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Thermal characteristics of polyurethane foams incorporated with phase change materials

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Abstract

Thermal energy storage plays an important role in heat management because of the demand for developed energy conservation, and has applications in diverse areas, from building heating/cooling systems which enable solar energy incorporation into the structure, to textiles and clothings providing an enhanced thermal comfort. In this study, we aimed to improve thermal characteristics of polyurethane rigid foams that have been widely used for thermal insulation as the ultimate energy savers due to their ability to form sandwich structures with various facer materials. Through a laboratory-scale work, two paraffin waxes acting as phase change materials, namely *n*-hexadecane and *n*-octadecane, each of which is capable of managing large heat storage/release, were directly incorporated into the polyurethane foams at different ratios. Polymerization modified by means of *n*-alkane addition could be achieved without any adverse effect. In order to determine both structural and thermal characteristics, seven types of foams produced were examined by FT-IR, SEM, DSC analyses, calorimeter bomb and mechanical tests. Results show that polyurethane foams can be designed as thermal insulators equipped with an improved buffering function against temperature changes. © 2007 Elsevier B.V. All rights reserved.

Keywords: Polyurethane foam; Thermal behaviour; Phase change materials; DSC; FT-IR; SEM

1. Introduction

Polyurethanes are polymers which contain urethane linkages and are produced by reacting diisocyanates with polyols and some supplementary chemicals and catalysts. The polyol is itself a low-molecular-weight polymer with hydroxyl end groups; the diisocyanate is often an isomer of toluene diisocyanate (TDI) or methylene diphenyl diisocyanate (MDI). The basic reaction between a diisocyanate and a polyol produces a polyurethane polymer with the liberation of heat.

Foaming occurs when a small amount of blowing agent and water is added during polymerization. Water reacts with isocyanate groups giving carbamic acids, which spontaneously lose CO_2 , thus generating the foam bubbles. The blowing catalyst composition provides the resulting polyurethane foam with improved breathability [1–5]. As well-known, polyurethanes are produced within an extensive range, including stretchable fibers, flexible foams, rigid lightweight foams, or tough, stiff elastomers, which allows them to be used in a wide diversity of consumer and industrial applications. Furniture, mattresses and automotive seating are made predominantly from flexible foams and semi-rigid foams. Footwear applications relate to elastomers; construction and insulation are of rigid foams. Other applications include coatings, adhesives, artificial leather, textile fibers and electronic applications, etc.

Polyurethane rigid foams have been widely used for thermal insulation as the ultimate energy savers. Compared with other insulating materials, they are highly competitive. The air trapped within the honeycomb like structure develops passive insulation characteristics of foam in addition to polyurethanes' heat absorption capacity. The lowest thermal conductivity, high mechanical and chemical stability at both high and low temperatures, the ability to form sandwich structures with various facer materials are their advantages. They are also chloroflorocarbon free and recyclable [6].

Thermal management named as the dynamic heat storage, has attracted more attention in the last decade because of the

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Chemical agent	IUPAC name and closed formula	Molar mass $(g mol^{-1})$	Amounts
Toluylene 2,4- diisocyanate (TDI),Merck	4-Methyl-m-phenylene diisocyanate, 2,4-(NCO) ₂ C ₆ H ₃ CH ₃	174.16	91.9 eq. mmol
Polyol	1,3-Propanediol, HO(CH ₂) ₃ OH	76.1	420.5 eq. mmol
DABCO (catalyst)	Triethylenediamine, 1,4-diazabicyclo[2.2.2]octane, C ₆ H ₁₂ N ₂	112.18	0.012 g
Stannus octoate (catalyst)	Tin 2-ethylhexanoate, [CH ₃ (CH ₂) ₃ CH(C ₂ H ₅)COO] ₂ Sn	405.10	0.036 g
Silicone oil (surfactant/stabilizer)	-	_	0.14 g
Methylene chloride (blowing agent)	Dicloromethane, CH ₂ Cl ₂	84.93	1.23 g
Water (blowing agent)	-	_	2-3 drops
Polyurethane hardener	Diphenylmethane 4,4-diisocyanate, $C_{15}H_{10}N_2O_2$	250.26	2–3 drops

Table 1Materials used in polyurethane synthesis

demand for developed energy conservation as well as improved thermal comfort. Thermal energy storage plays an important role in heat management and has applications in diverse areas, such as building heating/cooling systems which enable solar energy incorporation into the structure. Many natural and technical processes provide large amounts of excess heat. Successful applications of energy storage are still under investigation.

Heat storage materials are particularly attractive compounds or mixtures that provide high heat capacity per unit mass/unit volume and they have a buffering effect against temperature changes. Phase change materials (PCMs) capable of absorbing or releasing large amount of heat during phase transitions between two solid states and/or liquid and solid states are a subgroup of heat storage materials. They can be classified into two major categories: inorganic compounds and organic compounds. Inorganic PCMs include salt hydrates, salts, metals and their alloys, whereas organic PCMs are linear chain hydrocarbons known as paraffin waxes (or *n*-alkanes), poly ethylene glycols (PEGs) and fatty acids.

In general, the higher the PCMs' latent heat of phase change is, the more thermal energy a material can store. The phase transition process is completely reversible. Well-known PCMs are linear chain hydrocarbons known as paraffin waxes or *n*-alkanes. The melting points of *n*-alkanes depend on the length of the carbon atom chains, i.e. on the number of carbon atoms in the molecule. Long chain hydrocarbons with 13-28 carbon atoms have phase change temperatures ranging from -5 to $65 \,^{\circ}$ C. By selecting two or more different alkanes and forming a mixture thereof, a temperature stabilizing range can be widened for any desired application [7,8]. Compared to other PCMs, paraffin waxes have high energy storage densities, high boiling points and stability up to 250 °C. They are chemically inert, noncorrosive, long-lasting, inexpensive, ecologically harmless and non-toxic. These characteristics have made them the preferred PCMs for many commercial applications [7–11].

When a thermal insulator material is incorporated with PCMs to improve thermal comfort of end-use products, it can provide an enhanced heat capacity in addition to the existing passive insulation characteristic of the structure. Microencapsulation, coating, lamination, injection molding, foam manufacturing are some of the convenient processes for PCMs' incorporation into the structure. Although, polyurethane foams have been inserted into different composites as passive insulators, capturing of PCMs or microencapsulated PCMs in polyurethane foams has not been studied in detail [12].

In our study, we aimed to incorporate *n*-alkanes, namely *n*-hexadecane and *n*-octadecane, into polyurethane (PU) foams at different ratios directly in order to find out the enhanced buffering function of the products against temperature changes Then the thermal properties, microstructures, chemical composition and leakage properties of the PU foam samples had been studied by means of DSC, calorimeter bomb, SEM, FT-IR analysis and mechanical tests.

2. Experimental

This experimental work, deals with the manufacture of polyurethane composites containing PCMs that are used in the previous study. The enthalpy values of *n*-hexadecane and *n*-octadecane were obtained in DSC analyses as 185 J g^{-1} in between 10 and 26 °C and 234 J g⁻¹ in between 26 and 44 °C, respectively [11]. The materials used in polyurethane synthesis and the added PCM contents are given in Tables 1 and 2, respectively.

For the production of PU foams, TDI and silicone mixture was first stirred at 200 rpm at 20 °C for 10 min. While stirring, first the catalyst blend and then stochimetric amount of polyol and PCM were added successively. Polymerization proceeded under constant stirring and refluxing conditions for 8–10 min. Finally, 1 mL of methylene chloride and few drops water as blowing agents and the hardener were put into the polymer mixture to finish the reaction. Foaming occurred by a violent exothermic reaction. In the sample included Na₂CO₃·10H₂O, the same blowing effect was achieved without adding excess water due to the existence of water molecules in the hydrated salt.

To characterize the thermal behavior of the samples given in Table 2, DSC analyses were conducted on Perkin-Elmer Pyris1

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Sample code	Added PCM	Mass _{PCM} to mass _{PUmix} ratio
PU1	<i>n</i> -Hexadecane	1:5
PU2	<i>n</i> -Hexadecane	1:2.5
PU3	n-Hexadecane and Na ₂ CO ₃ ·10H ₂ O	1:1.6
PU4	<i>n</i> -Hexadecane	1:1.4
PU5	n-Hexadecane	1:1
PU6	n-Octadecane and PEG600	1:2
PU7	n-Octadecane	1:1.4

DSC under nitrogen atmosphere. During DSC analyses, test specimens were heated within a certain temperature interval ranging from 0 to 70 °C at 10 °C min⁻¹, which is common for polymer analysis [13,14]. Additionally, combustion heat capacities of certain samples were measured on PARR 1341 EE Model Plain Jacket Calorimeter calibrated with benzoic acid whereas, the water equivalent of it is 2426 cal °C⁻¹(10.141 kJ °C⁻¹). In order to identify the chemical structure of some PU foams and their includings, the infra red transmission spectra of specimens, dispersed in KBr pellets, were performed on Perkin-Elmer Fourier transform infrared spectrophotometer in between the wave numbers of 4000 and 450 cm⁻¹. SEM photos were also taken to explain the structural details of the foams by the SEM Instrument type JSM 6335F NT.

Leakage behaviors of foams, PU4 and PU7, were examined by a compression test procedure developed. First, a piece of coarse filter paper was weighed, and then, placed under about 5.0 g foam sample. The system was compressed by 12 kPa static load, used on Martindale abrasion tester, for 150 min under standard atmosphere conditions. The filter papers were removed and weighed again to check if there was any paraffin wax adsorption. Microscopic analysis was also conducted for visual comparison. Next, the same foam samples were immersed in 100 mL distilled water and waited for the next 60 days. After subsequent squeezing, the supernatant liquid samples were controlled whether they presented any oil phase by using separatory funnel.

3. Results and discussion

3.1. Characterization of manufactured polyurethane foams containing PCM or PCM microcapsules

3.1.1. FT-IR spectra evaluations

FT-IR spectra of the synthesized foams, namely PU4, PU7 and PU Control, are presented in Figs. 1–3. Table 3 gives the characteristics of transmission bands and the relative intensities ($\Delta T\%$) of the samples. The spectrum of PU Control presents all the distinctive bands of the polyurethane polymer. The spectra of experimental groups are compared with that of PU Control.

The band of -OH stretching vibration at 3436–3350 cm⁻¹ is associated with the free H₂O, -OH groups of non-bonded polyol or -OH groups within the polymer structure. Its strength is almost the same for all samples. The intensities of transmission bands for $-CH_2$ and -CH chain formation at 2972–2953 cm⁻¹, decrease for PU4 when compared with that of the control group due to the discontinuity of PU chains caused by PCM addition to the structure. Similarly, peaks related to -CN and -C=O at 2273 and 1710 cm⁻¹ observed in the spectrum of control group disappear in the spectra of PU4 and PU7. This also indicates incompleteness of PU chains arising from the addition of a secondary material into the structure.

The intensity increases in peaks for $-CH_2$ at 2953.9 and 2916.8 cm⁻¹ of PU7 is associated with capturing *n*-octadecane with 18 carbon atoms. As a matter of fact, the newly formed peaks of PU7 at 2871.4, 2849.7 and 1471.9 cm⁻¹ related to $-CH_3$, $-CH_2$, -CH groups of *n*-octadecane, which have strong relative transmissions of 31.5, 61.5 and 42.5, are not detected in the FT-IR spectrum of control group. These characterized peaks are the evidence of a successful *n*-octadecane trapping in PU foam [15–17]. Likewise $-CH_3$ and $-CH_2$ bands at 2853.4 and 1469.6 cm⁻¹ wave number specify *n*-hexadecane trapped in PU4.

3.1.2. SEM photos of foam structures

SEM photos of some PU samples are shown in Figs. 4–7. Figs. 6–7 clearly illustrate the micro-cells comprising some PCM micelles. The excellent honeycomb structure obtained during foam formation made considerable amount of still air trapping possible, thus, leading to an increased passive insulation. Although the presence of PCM micelles in cells can easily be distinguished, PCM addition into the structure was not so easy due to the violent foaming reaction. The body in Fig. 5 is a PU composite including *n*-octadecane and PEG600. It seems that PEG600 involved in the polymerization reaction as a cross



Fig. 1. FT-IR spectrum of PU Control.



Fig. 3. FT-IR spectrum of PU7.



Fig. 4. PU1 containing *n*-hexadecane: (a) magnification ×1000; 10.0 kV and (b) magnification ×10,000; 10.0 kV.

Table 3	
Characteristics of transmission bands and the relative intensities (ΔT %) of FT-IR spec	tra

Vibrating group	Type of vibration	Wave number ν (cm ⁻¹)	$\Delta T(\%)$		
			PU Control	PU4	PU7
-OH	Stretching	3436–3350	39.3	31	25.5
CH ₂ ;CH	Stretching; stretching in an acid	2972–2953	33.3	21.5	40.5
CH ₂ ;CH	Stretching; stretching in an acid	2930-2916	37.3	35.5	87.5
CH ₃ , CH ₂	Stretching	2872-2853	0	26	31.5
CH ₃ , CH ₃	Stretching	2850	0	0	61.5
-C-N	Stretching	2273	8.3	0	0
-C=0	Stretching	1710	38.8	0	0
-C=0	Stretching	1648–1644	39.8	22	20
-C=0	Stretching	1605–1601	41.8	20.5	23
–N–H; –C–N	Stretching	1549–1536	47.3	23.5	20
-CH ₂	Bending	1472–1454	0	18	42.5
-С-Н; -С-С	Bending in plane	1413–1411	31.3	12.5	9.5
-C-N	Stretching	1377–1373	27.3	13	11.5
-C-OH	Stretching	1245–1222	39.8	18.5	16
-C-O-C	Vibrating	1111-1096	38.3	21.8	18
CH ₂ ;CH	Rocking; bend out plane	934–927	4.3	2.5	1
CH ₂ ;CH	Rocking; bend out plane	871	3.3	2.2	0
CH ₂ ;CH	Rocking; bend out plane	813-810	11.8	7.8	5.5
CH ₂ ;CH	Rocking; bend out plane	755–754	10.3	5	0
-СН2; -С-Н	Rocking; bend out plane	718–701	12.3	7.5	16.5

linking agent which resulted in a long chain bulky structure surrounding *n*-octadecane molecules.

3.1.3. Leakage behavior

Leakage behavior of foam samples is an important property to facilitate production, handling and application. Table 4 summarizes the results of leakage tests conducted for PU4 and PU7 where the ratios of PCM mass to PU mixture mass are both 1:1.4.

The changes in filter papers' masses observed after compression of samples by 12 kPa static load for 150 min can be assumed as negligible, which probably result from the unsteady humidity exchange between air and papers. During visual assessments under optical microscope, only a very few number of oily spots was detected on filter paper of foam PU4, and no oil spot was observed for PU7. After keeping samples in water for the next 60 days the supernatant liquids left in separatory funnels were compared and oil droplets on the surface of water were watched only for PU4. This shows that the durability of the manufactured foams could be essentially maintained. As the honeycomb structure of polyurethane foam becomes firmer, the durability of it will increase and the leakage possibility of PCM material will decrease. For PU7, capturing *n*-octadecane, for instance, there is no leakage of PCM, which gives promise for PCM containing polyurethane foam production industrially. On the other hand, PU4, containing *n*-hexadecane, caused a little oil phase during leakage tests probably because of the relatively smaller molecules of *n*-hexadecane escaped from honeycomb cells. Nevertheless, this difficulty can be overcome through the production of firmer structures and the protective finishing treatments available for tightness and inflammability [18].

3.2. The thermal properties of polyurethane foams

3.2.1. DSC analyses results

DSC analyses of foam samples, PU1–7, resulted in wellperformed endothermic enthalpy changes during heating in between 0 and 70 °C at the rate of $10 °C min^{-1}$. Table 5 sum-



Fig. 5. PU6 containing *n*-octadecane and PEG600: (a) magnification ×5000; 10.0 kV and (b) magnification ×5000; 10.0 kV.



Fig. 6. PU3 containing *n*-hexadecane and Na₂CO₃·10H₂O: (a) magnification ×20; 10.0 kV, (b) magnification ×500; 10.0 kV and (c) magnification ×10,000; 10.0 kV.

marizes the observed phase transition intervals as well as ΔH (J g⁻¹) values. In each case, the phase transition interval of the manufactured PU foam greatly coincides with that of the contained paraffin wax as given in the previous study [11]. Considering the enthalpy values of *n*-hexadecane and *n*-octadecane,

185 J g⁻¹ in between 10 and 26 °C and 234 J g⁻¹ in between 26 and 44 °C, respectively, ΔH values especially those obtained for foams PU4–7 are found remarkable in terms of their contribution to the heat capacity and dynamic thermal management of the final product.



Fig. 7. PU5 containing *n*-hexadecane: (a) magnification ×500; 10.0 kV, (b) magnification ×20,000; 10.0 kV and (c) magnification ×30; 10.0 kV.

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Leakage test results and observations for polyurethane foam samples
Table 4

Foam code	Mass of foam (g)	Mass of filter paper			Microscopic observation on filter paper	Phases of supernatant liquid in separatory funnel	
		Initial (g)	Final (g)	Change (%)	(after 12 kPa load application for 150 min)	(after keeping samples in water for the next 60 days)	
PU4	4.75	0.591	0.592	0.10	A few number of oil spots	A few number of oil droplets	
PU7	4.62	0.585	0.586	0.10	No oil spot	No oil phase	

Table 5

Phase transition characteristics of PU foams containing paraffin waxes

Foam type/added PCM		Transition interval		Peak $T(^{\circ}C)$	$\overline{\Delta H \left(\mathrm{J}\mathrm{g}^{-1} \right)}$	
		Onset $T(^{\circ}C)$	End $T(^{\circ}C)$			
PU1	n-Hexadecane, 1:5	18.3	22.9	21.1	11.8	
PU2	<i>n</i> -Hexadecane, 1:2.5	18.7	21.4	20.4	11.6	
PU3	<i>n</i> -Hexadecane and Na ₂ CO ₃ ·10H ₂ O, 1:1.6	17.1	20.6	19.7	3.4	
PU4	<i>n</i> -Hexadecane, 1:1.4	16.2	22.4	19.4	40.3	
PU5	<i>n</i> -Hexadecane, 1:1	14.5	20.6	19.0	36.8	
PU6	n-Octadecane and PEG600, 1:2	29.0	46.7	31.7/38.8	34.5	
PU7	n-Octadecane, 1:1.4	27.8	36.0	31.7	77.8	

Figs. 8 and 9 illustrate the specific enthalpy changes of PU foams in terms of $J g^{-1} (^{\circ}C)^{-1}$. The specific heat capacity of PU control was only $0.32 J g^{-1} (^{\circ}C)^{-1}$ for 5 to 55 °C against to the quite high values of other PU foams containing PCMs. DSC curves of foam samples PU4–7 are given in Figs. 10–13.

In general, raising added PCM content in polyurethane formation from 1:5 to 1:1 by mass enhanced the heat absorption capacity of the sample (see Figs. 8–9). On the other hand, relatively small changes in ratios of PCM mass to PU mixture mass did not cause any significant difference in ΔH (J g⁻¹) values, i.e. for PU4 and PU5 (see Table 5 and Figs.10 and 11). However, these results are the evidence that *n*-hexadecane can be incorporated into the PU structure effectively, and this process can be improved if the polymerization conditions are completely taken under control.



Fig. 8. Comparison of the enthalpy changes of PU foams (PU Control, PU1–5) in terms of J $g^{-1} \circ C^{-1}$ during their heating to 70 °C at 10 °C min⁻¹.



Fig. 9. Comparison of the enthalpy changes of PU foams (PU Control, PU6–7) in terms of J g⁻¹ °C⁻¹ during their heating to 70 °C at 10 °C min⁻¹.



Fig. 10. The DSC curve of the foam PU4, containing *n*-hexadecane, 1:1.4 by mass, heating to 70 °C at 10 °C min⁻¹ (sample weight is 15.0 mg).

Foam type/added PCM		Mass of sample (g) 0.06	<i>T</i> _{initial} (°C) 24.7	<i>T</i> _{final} (°C) 24.8	Heat capacity of ignition (cal g ⁻¹) 4852	Heat capacity of ignition (J g ⁻¹) 20281.4	$\frac{H_{\text{sample}} - H_{\text{control}}}{(\text{J g}^{-1})}$	H _{sample} /H _{control} (%) 100
PU7	n-Octadecane	0.28	25.2	26.1	8144.4	34043.7	13762.4	168

Heat capacities of ignition measured with calorimeter bomb (T_{initial} and T_{final} are the internal temperatures of calorimeter before and after ignition respectively)



Table 6

Fig. 11. The DSC curve of the foam PU5, containing *n*-hexadecane, 1:1 by mass, heating to 70 °C at 10° C min⁻¹ (sample weight is 15.0 mg).

The enthalpy change of the foam PU3 with the added *n*-hexadecane and Na₂CO₃·10H₂O, 1:1.6 by mass, is shown in Fig. 8. In the production of this kind of composite, it was observed that sodium carbonate did not show any PCM characteristic and reacted as a blowing agent just because one mole of salt contains 10 moles of crystal water. Therefore, during the synthesis of PU premix, including roughly 50% PCM mixture, the polymerization ended with an instantaneous exothermic reaction and only a small amount of *n*-hexadecane could be captured in the foam structure ($\Delta H = 3.4 \text{ J g}^{-1}$).

DSC graph of the foam PU6 containing 50% *n*-octadecane and PEG600 mixture, in Fig. 12, yielded one peak and one shoulder at 31.7 and 38.8 °C, respectively, which is in accordance with that of *n*-octadecane. The molecules of PEG600 probably



Fig. 12. The DSC curve of the foam PU6, containing *n*-octadecane and PEG600, 1:2 by mass, heating to $70 \,^{\circ}$ C at $10 \,^{\circ}$ C min⁻¹ (sample weight is 13.5 mg).

involved in the reaction as a polyol monomer and made contribution to develop cross linking in the structure, but no further improvement in fusion enthalpy was obtained due to it. Moreover, the phase transition interval seems to be extended up to 47 °C. This may because some of the 1,3-propanediol molecules did not react in PU foam production. The specific heat capacity of 1,3-propanediol at 320 K (47 °C) is 201.211 J mol⁻¹ K⁻¹ or 2.644 J g⁻¹ K⁻¹[19]. Thus, the enthalpy change in the latter part of the graph can be explained by free polyol's absorption of heat to a little extent when the environmental temperature increases.

Fig. 13 shows the DSC result of the foam PU7 which comprises a substantial amount of *n*- octadecane. The enthalpy change obtained, 77.8 J g^{-1} , indicates that the foam will provide a good dynamic heat absorption/release property depending on the environmental temperature changes in addition to the high passive insulation characteristic of it.

3.2.2. Results of calorimeter bomb experiments

PU Control, the foams having the highest fusion enthalpies in DSC analyses, PU4 and PU7, were taken into account and their heat capacities of ignition were tested with a calorimeter bomb. Table 6 presents heat capacities of the individual samples and their comparison with the heat capacity of PU Control during their combustions.

As shown from Table 6, apart from their fusion enthalpies, also the ignition heat capacities of PU4 and PU7 are greater than that of PU Control, 155 and 168%, respectively. These results



Fig. 13. The DSC curve of the foam PU7, containing *n*-octadecane, 1:1.4 by mass, heating to 70 °C at $10 \circ$ C min⁻¹ (sample weight is 15.2 mg).

support that a substantial increase in the heat capacity of the PU foam samples could be achieved by the PCM incorporation process.

4. Conclusion

Based on comprehensive FT-IR, SEM, DSC analyses and calorimeter bomb and leakage tests, we have shown that thermal characteristics of polyurethane foams could be modified by means of PCM addition during polymerization synthesis.

Microstructures and chemical compositions of the experimented PU samples were found clearly different from the structure of PU Control in FT-IR analyses, and it was verified that they comprised the functional groups indicating the existence of linear chain hydrocarbons, say *n*-hexadecane and *n*-octadecane. SEM photos illustrate the PCM micelles trapped in cells of the perfect honeycomb structure. Polyurethane foams containing PCMs can be assumed to be leakage protected and this gives promise for PCM containing polyurethane production industrially.

Phase transition intervals of DSC graphs obtained for PU foams containing PCM(s) at different ratios all coincide with those of *n*-hexadecane and *n*-octadecane and enthalpy changes observed are considerable for the samples where the ratios of PCM to polymer mixture are relatively high, say 1:1.4 and 1:1 by mass. Heat capacities measured in calorimeter bomb experiments also verifies the enhanced thermal capacities of the samples.

By taking into account these test results we have concluded that the sample PU7 containing a considerable amount of *n*octadecane showed a satisfactory performance in all aspects and passed for thermal, structural and durability characteristics for further industrial applications. The sample PU4 containing a considerable amount of *n*-hexadecane is another remarkable one providing good thermal and structural characteristics, and the little leakage problem can be eliminated through well-organized process conditions and/or some available protective finishes. In conclusion, polyurethane foams can be designed as thermal insulators equipped with an improved buffering function against temperature changes.

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References

- G.R. Petrella, Blowing reaction catalyst composition that provides cell opening of the resulting polyurethane foam, U.S. Patent 5,039,713 (1991), available from http://www.freepatentsonline.com/5039713.html.
- [2] D.C. Krueger, L.D. Christman, H.A. Rothacker, B.T. Lee, Rigid polyurethane foams containing lithium salts for energy absorbing applications, U.S. Patent 5,258,416 (1993), available from http://www. freepatentsonline.com/5258416.html.
- [3] Y. Tamano, M. Ishida, S. Okuzono, Amine catalyst for producing polyurethane and process for producing polyurethane, U.S. Patent 5,374,666 (1994), available from http://patft.uspto.gov/.
- [4] H. Seyanagi, I. Kaoru, K. Ogawa, T. Masui, K. Ono, Process for producing polyurethane foam, U.S. Patent 7,098,255 (2006), available from http://patft.uspto.gov/.
- [5] C. Beck, J. Wagner, H. Ehbing, Polyurethane foam, U.S. Pat. 20050043425 (2005), available from http://www.freepatentsonline.com/ 20050043425.html.
- [6] A. Demharter, Polyurethane rigid foam: a proven thermal insulating material, Cryogenics 38 (1998) 113–117.
- [7] K. Saeki, H. Matsukawa, M. Satomura, Method for preparing microcapsules, U.S. Patent 4,251,386 (1981), available from http://patft.uspto.gov/.
- [8] B. Zalba, J. Marin, L.F. Cabeza, H. Mehling, Review on thermal energy storage with phase change: materials, heat transfer analysis and applications, Appl. Therm. Eng. 23 (2003) 251–283.
- [9] M.H. Hartmann, Stable phase change materials for use in temperature regulating synthetic fibers, fabrics and textiles, U.S. Patent 6,689,466 (2004), available from http://patft.uspto.gov/.
- [10] A.M. Khudhair, M.M. Farid, A review on energy conservation in building applications with thermal storage by latent heat using phase change materials, Energy Conversion Manag. 45 (2004) 263–275.
- [11] N. Sarier, E. Onder, The manufacture of microencapsulated phase change materials suitable for the design of thermally enhanced fabrics, Thermochim. Acta 452 (2007) 149–160.
- [12] R.L. Everitt, P.R. Harrison, R.V. Onufrak, Energy absorbing, water blown, rigid polyurethane foam, US Patent 6,028,122 (2000), available from http://www.freepatentsonline.com/6028122.html.
- [13] S. Giraud, S. Bourbigota, M. Rocherya, I. Vromana, L. Tighzertb, R. Delobelc, F. Poutch, Flame retarded polyurea with microencapsulated ammonium phosphate for textile coating, Polym. Degrad. Stab. 88 (2005) 106–113.
- [14] X.-X. Zhang, Y.-F. Fan, X.-M. Tao, K.-L. Yick, Crystallization and prevention of supercooling of microencapsulated *n*-alkanes, J. Colloid Interface Sci. 281 (2) (2005) 299–306.
- [15] D. Saihi, I. Vroman, S. Giraud, S. Bourbigot, Microencapsulation of ammonium phosphate with a polyurethane shell part I: coacervation technique, React. Funct. Polym. 64 (2005) 127–138.
- [16] R. Yang, H. Xu, Y. Zhang, Preparation, physical property and thermal physical property of phase change microcapsule slurry and phase change emulsion, Sol. Energy Mater. Sol. Cells 80 (2003) 405–416.
- [17] K. Choi, G. Cho, P. Kim, C. Cho, Thermal storage/release and mechanical properties of phase change materials on polyester fabrics, Textile Res. J. 74 (4) (2004) 292–297.
- [18] S.S. Simpson, Polyurethane foam composition and method of manufacture thereof, U.S. Patent 6,803,495 (2004), available from http:// patft.uspto.gov/.
- [19] V. Shatikian, G. Ziskind, R. Letan, Numerical investigation of a PCMbased heat sink with internal fins, Int. J. Heat Mass Transfer 48 (2005) 3689–3706.