Carbohydrate Polymers 101 (2014) 912–919

Contents lists available at ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

New approaches to improving thermal regulating property of cellulosic fabric

Ahmed G. Hassabo*

National Research Centre, Textile Research Division, Cairo, Egypt

ARTICLE INFO

Article history:
Received 9 August 2013
Received in revised form
26 September 2013
Accepted 1 October 2013
Available online 16 October 2013

Keywords:
Paraffin wax
Butanetetracarboxylic acid
Phase change material (PCM)
Duration index
Cotton fabric

ABSTRACT

To enhance the thermoregulation property of cotton fabric, new materials have been prepared to be used for encapsulating phase change materials (PCMs). The new material has been prepared via esterification reaction between different carboxylic acids and different fatty acids crossed with diglycol compounds, these materials were characterised to be used as hosting materials for octadecane, which is heat storing material suitable for textile applications. FT-IR and DSC analysis were used to characterise the prepared hosting material. The prepared materials have special shape which has different cavity distance between its side chains, and also have a reactive group on the backbone of its structure which make these materials able to react chemically with cotton fabric to help it to be not leakage from the treated surface (permanent) and the material will be stable on the fibre surface even after washing. When applied onto textile materials, the treated fabric shows good thermoregulation property.

1. Introduction

In textile industry, protection from extreme environmental conditions is a crucial requirement. Clothing that protects us from extreme cold, intensive heat, open fire, high voltage etc are some of the illustrations. One of the best ways to functionalise the fibres surface is the deposition of some intelligent molecules on the fibre surface in order to gain a new property.

Any material absorbs heat during heating process while its temperature is rising constantly. The heat stored in the material is released into the environment through a reverse cooling process. During the cooling process, the material temperature decreases continuously. A normal textile material absorbs about one kilo joule of heat per kilogram while its temperature rises by 1 °C (Bendkowska, Tysiak, Grabowski, & Blejzyk, 2005; Shin, Yoo, & Son, 2005).

The phase-change materials (PCMs) are used to store latent heat. The storage of latent heat or thermal regulation is based on the transition of the PCM from a phase to another. When such material is heated to its melting point, it absorbs heat during the change of phase from solid to liquid state and releases heat when changes back from liquid to solid state.

A paraffin-PCM, for example, absorbs approximately 200 kJ/kg when it undergoes a melting process. If a textile would absorb the same amount of heat its temperature would raise by 200 °C. The high amount of heat absorbed by the paraffin in the melting process is released into the surrounding area on cooling starting at the PCM's crystallisation temperature. After comparing the heat storage capacities of textiles and PCM, it is obvious that by applying paraffin-PCM to textiles their heat storage capacities can be substantially enhanced (Shin et al., 2005).

The paraffins are either in solid or liquid state. In order to prevent the paraffin's leakage while in the liquid state, it is enclosed in small spheres with diameters of only a few micrometres. These microscopic spheres containing PCM are called PCM-microcapsules. The micro-encapsulated paraffin is either permanently locked like in acrylic fibres and in polyurethane foams, or coated onto the surface of a textile structure.

An alternative way to deposit the organic PCM materials on textiles is to encapsulate them in another organic material which may prevent the flow of the melted PCM from the surface. One of the simplest ideas is to prepare composites of PCM/polymer in which the polymer has side chains, the gap between two chains being able to accommodate crystal of PCM. The encapsulation of PCM is the most advantageous technique to merge the expected enriched heat performance with the other textile qualifications on the same product (Lan, Tan, Shi, & Gao, 2009). The incorporation of PCMs into textiles in the form of a shell-core matrix brings many opportunities such as prevention of PCM dispersion in the structure, less evaporation and minimum interaction with the environment, increased heat transfer area, long shelf-life on a garment for normal

* Tel.: +20 11 29 76 999 1.
E-mail addresses: aga.hassabo@hotmail.com, aga.hassabo@yahoo.com

0144-8617/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carbpol.2013.10.006

fabric-care processes, and no adverse effect on the textile properties. The encapsulated PCM materials are usually embedded in a thermally conductive medium. The characteristics of capsules, phase change material and conductive medium can be designed to provide the enhanced thermal management in a wide variety of applications.

The main problem of the PCM material is the leaking from the surface, so to overcome this problem, a hosting material should be used as a carrier for the PCM material to hold it and prevent it from leaking, and these hosting materials are deposited on the fibre surface through a polymer matrix e.g. arabic gum (Bayés-García et al., 2010; Mondal, 2008), dimethyloldihydroxy ethylene urea (DMDHEU) (Erkan, 2004), polyethyleneglycol (Onofrei, Rocha, & Catarino, 2010), and many other matrix. Therefore, in this study, a new PCM hosting material will be prepared and characterised. These hosting materials have a different structure than all the other hosting materials, that, it have a side functional group in the long of its structure (OH and COOH), these functional groups allow the hosting material to bonded chemically to the fibre surface, which make the PCM/hosting materials permanent on the surface against washing processes.

Micro-PCMs have been studied as active or pumped coolants (Fossett, Maguire, Kudirka, Mills, & Brown, 1998; Mulligan, Colvin, & Bryant, 1996; Yamagishi, Takeuchi, Pyatenko, & Kayukawa, 1999), as solar and nuclear heat storage systems (Chaurasia, 1981; Hawlader, Uddin, & Zhu, 2002), and as backed beds heat exchangers (Bryant, 1999). Micro-PCMs have also been used in the manufacture of thermo regulated fibres (Bryant, 1992), fabrics, and foams (Hittle & André, 2002). Yamagishi, Sugeno, Ishige, Takeuchi, and Pyatenko (1996) studied the melting and crystallisation processes of microencapsulated n-tetradecane and n-dodecane with a melamine formaldehyde and gelatine shell and microcapsule diameters in the range of 5–1000 μm. The degree of super-cooling of micro-encapsulated n-tetradecane and microencapsulated n-dodecane increased when the diameter was lower than 100 μm (Himran, Suwono, & Mansoori, 1994; Zhang, Fan, Tao, & Yick, 2005).

The PCM polymer composites are characterised by two thermodynamic parameters, namely the temperature at which the phase change (fusion/crystallisation) occurs, and the enthalpy which accompany the change of phase, ΔH. For the engineering of insulation, there are also other indexes, which are defined for helping to choose a material for a specific use. For textile users such indexes are the duration index (DI) (Mottinger, 1999), and the total resistance to dry heat transfer (R) (Doerr, 1997; Shim, McCullough, & Jones, 2001).

2. Experimental

2.1. Materials

2.1.1. Fabrics

100% bleached, scoured cotton fabric (poplin) plan weave (23 ends and 23 pick/cm) was supplied by "Misr El-Beida Dyers", Egypt. The fabric was not subjected to any type of finishing treatments. The fabric was further washed with a solution containing 5 g/l sodium carbonate and 5 g/l non-ionic detergent at boil for 30 min. It was then rinsed with hot and cold water and left to dry in air at ambient temperature.

2.1.2. Chemicals

Tartaric acid (TA), citric acid (CA), butanetetracarboxylic acid (BA), 1,2-ethanediol (EG), 1,4-butanediol (BG), 1,6-hexanediol (HG), palmitic acid (PA), stearic acid (SA). Fatty acids were dehydrated by heating at 110 °C for 2 h in a circulating air oven.

2.2. Methods

2.2.1. Preparation of pre-PCM hosting materials

0.1 mole of the acid (TA, CA and BA) and the equivalent amount from diglycol to carboxylic group of multicarboxylic acid (two carboxylic group for CA and BA, and one carboxylic group for TA) are melted together at 60 °C and thoroughly mixed in the 500 ml round flask that contains some porcelain balls (2 mm diameter). Then, Dean and Stark apparatus was fitted onto the flask that introduced into a thermostatic oil bath. The temperature was then raised to 115 °C and the reaction mixture kept for 2 h at this temperature, then the flask was taken out of the bath, cooled to room temperature, and reaction products were analysed. The products were marked as listed in Table 1.

2.2.2. Preparation of PCM hosting materials

0.1 mole of the pre-PCM host materials and the equivalent amount from fatty acid (SA and PA) to the free hydroxyl group of pre-PCM host materials are melted together at 60 °C and thoroughly mixed in the 500 ml round flask that contains some porcelain balls (2 mm diameter). Then, Dean and Stark apparatus was fitted onto the flask that introduced into a thermostatic oil bath. The temperature was then raised to 115 °C and the reaction mixture kept for 2 h at this temperature, then the flask was taken out of the bath, cooled to room temperature, and reaction products were analysed. The products were marked as listed in Table 1.

2.2.3. Preparation of PCM Composites

The PCMs composites are prepared by mixing different hosting materials (CES, CBS or CHS), with paraffin compound (n-octadecane; $C_{18}H_{38}$) in different molar ratio (Polymer to Paraffin of 1:1, 1:2, 1:4 and 2:1) at high temperature (110 °C) for a 14 h, and then used for the further analysis.

2.2.4. Coating of cotton fabrics with PCM compound

Two coating processes are used to coat cotton fabric with PCM materials, the first method is one step coating method (coating using PCM composites, the paraffin was encapsulated inside the PCM hosting material before coating process), the second method is two step coating method (coating using PCM hosting material, the fabric was immersed firstly in the PCM hosting material then immersed in the paraffin compound.

2.2.4.1. Coating using PCM composites. An emulsion of PCM composite material in water was prepared as follow, 10 g (PCM composite/water) was transferred to one necked round flask, and then 990 ml water was added and sonicated at 50 °C for 10 min.

The fabrics were immersed into the coating dispersion solution at 40–50 °C; the coating process was occurred at acidic pH, in presence of Lewis acid. The weight pickup is adjusted to be 80%. Coated fabric samples were fixed in an oven and the temperature increased gradually from 60 to 110 °C for 5 min then conditioned for the subsequent 24 h.

To determine the actual incorporation percentages of the PCM materials transferred to the sample, which depends also on the coating thickness, coated and uncoated pieces of fabric were weighed.

2.2.4.2. Coating using PCM hosting material. An emulsion of PCM hosting material in water was prepared as follow, 10 g (PCM hosting material) was transferred to one necked round flask, and then 990 ml water was added and sonicated at 50 °C for 10 min.

The fabrics were immersed into the PCM hosting material emulsion at 40–50 °C, the coating process was occurred at acidic pH, in presence of Lewis acid. The weight pickup is adjusted to be 80%. Coated fabric samples were fixed in an oven and the temperature

Table 1
List of pre-PCM and PCM hosting labels.

Multicarboxylic acid	Diglycol	Pre-PCM label	PCM hosting label Fatty acid type	
			Palmitic acid (PA)	Stearic acid (SA)
Tartaric acid (TA)	1,2-Ethanediol (EG)	TA-EG	TEP	TES
	1,4-Butanediol (BG)	TA-BG	TBP	TBS
	1,6-Hexanediol (HG)	TA-HG	THP	THS
Citric acid (CA)	1,2-Ethanediol (EG)	CA-EG	CEP	CES
	1,4-Butanediol (BG)	CA-BG	CBP	CBS
	1,6-Hexanediol (HG)	CA-HG	CHP	CHS
Butanetetracarboxylic acid (BA)	1,2-Ethanediol (EG)	BA-EG	BEP	BES
	1,4-Butanediol (BG)	BA-BG	BBP	BBS
	1,6-Hexanediol (HG)	BA-HG	BHP	BHS

increased gradually from 60 to 110 °C for 5 min then conditioned for the subsequent 24 h. Treated fabrics were then padded in the emulsion of the paraffin (n-octadecane, 3 g/l). Coated fabric samples were then fixed in a drying oven for 15 min and the temperature increased gradually from 60 to 80 °C and then conditioned for the subsequent 24 h.

2.3. Measurements

2.3.1. Differential scanning calorimetry (DSC)

DSC measurements for measuring the melting and the crystallisation behaviour of the substances were carried out on Netzsch DSC 204. The measurements were run using nitrogen flow at 20 ml/min as purge gas. The weighted samples, each of approximately 7 mg, were closed in aluminium pans, which were perforated prior to be placed in DSC device. An empty aluminium pan was used as reference. The temperature programme consisted of heating, cooling and heating steps. Temperature ranged from 0 °C to 70 °C, with 10 °C min^{-1}. The melting temperature and enthalpy ΔH were evaluated from the onset and area, respectively, of the peaks recorded during the second heating. DSC temperature and heat flow was calibrated with indium.

2.3.2. Scanning electron microscopy (SEM)

Scanning electron microscope (SEM) measurement of the PCM capsules was carried out on Hitachi 5-4800 FESEM (Field-Emission SEM). Surface morphology of the composite films was studied using scanning electron microscope HITACHI S-3000 microscope S, at 15 kV acceleration voltage, after gold coating.

2.3.3. Fourier transform infra-red spectroscopy (FT-IR)

Fourier transform infrared spectroscopy (FT-IR) was performed by using a Nicolet Impact 400 spectrophotometer to determine the functional groups in the samples. Resolution for the infrared spectra was 4 cm^{-1} and there were 32 scans for each spectrum. The tester collected transmittance of the infrared in the film between 400 and 4000 cm^{-1}.

2.3.4. Duration index (DI)

Duration index is a parameter characterising the material and the temperature at which it is aimed at functioning; the resistance to dry heat transfer is an index which is related also to the textile material on which PCM is applied.

The duration index (DI) (J/cm^3 K), which allows comparing how long a PCM will remain at a constant temperature during the phase change, is defined by (Mottinger, 1999):

$$DI = \frac{\Delta H \rho}{\Delta T}$$

where ΔH is the enthalpy of PCM change of state, ρ is the PCM density and ΔT is the temperature difference between those of change of state and the temperature of interest (ambient, or body temperature).

2.3.5. Stability test

Stability of the PCM/octadecane on the surface of cotton fabric were tested according to the filter paper test method (Hassabo, 2011).

3. Result and discussion

3.1. Preparation and characterisation of pre-PCM hosting materials

The pre-PCM materials were produced; i.e. nine pre-PCM materials were prepared and characterised. These materials were prepared by reaction between multicarboxylic acid (tartaric acid, citric acid and butanetetracarboxylic acid) and diglycol materials (ethandiol, butanediol and hexanediol). These materials were characterised by FT-IR and DSC analysis.

3.1.1. FT-IR analysis

Pre-PCM hosting materials were characterised using FT-IR analyser; the IR spectra of some prepared compound are illustrated in Fig. 1. It is clear that, the characteristic peaks for pure reactants (OH for di glycol and COOH for multicarboxylic acid) are clear at (3350 and 1710 cm^{-1}) for hydroxyl and carboxyl groups respectively. A decrease in intensity at 3350 cm^{-1} is attributed to a decrease in the total numbers of hydroxyl groups through ester formation between glycol and acid. In addition, increasing of the intensity peak at 1630 cm^{-1} in the pre-PCM might correspond to the carbonyl group due to ester formation.

3.1.2. DSC analysis of pre-PCM hosting materials

The DSC results were obtained from second heating of DSC (1st heating from 0 to 100 °C, then cooling from 100 to 0 °C and then second heating from 0 to 100 °C, all these three steps were carried at 10 °C min^{-1}) for the pure and prepared compounds are shown in Tables 2 and 3 respectively. It is observed that (a) for the diglycol and fatty acid; increasing the number of methylene group causes increasing in the melting temperature and the total enthalpy of the PCM host materials, meaning that, hexandiol and stearic acid give more latent heat storage than the other diglycol and fatty acid, (b) for the multicarboxylic acid; presence of alcohol or carboxyl group free in the PCM host materials cause high latent heat storage, and this heat increased by increasing the number of free carboxyl group. In addition, carboxyl group give more latent heat than alcoholic group.

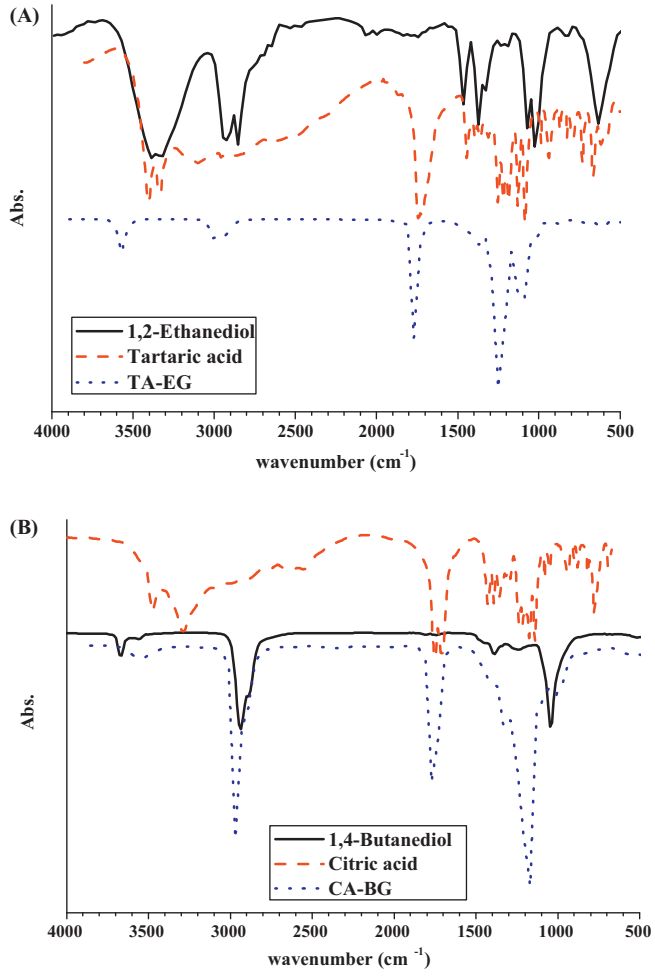

Fig. 1. FT-IR spectra of pre-PCM hosting materials compared with its pure materials. (A) TA-EG; (B) CA-BG.

3.2. Preparation and characterisation of PCM hosting materials

3.2.1. Optimisation and preparation of PCM composite

In order to have PCM composite with high storage heat, the reaction condition was optimised. Polymers were react with one of the paraffin compounds (n-octadecane) with different molar ratio, to obtain co-crystallisation, and measured on DSC for determine the temperature and heat of the phase change process, in order to choose the best formulation to prepare PCM composite with suitable melting temperature and heat storage.

Polymer/paraffin composite which merges paraffin thermal characteristics (melting point and melting enthalpy) with the polymer compounds was successfully produced. This methodology may be used with various polymers with the aim to produce PCM composites which needs to have a melting transition occurring within the temperature range of interest (30–40 °C) and an enthalpy of at least 200 J/g, for being of interest.

Four hosting material were selected depending on their enthalpy and peak temperature (those have enthalpy more than 230 J/g and peak temperature more than 31 °C), the code of these materials are THS, CHS, BHP and BHS and there enthalpy and temperature peak values are listed in Table 3.

Table 2
DSC data for pure compounds from 2nd heating.

Compounds	2nd heating		
	T_o (°C)	T_p (°C)	ΔH (J/g)
1,2-Ethanediol	−13.4	−16.8	10.3
1,4-Butanediol	16.2	18.3	76.6
1,6-Hexanediol	38.5	40.8	21.6
Tartaric acid	170.6	173.2	15.3
Citric acid	155.7	159.4	18.5
1,2,3,4-Butanetetracarboxylic acid	196.8	200.1	35.2
Palmitic acid	73.6	76.8	154.9
Stearic acid	65.2	69.7	166.5

Table 3
DSC data for prepared PCM host materials from 2nd heating.

Fatty acid	Pre-PCM host materials	Label	2nd heating		
			T_o (°C)	T_p (°C)	ΔH (J/g)
Palmitic acid (PA)	TA-EG	TEP	23.1	26.3	162.45
	TA-BG	TBP	24.2	28.6	172.62
	TA-HG	THP	24.6	29.3	222.12
	CA-EG	CEP	23.2	27.1	165.33
	CA-BG	CBP	24.3	29.3	175.50
	CA-HG	CHP	24.6	30.2	225.22
	BA-EG	BEP	25.4	30.6	180.36
	BA-BG	BBP	27.4	31.1	190.53
	BA-HG	BHP	29.9	35.6	240.03
Stearic acid (SA)	TA-EG	TES	24.2	27.5	172.89
	TA-BG	TBS	27.0	29.9	183.06
	TA-HG	THS	29.7	32.2	232.56
	CA-EG	CES	27.4	30.9	175.77
	CA-BG	CBS	28.2	31.1	185.94
	CA-HG	CHS	30.9	33.5	235.44
	BA-EG	BES	29.7	31.2	190.80
	BA-BG	BBS	30.1	31.9	200.97
	BA-HG	BHS	32.1	35.8	250.47

3.2.1.1. Effect of polymer:paraffin molar ratio. An alternative way is to prepare composites of paraffin-polymer in which the polymer has side chains, and the gap between two chains is equal to the size of paraffin molecule, and is able to participate to the co-crystallisation of the two components. This may produce eutectic crystals with enhanced properties.It is expected that using such a compound for further co-crystallising with other paraffin molecules will result in improved paraffin/polymer composites, able to store more heat than the usual mixtures.

Further, the mixture of polymer with paraffin may form a mixed crystal (an eutectic). A eutectic system is a mixture of chemical compounds or elements that has a single chemical composition that solidifies at a lower temperature than any other composition. This composition is known as the eutectic composition and the temperature is known as the eutectic temperature. On a phase

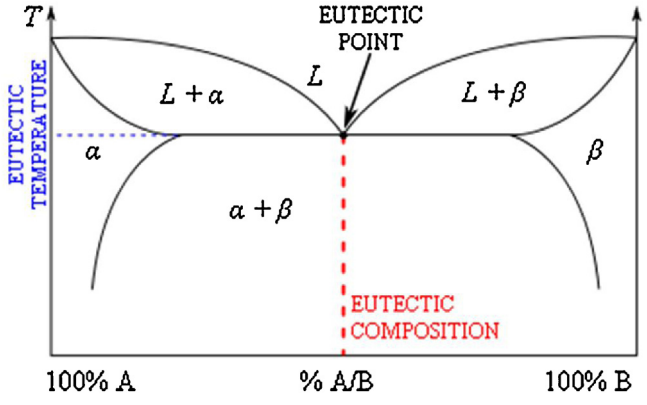

Fig. 2. A binary phase diagram showing the eutectic composition, eutectic temperature, and the eutectic point.

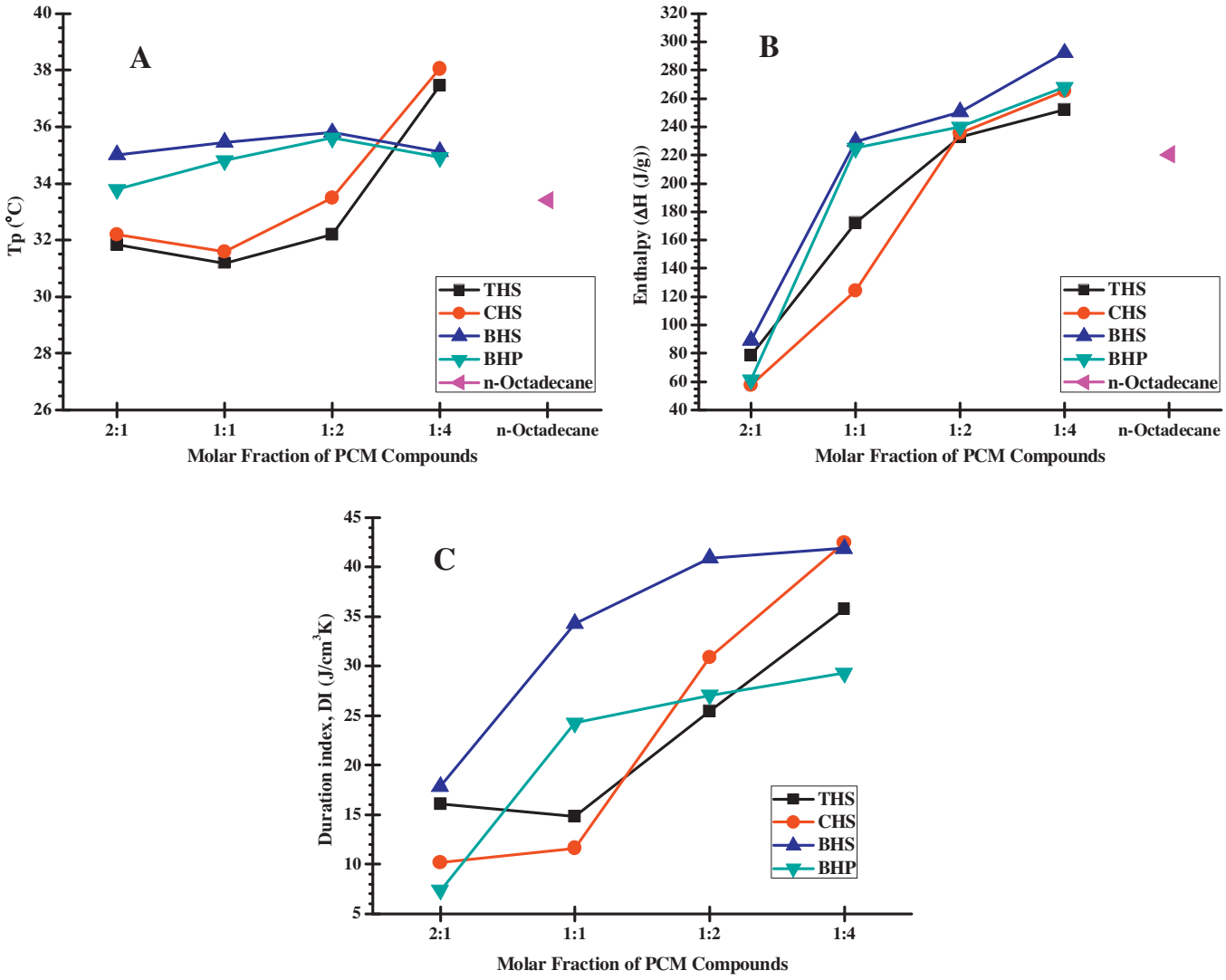

Fig. 3. Comparison of DSC recorded data for the PCM/n-octadecane with different molar ratio. (A) Temperature of melting; (B) enthalpy of phase transition; (C) duration index (DI). Duration index (DI) based on ΔT from melt point to body temperature (37 °C) and average density of 0.8 g/cm^3.

diagram the intersection of the eutectic temperature and the eutectic composition gives the eutectic point (Smith & Hashemi, 2006).

The formation of the eutectic crystal is identifiable on a diagram of the phase change temperature versus molar fraction of components as a minimum, as shown in an ideal case in Fig. 2.

Following these considerations we have screened several polymers and paraffins for identifying the mixtures which storing the largest amount of heat and having the phase change transition within the range of body temperature.

Because the desired phase-change effect of the paraffin, more paraffin means larger amount of latent heat is stored/release during a cycle. On the other side, the paraffin content of the composite is limited by the amount of polymer which is required for arresting it.

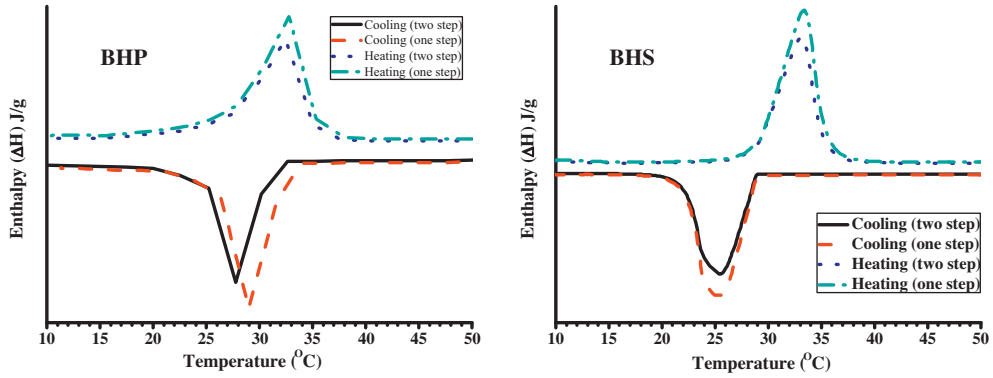

Fig. 4. DSC curves of coated cotton fabrics with BHS and BHS with n-octadecane (cooling and 2nd heating).

Table 4
Effect of molar ratio on T_o, T_p and ΔH of second heating for PCM compounds prepared using n-octadecane.

Polymer	Molar ratio	1st heating			1st cooling			2nd heating			DI[a] (J/cm^3 K)
		T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)	
THS	2:1	25.56	31.13	162.13	22.48	27.43	214.62	26.15	32.84	78.42	16.10
	1:1	27.57	33.87	190.20	20.47	25.16	163.74	27.69	33.99	172.22	14.80
	1:2	32.89	35.66	241.81	21.42	23.26	200.88	29.70	32.20	232.60	25.49
	1:4	31.12	37.21	259.65	28.75	34.35	259.94	31.36	37.45	252.34	35.77
CHS	2:1	25.40	31.11	152.24	20.76	25.48	161.73	23.82	31.19	57.46	10.16
	1:1	28.34	31.47	154.95	24.92	27.64	128.42	28.46	31.59	124.05	11.62
	1:2	30.78	33.38	239.81	28.09	30.51	229.71	30.90	33.50	235.44	30.88
	1:4	32.12	38.17	267.55	28.34	33.74	264.68	32.00	38.05	265.44	42.46
BHP	2:1	29.25	32.55	84.83	24.46	27.24	77.35	30.33	33.79	61.37	7.37
	1:1	30.33	35.71	226.08	24.14	28.37	212.77	29.57	34.81	224.94	24.23
	1:2	29.57	35.26	236.10	23.49	27.91	223.17	29.90	35.60	240.03	27.05
	1:4	29.90	35.15	273.50	27.07	31.87	237.24	29.68	34.92	268.05	29.31
BHS	2:1	32.90	34.90	88.75	31.76	33.66	85.83	33.01	35.01	89.15	17.88
	1:1	31.76	35.57	230.31	30.39	34.11	220.62	31.64	35.46	229.64	34.30
	1:2	31.99	35.69	249.54	30.85	34.45	240.65	32.10	35.80	250.47	40.89
	1:4	31.30	35.01	238.66	30.16	33.77	229.64	31.42	35.12	292.26	41.88

Reaction condition: time: 14 h; temperature: 100 °C; paraffin:n-octadecane; M.R.: PCM hosting:octadecane; T_o: onset temperature; T_p: keeping temperature; ΔH: enthalpy.
[a] Duration index: based on ΔT from melt point to body temperature (37 °C) and average density of 0.8 g/cm^3.

Four selected PCM hosting material were chosen for the further analysis depending on their DSC result (ΔH, T_p and T_o) (THS, CHS, BHP and BHS). N-octadecane was used in four different molar ratios, calculated to the corresponding hosting material, 1:1, 1:2, 1:4 and 2:1 hosting material: paraffin. The DSC results from second heating for PCMs are shown in Table 4 and Fig. 3.

One may notice that the DSC signal records, in most of the cases, a single endothermic effect at heating and a single exothermic effect at cooling, corresponding to the melt/crystallisation of the paraffin.

It is obvious from the second heating result that, for PCM-polymer composites prepared from stearic acid and 1,6-hexanediol, the type of the multicarboxylic acid is affecting the enthalpy and temperature peak by increasing the number of carboxyl groups in the multicarboxylic acid (tartaric acid (THS) then citric acid (CHS) and then butanetetracarboxylic acid (BHS)). In addition, the enthalpy decreasing from the 33.3% (2:1) till 50% (1:1) molar ratio and then by increasing the molar ratio till 80% (1:4) the ΔH value was increased and the keeping temperature (T_p) was increasing by increasing the paraffin percent in the mixture.

Furthermore, for the hosting materials from butanetetracarboxylic acid and hexanediol, the type of fatty acid is affecting the DSC results (enthalpy and keeping temperature), e.g. increasing the number of methylene group in the fatty acid backbone cause increasing the enthalpy and keeping temperature, stearic acid give more latent heat storage for the PCM composite material than palmitic acid (BHS > BHP).

Fig. 3 shows that the PCM composites which produced from THS and CHS only has eutectic point, and it can defined as eutectic composition. The other PCM polymer composites are not eutectic composition and commonly defined as *hypoeutectic* or *hypereutectic*. Hypoeutectic composition is composition to the left of the eutectic point and hypereutectic composition is compositions to the right (Smith & Hashemi, 2006).

As it appears, the temperatures of phase transition recorded for the mixtures (Fig. 3A) is close to those of the pure paraffin in most of the cases. On the other side, at such low molar fraction of paraffin in the mixture the heat of fusion is quite low, below 100 J/g, which makes the products less interesting for practical application (Fig. 3B).

From point of view of the duration index, the PCM composites are ranked in Fig. 3C. The calculations are based on the insulating at body temperature of 37 °C. The values of duration index show that out of the four PCM hosting material for making the composites with n-octadecane those which make the best material (having the highest duration index) are BHS and CHS. Also one may notice that in all cases the mixtures in molar ratio 1:4 monomer to paraffin are the best ones, and those in molar ratio of 2:1 are the worst.

For evaluation, the data of Table 4 are compared with the temperature and enthalpy of phase change process of the pure n-octadecane. The pure n-octadecane melts at 28 °C and has the enthalpy of melting of 242.5 J/g (Zhang, Frenkel, March, & Wilhoit, 1995). The comparison of the data of Table 4 and the pure paraffin is illustrated in Fig. 3. From above data the affected molar ratio to produced PCM compounds with high keeping temperature T_p and enthalpy ΔH is polymer:paraffin 1:2 (33.33% polymer and 66.66% paraffin).

3.2.2. Textile application

The textiles (clothing, interior textiles, and technical textiles) are used as thermal insulators, adding PCM to such textile is considered to improve the insulating performance for suppressing temperature variations (Mondal, 2008). The phase change materials play the role of a buffer in the insulator by storing and releasing heat under the change of environmental temperature (Mondal, 2008). This effect has to be quantified for evaluating the efficiency of a PCM material.

3.2.2.1. DSC analysis. The DSC results of coated cotton fabrics with PCM polymer composites (BHS and BHP) are illustrated in Fig. 4 and Table 5, from second heating, it can seen that, using one step coating method (coating using PCM composites, the paraffin was encapsulated inside the PCM hosting material before coating process) give the fabric thermo-regulating property more than using two step coating method (coating using PCM hosting material, the fabric was immersed firstly in the PCM hosting material then immersed in the paraffin compound). In addition, treated cotton fabric with BHS/octadecane composite has higher duration index value than cotton fabric treated with BHP/octadecane composite.

Finally, it can be concluded that cotton fabric coated with PCM polymer composite has better result than the uncoated fabric.

3.2.2.2. Morphological analysis. Fig. 5 illustrates the scanning electron microscope image of the untreated fabric (A), treated fabric with BHS/octadecane (B) and treated fabric with BHS/octadecane after 10 cycle of washing (2 g/l non-ionic detergent for 15 min at

Table 5
DSC and DI results of coated fabric with PCM polymer composites.

PCM composite	Coating method	1st heating			1st cooling			2nd heating			DI[a] (J/cm^3 K)
		T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)	T_o (°C)	T_p (°C)	ΔH (J/g)	
BHS	One step	28.10	32.60	219.37	24.33	27.88	207.98	28.30	32.65	193.21	17.27
	Two step	27.83	32.45	218.87	23.93	28.07	205.94	28.05	32.50	182.64	16.79
BHP	One step	27.39	32.83	213.30	21.00	25.31	201.14	27.65	33.35	177.67	15.20
	Two step	27.31	32.74	212.80	20.85	25.38	200.04	27.57	33.07	171.29	14.52

Reaction condition: time: 14 h; temperature: 100 °C; M.R.: hosting material:octadecane (1:2); T_o: onset temperature; T_p: keeping temperature; ΔH: enthalpy.
[a] Duration index: based on ΔT from melt point to body temperature (37 °C) and average density of 0.8 g/cm^3.

40 °C). It is seen that, a homogeneous distribution of spherical particles deposited on the surface of the cotton fibre. These particles are representing the PCM materials which are reacted with cotton fibre through the hydroxyl group producing a chemically bonded, which make the PCM material more stable and did not leak from the fibre surface after washing.

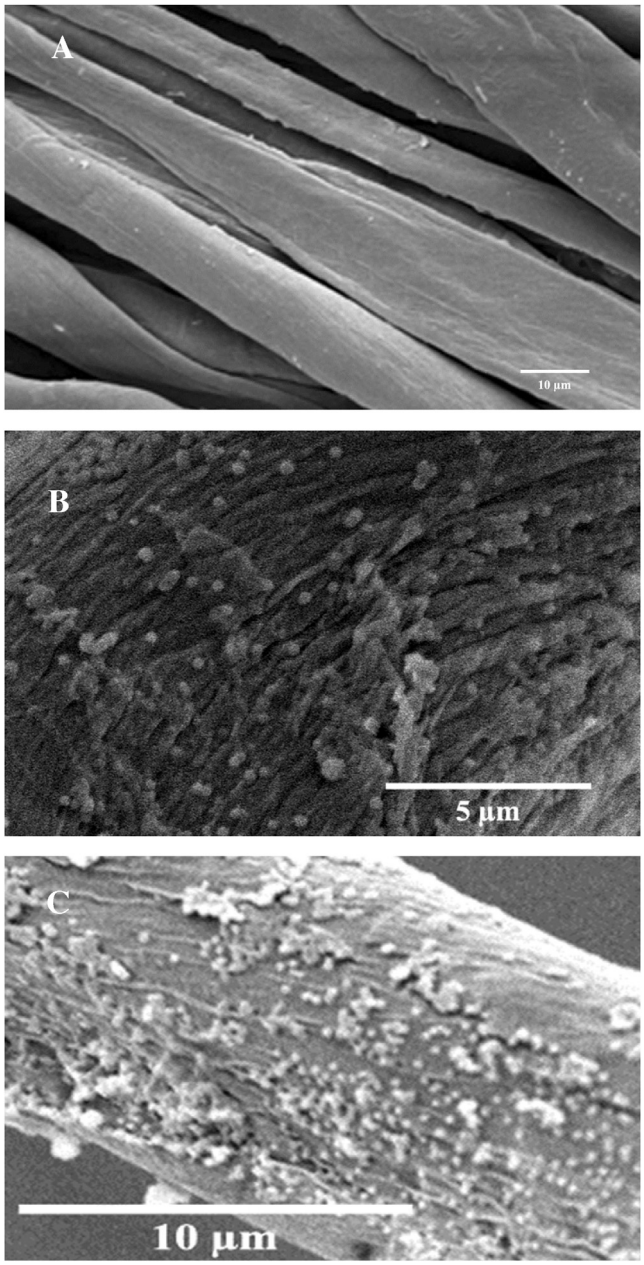

Fig. 5. Scanning electron micrograph (SEM) of untreated and treated fabrics with BHS/octadecane. (A) Untreated cotton fibre; (B) treated cotton fibre with PCM materials; (C) treated cotton fibre with PCM materials after 10 cycle washing.

3.2.2.3. Stability test. For checking the stability of the composite, the treated fabric was washed (2 g/l non-ionic detergent for 15 min at 40 °C) and then heated from room temperature till 45 °C, a temperature that is higher than the complete melting temperature of the PCM capsules. After that, the fabric is put on a filter paper and kept at 45 °C in the oven for 15 min. After 24 h no oil drops are noticeable, which shows that although melting, the PCM material is still held up well by the polymer matrix. We consider that, this is due to capillary forces (capillary forces is the movement of a liquid along the surface of a solid caused by the attraction of molecules of the liquid to the molecules of the solid) existing between the polymer and the melted paraffin (Beginn, 2003), and also, because the chemically bonded between the fabric and the PCM composite.

4. Conclusion

The preparation method of the PCM hosting materials used in this study has succeeded with high heat storage capacities. The achieved enthalpies of PCM hosting materials were found proportional to those of hydrocarbons in temperature intervals corresponding to the phase transitions of PCMs.

Butanetetracarboxylic acid/hexanediol/stearic acid/n-octadecane composite has an excellent thermo-regulation property in comparing with the other prepared composites. Also, all the composites based on butanetetracarboxylic acid or hexandiol or stearic acid give better thermoregulating property than the other multicarboxylic acids or other diol or other fatty acid respectively. Stability test and scanning electron micrograph approved that, the PCM polymer composite is still held up well on the cotton surface by the polymer matrix even after 10 cycle washing.

By application onto cotton fabric, it is clear that, a homogeneous distribution of spherical particles deposited on the surface of the coated cotton fibre. These particles are representing the PCM materials which are reacted with cotton fibre, which make the PCM material more stable and did not leak from the fibre surface after washing. In addition, the coated one has better result than its uncoated cotton fabrics.

Acknowledgement

The author gratefully acknowledges National Research Centre, for financial support and for facilities provided through project ID: P90303.

References

Bayés-García, L., Ventolà, L., Cordobilla, R., Benages, R., Calvet, T., & Cuevas-Diarte, M. A. (2010). Phase change materials (PCM) microcapsules with different shell compositions: Preparation, characterization and thermal stability. *Solar Energy Materials and Solar Cells, 94*(7), 1235–1240.

Beginn, U. (2003). Applicability of frozen gels from ultra high molecular weight polyethylene and paraffin waxes as shape persistent solid/liquid phase change materials. *Macromolecular Materials and Engineering*, *288*(3), 245–251.
Bendkowska, W., Tysiak, J., Grabowski, L., & Blejzyk, A. (2005). Determining temperature regulating factor for apparel fabrics containing phase change material. *International Journal of Clothing Science and Technology*, *17*(3/4), 209–214.
Bryant, Y. G. (1992). 2.0 new textiles-new technologies. In *Techtextile Symposium* Frankfurt, (p. 1).
Bryant, Y. G. (1999). Melt spun fibers containing microencapsulated phase change material. *HTD. Advances in Heat and Mass Transfer in Biotechnology ASME*, *363*(BED-44), 225–234.
Chaurasia, P. B. L. (1981). *Research and Industry*, *26*, 159.
Doerr, D. F. (1997). *Heat stress assessment and a countermeasure*. West Melbourne, FL: Biomedical Laboratory Kennedy Space Center.
Erkan, G. (2004). Enhancing the thermal properties of textiles with phase change materials. *Research Journal of Textile and Apparel*, *8*(2), 57–64.
Fossett, A. J., Maguire, M. T., Kudirka, A. A., Mills, F. E., & Brown, D. A. (1998). *Journal of Mechanical Design - Transactions of the ASME*, *120*, 238.
Hassabo, A. G. (2011). *Synthesis and deposition of functional nano-materials on natural fibres. DWI an der RWTH-Aachen*. Aachen, Germany: RWTH-Aachen University (Ph.D. Thesis).
Hawlader, M. N. A., Uddin, M. S., & Zhu, H. J. (2002). Encapsulated phase change materials for thermal energy storage: Experiments and simulation. *International Journal of Energy Research*, *26*(2), 159–171.
Himran, S., Suwono, A., & Mansoori, G. A. (1994). Characterization of alkanes and paraffin waxes for application as phase change energy storage medium. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects*, *16*(1), 117–128.
Hittle, D. C., & André, T. L. (2002). *ASHRAE Transaction: Research*, *180*, 175.
Lan, X.-Z., Tan, Z.-C., Shi, Q., & Gao, Z.-H. (2009). Gelled $Na_2HPO_4{\cdot}12H_2O$ with amylose-g-sodium acrylate: Heat storage performance, heat capacity and heat of fusion. *Journal of Thermal Analysis and Calorimetry*, *96*(3), 1035–1040.
Mondal, S. (2008). Phase change materials for smart textiles – An overview. *Applied Thermal Engineering*, *28*(11–12), 1536–1550.
Mottinger, B. (1999). *Space hardware design final project, asen 4512*. USA: University of Colorado.
Mulligan, J. C., Colvin, D. P., & Bryant, Y. G. (1996). Microencapsulated phase-change material suspensions for heat transfer in spacecraft thermal systems. *Journal of Spacecraft and Rockets*, *33*(2), 278–284.
Onofrei, E., Rocha, A. M., & Catarino, A. (2010). Textiles integrating PCMs – A review. *BULETINUL INSTITUTULUI POLITEHNIC DIN IAŞI Publicat de Universitatea Tehnică "Gheorghe Asachi" din Iaşi SecŃia, LVI (LX)*(2), 99–110.
Shim, H., McCullough, E. A., & Jones, B. W. (2001). Using phase change materials in clothing. *Textile Research Journal*, *71*(6), 495–502.
Shin, Y., Yoo, D. I., & Son, K. (2005). Development of thermoregulating textile materials with microencapsulated phase change materials (PCM). II. Preparation and application of PCM microcapsules. *Journal of Applied Polymer Science*, *96*(6), 2005–2010.
Smith, W. F., & Hashemi, J. (2006). *Foundations of materials science and engineering*. McGraw-Hill.
Yamagishi, Y., Sugeno, T., Ishige, T., Takeuchi, H., & Pyatenko, A. T. (1996). An evaluation of microencapsulated PCM for use in cold energy transportation medium. *Proceedings of the Intersociety Energy Conversion Engineering Conference*, *3*, 2077.
Yamagishi, Y., Takeuchi, H., Pyatenko, A. T., & Kayukawa, N. (1999). Characteristics of microencapsulated PCM slurry as a heat-transfer fluid. *AIChE Journal*, *45*(4), 696.
Zhang, X. X., Fan, Y. F., Tao, X. M., & Yick, K. L. (2005). Crystallization and prevention of super-cooling of microencapsulated n-alkanes. *Journal of Colloid and Interface Science*, *281*, 299–306.
Zhang, Z.-Y., Frenkel, M., March, K. N., & Wilhoit, R. C. (1995). *Thermodynamic properties of organic compounds and their mixtures, subvolume a: Enthalpies of fusion and transition of organic compounds*. USA: Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology, The Texas A&M University.