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Nonwovens with Thermal Storage Properties Based on Paraffin–Modified Polypropylene Fibres

Abstract

A series of nonwovens with various mechanical and thermal properties was prepared by a textile technique based on melt-spun continuous PP fibres modified with paraffin as a phase change material (PCM). The PCM is not encapsulated; it forms a structure like "islands in the sea" in the PP fibres. This permits the addition of a larger amount of the active substance to the fibre than in the encapsulated version. The nonwovens made of such fibres retained high thermal resistance. Paraffin was added to the PP fibre in amounts of 10 - 30 wt%; 20 wt% appeared to be best in terms of thermal properties and processability. To prevent fibre to fibre sticking at elevated temperatures, the nonwovens were made of a blend of paraffin-modified and standard PP fibres in variable proportions. The thermal activity determined by the kind of paraffin used was estimated to be in the range of 30 - 60 °C. The fibre heat accumulation capacity stemming from the phase transition in the PCM was in the range of 3.6 - 19.4 kJ/m^2, at a thermal regulation factor (TRF) from 0.8 to 0.4.

Key words: *PCM, PCM fibres, PCM nonwovens, TRF coefficient, paraffin.*

Introduction

For many years, highly processed modern materials with unique and useful properties have aroused the interest of the textile industry. So-called smart fibres [1 - 3] are seen as being particularly interesting for the future. These fibres have built-in functional agents that react to external factors like temperature, humidity, chemicals, electromagnetic fields, and atmospheric pressure by changing the fibre's properties. Presently, such materials are classified as thermoregulating materials capable of accumulating heat, materials with shape memory, semipermeable membranes, electro-conductive textiles, textiles that control vital functions, IR-invisible, self-cleaning, anti-allergic and anti-mite fibres and the like. Commercially produced [13] thermoregulating fibres with a phase change material (PCM) occupy an important place among modern materials [4 - 12]. These fibres are capable of accumulating heat at rising ambient temperature and releasing the heat at decreasing temperature. This feature of PCM-containing materials provides the opportunity of controlling the temperature of a protected object to a certain degree. When adequately designed, these fibres may serve as materials to prepare special functional clothing according to the principle of "not too hot, not too warm" [13]. These fibres emerged about 30 years ago as polyester, polyamide, cotton, and woollen fabrics soaked with

an aqueous solution of polyethylene glycols and dried afterwards [4]. NASA carried out research in the early 1980s [14] on protective clothing for astronauts employing the encapsulation technique (the PCM agent is trapped in a protective capsule) [8]. Presently, over 500 natural and synthetic substances comprise the PCM category [6, 8, 14, 15], including hydrated organic salts, linear hydrocarbons (so-called n-paraffin), polyethylene glycols, fatty acids, and others. All these feature phase transition in the temperature range of -5 to +70 °C and enthalpy of the transition in the range of 120 - 250 kJ/kg. There are several ways to introduce CPM to textiles.

The literature [14] quotes the following main methods:
- "In fibre": PCM-containing microcapsules are added in the course of fibre manufacture to the polymer melt or solution which is processed into fibres by melt, dry or solution spinning. Attempts have also been made to build the PCM into the polypropylene sheath/core bicomponent fibres as the core component [16]. Recently, various versions have been proposed to put the PCM into fibres [17]. Commercial solution-spun PAN and cellulosic fibres containing microcapsules are available under the trade name Outlast [13].
- Coating: The PCM substance is fragmented into micro-beads, encapsulated or dispersed, along with auxiliary agents like dispersants and foam breakers into an aqueous suspension that is applied superficially or in the

mass by various textile techniques. A number of paraffin hydrocarbons serve as the PCM substance. This method is used by Frisby Technologies Inc.
- Lamination: A thin, PCM-containing film is laminated from the inside of the textile material, on the contact side with human skin. The film ought to be water vapour-permeable. This method is used in the manufacture of surgical aprons, uniforms and clothing for clean rooms [14]. In addition to films, PCM-containing foams are also applied in lamination.

It must be stressed that the addition of the encapsulated PCM directly to the fibre ("in fibre") is indeed quantitatively limited both by the fibre-forming technique and the need to preserve adequate fibre properties. Usually, the maximum that can be added does not exceed 15%. In the remaining methods, higher amounts are possible, but this leads to the disadvantage of reduced thermal insulation and increased surface mass caused by the presence of the capsules in the inter-fibre space of fabrics or nonwovens [18].

The aim of this work was to assess the suitability of modified PP fibres in the manufacture of nonwovens with special thermal properties. The modified PP fibre was prepared by melt spinning from a blend of PP and solid cosmetic paraffin which played the role of PCM. The paraffin was mixed directly with the PP in the melt without encapsulation. In terms of morphology, the material of obtained PP/paraffin fibres represented an "islands in

the sea" type, paraffin being the "islands" while PP makes the "sea".

Experimental part

Fibre-forming raw material

To form the fibres, blends were prepared of PP (Malen P type F 401 made by PKN Orlen, Poland) characterised by a melt flow index of $MFI_{230^{\circ}C}$ = 2.4 - 3.2 g/10 min, and solid paraffin (FP V and FP VI, produced by Pharma Cosmetic, Poland). Blends containing 10, 20 and 30 wt% paraffin were prepared in a single-screw extruder by multiple pressings through the extruder.

In each of the single runs, no more than 7% of paraffin was added, calculated on the basis of the remaining portion. The blending began at 238 °C, and the temperature was reduced to 198 °C in the consecutive runs.

Formation of the fibre

From the PP/paraffin blend, a fibre was prepared in a two-step process comprising spinning and drawing. Multifilaments were spun on an experimental extruder spinning bank at a temperature of 200 °C for the blend with 30 wt% paraffin and 230 °C for the blends containing 20 and 10 wt% paraffin. A nine-hole spinneret was used; the spinning speed was 600 m/min and throughput was 20.0 g/min.

The spinfinish Silastol 80 G31 (Schill & Seilacher GmbH) was applied in the course of spinning as a 20% aqueous emulsion. The multifilament yarn was drawn on a Rieter draw-winder at a draw ratio of 3.52 and a speed of 267 m/min. During drawing, the multifilaments were joined from nine spools, and then a cable was formed on a Barmag winder
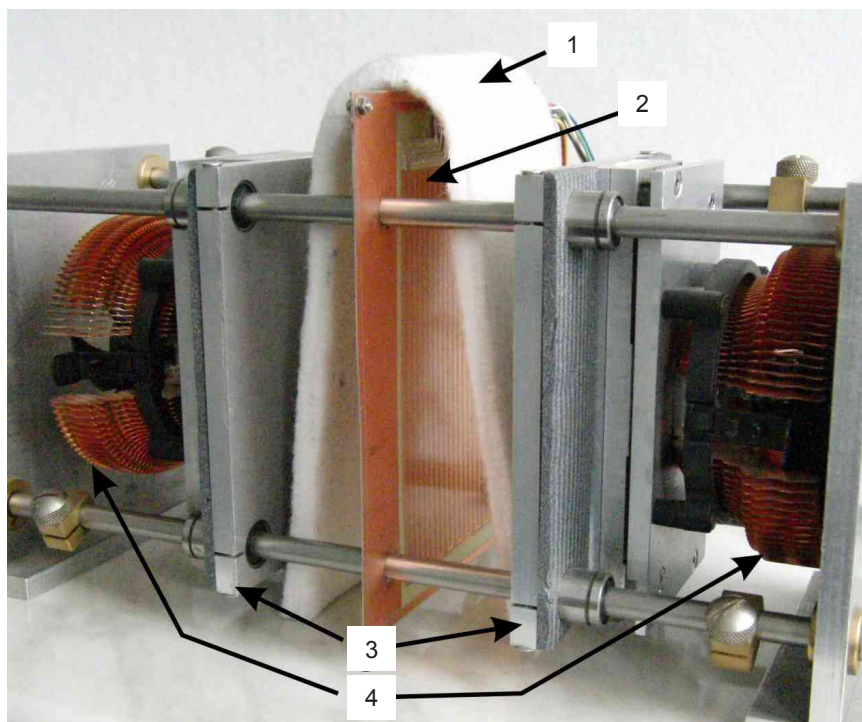
Figure 1. *Photo of the measurement cell of the TRF testing apparatus during preparation for measurements. The arrows indicate 1 – the sample of the nonwovens tested, 2 – the measurement plate, 3 - cold plates thermostatted with the use of air-cooled Peltier modules (4).*

EKS 210V consisting of 9×9×9 = 729 filaments. Two-step crimping was accomplished on an experimental thermomechanical device in which the cable was first crimped by three to four tiny crimps/cm and then "bent" by about 90° in 2 cm intervals. The crimps were fixed at 70 °C. The crimped cable was cut to a 52 mm staple length.

Formation of the nonwovens

To provide a proper feedstock for controlled carding, the prepared crimped staple PP/paraffin fibre was disintegrated to a mass of single loose fibres. From the loose PCM fibres, a card was formed by multiple overlapping of the fleece to arrive at the assumed surface mass. That was done on a laboratory Befama 3K

roller card. To provide a stable product, the formed three-layer fleece was needled at a density of 16 stiches/cm² on a Vulkan needling machine.

Analytical methods

Inspection of the fibre surface – A SEM Quanta 200 scanning electron microscope (FEI Co., USA) was used to this end. The images were recorded under high vacuum using the standard Everhart-Thornley detector at a voltage of 25 kV. The software analySIS Docu (Soft Imaging System Co.) was used to assess the thickness of the fibres.

Thermal properties - Phase transitions were examined using a DSC-2 differential scanning calorimeter and Diamond
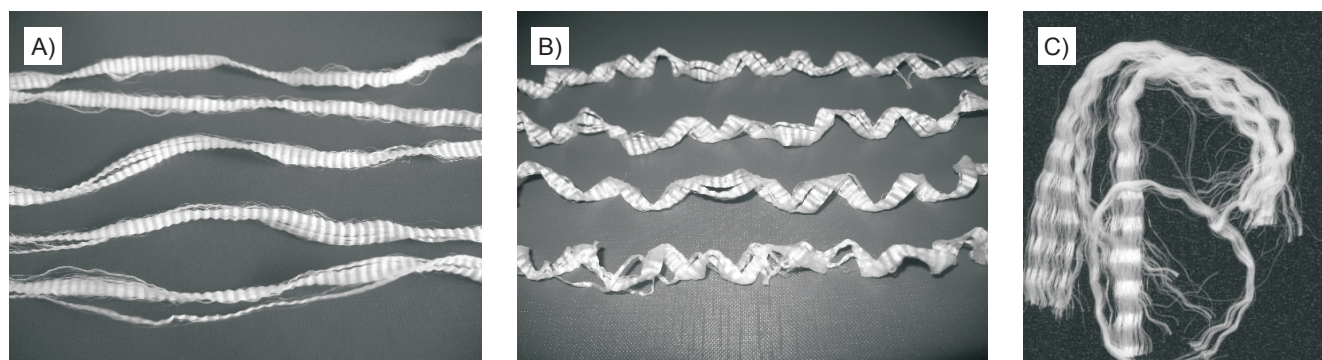
Figure 2. *Photographs of the two-step preparation of crimped paraffin-modified PP fibres in cable form. A - fine crimped cable; B - coarse crimped cable; C- crimped cable after cutting with visible loose fibres.*

Table 1. *Physical-mechanical properties of crimped PP fibers modified with paraffin.*

Parameter	Unit	1st crimping step		2nd crimping step	
		paraffin content		paraffin content	
		20%wt	30%wt	20%wt	30%wt
Linear density	dtex	12.4 ± 0.8	12.9 ± 0.2	12.4 ± 0.2	14.7 ± 0.7
	CV%	5.19	1.16	1.55	3.92
Breaking force	cN	42.6 ± 3.4	33.7 ± 2.1	30.7 ± 13.4	26.8 ± 1.3
	CV%	19.0	15.0	10.3	11.9
Tenacity	cN/tex	34.4	26.1	24.8	18.2
Elongation	%	226 ± 14	289 ± 27	19 ± 2	26 ± 2
	CV%	14.7	22.6	26.1	18.3
Loop breaking force	cN	65.1	55.3	54.9	45.0
	CV%	6.97	6.44	8.61	7.39
Loop tenacity	cN/tex	26.2	21.4	22.1	15.3
Relative loop tenacity	%	76.2	63.5	89.1	84.1
Young's modulus	cN/tex	187	128	755	483

Figure 3. *SEM photos of the surface and cross section of PP fibres modified with paraffin; a) paraffin 10%wt, b) paraffin 20%wt, c) paraffin 30%wt.*

(Pyris software) from Perkin-Elmer Co, USA.

Physical-mechanical properties of the fibres and nonwovens were assessed according to Polish standards.

The following measurements were made on the staple fibre:
- tenacity PN-EN ISO 5079
- elongation at break PN-EN ISO 5079
- loop tenacity PN-85/P-04761/04
- linear density PN ISO 1973
- initial drawing modulus PN-84/P-04669

Measurements on the nonwovens:
- thickness PN-EN ISO 9073-2:2002
- surface mass PN-EN 29073-1:1994
- breaking force, elongation at break PN-EN 29073-3:1994

The apparent nonwovens density was calculated as the quotient of surface mass and thickness.

Assessment of temperature regulation factor (TRF) – The device for this measurement was constructed by the Team of Special Fibres of IBChF according to outlines laid down in a standard [19] adapted, however, to slightly finer nonwovens samples. ***Figure 1*** shows the measuring cell of the device; it contains a hot plate in thermal contact with the nonwoven sample tested, and through the sample, with cold plates on both sides. The cold plate temperature was kept constant (thermostat), simulating the assumed ambient conditions. The measuring plate was prepared as a plated printed circuit on an electric insulator layer with a negligible thermal capacity. It was arranged in such way that the heaters and thermometers of the copper paths (after etching of the copper film) coincided on both sides. During the measurement, the plate was heated in such a way that its temperature changed according to a sine curve (period of 900 s), and the heat absorbed by the nonwoven sample was registered. DASYLab software and an A/C and C/A DaqBoard/2000 (IOtech Co) transducer card were used in the control system. The device was also used in the measurement of heat transfer resistance. The TRF parameter was calculated according to [20] from the equation:

$$TRF = \frac{(T_{max} - T_{min})}{(q_{max} - q_{min})} \times \frac{1}{R} \qquad (1)$$

where:
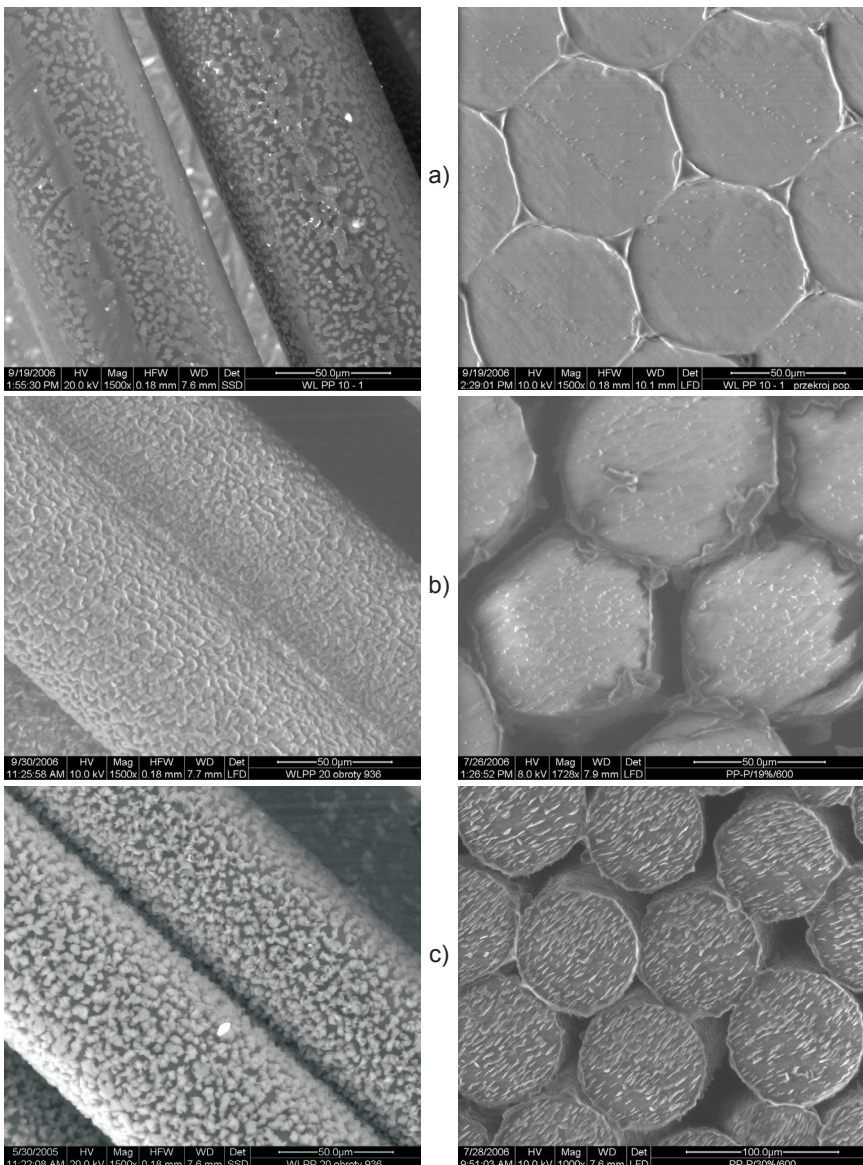
T_{max} and T_{min} is the temperature adequate to the maximum, q_{max}, and minimum, q_{min}, heat flux streaming through the material tested.

This is a non-dimensional parameter with a value in the 0 to 1 range. A value of 1 indicates thermally inactive materials (no PCM content) and decreases along with the material's ability to accumulate heat, provided that the thermal resistance does not decrease too much. It implies that the addition of the PCM does not always lead to a favourable (low) value of the TRF parameter.

■ Results and discussion

A careful selection of the PP quality was needed for the melt spinning of the PP/paraffin blend since the processing of the melt was burdensome at temperatures beyond 200 °C, caused by evaporation of the paraffin. After introductory attempts with various PP granulates, including the grade with $MFI_{230^oC} = 25 - 35$ g/10 min, $MFI_{230^oC} = 11 - 16$ g/10 min, samples could have been prepared in the amount of several kilograms of the modified PP fibres containing paraffin with a percentage content of 10, 20 and 30 wt%. The finally used PP granulate featured an MFI_{230^oC} of 2.4 - 3.2 g/10 min. For subsequent processing, the spun multifilaments were joined to a 9×9×9 multifilament system. Under pressure, the fibres are prone to stick to each other at elevated temperatures. This was the reason for using a unique two-step crimping method which enabled the preparation of staple fibres fit for further processing into the nonwovens. *Figure 2* shows the appearance of the fibre cable after the consecu-tive steps of crimping and the prepared staple fibre. In *Table 1* are presented the physical-mechanical parameters of the staple fibre after the consecutive steps of crimping and stabilisation. After the first crimping step, the fibre revealed high elongation which could cause disturbances during processing into the nonwovens. The second crimping step in which the fibre was bent at an angle of 90° and stabilised not only produced an additional crimp but also caused a distinct change in the fibre's mechanical properties. Tenacity was slightly decreased, while the initial modulus increased considerably and elongation decreased, largely easing processing into the nonwovens.

Figure 3 shows SEM micro-photos of the fibre surface and cross-section. Paraffin appears as lighter spots both in the cross-section and on the fibre surface. The amount discerned in this examination was equal to the actual mass proportion in the material used for spinning. This type of paraffin is brittle under ambient conditions, but adheres firmly to the fibre surface and is quite resistant to mechanical abrasion. As can be seen in *Figure 4*, the paraffin, though deformed, did not fall off the surface during cold drawing of the modified fibre. Addition of non-encapsulated paraffin as the PCM to the fibre-forming PP material led to an "island in the sea" structure which can be seen in the images of the fibre cross-sections. Quantitative examination was performed by means of the DSC method which enabled the assessment of thermal effects accompanying the proceeding phase transitions. In *Figure 5.A*, the DSC curve is shown for the heating and cooling of a fibre sample of PP, modified
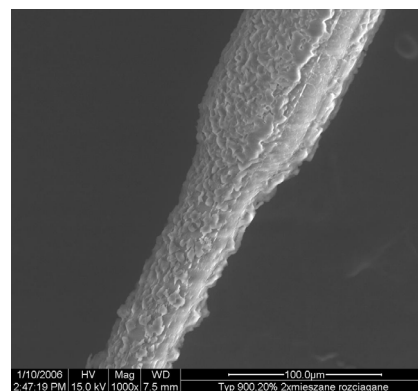
Figure 4. SEM photo of a neck appearing during cold drawing of the PP fibre modified with paraffin. The paraffin layer is not damaged during the drawing process.

with a paraffin content of 20 wt% in the full range of the reversible phase transitions. The qualitative analysis suggested that the paraffin and PP were a physical blend of two components. Melting and crystallisation typical of the singular components were separated, reflecting the phase division in the fibre. In *Figure 5.B*, the DSC curves are presented only in the paraffin range. The paraffin in the fibre changed its state of aggregation when heated, while the PP resin remained in the solid state, maintaining the fibre shape.

The DSC investigations in the paraffin range were performed cyclically in quick succession and, after 30 repeated cycles, no systematic quantitative changes were observed. However, the measured enthalpy of the paraffin component appeared to be lower than expected, which was particularly pronounced in the fibre modified with a 10 wt% portion of paraffin. With such fibres, broader testing
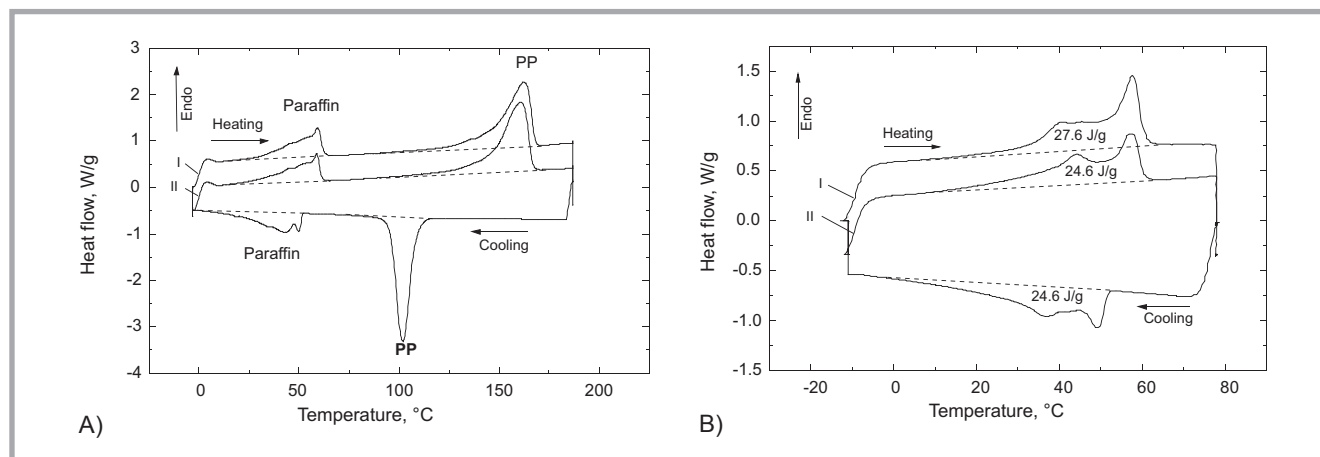
Figure 5. DSC curves of heating (I-first; II-second) and cooling at 20 °C/min for the paraffin- modified PP fibres A – full temperature range of reversible phase transitions (paraffin content of 20 wt%), B –temperature range restricted to paraffin thermal activity (PP left in solid state, paraffin content of 30 wt%).

Table 2. Enthalpy and specific enthalpy of paraffin component melting in PP fibres (PP/paraffin) with variable composition. Reproducibility of the crystalline phase of the paraffin component is given as well as its relative ability to crystallise; ΔHmp- melting enthalpy of paraffin in the mass amounts to 196.9 J/g in heating I and 194.2 J/g in heating II.

Content of parafin in fibre, wt%	Heating I $\Delta H_{m\,I}$, J/g		Heating II $\Delta H_{m\,II}$, J/g		Reproducibility of crystalline phase, $\dfrac{\Delta H_{mI}}{\Delta H_{mI}} \times 100\%$ %	Relative ability to crystallise $\dfrac{\Delta H_{mI}}{\Delta H_{mI}} \times 100\%$ %
	Per 1 g of sample	Per 1 g of component	Per 1 g of sample	Per 1 g of component		
10	9.9	99	4.9	40.0	40.0	20.6
20	27.6	138	24.6	123.0	89.0	63.3
30	38.1	127	38.0	126.7	99.7	65.2

was performed by estimating the melting enthalpy of the paraffin component in samples taken at varied storage times at ambient temperature after crystallisation in the DSC apparatus. The increase in the paraffin component enthalpy from 40 J/g to 100 J/g after 25 days is shown in **Figure 6**. It may be concluded that the paraffin must have formed a partially chemical blend with the PP during the melt blending and slow phase isolation proceeded only after the temperature decreased. The causes of the observed phenomenon may also be explained to a certain degree with the appearance of paraffin micro-regions deprived of impurities and forming crystal nuclei. Because of the observed lower crystallisation ability of the paraffin component, the DSC examination was broadened and two parameters were added to the characteristics of the behaviour of the prepared materials:

1. Reproducibility of the crystal phase in the thermal cycle measured as:

$$\frac{\Delta H_{mI}}{\Delta H_{mI}}x100\% \qquad (2)$$

where: ΔH_{mII} is the melting enthalpy of the paraffin component in the second heating phase, ΔH_{mI} is the melting enthalpy of the paraffin component in the first heating phase.

2. Relative crystallisation capacity measured as:

$$\frac{\Delta H_{mI}}{\Delta H_{p}}x100\% \qquad (3)$$

where: ΔH_{mII} is the melting enthalpy of the paraffin component in the first heating phase, ΔH_{mp} is the melting enthalpy of the paraffin in the mass in the second heating phase (194.2 J/g).

The first of these parameters characterises the ability to re-establish the crystalline phase in the paraffin portion when the test material is submitted to the first cycle of temperature change in the DSC apparatus (in the range of phase transitions in paraffin). The parameter may depend upon the thermal conditions of nonwovens storage and is therefore related to the thermo-control properties of the nonwovens. A higher value of this parameter means better stability. The second parameter expresses the ability to re-establish the crystalline phase in the paraffin in the product in proportion to paraffin in the mass and is related to the efficacy of the use of paraffin as a PCM. The most desired value is close to 100% of both parameters (a physical blend with an undisturbed ability to crystallise). The proposed parameters were estimated for all paraffin-modified PP fibres, and are presented in **Table 2**. Very low values of both parameters were found for the PP fibres modified with 10 wt% paraf-

fin. Unstable behaviour may therefore be expected regarding the thermal properties of such fibres as well as a very low thermal efficiency. Conversely, PP fibres modified with a higher paraffin content showed a high ability to restore crystalline phase in the thermal cycle that suggests stable thermal activity in the final product. The relative crystallisation ability of the paraffin component of the fibres at a level of 63 - 65% seems to be a feature assigned to the system of only these components. In other words, the use of another kind of paraffin or PP could cause a change in this parameter. In the light of these results, fibres with low content of paraffin were abandoned. A blend of PP fibres modified with 20 wt% paraffin with standard staple PP fibres (4.4 dtx, 40 mm) was used in the weight proportions of 35/65 and 85/15 to provide good processability and adequate mechanical properties of the product. The use of PP fibres modified with 30 wt% of paraffin will be the subject of future research.

The physical-mechanical properties of the nonwovens prepared are presented in **Table 3**. A strong, nonlinear increase in tenacity in both directions can be seen with increasing thickness of the nonwovens. The effect was seen in both the 35/65 and 85/15 blends, accompanied by an increase in the apparent density and elongation at break. It appears that this is the result of obtaining a greater degree of consolidation of the fibres in the nonwovens. The obtained thermal properties deserve particular attention. All of the nonwovens showed a relatively high thermal resistance, which may stem from their thickness of 5 - 10 mm and high inherent thermal insulation typical for this sort of material. This feature may be disturbed by the introduction of an encapsulated PCM into the areas between the fibres, as is the case in alternative technologies, resulting in certain decrease in thermal insulation [18]. On the other hand, the thermal conductivity

Table 3. Physical-mechanical and thermal properties of PCM nonwoven material.

Content modified PP/PP, wt%	Thickness, mm	Surface mass, g/m²	Apparent density, kg/m³	Breaking force, N		Elongation at break, %		Melting enthalpy of paraffin in nonwovens during second heating		Thermal resistance m²×°C/W	TRF
				Longitudinal direction	Lateral direction	Longitudinal direction	Lateral direction	Expected, kJ/m²	Measured, kJ/m²		
35/65	6.26 ± 0.31	496 ± 28	79.2	72.5 ± 32.6	33.3 ± 13.4	103 ± 21	101 ± 9	4.57	4.81	0.129	0.724
35/65	5.38 ± 0.19	405 ± 8	75.3	288 ± 28	171 ± 45	199 ± 16	163 ± 24	3.73	3.69	0.119	0.823
35/65	7.37 ± 0.40	765 ± 15	103.8	1099 ± 162	1263 ± 42	289 ± 5	273 ± 32	7.04	7.27	0.139	0.601
85/15	9.53 ± 0.45	1044 ± 36	109.5	957 ± 87	391 ± 239	164 ± 3	128 ± 48	23.34	19.42	0.156	0.401
85/15	4.54 ± 0.29	291 ± 33	64.1	56.8 ± 31.0	6.79 ± 2.15	42.6 ± 5.0	83.8 ± 10.4	6.51	6.46	0.108	0.829
85/15	6.55 ± 0.22	542 ± 66	82.7	42.2 ± 17.4	12.1 ± 2.4	68.9 ± 5.7	70.0 ± 10.5	12.12	11.92	0.137	0.633
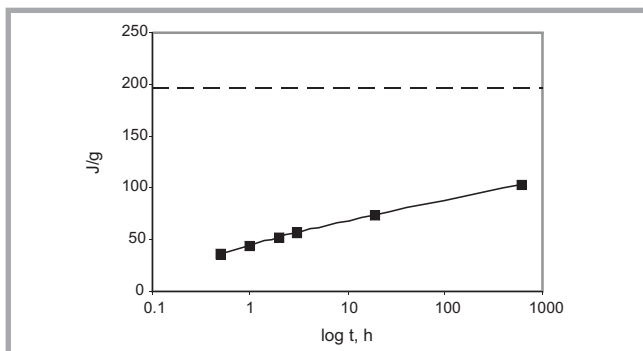
Figure 6. *Dependence of paraffin melting enthalpy (on 1 gram of the paraffin component) in PP fibres modified with 10 wt% paraffin on the its crystallization time during storage of the fibre at ambient conditions. The dashed line indicates the level of paraffin melting enthalpy in the mass.*
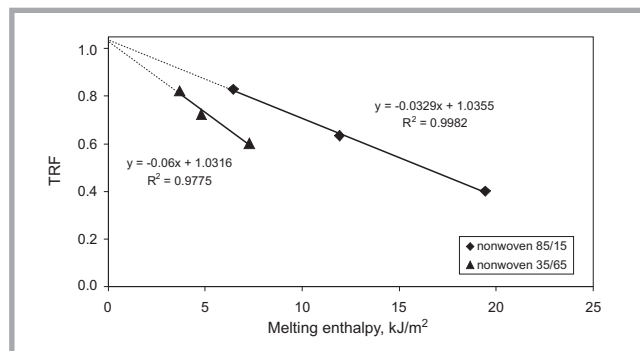
Figure 7. *Dependence of the TRF coefficient upon melting enthalpy of the paraffin component per unit of the nonwoven surface.*

coefficient calculated from the data in *Table 3* concerning the nonwovens described herein shows an undesired linear growth with increasing apparent density. However, higher apparent density means greater mechanical strength, which may be necessary in many applications. The previously indicated thermal behaviour stability of the PCM component in the nonwoven fibres enables a reliable prediction of the heat accumulation ability of the nonwovens; see *Table 3* (melting enthalpy of paraffin in nonwovens during the second heating phase). Presently, the TRF coefficient seems best characterised in the nonwovens prepared in relation to the introduced PCM. The values of this coefficient reached a level of 0.4, while maintaining thermal resistance, suggestive of high thermo-regulation ability, at least in some of the nonwovens. The dependence of the TRF coefficient drawn from the function of melting enthalpy on the nonwovens surface unit is shown in *Figure 7*. A strict linear dependence was achieved for every kind of nonwovens. Extrapolation to a zero content of PCM yielded the expected value of 1 with good accuracy. The linear dependence between these parameters has been reported in another study [18].

■ **Summary**

A method was devised for the experimental-scale preparation of staple PP fibres modified with paraffin acting as a PCM. The paraffin was not encapsulated, hence a structure of "islands in the sea" was obtained, with paraffin being the "islands" and PP the "sea". Such an arrangement offers the opportunity for a higher content of the active substance in the fibre compared to the encapsulated version and, additionally, the nonwovens prepared maintain high thermal resistance. Needle punched nonwovens were prepared from a blend of PP fibres modified with a 20 wt% content of paraffin and regular PP fibres in weight proportions of 35/65 and 85/15. The nonwovens featured a relatively high apparent density of 64 - 110 kg/m^3 and a high heat accumulation capacity of 3.7-7.3 kJ/m^2 in the 35/65 material and 6.5-19.4 kJ/m^2 in the 85:15 material. The TRF coefficient value was 0.4 along with the preserved high thermal resistance of 0.156 m^{2}xK/W, indicating the high thermo-regulating ability of at least some of the nonwovens prepared.

References

1. Van Langenhove L, Hertleer C. Smart clothing: a new life. *International Journal of Clothing Science and Technology* 2004; 16, 1/2: 63-72.
2. Tao X. *Smart Fibres, Fabrics and Clothing.* Woodhead Publishing Ltd., 2001.
3. Vincenzini P, Paradiso R. *Smart textiles.* Trans Tech Publications Limited, 2009.
4. Vigo TL, Bruno JS. Temperature-adaptable textiles containing durably bound polyethylene glycols. *Text Res J.* 1987; 57 (7): 427-429.
5. Zuckerman JL, Pushaw RJ, Perry BT, Wyner DM. *Fabric coating containing energy absorbing phase change material and method of manufacturing same.* US Patent 6 514 362, 2003.
6. Pause B. Thermal insulation effect of textiles with phase change materials. *TTI* 1999; 9: 21-26.
7. Shim H, McCullough EA, Jones BW. Using Phase Change Materials in Clothing. *Tex. Res. J.* 2001; 71 (6): 495-502.
8. Bendkowska W. Microencapsulation technology in textile industry. Part I: A basic overview (in Polish). *Przegląd Włókienniczy* 2006; 3: 36-39.
9. Bryant YG, Colvin DP. *Fibre with reversible enhanced thermal storage properties and fabric made there from.* US Patent 4 756 958, 1988.
10. Colvin DP, Bryant Y.G. *Thermally enhanced foam insulation.* US Patent 5 637 389, 1996.
11. . Bryant YG, Colvin DP. *Fabric with reversible enhanced thermal properties.* US Patent 366 807, 1994.
12. Pushaw RJ. *Coated skived foam and fabric article containing energy absorbing phase change material.* US Patent 5 677 048, 1997.
13. www.outlast.com
14. Mondal S. Phase change materials for smart textiles – An overview. *Applied Thermal Engineering* 2008; 28: 1536-1550.
15. Cabeza LF, Castellon C, Nogues M, Medrano M, Leppers R, Zubillaga O. Use of microencapsulated PCM in concrete walls for energy savings. *Energy and Buildings* 2007; 39: 113-119.
16. Magill MC, Hartman MH, Haggard JS. Multi-component fibers having enhanced reversible thermal properties and methods of manufacturing thereof. WO/2006/086031.
17. Magill MC, Hartman MH, Haggard JS, Brang JE. *Multi-component fibers having enhanced reversible thermal properties.* US Patent 7 666 500, 2010.
18. Bendkowska W, Wrzosek H. Experimental study of the thermoregulating of nonwovens treated with microencapsulated PCM. *Fibres & Textiles in Eastern Europe* 2009; 17, 5(76): 87-91.