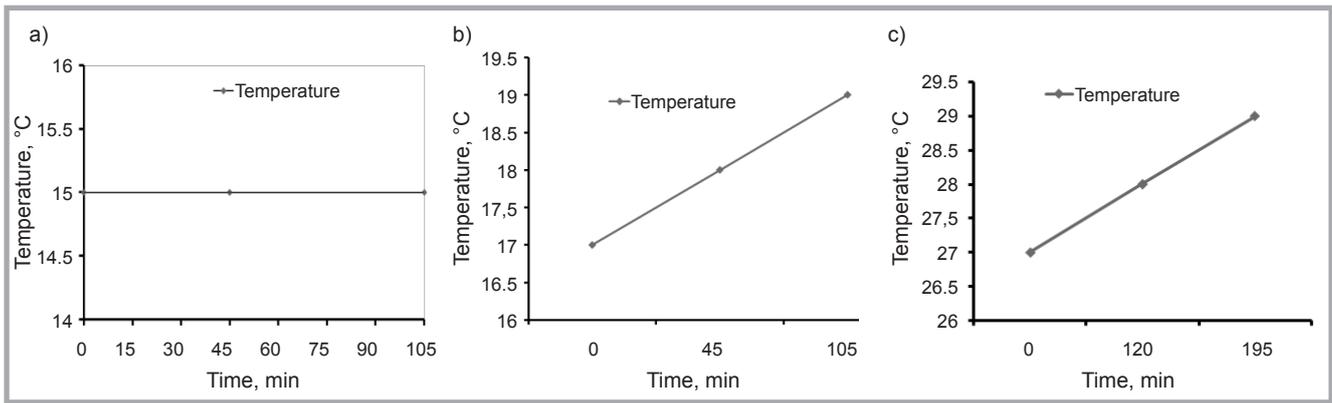


Figure 3. Temperature profile of isolated water: a) without feet, and b) with feet – cold water 17 °C, c) with feet – ambient water 27 °C.

105 minutes it rises to 18 °C and 19 °C, respectively, for cold water. Also the initial water temperature is 27 °C, and after 120 and 195 minutes it rises to 28 °C and 29 °C, respectively, for ambient water. These findings confirm that the change in the isolated water temperature is only due to the release of energy from the feet due the natural metabolic function of the body, and is not due to the influence of the atmosphere, as the temperature of the isolated water without feet did not undergo any change but remained only at 15 °C over the test period of 105 min. Hence the rise in temperature of isolated water in the presence of feet can be used as a measure of the energy, as shown in **Table 4**.

It is clear from the calculation above that the average energy released by a foot is 418 J/min and 225 J/min for cold water and ambient water, respectively, which might vary slightly from person to person; however, this can be considered as a reference value. This paves the way for finding out the quantity of μ PCM required for the thermoregulation of feet for a definite period of time, whose calculation is presented in **Table 5**.

These calculations clearly highlight that the heat loss of feet tested with ambient temperature water was lower, taking about 195 min for a 2 °C rise, while it was only 105 min with cold (17 °C) water. Thus the energy loss decreases almost two fold under these two conditions i.e. 418 J/min with cold water test and 225 J/min with the ambient water test. Hence the total quantity of μ PCM required for 1 h thermoregulation also decreases almost twice i.e. from 121 g to 65 g. Although the decrease seems to be double with the modified testing conditions, the 65 g of μ PCM appears to be

a high value particularly when compared with the actual socks average weight of about 18 g. At this point, some more important physical factors, as given in **Table 6**, have to be considered to arrive at a decision on the quantity of μ PCM required for a definite period of thermoregulation. The thermal conductivity of air is only 0.024 W/m.K, while that of water is 0.563

W/m.K, which is ~ 24 times higher than for air. This clearly indicates that when bare feet are exposed to air, the rate of heat loss will be much lower than inside water. Therefore considering the same ambient temperature, the heat loss rate would be, considering other unknown factors, approximately 24 times less than what is observed with the water experi-

Table 4. Energy released by foot in joules per minute for cold water (17 °C) and ambient water (27 °C).

1 calorie	: 1 g of water rising in temperature to 1 °C
Weight of water taken	: 10.5 L (10.5 kgs or 0.01 m ³)
Cold water, 17 °C	
Total temperature rise in 105 min	: 2 °C
Therefore the total energy transfer (Calories) from feet to water for 105 min is given by	
= Weight of water in gm × temperature rise	
= 10500 × 2 = 21000 Calories	
= 87780 Joules (1 Calorie = 4.18 Joules)	
The total energy transfer (Calorie) from feet to water for 1 min is given by	
= 87780 Joules/105	
= 836 Joules/min	
Energy released by foot	
= Energy released by feet/2	
= 836/2	
= 418 Joules/min	
Ambient water, 27 °C	
Total temperature rise in 195 min	: 2 °C
Therefore the total energy transfer (Calories) from feet to water for 195 min is given by	
=Weight of water in gm × temperature rise	
= 10500 × 2 = 21000 Calories	
= 87780 Joules (1 Calorie = 4.18 Joules)	
Total energy transfer (Calories) from feet to water for 1 min is given by	
= 87780 Joules/195	
= 450 Joules/min	
Energy released by foot	
= Energy released by feet/2	
= 450/2	
= 225 Joules/min	

Table 5. Quantity of μ PCM required for a definite period (h) of thermoregulation for cold water (17 °C) and ambient water (27 °C).

Cold water, 17 °C		Ambient water, 27 °C	
Heat of fusion of μ PCM	: 207 J/g	Heat of fusion of μ PCM	: 207 J/g
Quantity of μ PCM required : (Energy released by foot/h)/Heat of fusion of μ PCM		Quantity of μ PCM required : (Energy released by foot/h)/Heat of fusion of μ PCM	
	: (418 × 60)/207		: (225 × 60)/207
	: 121 g		: 65 g

Table 6. Physical parameter governing thermoregulation.

Physical parameter	Values	Remarks
Thermal conductivity of air	0.024 W/m.K	Thermal conductivity of air is ~ 24 times lower than water
Thermal conductivity of water	0.563 W/m.K	
Specific heat capacity of water at 25 °C	4.181 J	Specific heat capacity of water is 4.131 times higher than air
Specific heat capacity of air at ambient conditions	1.012 J	

Table 7. Summary of quantity of μ PCM required for 1 h thermoregulation

Condition of testing	Quantity of μ PCM for 1 h thermoregulation, g	Times the preceding cells of column two
Cold water (17 °C)	121.00	–
Ambient water (27 °C)	65.00	1.86
Using ambient air	0.657	184 & 99
Using ambient air with a factor of safety of 1.5	0.986	123 & 66

Table 8. Time-temperature profile of air inside the test chamber with feet.

Time	Temperature of air	Sensation
6:30 pm	26 °C	Without feet
6:30 pm	26 °C	With feet normal
7:00 pm	29 °C	Hot, some sweat, with discomfort
9:00 pm	30 °C	Hot, high sweat, with discomfort
9:30 pm	30 °C	Hot, high sweat, with discomfort, bad odour from feet after removing

Table 9. Summary of energy release and quantity of μ PCM required.

Condition	Energy release, J/min	Quantity of μ PCM for 1 h thermoregulation, g	Quantity of μ PCM for 10 h thermoregulation, g
Air approximated using water experiment	2.27	0.658	6.58
Air approximated using water experiment with a factor of safety of 1.5	3.41	0.986	9.86
Using ambient air	1.20	0.350	3.50
Using ambient air with a factor of safety of 1.5	1.80	0.525	5.25

ments. Furthermore from **Table 6** it can be observed that the specific heat capacity of water is 4.131 times higher than of air, meaning that water would take 4.131 times higher energy than air to undergo a 1 °C rise. Hence, the net energy release rate under ambient conditions in the presence of air would be ~ 99 times (4.131×24) less than the rate of energy release in the presence of water. Therefore the energy released by feet would be only 4.55 J/min (i.e. 450/99) and for a foot it would be 2.27 J/min. Considering this rate of heat loss, the quantity of μ PCM required is calculated as below.

Quantity of μ PCM required for a definite period (h) of thermoregulation

Quantity of μ PCM required

- : (Energy released by foot/h)/Heat of fusion of μ PCM
- : $(2.27 \times 60)/207$
- : 0.658 g

μ PCM required for 10 h

- : μ PCM required for 1 h $\times 10$
- : 0.658×10
- : 6.58 g

Thus, based on the above calculations developed with the experiment's values of energy release from average human feet using cold (17 °C) water and am-

bient water (27 °C), it can be inferred that it requires 121 g of μ PCM for 1 h thermoregulation for cold water experiments, while it is only 65 g of μ PCM for 1 h thermoregulation for ambient water experiments with an approximately two-fold decrease. With practical consideration of where the air would actually be a fluid, and hence considering the thermal conductivity of air and relating it to the water experiments, it is found that the μ PCM requiring 1 h thermoregulation is only 0.658 g, being a large decrease compared to the water experiments i.e. 184 times lower μ PCM compared to cold water and 99 times lower μ PCM compared to ambient water. These values are summarised in **Table 7**.

With these findings, it can be inferred that the socks should have 0.658 g μ PCM for 1 h thermoregulation. But for practical purposes, considering office hours, it would be appropriate to consider about 10 h, and hence a total μ PCM of 6.58 g should be present in the socks for their efficient use. Additionally in order to address some of the unknown factors, a factor of safety of 1.5 is multiplied with the quantity of μ PCM required under ambient air conditions, and hence the values turn out to be 0.986 g and 9.86 g for 1 h

and 10 h thermoregulation, respectively. In order to confirm the predictions derived from water based experiments, a further trial using only air inside the chamber was made, details of which are presented and discussed in the subsequent section.

Energy release study with air inside the chamber

An energy release study experiment with air was conducted using the same chamber of 318 mm (L) \times 216 mm (B) \times 292 mm (H) which is described in the experimental section (**Figure 1**) Similar to the water experiments, the same adult feet are inserted through the holes and the rise in temperature is measured by a thermometer through the hole provided in the chamber for the purpose. The results of these tests are presented in **Table 8**, from which it can be observed that the temperature of the air increases in the short time of 30 min from the ambient temperature of 26 °C to 29 °C – a total of 3 °C. Furthermore the temperature rise is slow i.e. the rise is only 1 °C for the next 2 h and remains same for the next half an hour, indicating a very slow increase in temperature. Such results obtained are interesting, being in a comparatively much shorter time than in the water experiments i.e. in cold water (17 °C) the experiment took 105 min for a 2 °C rise and in the ambient water experiment – 195 min for a 2 °C rise. This can be understood by relating the basic difference in the specific heat capacity and thermal conductivity of water and air, whose values are presented in **Table 5** and discussed in the previous section.

Based on the values obtained in the energy release study with air inside the chamber, as in **Table 8**, energy released by a foot in Joules per minute can be calculated as follows:

Energy released by a foot in Joules per minute for air

- Chamber size in mm : 318 (L) \times 216 (B) \times 292 (H)
- Specific heat capacity of air : 1 J/g \cdot K
- Density of air : 1.225 kg/m³ (0.001225 g/cc)
- Weight of air inside the chamber : Volume in CC \times Density of Air in g/cc
- : 20057×0.001225
- : 24 g

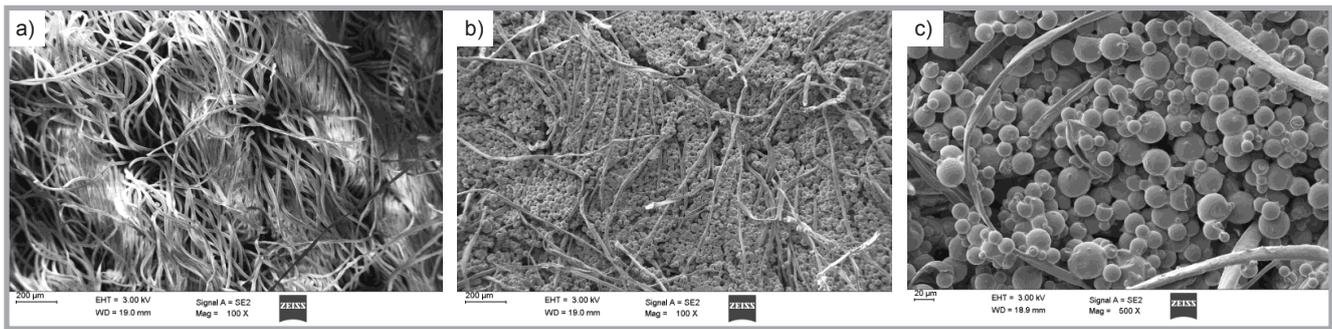


Figure 4. SEM photographs of a) untreated socks, b) μ PCM treated socks at 100 \times , and c) μ PCM treated socks at 500 \times .

Temperature rise inside the chamber in 30 min : 3 °C
Therefore energy released by feet in 30 min is given by

$$\begin{aligned} & \text{Temperature rise inside the chamber} \\ & \text{in 30 min} \times \text{Weight of air in g inside} \\ & \text{the chamber} \times \text{Specific heat capacity} \\ & \text{of air in J/g}\cdot\text{K} \\ & : 3 \times 24 \times 1 \\ & : 72 \text{ J} \end{aligned}$$

It implies that a total of 72 J was released from two feet in half an hour. Thus the energy release per min per foot is given by,
Energy released by feet in 30 min/30/2
= 72/30/2 = 1.2 J/min

It is clear from the calculation above that the average energy released by a foot is 1.2 J/min under the conditions above. This value is 1.89 times less than the value 2.27 J/min approximated in the water experiments. This might be because of the inherent difference between the theoretical predictions and actual experiments, where some of the unknown factors might have some influence on the actual experimental values. However, the lower value in the air experiment is a good indication that the total quantity of μ PCM required for a definite period of thermoregulation would be less. Hence the total quantity of μ PCM required for thermoregulation using the air experimental energy release rate is calculated as below and discussed.

Quantity of μ PCM required for a definite period (h) of thermoregulation for air

Heat of fusion of μ PCM
: 207 J/g
Quantity of μ PCM required
: (Energy released by foot/h)/
Heat of fusion of μ PCM
: 1.2 \times 60/207
: 0.35 g
 μ PCM required for 10 h
: μ PCM required for 1 h \times 10
: 0.35 \times 10
: 3.5 g

The final values of the energy release rate and quantity of μ PCM for air as a medium from the water experiment approximation and air experiment are summarised in **Table 9**.

It can be observed from **Table 9** that in every reading i.e. the energy release, quantity of μ PCM for 1 h and 10 h thermoregulation, a factor of 1.89 times remains the same as a fundamental difference between the air medium approximated through water experiments and the actual air medium experiment. Furthermore it can be observed that about 10 g of μ PCM is required for 10 h thermoregulation based on the air medium approximated through water experiments with a factor of safety of 1.5, and in the case of actual air medium experiments it is only about 5 g. When these values are related to the weight of an actual sock, which is about 20 g, almost 50% weight is added to the socks if 10 g of μ PCM is considered for application as per air medium approximation. However, it is only 25% weight addition if 5 g of μ PCM is considered for application as per the actual air medium experiment. It can be finally inferred that within the limits, the lowest value 3.5 g i.e. the actual air medium experiment without a factor of safety, and the highest value 9.86 g for the air medium approximation with a factor of safety, one may choose the μ PCM quantity for application on socks for 10 h

thermoregulation. However, considering the practical situation, the inclusion of some factor of safety, say about 1.5, would doubly ensure the purpose, and hence the value of 5 g addition could be recommended for 10 h thermoregulation of the average human adult foot. Furthermore it can also be recommended to incorporate some μ PCM in shoe parts to have improved and long lasting thermoregulation. The average weight of a shoe ranges from 400 g – 700 g, and hence the addition of 5 to 10 g of μ PCM would practically not alter the weight of the shoe. Additionally socks can also be treated with a low quantity of μ PCM for coupled and improved performance.

Surface morphology of PCM treated fabrics

The surface morphology of phase change materials was analysed using SEM.

Treated socks were examined for the deposition of micro-encapsulated PCM (μ PCM) in the yarn interstices. **Figure 4.a** shows untreated socks, **Figure 4.b** – micro encapsulated PCM treated socks at low magnification, and **Figure 4.c** microencapsulated PCM (μ PCM) treated socks at high magnification. It can be seen from **Figure 4.a** that the untreated socks do not have any micro encapsulated PCM (μ PCM) (**Figure 4.a**). However in the microencapsulated PCM treated socks, the presence of good

Table 10. Summary of subjective wear trial of μ PCM treated socks. Note: N – no, S – slightly, Y – yes.

Weight of μ PCM in a sock, g	% of μ PCM in 20 g socks	Heat sensation at different time intervals, min									
		30	60	90	120	180	240	300	360	480	600
0.2	1	N	S	Y	Y	Y	Y	Y	Y	Y	Y
0.4	2	N	N	S	S	Y	Y	Y	Y	Y	Y
1.0	5	N	N	N	N	N	S	Y	Y	Y	Y
3.0	15	N	N	N	N	N	N	N	N	N	S
5.0	25	N	N	N	N	N	N	N	N	N	N

round, regular-shaped capsules in a large quantity is easily perceived in **Figure 4.b** as well as in **Figure 4.c** i.e. the presence of good round, regular-shaped shaped micro capsules are seen. Hence this supports the previous findings of the stability study of micro-capsules in section heat and solvents; thus the presence of PCM in a well-encapsulated polymer wall is not affected by both the temperature and solvents.

Wear trials of μ PCM treated socks

Biased on the predictions made in the preceding sections, a sock was treated with varying quantities of μ PCM by the Pad-Dry-Cure method, as described in the experiment sections and shown in **Table 10**.

Quantities of μ PCM ranges are kept within sensible ranges of thermoregulation as per the calculations i.e. from 0.2 g to 5 g, ranging from 1% to 25% per weight of the socks accordingly. The socks were given for wear trial and the heat accumulated inside the shoe was compared by the wearer against the other untreated sock on the other leg. The findings were recorded against the respective quantity of μ PCM. Subjective measurements were taken by 20 people, and more than 50% of the wear trial measurements were tabulated. It can be observed from **Table 10** that for a low quantity of μ PCM, the thermoregulation time was very short, up to only 30 min, and for a high quantity of μ PCM – even up to 10 h.

The performance of the other sock lies in between these extremes. These findings are in good agreement with the theoretical predictions of the preceding sections. As in **Table 8**, μ PCM of 5 g which was derived from a factor of safety of 1.5 worked well for 10 h, as well as the 3 g of μ PCM, being almost close to 10 h, which is slightly less than without a factor of safety. Hence the predictions made in this paper are experimentally verified and the values recommended can be used for selecting the quantity of μ PCM application on socks based on the time of thermoregulation required.

Conclusions

The heat capacity of pure PCM and microencapsulated PCM – n-octadecane (μ PCM), were found to be 231 J/g and 207 J/g, respectively, as analyzed through DSC. Correspondingly the core content

of μ PCM was calculated to be 89% from the heat capacities of μ PCM and pure PCM. μ PCM did not show any leakage and colour change at 150°C, even up to 90 min. When tested for solvent stability, μ PCM showed a core content of 72% and 65% against cyclohexane and benzene for 10 min washing. Theoretical prediction of the quantity of μ PCM was made using an in-house tester for calculating the energy release rate by human feet by means of two distinct methods using water and air as a medium. In the water medium experiments, the effect of two different initial temperatures i.e. 17 °C & 27 °C were studied in which the energy release rate was found to be 418 J/min and 225 J/min per foot, respectively. Using the water experiments with a 27 °C initial temperature, theoretical prediction of the energy release rate using air as a medium were deduced to be 2.27 J/min considering the thermal conductivity and specific heat capacities of water and air through establishing a factor of 99. The theoretical prediction was verified experimentally with only air as a medium in the tester, where the energy release rate was found to be 1.2 J/min, being 1.89 times less than the theoretical prediction. Such a difference was attributed appropriately. A factor of safety of 1.5 was used for all the energy release values and the total quantities of μ PCM ranged from 3.5 g to 9.86 g for 10 h thermoregulation for only the ambient air experiment and theoretically predicted value with a factor of safety, respectively. Finally the socks were treated with 0.2 g to 5 g of μ PCM, corresponding to the energy release values proposed, and were evaluated for thermoregulation over various time periods through wear trials. It was found that the thermoregulation period of the μ PCM treated socks was proportional to their add-on weight and were in close agreement with the theoretical predictions proposed. SEM images of the treated socks indicated the presence of microcapsules of regular size and shape.

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