Research Article

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Enhancement of thermal properties of bio-based microcapsules intended for textile applications

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Abstract: The thermal properties of bio-based phase change material (PCM) microcapsules and their separate components, core and shell, were investigated considering the influence of used thermal enhancer. As a core, bio-based PCM, capric acid (CA), was used. Biodegradable material, such as polylactic acid (PLA), was used as a shell. To improve the thermal conductivity of PLA/CA microcapsules, the multiwall carbon nanotubes (MWCNTs) were used as a thermal enhancer. Composites of PCM with different concentrations of MWCNT as well as composites of PLA with these carbon compounds were prepared and investigated to assess how MWCNT influences the thermal conductivity of the core and the shell. The heat storage and release capacity, as well as the phase change temperatures of CA/MWCNT composites and manufactured PCM microcapsules, were determined using differential scanning calorimetry. To evaluate the thermal conductivity of prepared composites and to compare it with the conductivity of pure materials (without MWCNT), their thermal resistance was measured using the guarded-hotplate test method. To obtain the supplementary information and to assess the dynamic behavior of used PCM during the temperature changes, another technique, such as monitoring of a cold/hot plate with an IR camera, was used. The results of these measurements showed that introduced MWCNT increases the thermal conductivity of PCM used for the core and the conductivity of films prepared from PLA. Consequently, with reference to the

results obtained, it could be stated that the introduction of MWCNT into PLA/CA microcapsules improved the thermal properties of these microcapsules. However, it was determined that too large concentration of MWCNT reduces an enthalpy of melting and crystallization of tested PCM and PCM microcapsules. Therefore, during the investigation, an optimal concentration of MWCNT additives has been determined.

Keywords: textiles, bio-based PCM, carbon nanotubes, heat storage, heat release, differential scanning calorimetry

1 Introduction

One of the main purposes of wearing clothes is the comfort of the body. Comfort can be classified into four major classes such as thermal or thermophysiological comfort, sensorial comfort, physiological comfort, and garment fit [1]. The thermal factor is the most decisive one affecting the comfort level [2]. Thermal energy storage is the main concept of making thermoregulated fabrics. Thermal energy can be stored as sensible heat, latent heat, or thermochemical energy. The latent heat storage method is mostly used for thermoregulated fabric as in latent heat storage method high storage density is possible to achieve under nearly isothermal conditions [1,3]. Phase change materials (PCMs) represent an interesting potential energy carrier due to their high latent heat and capacity for energy transfer [4–6]. Organic PCMs can be divided into main parts, such as pure alkanes, paraffins, fatty acids and their derivatives, and polyols [7]. Researchers used a broad range of PCM materials such as eicosane [8], *n*-octadecane [9], fatty acids, such as stearic acid, palmitic acid, myristic acid, and lauric acid, and their blends [10,11], polyethylene glycol (PEG-100) [12], PEG 100 with Na-alginate [13], paraffin and nanomagnetite [14], butyl stearate [15], and others. Organic PCMs are a particularly well-suited candidate for energy storage owing to their especially high latent heat. For textiles application, the paraffinic

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petroleum-based phase-changing materials are the most commonly used, which are characterized by relatively high latent heat. However, their broad applications are limited due to high flammability and low thermal conductivity [16,17]. Furthermore, fossil fuels are used for the production of paraffin; therefore, it is not considered to be eco-friendly material. Only recently a new alternative of non-paraffinic PCM, the use of fatty acids or their esters was introduced. Despite the suitable origin of these bio-sourced materials, they have a major drawback, low thermal conductivity, which severely reduces the rate of heat storage and extraction during the melting and solidification cycles. The thermal conductivity of most PCMs, including bio-based PCMs, is typically in the range of 0.15–1 W/mK [17], and it means these are too low to provide a required heat exchange rate between the PCM and substrate. Therefore, a thermal conductivity enhancer would be useful to use efficiently the thermal energy stored in the PCM. Using bio-based PCM filled with high thermal conductivity materials could be a good strategy to enhance the thermal properties of the PCM. The thermal conductivity of PCM could be enhanced by using metal fillers, carbon nanofiber fillers, carbon nanotubes, expanded graphite, or exfoliated graphite nanoplatelets [14,18–22]. The thermal conductivity of carbon-based fillers is considerably high and their densities are lower than those of metals. The form of thermal conductivity enhancers also influences their effectiveness.

It is common knowledge in heat transfer that when lateral surface area increases, the heat transfer rate also increases [15]. Consequently, rod-type fins, such as carbon nanotubes, could perform better than plate-type ones, for example, expanded graphite or exfoliated graphite nanoplatelets. Therefore, in this study, carbon nanotubes were selected as efficient thermal conductivity enhancers for PCM intended for textile applications.

PCM has been applied to textiles in a variety of processes such as coating, lamination, finishing, melt spinning, bi-component synthetic fiber extrusion, injection molding, and encapsulation [5]. Our goal was to manufacture bio-based PCM microcapsules intended for textile applications and explore their thermal properties. As a core, bio-based PCM, capric acid (CA), was used. Biodegradable material, such as polylactic acid (PLA), was used as the shell.

PLA is a linear aliphatic thermoplastic polyester that can be derived from renewable resources [23,24]. Usually PLAs are used for the pharmaceutical field [25] as contrast agents in ultrasound imaging [26] and others.

Microencapsulated PCMs can be incorporated into textile structures to produce fabrics with thermoregulating

properties [27]. The most convenient form of their use in the textile industry is core-shell microcapsules. Many researchers had produced microcapsules [28–36].

This study aimed to investigate the possibility to improve the thermal conductivity of produced microcapsules, using multiwall carbon nanotube (MWCNT) as a thermal enhancer. Therefore, the thermal properties of bio-based PCM microcapsules and their separate components, core and shell, were investigated considering the influence of used thermal enhancer.

The analysis of the textile materials with incorporated synthesized PCM microcapsules will complement the research works presented in this paper as a subsequent, separate publication.

2 Methods

2.1 Materials

As the core for the synthesis of microcapsules, bio-based PCM, CA, was used. Biodegradable material, such as PLA, was used as the shell. To improve the thermal conductivity of PLA/CA microcapsules, the MWCNTs were used as a thermal enhancer.

CA (decanoic acid, 99%) of analytical grade was bought from ACROS organics. For the improvement of thermal properties of PCM MWCNT NC7000 aqueous dispersion AQUACYL AQ0302 (producer Nanocyl SA) was used. PLA (Ingeo 6202D Nature works) was used to fabricate the shell of microcapsules.

To analyze the impact of thermal enhancer, MWCNT, on thermal properties of PCM microcapsules, primarily the influence of MWCNT for the thermal conductivity of core and shell was investigated, as it is not possible to control separately the amount of MWCNT in the core and the shell during the encapsulation process. Due to this, separate composites, CA/MWCNT and PLA/MWCNT, were prepared and tested.

2.1.1 Preparation of CA/MWCNT composites

Preparation of composite was carried out by mixing a CA with different contents of MWCNTs (0.5%, 1%, and 3%) using a magnetic stirrer, and after mixing additionally with a mechanical stirrer for 120 min at the rate of 600 rpm/min and a temperature of 60°C (Figure 1 and Table 1). The prepared composites were poured into Petri plates with the same size of 90 mm diameter and 15 mm height, which were intended for further investigation as the core of microcapsules.

Figure 1: Preparation of CA/MWCNT composite.

Table 1: Description of samples

CA (only capric acid)
CA-0.5C – capric acid with 0.5% MWCNT
CA-1C – capric acid with 1% MWCNT
CA-3C – capric acid with 3% MWCNT

2.1.2 Preparation of PLA/MWCNT composites

To prepare PLA/MWCNT composites, MWCNT was incorporated into the shell material, PLA. The dependence of PLA thermal conductivity on the quantity of incorporated MWCNT was measured. The films from PLA/MWCNT composites were produced by the following sequence: applying dispersion apparatus T25 digital ULTRA-TURRAX (IKA) 1% and 3% of MWCNTs were incorporated into the solution of the PLA in dichloromethane (DCM), then films of 16 cm × 16 cm size produced were left in the room temperature for the formation. In this way, films from shell material PLA, only PLA (control sample) and PLA with additives 1% and 3% MWCNT, were produced (Table 2).

2.1.3 Preparation of coated samples

To assess the dynamic thermal behavior of used PCM (see Section 2.2.3), the prepared CA/MWCNT composites were coated manually on the 3D PES knitted fabric by the screen printing method. In this study were investigated – 3D PES knitted fabric without coating, coated

Table 2: Description of samples

PLA – 0 (only PLA [control sample])
PLA-C1 – PLA with 1% MWCNT
PLA-C1 – PLA with 3% MWCNT

Table 3: Description of samples

F-K – control specimen (3D PES knitted fabric, further – fabric)
F-CA – fabric coated with CA
F-CA 0.5C – fabric coated with CA + 0.5% MWCNT
F-CA 1C – fabric coated with CA + 1% MWCNT
F-CA 3C – fabric coated with CA + 3% MWCNT

with pure CA and CA/MWCNT (0,5%, 1% and 3%) composites (Table 3).

2.1.4 Encapsulation

PLA was used to fabricate the shell of the microcapsules. CA (decanoic acid) (Acros Organics BVBA) was used as the core of the microcapsules. Polyvinyl alcohol (PVA; Acros Organics BVBA), with an average molecular weight of 1,46,000–1,86,000 g mol⁻¹ and 87%–89% hydrolyzed, was used as the emulsifier. DCM (Chempur), with a density of 1,320 kg–m⁻³, was used as the solvent for the oil medium. Deionized water was used as an aqueous medium. All materials and chemicals were used as received. The physical properties of PLA and CA (decanoic acid) are summarized in Table 4.

Microencapsulation of the capric core in the PLA shell was conducted by the solvent evaporation method accompanied by oil in water emulsification [23]. In general, the fabrication process involves four main steps: (1) dissolution of CA and PLA in DCM; (2) emulsification of this organic phase (i.e., dispersed phase) in a continuous aqueous phase of deionized water containing PVA; (3) extraction and evaporation of solvent from the dispersed phase, which transforms the dispersed phase into solid microspheres (i.e., microcapsules); and (4) recovery and drying of microcapsules to eliminate residual solvent and emulsifier. For the

Table 4: Physical properties of PLA and of CA (decanoic acid)

Materials	Density (kg m ⁻³)	Crystalline melting temperature (°C)	Glass transition temperature (°C)	Boiling temperature (°C)
PLA	1,240	170	58–61	—
CA (decanoic acid)	890	30–32	—	268–270

aqueous phase, a 5% PVA solution was prepared by dissolving 5 g of PVA in 95 mL of deionized water. The solution was cured for 30 min at room temperature. After it swelled, it was heated up to 80°C for 2 h to completely dissolve PVA. The oil phase, 1.2 g of PLA, and 1 g of CA were added to 29 mL of DCM. The oil phase was cured for 2 h to obtain a PLA–CA solution. When the preparation of both phases was conducted, 10 g of PLA–CA solution was added to 80 g of PVA solution. The oil–water system was first stirred by a magnetic stirrer at 300 rpm for 3 h at room temperature. Then, emulsion was stirred at 1,000 rpm for 10 min using a mechanical stirrer. In the next steps, DCM was evaporated by elevating the emulsion temperature to 45°C while the emulsion was continuously stirred at 200 rpm for 1 h. The solution was kept at room temperature for 24 h to precipitate the fabricated microcapsules. Then, microcapsules were repeatedly washed with deionized water at 60°C and were filtrated to remove the PVA residues. The filtrated microcapsules are first dried in an oven and then in a desiccator (Figure 2). Similarly, the microcapsules were prepared with the CA and 1% MWCNT. The composite CA 1C, whose preparation is described in Section 2.1.1, was used.

2.2 Methods of investigation

2.2.1 Heat storage and release capacity determination (of CA, CA/MWCNT composites, and microcapsules)

The heat storage and release capacity, as well as the phase change temperatures of PCM – pure CA and CA/MWCNT composites and microcapsules as well, were determined by the standard method EN 16806-1, using differential scanning calorimetry (DSC; Instrument, DSC Q10). The samples underwent a heating–cooling–heating cycle from –20°C to 60°C at a heating and cooling rate of 5°C/min.

2.2.2 Thermal conductivity (of CA, CA/MWCNT composites and PLA, PLA/MWCNT composites)

The thermal conductivity of the shell (PLA) and core materials (CA), used for the manufacturing of bio-based

PCM microcapsules, was evaluated based on the measurements of reciprocal parameter – thermal resistance (R_{ct}).

To this purpose, the films made from the shell material, PLA and PLA composites with different loadings of carbon nanotubes (MWCNT), were prepared and measured. The thermal resistance values of the core, pure CA, and the composites of CA with MWCNT were also measured.

R_{ct} under steady-state conditions was measured using sweating guarded-hotplate (apparatus-M259B Sweating guarded hotplate) according to the modified standard method ISO 11092:2014. The principle of this method is that the specimen to be tested is placed on an electrically heated plate with conditioned airflow across and parallel to its upper surface. For the determination of thermal resistance, the heat flux through the test specimen is measured after the steady-state conditions have been reached.

The thermal resistance R_{ct} (m²K/W) was measured in the following way: the difference of the temperature between the two faces of the material was divided by the resultant heat flux per unit area in the direction of a steadily applied temperature gradient.

During the test, an area of measurement unit of 0.04 m² was diminished till 0.004 m² by covering it with the thermal insulating material. The samples of films prepared from the shell material were placed directly on the measuring unit, an electrically heated plate, and the samples of core material were placed into the tubes with a bottom of liquid–water impermeable cellophane membrane (to prevent PCM leakage during its melting).

Thermal resistance was calculated using the following formula:

$$R_{ct} = \frac{(T_m - T_a)A}{H - \Delta H_c} - R_{cto} [\text{m}^2 \text{ K/W}]$$

where T_m = 35°C (temperature of the measuring unit), T_a = 20°C (air temperature in the test enclosure), H is the heating power supplied to the measuring unit, in watts, A is the area of measuring unit in square meters, R_{cto} is the apparatus constant, in square meters kelvin per watt, $\Delta H_c = 0$ (correction term for heating power), coefficient

Figure 2: (a) Preparation of microcapsules and (b) image of the prepared microcapsules.

of the thermal conductivity λ , W/(m K), was calculated using the formula:

$$\lambda = D/R_{ct} \text{ [W/(m K)]}$$

where D is the thickness of the sample (m) and R_{ct} is the thermal resistance ($\text{m}^2 \text{K/W}$).

2.2.3 Evaluation of dynamic thermal behavior (of coated fabrics)

To obtain the supplementary information and to assess the dynamic thermal behavior of used PCM when the temperature changes, another technique, such as monitoring of a cold/hot plate with an IR camera, was used. For this purpose, textile samples coated with PCM, pure CA and of CA/MWCNT composites, were prepared and tested.

The electrically heated measuring unit of apparatus, M259B Sweating guarded hotplate, was used as a plate. Test samples were placed across the measuring unit, with the backside (not coated with PCM) toward the measuring unit (face side on the top). The samples were heated approximately till the melting temperature of the used PCM. The outer surface temperature of the samples was periodically recorded with a calibrated thermal imaging camera, InfraCam (FLIR SYSTEMS AB, Sweden), operating in the mid-infrared wavelength range ($7.5\text{--}13\ \mu\text{m}$) and providing detailed thermographic images. For the analysis of images, FLIR tools+ software was used.

2.2.4 SEM (of microcapsules)

PLA/CA synthesized microcapsules morphology was investigated by scanning electron microscopy (SEM) using Quanta 200 FEG device (FEI Netherlands) at 20 keV (low vacuum). All microscopic images were taken

in the same technical and technological conditions: electron beam heating voltage $-20.00\ \text{kV}$, beam spot -5.0 , magnification $-500\times$, $5,000\times$, working distance $-6.0\ \text{mm}$, low vacuum $-80\ \text{Pa}$, and detector – LFD.

Ethical approval: The conducted research is not related to human or animal use.

3 Results and discussion

As it can be seen from the results presented in Table 5 and Figure 3, the incorporation of MWCNT into CA (MWCNT NC7000 aqueous dispersion AQUACYL AQ0302 (producer Nanocyl SA)) has a certain influence on the enthalpy and phase change temperatures of investigated PCM. In all cases, the presence of MWCNT reduces the peak of melting temperature by about 1°C and the peak of crystallization temperature is even less. However, the onset of melting temperature of the composites differs relatively significantly from CA melting start temperature, that is, to say, the additives of MWCNT accelerate the melting process of CA. The influence of used carbon compounds on the reduction of CA onset melting temperature depends on its concentration in composite – the higher the MWCNT concentration, the lower the melting start temperature (Table 5). Although the addition of MWCNT has a negligible effect on the peak of melting and crystallization temperatures of CA, it reduces the enthalpy of fusion and crystallization as the concentration increases. Only samples of composites with 0.5% of MWCNT have similar heat storage and release capacity as pure CA. The increase in MWCNT concentration up to 1% or 3% reduces the enthalpy of fusion by about 5% and the enthalpy of crystallization by about 10% and thereby turns down the heat storage and release capacity of used PCM.

Table 5: Thermal properties of investigated PCM and its composites with carbon nanotubes determined using the DSC method

Sample code	Melting		Crystallization					
	Peak melting temperature, $T_{p,m}$, °C	Extrapolated onset melting temperature, $T_{ei,m}$, °C	Extrapolated end melting temperature, $T_{ef,m}$, °C	Enthalpy of fusion, ΔH , J/g	Peak crystallization temperature, $T_{p,c}$, °C	Extrapolated onset crystallization temperature, $T_{ei,c}$, °C	Extrapolated end crystallization temperature, $T_{ef,c}$, °C	Enthalpy of crystallization, ΔH , J/g
CA	33.73	26.23	43.10	144.9	26.30	27.00	14.73	151.7
CA-0.5C	32.57	24.00	40.83	148.0	26.55	27.67	16.13	153.4
CA-1C	32.65	21.85	41.91	138.0	26.09	27.45	15.95	139.5
CA-3C	32.35	19.55	41.35	138.3	25.25	27.70	14.05	132.2

From the results of DSC analysis, it can be concluded that the optimal amount of MWCNT in composites with CA could be in the interval from 0.5% to 1%, as the higher amount of additive reduces positive properties of heat storage and release capacity of CA.

The DSC test was performed with microcapsules as well. There were two kinds of microcapsules used with PLA/CA and with PLA/CA and with 1% of MWCNT (PLA/CA + C).

The morphology of PLA/CA synthesized microcapsules was investigated using SEM (Figures 4 and 5). These figures illustrate the microscopic morphology of microcapsules fabricated by different recipes with and without WMCNT. The micrographs reveal that all microcapsules were spherical and had a considerably smooth surface. Some pores were observed to be on their surface and were believed to be caused by the evaporation of DCM from the inner region of the emulsion. Figure 5b is a microscopic picture of microcapsule darkening possibly due to the introduction of WMCNT into the composition of the microcapsules. Both types of microcapsules have morphologically similar images. Differences are only observed from the result obtained in the size distribution of microcapsule (Figures 6 and 7). A larger distribution of particle size is observed, within microcapsules containing WMCNT. Although the manufacturing conditions of both types of microcapsules were the same, only the composition differed, the use of WMCNTs is likely to have influenced the size of the microcapsules and the diameter of distribution results.

For the DSC test, four specimens of each kind of microcapsules were used. Results are presented in Table 6.

The phase change latent heat of microcapsules can be determined by calculating the area under the endothermic peak. The encapsulation efficiency of PLA/CA microcapsules can be calculated using the following equation:

$$\text{Encapsulation efficiency} = (\Delta H / \Delta H_{\text{PCM}}) \times 100\% \quad (1)$$

where ΔH and ΔH_{PCM} are the latent heat of fusion of microcapsules and CA, respectively.

The peak of melting temperature, enthalpy of fusion, and enthalpy of crystallization were determined. The results revealed that melting and crystallization temperatures of PCM in the microcapsules are equal. The results show that the beginning and the end of the glass transition remain unchanged. Also, the enthalpy of fusion of PLA/CA + C is lower than PLA/CA only in 4%, for example, MWCNT reduces the enthalpy of fusion only in 4%. Also, the content of MWCNT 1% slightly

Figure 3: DSC thermal curves of tested PCM and prepared composites: CA (a), CA/0.5% MWCNT (b), CA/1% MWCNT (c), and CA/3% MWCNT (d).

Figure 4: SEM micrograph of microcapsules (PLA/CA (a) and PLA/CA + C (b)).

reduces enthalpy of crystallization, but further results of thermal behavior of PCM and PCM + MWCNT on fabric

showed that the MWCNT content increases the rate of glass transition.

a)

b)

Figure 5: SEM micrograph of microcapsules (PLA/CA (a) and PLA/CA + C (b)) (bigger increase).

Figure 6: Distribution of particle size in the microcapsules PLA/CA.

To evaluate the thermal comfort and to assess the thermal behavior of PCM and its composites (core of microcapsules) and PLA, and also its composites (shell of microcapsules), the thermal resistance test was performed. According to the obtained results of thermal resistance, the coefficients of thermal conductivity and surface resistivity were calculated. For this purpose, CA and CA composites with MWCNT and the PLA and PLA

composites with MWCNT were tested. As shown in Tables 7 and 8, although the thickness of PCM layers D is not precisely the same, but the same rank, MWCNT influences the coefficient of thermal conductivity of PCM, coefficient of thermal conductivity is increasing according to the increase in MWCNT in PCM. The same process can be noticed in PLA and PLA composites with different loadings of MWCNT. The coefficient of thermal

Figure 7: Distribution of particle size in the microcapsules PLA/CA + C.

Table 6: Thermal properties of investigated microcapsules with PCM and with PCM with carbon nanotubes determined using the DSC method

Sample code	Melting		Encapsulation efficiency, % (by latent heat of melting)		Crystallization		Enthalpy of crystallization, ΔH , J/g
	Peak melting temperature, $T_{p,m}$, °C	Extrapolated onset melting temperature, $T_{el,m}$, °C	Extrapolated end melting temperature, $T_{ef,m}$, °C	Enthalpy of fusion, ΔH , J/g	Peak crystallization temperature, $T_{p,c}$, °C	Extrapolated onset crystallization temperature, $T_{el,c}$, °C	
PLA/CA	33.82	26.28	42.02	35.99	24.29	15.92	21.70
Standard deviation	0.63	0.22	1.01	2.30	0.12	1.13	2.49
PLA/CA + C	33.83	26.62	42.04	30.86	24.31	16.28	18.31
Standard deviation	0.34	0.50	0.13	2.32	0.21	1.06	0.71

Table 7: Thermal conductivity of core material (pure CA and composites of CA with MWCNT)

Code of sample	Thickness of PCM layer D , mm	Coefficient of thermal conductivity λ , W/(m K)
CA	9	0.214
CA-0.5C	9	0.225
CA-1C	8	0.242
CA-3C	10	0.272

conductivity is rising according to the increase in MWCNT amount in PLA. Moreover, the surface resistivity of PLA composites is decreasing when the quantity of MWCNT increases.

To obtain supplementary information and to assess the dynamic thermal behavior of used PCM when the temperature changes, another technique, monitoring of a cold/hot plate with an IR camera, was applied. For this purpose, textile samples, control sample, and samples coated with pure CA and with CA/MWCNT composites were prepared and tested. Textile material was used just as the basis for coating since the main aim of this test was to evaluate the thermal behavior of CA and CA/MWCNT composites.

As shown in Figure 8 and Table 9, MWCNT influences the thermal behavior of used PCM, the surface temperature of fabrics coated with composites increases more rather than in samples with pure CA. The concentration of MWCNT has no considerable impact on the rate of surface heating. The results of these measurements prove the influence of MWCNT on the acceleration of the CA melting process and positive effect on the thermal properties of used bio-PCM.

Figure 9 presents an example of how the surface of fabric samples heats. Figure 9 shows the surface of tested samples heated for 5 min. There are only instant images of samples. For the analysis of images FLIR tools + software was used, and the mean temperature was calculated (Table 9).

4 Conclusion

The thermal properties of bio-based PCM microcapsules and their separate components, core and shell, were investigated considering the influence of used thermal enhancer. Composites of PCM with different concentrations of MWCNT as well as composites of PLA with these carbon compounds were prepared and investigated to assess how MWCNT influences the thermal conductivity

Table 8: Thermal conductivity and electrostatic properties of films from shell material (PLA and PLA composites with different amounts of MWCNT)

Code of sample	Thickness of film D , mm	Coefficient of thermal conductivity λ , W/(m K)	Electrostatic properties*	
			Surface resistivity ρ , Ω	Electrical resistance through the material (vertical resistance) R_y , Ω
PLA-0	1.24	0.1	7.92×10^{13}	5.2×10^{12}
PLA-C1	1.04	0.2	5.86×10^5	$< 2 \times 10^3$
PLA-C3	1.28	0.25	3.58×10^4	$< 2 \times 10^3$

*Electrostatic properties were determined according to the standard methods – EN 1149-1 and EN 1149-2.

Figure 8: Dynamic thermal behavior of textile samples coated with pure CA and composites of CA with MWCNT, during heating.**Table 9:** Temperatures of textile samples coated with pure CA and composites of CA with MWCNT during heating

Code of sample	Time of retention on the heating plate, min									
	Temperatures of sample, °C									
	1	2	3	5	7	10	11	12	17	22
F-K (control sample)	28.6	29.1	31	31.9	31.8	32	32.1	32.1	32.1	32.3
F-CA	27.9	27.9	29.1	29.5	30.1	30.6	30.8	31.1	30.9	30.8
F-CA 0.5C	27.8	28.8	30.3	30.3	30.4	30.5	31	30.9	30.9	31
F-CA 1C	27.6	29	29.9	30	30	30.5	31	31	30.4	30.4
F-CA 3C	27.6	29	29.9	30.5	30.8	31	31	31.1	31.2	31.3

Figure 9: Thermographs of samples after 5 min of heating.

of the core and the shell. The heat storage and release capacity, as well as the phase change temperatures of CA/MWCNT composites and manufactured PCM microcapsules, were determined using DSC. To analyze the thermal behavior of core and shell of microcapsules, the thermal resistance test was conducted. To obtain supplementary information and to assess the dynamic behavior of used PCM and its composites with MWCNT, when the temperature changes, monitoring of a cold/hot plate with an IR camera was carried out.

It was determined that the presence of MWCNT reduces the peak of the melting temperature of CA about 1°C and even less peak crystallization temperature. Although the addition of MWCNT has a negligible effect on the peak melting and crystallization temperatures of CA, it reduces the enthalpy of fusion and crystallization as the concentration increases. Compared with studies of other authors, the obtained results are compatible enough [20,35]. According to the gained results, it could be stated that the optimal amount of MWCNT in composites with CA could be in the interval from 0.5% to 1%, as the higher amount of additive reduces positive properties of heat storage and release capacity of CA. The same process is noticed in the results of the microcapsule investigation, and the reduction of the melting and crystallization enthalpy in microcapsules, which was produced with MWCNT, can be observed. The same process is noticed in works of other authors, who investigated different carbon additives [37]. The coefficient of thermal conductivity and the thermal resistivity showed that MWCNT improved the thermal behavior of core and shell materials of microcapsules. Analysis of thermal behavior of the prepared composites also has proven the influence of MWCNT on the acceleration of CA melting process and positive effect on thermal properties of used bio-based PCM.

Conflict of interest: The authors declare no conflict of interest.

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