



Fatty acid alkyl ester nanowebs suitable for renewable thermal energy storage

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ARTICLE INFO

Keywords:

Phase change material
Fatty acid alkyl esters
Thermal
DSC
Coaxial electrospinning
Nanowebs

ABSTRACT

Owing to their high heat absorption and release capacities, chemical and thermal stability, non-toxicity, two fatty acid alkyl esters (FAAEs), methyl palmitate (MP) and isopropyl palmitate (IPP), were investigated for their use as thermal energy storage (TES) material in a shape stabilized form. Four nanowebs were developed via coaxial electrospinning, using poly(acrylonitrile) (PAN) or poly(methacrylic acid-co-ethyl acrylate) (PMEA) shell to envelope MP or IPP core. Scanning electron microscope (SEM), transmission electron microscope (TEM) images confirmed cylindrical nanofiber formation, demonstrating a coaxial sheath-core morphology. The phase change enthalpies of PAN-MP, PMEA-MP nanowebs, with average diameters of 259–289 nm, were 71 J g^{-1} and 86 J g^{-1} at $28\text{--}32^\circ\text{C}$, and those of PAN-IPP, PMEA-IPP were 72 J g^{-1} and 60 J g^{-1} at $7\text{--}15^\circ\text{C}$ during heating cycle in differential scanning calorimeter (DSC) analyses. A composite including PAN-MP nanoweb performed enhanced thermo-physical properties than its control counterpart.

1. Introduction

Nowadays, research groups from various disciplines and industry practitioners are interested in the thermal regulation function of new materials and composites in a very broad sense. The global demand for energy saving technologies, more comfortable, healthier and eco-friendly products and sustainable designs has been the main driving force of developing various goods with superior thermal properties. Organic phase change materials (PCMs), that can store and release large quantities of latent heat during a phase change process, offer noteworthy potential to improve the thermal energy storage capacity of a given material, which can be applied in many cooling and heating applications across various industries, such as thermal management and thermal comfort in buildings [1], outdoor and indoor apparels, sports and medical thermoregulating textiles [2,3], space and water heating [4], solar energy storage systems [5], transport packaging [6] and so forth.

Fatty acid alkyl esters (FAAEs), sustainably obtained from common vegetable and animal oils through transesterification of fatty acids with alcohols, have recently become of interest scientifically as potential bio-based PCMs [7] owing to their considerable characteristics such as suitable melting temperature ranges, high heat of fusion, chemical and thermal stability, good smell, non-toxicity and biodegradability. They can make thousands of melting and freezing cycles without thermal

degradation. Depending on the chain length and bond types, their phase transition temperature intervals are indicated in the literature in the range of -36 to 70°C , and the corresponding heat capacities in the range of $90\text{--}250 \text{ J g}^{-1}$, which make them suitable for heat storage applications at low and moderate temperatures [8]. Recent studies performed by various research groups, including Röttig et al. [9], Sari and his coworkers [7], Liston et al. [10], Ma et al. [11], Hajilar and Shafei [12] are mainly related with the syntheses and thermal properties of FAAEs.

Developing new energy-saving composites with improved thermal performances and durability has been the research focus for promoting the applicability of PCMs at the industrial scale [13]. Recently, coaxial electrospinning has attracted attention as a straightforward, convenient and flexible technique for encapsulating both hydrophilic and oleophilic PCMs in a variety of polymers. The nanofibers made up of a PCM core and a polymer shell possess remarkable advantages, such as achieving high encapsulation efficiency, preventing the leakage of PCMs within the structure, forming a large surface area with the numerous nanofibers, being lightweight, holding good mechanical strength, and allowing direct use in various composites [14]. McCann et al. first applied this technique to PCMs in 2006. They fabricated phase change nanofibers of *n*-alkanes encapsulated in Polyvinylpyrrolidone (PVP) shell via melt coaxial electrospinning [15]. Since then, various ultrafine PCM-polymer nanowebs including poly

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<https://doi.org/10.1016/j.tca.2020.178698>

Received 17 January 2020; Received in revised form 18 June 2020; Accepted 18 June 2020

Available online 20 June 2020

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(ethylene glycol) (PEG)-polyvinylidene fluoride (PVDF) [16], PEG-cellulose acetate (CA) [17,18], PEG-poly (acrylonitrile) (PAN) [19], PEG-poly(amide 6) (PA6) [20], hexadecane-poly(urethane)(PU) [21], *n*.alkane-PVP [22], paraffine wax-PAN [23] via coaxial electrospinning technique have been consecutively reported.

Recently, a few numbers of studies focused on the incorporation of fatty acid alkyl esters into the nanowebs. Li et al. prepared mixtures of PAN solution and five fatty acid esters, say methyl palmitate, ethyl stearate, ethyl palmitate, and butyl stearate, by adding loaded with different practicable mass percentages, and produced phase change composite nanofibers via single electrospinning. The nanofibers which perform phase transitions within temperatures of 20–30 °C with considerable enthalpies were found suitable for smart textile and temperature regulating fiber applications [24]. Chen et al. synthesized fatty acid mixed esters, with the onset phase change temperature around 32 °C, by grafting palmitic-stearic binary acids onto hydroxypropyl cellulose skeleton to have thermoplastic copolymers, prospective for thermal energy storage applications in textiles and energy efficient buildings [25]. Huizhen and Qufu prepared form-stable phase change composite fibrous membranes by physical adsorbing of fatty acid esters and their eutectic mixtures with the melting temperatures of about 20–33 °C, including butyl stearate, capric-myristic acid binary eutectic, capric- palmitic-stearic acid ternary eutectic, into electrospun PAN/silver nanoparticles nanofibrous supporting membranes and sought for their thermal properties [26]. Wi et al. produced shape-stabilized phase change materials by impregnating two fatty acid esters, say coconut oil and palm oil, into exfoliated graphite nanoplatelets, the supporting material, for saving energy in buildings [27].

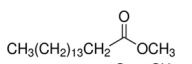
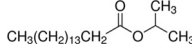
The aim of this study is to develop new thermal energy storage (TES) materials, capable of storing and retrieving a considerable amount of heat repeatedly, while providing chemical and thermal stability. Although the use of bio-based FFAEs in different fields as PCMs has attracted attention, their preparation and application in various engineering designs in the form of electrospun form stable nanowebs is very limited. Among possible choices, coaxial electrospinning of two fatty acid alkyl esters, i.e. methyl palmitate (MP) and isopropyl palmitate (IPP), were investigated in this study. Two types of copolymers, namely poly (acrylo nitrile) (PAN) and poly(methacrylic acid-co-ethyl acrylate) (PMEA), were chosen as shell materials in the process, to seek the producibility of sheath/core structures as TES materials in a range of applications. The properties of the developed nanowebs were examined in detail by structural and thermal analyses, and the contribution of one type of FFAE nanowebs to the thermal properties of a composite was investigated via its implementation into a textile based multilayer structure. Considering the attained thermal performances of these nanowebs, it is suggested that they will constitute an important alternative for different micro and macro scale composites as thermally active functional layers.

2. Experimental

2.1. Materials

Two fatty acid alkyl esters (FAAEs), given in Table 1, were the core materials of electrospinning process. They were technical grade (98 %) and used without further purification (Sigma-Aldrich Inc.).

Table 1
Fatty acid alkyl esters used in the production of nanowebs.

Fatty acid ester	Synonym	Formula	Molecular weight MW (g mol ⁻¹)
Methyl palmitate (MP)	<i>n</i> -Hexadecanoic acid methyl ester (Methyl hexadecanoate)		270.45
Isopropyl palmitate (IPP)	Hexadecanoic acid 1-methylethyl ester (Isopropyl hexadecanoate)		298.50

Two different copolymers, namely poly (acrylo nitrile) (PAN) and poly(methacrylic acid-co-ethyl acrylate) (PMEA), were used as shell materials in the sheath-core nanofiber production, considering their non-reactivity, good mechanical and thermal properties and suitability for the fabrication of nanofibers. PAN, consisting of 99.5 % of Acrylonitrile (AN) and 0.5 % of Maleic anhydride (MAH), (H₂CHCN)_n, was supplied from Good Fellow Cambridge Limited (Ermine Business Park, Huntingdon, England; CAS No: 25014-41-9) in powder form. Its average molecular weight was 150,000 g mol⁻¹, its density was 1.18 g cm⁻³, and its mean particle size was 50 μm [28]. PMEA with the methacrylic acid groups of 46.0–50.6 %, having the glass transition temperature of 96 °C ± 5 °C and the molecular weight of 320,000 g mole⁻¹ was kindly supplied from Evonik Company (USA) in powdered form under the trade name of Eudragit L100-55* [29].

The chemical reagents, namely dimethyl acetamide (DMAc, C₄H₉NO) and ethanol (98 %), from Sigma-Aldrich Inc., were used to prepare shell solutions of PAN and PMAE, respectively. The core solutions were prepared using the same solvent of its shell counterpart, either DMAc or ethanol, in order to reduce the interfacial surface tension between shell and core solutions in the coaxial electrospinning process.

2.2. Coaxial electrospinning of PAN-FAAE and PMEA-FAAE nanowebs

Nanowebs composed of sheath-core nanofibers of FFAEs, were produced using a coaxial electrospinning device (Yflow Co., Spain) [30], which was provided with a spinneret of two coaxial needles, a grounded flat collector, a double polarized system (–30 kV, +30 kV) and a Taylor cone visualization system as explained in detail in our previous study [31]. The core solution was pumped from inner needle and the shell solution was pumped from outer needle. The collector was placed 15 cm far from the spinneret. Electrospinning process was proceeded at 25 °C. The process parameters of the produced nanowebs were those allowed compound Taylor cone formation, anchored at the tip of the nozzle. Different samples of PAN-FAAE and PMAE-FAAE nanowebs were produced with the given process parameters (See Table 2).

In coaxial electrospinning of PAN-FAAE nanowebs, 6 w% PAN shell solution (in DMAc) and 20 w% MP and 20 w% IPP solutions (in DMAc) were prepared as stock solutions. To prepare the shell solution of PAN, 150 mL of DMAc and 6 w% PAN were added to a glass bottle and stirred at 500 rpm at 35–40 °C for 4 h to obtain a transparent solution. To prepare the core solutions, 20 w% MP and 20 w% IPP, were dissolved in DMAc by stirring each mixture at 500 rpm under ambient conditions for 15 min. In coaxial electrospinning of PMAE-FAAE nanowebs, 15 w% PMAE shell solution (in ethanol) and 20 w% MP and 20 w% IPP solutions (in ethanol) were prepared as stock solutions by stirring them at 500 rpm under ambient conditions for 2 h. Considering the concentrations of the shell and core solutions, ratios of the core materials in sheath-core structures (RW_{core}) by weight were calculated as 0.769 and 0.571 for PAN-FAAE and PMAE-FAAE nanowebs, respectively.

The solutions' characteristics were determined before using them in the nanoweb production process. Table 3 shows the dynamic viscosity, surface tension and conductivity values of the prepared solutions along with the corresponding core/shell ratios. The dynamic viscosity measurements of shell and core solutions were performed using an SNB-1

Table 2

Coaxial electrospinning parameters of PAN-FAAE and PMAE-FAAE nanoweb.

Shell Solution	Core Solution	Nanoweb Sample Code	Shell pump rate (mL h ⁻¹)	Core pump rate (mL h ⁻¹)	Injector voltage (kV)	Collector voltage (kV)	Time (min)
6 % PAN (DMAc)	–	PAN (Control)	0.03	–	7.0	–7.0	30
15 % PMAE (Ethanol)	–	PMAE (Control)	0.03	–	11.0	–11.0	30
6 % PAN (DMAc)	20 % Methyl Palmitate (DMAc)	PAN-MP1	1.50	0.50	6.0	–5.4	60
		PAN-MP2	1.50	0.50	6.0	–5.0	60
		PAN-MP3	1.50	0.50	6.0	–5.2	60
		PAN-MP4	1.50	0.50	6.0	–5.5	60
6 % PAN (DMAc)	20 % Isopropyl Palmitate (DMAc)	PAN-IPP1	1.50	0.50	6.0	–5.0	60
		PAN-IPP2	1.50	0.50	6.0	–5.2	60
		PAN-IPP3	1.50	0.50	6.0	–4.7	60
15 % PMAE (Ethanol)	20 % Methyl Palmitate (Ethanol)	PMAE-MP1	2.00	1.00	11.0	–10.0	30
		PMAE-MP2	2.00	1.00	11.5	–11.0	30
		PMAE-MP3	2.00	1.00	12.5	–12.0	30
		PMAE-MP4	2.00	1.00	12.5	–12.0	30
15 % PMAE (Ethanol)	20 % Isopropyl Palmitate (Ethanol)	PMAE-IPP	2.00	1.00	12.0	–11.0	30

model Stepless Speed Regulation Rotary Display Viscometer at the shear rate (R) of 60 rpm and at 25 °C [32]. The surface tensions of the solutions were measured with a Neubert Glass model Traube Stalagmometer according to a previously reported method [33]. The electrical conductivity measurements of solutions were performed at 25 °C using a Mettler Toledo S80 model Multi Conductometer between 0.001 $\mu\text{S cm}^{-1}$ and 1000 mS cm^{-1} . The conductometer was calibrated with a standard solution (84 $\mu\text{S cm}^{-1}$), and the cell constant was taken as ≤ 0.1 .

As shown from Table 3, in PAN-FAAE coaxial electrospinning processes, the core viscosities were preserved to be one hundredth of the shell viscosity ($\eta_{\text{core}}/\eta_{\text{shell}} = 0.01$) in relation with the chosen concentrations; the surface tensions were held nearly the same for core and shell solutions ($\gamma_{\text{core}}/\gamma_{\text{shell}} = 0.9$) by using the same solvent; the electrical conductivities of the core solutions were obtained as two to three percent of the shell solution ($\sigma_{\text{core}}/\sigma_{\text{shell}} = 0.02 - 0.03$), all sufficient to achieve continuous nanofiber formation [34]. Similarly, PMAE-FAAE nanoweb were produced in coaxial electrospinning process with the core/shell viscosity ratio of one percent ($\eta_{\text{core}}/\eta_{\text{shell}} = 0.01$), surface tension ratio of the same order ($\gamma_{\text{core}}/\gamma_{\text{shell}} = 1.2$), and electrical conductivity ratio of three thousandth ($\sigma_{\text{core}}/\sigma_{\text{shell}} = 0.003-0.004$).

2.3. Characterization of PAN-FAAE and PMAE-FAAE nanoweb

The Fourier transform infrared (FTIR) transmission spectra of PAN-FAAE and PMAE-FAAE nanoweb were recorded between 4000 and 650 cm^{-1} at a resolution of 4 cm^{-1} using a Perkin Elmer Spectrum 100 FTIR spectrometer equipped with a universal attenuated total reflection (ATR) accessory. The Scanning Electron Microscope (SEM) images of nanoweb were taken by EVO® LS 10 model Zeiss type SEM (LaB6-Tungsten filament at 10–15 kV). To prepare the SEM samples, dried nanoweb were placed on standard mounts (15 mm in diameter and 2 mm in depth) under vacuum and coated with a 1–2 nm thick

conductive layer of gold to prevent charging during imaging. The diameters of nanofibers were analyzed directly from SEM images using “ImageJ-DiameterJ” software for 100 nanofibers on average [35]. The Transmission Electron Microscope (TEM) images of nanoweb were taken by JEOL JEM-2100 model TEM at 200 kV. Samples were prepared by scraping the nanofiber surface thinly and then by slightly rubbing 400 mesh Cu grid surface from the bottom of itchy surface to remain nanofiber on the grid surface.

The thermogravimetric (TG) analyses were carried out from 30 to 700 °C at 10 K min^{-1} ($^{\circ}\text{C min}^{-1}$) heating rate under a dry nitrogen atmosphere purged at 20 mL min^{-1} by a SEIKO EXSTAR 6200 Model TG/DTA instrument. The differential scanning calorimeter (DSC) analyses were conducted to examine the thermal properties of the fatty acid esters and their electrospun nanoweb comparatively, using a Perkin Elmer DSC 4000 differential scanning calorimeter with an accuracy of ± 0.001 . A nitrogen flux (20 mL min^{-1}) was used as the purge gas for the furnace. The temperature scans were run on samples as 10 successive heating-cooling cycles at 10 K min^{-1} ($^{\circ}\text{C min}^{-1}$). Methyl palmitate and its nanoweb were tested between -5 and 45 °C and isopropyl palmitate and its nanoweb were tested between -30 and 30 °C. At the beginning, 5–10 mg test specimen was placed in a closed pan, brought to the starting temperature and waited at that temperature for 1 min to attain a thermal equilibrium. The test sample was then heated to the final temperature, waited for 1 min and finally cooled to the predetermined starting temperature again. Both the temperature and enthalpy changes of the test sample were entirely analyzed in each cycle and this process was proceeded until ten successive heating-cooling cycles were completed. This DSC analysis was repeated for three different test specimens randomly taken from each of the produced nanoweb. Besides, two DSC analyses for one PAN-MP and one PAN-IPP sample were conducted for a hundred heating-cooling cycle to examine the long-term phase change repeatability of FAEs nanoweb.

Table 3

The dynamic viscosity, surface tension and conductivity results for the core and shell solutions used in coaxial electrospinning of PAN-FAAE and PMAE-FAAE nanoweb (T = 25 °C).

Solution	Dynamic Viscosity(η) (Pas)	$\eta_{\text{core}}/\eta_{\text{shell}}$	Surface Tension (γ) (mN cm ⁻¹)	$\gamma_{\text{core}}/\gamma_{\text{shell}}$	Conductivity (σ) ($\mu\text{S cm}^{-1}$)	$\sigma_{\text{core}}/\sigma_{\text{shell}}$
6 w% PAN(DMAc)	0.752	–	35.56	–	17.190	–
20 w% MP(DMAc)	0.008	0.011	31.88	0.9	0.355	0.020
20 w% IPP(DMAc)	0.009	0.012	30.75	0.9	0.456	0.030
15 w% PMAE (Ethanol)	0.384	–	18.80	–	55.900	–
20 w% MP (Ethanol)	0.007	0.018	22.32	1.2	0.223	0.004
20 w% IPP (Ethanol)	0.007	0.018	22.17	1.2	0.185	0.003

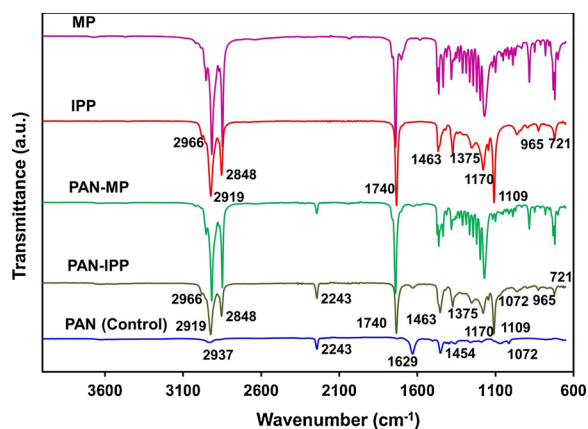


Fig. 1. Comparative ATR-FTIR transmission spectra of FAAE's, PAN (Control) and PAN-FAAE nanowebs.

3. Results and discussion

3.1. ATR-FTIR results of PAN-FAAE and PMAE-FAAE nanowebs

ATR-FTIR transmission spectra of FAAE, PAN (Control) and PAN-FAAE nanowebs are given in Fig. 1, comparatively. The ATR-FTIR spectra of MP and IPP comprise all characteristic transmission bands of fatty acid alkyl esters. Due to the different numbers of alkyl groups and different chemical arrangements, subtle differences can be observed between the spectra of MP and IPP. The intensive bands observed at 2919 cm^{-1} and 2848 cm^{-1} were attributed to asymmetric and symmetric stretching vibrations of $-\text{CH}_3$ and $-\text{CH}_2$ groups, respectively [36]. The band at 1463 cm^{-1} corresponded to scissors deformation of $-\text{CH}_2$ groups. All strong, moderate and weak bands appeared between 1460 and 800 cm^{-1} were due to the scissoring, rocking and twisting vibrations of $-\text{CH}_2$ groups. O–C and C=O stretching vibrations of O–C=O groups, typical of esters, were detected at 1740 cm^{-1} and 1170 cm^{-1} , respectively [36].

The distinctive bands for the bonds in CH_2 , $\text{C}\equiv\text{N}$, C=O, C–O groups of PAN at 2937 cm^{-1} , 2243 cm^{-1} , 1454 – 1355 cm^{-1} and at 1072 cm^{-1} , arisen from the stretching vibrations of the C–H bonds in $-\text{CH}$, $-\text{CH}_2$ and $-\text{CH}_3$ groups, the stretching vibrations of the $\text{C}\equiv\text{N}$ bonds, twisting vibrations of the $-\text{CH}_2$ and $-\text{C}\equiv\text{N}$ groups, and stretching vibrations of the O–C and C=O bonds in the O–C=O groups in PAN chains, respectively [19,37–39].

All characteristic bands of PAN and FAAEs were distinctively observed in ATR-FTIR spectra of PAN-FAAE nanowebs e.g. the bands at 2919 cm^{-1} , 2850 cm^{-1} , 1739 cm^{-1} and 1169 cm^{-1} were associated with FAAE alkyl and ester groups, and the bands at 2243 cm^{-1} and 1072 cm^{-1} were related to PAN chains.

FTIR spectrum of PMAE (Control) in Fig. 2, demonstrated typical bands associated with the bonds in CH_2 , C=O, C–O and O–H groups. The band at 2982 cm^{-1} was related to the stretching vibrations of C–H bonds in CH , $-\text{CH}_2$ and $-\text{CH}_3$ groups. The strong bands at 1699 cm^{-1} , 1252 cm^{-1} , 1159 cm^{-1} and the medium intensity band at 1020 cm^{-1} appeared due to the stretching vibrations of the O–C and C=O bonds in O=C–O groups of PMAE. The medium intensity bands at 1447 cm^{-1} and 1383 cm^{-1} were because of the characteristic O–C twisting vibrations of O–C=O groups [40].

The distinctive vibrations of PMAE and FAAE groups were clearly observed in the FTIR spectra of PMAE-FAAE nanowebs, e.g. the bands at 2919 cm^{-1} , 2848 cm^{-1} , 1740 cm^{-1} and 1463 cm^{-1} of FAAE groups, and the bands at 1699 cm^{-1} , 1447 cm^{-1} , 1252 cm^{-1} and 1159 cm^{-1} of PMAE groups, all indicating sheath-core structures of nanofibers. In addition, no dissimilar transmission bands were observed in FTIR spectra of PAN-FAAE and PMAE-FAAE nanowebs compared to those of shell and core components, demonstrating a spontaneous coaxial

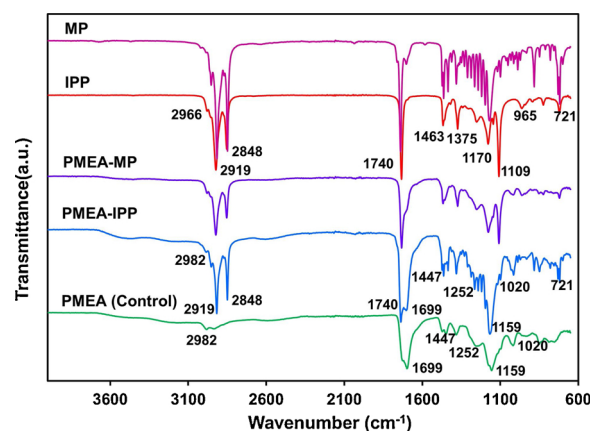


Fig. 2. Comparative FTIR transmission spectra of FAAE's, PMAE (Control) and PMAE-MP nanowebs.

electrospinning process without chemical interactions between the materials used. As a result, FTIR spectra of the nanowebs points to the evidences of enveloping of the core macromolecules by shell material, parallel to the given TEM results.

3.2. SEM and TEM results of PAN-FAAE and PMAE-FAAE nanowebs

The representative SEM images acquired from four PAN-FAAE and PMAE-FAAE nanoweb samples are given in Fig. 3. The TEM images demonstrating the coaxial sheath-core morphologies of these nanowebs are given in Fig. 4.

As seen in Fig. 3, each of the PAN-MP, PAN-IPP, PMAE-MP and PMAE-IPP nanowebs consisted of randomly oriented overlaid fibers; they were morphologically uniform and mostly cylindrical without microscopically identifiable beads and beaded nanofibers [41] and [42].

The fiber diameters analyses of PAN-FAAE and PMAE-FAAE nanowebs were performed on the SEM images given in Fig. 3 using “ImageJ-DiameterJ” software [35]. The diameter distributions of PAN-MP and PAN-IPP nanowebs were in the ranges of 25 – 700 nm and 33 – 833 nm , where their average diameters were estimated $287 \pm 152\text{ nm}$ and $270 \pm 91\text{ nm}$, respectively. The fiber diameter of PMAE-MP nanowebs extended from 33 to 1367 nm with the average of $259 \pm 81\text{ nm}$; while that of PMAE-IPP nanowebs varied between 48 and 1048 nm with the average of $289 \pm 106\text{ nm}$, thus all of the samples consisted of sub-micron and nano scale fibers and had the average diameters less than 300 nm .

The TEM images of all four types of nanowebs, given in Fig. 4a–d, clearly show that the shell material, either PAN or PMAE, successfully encapsulated the core material, either MP or IPP to form the nanofiber. In longitudinal TEM images of nanofibers, the outer shell layer, was identified by the lighter shade, which encircling the FAAE core, identified by the darker shade. Neither SEM nor TEM results show a phase separation or mixing of the shell and core solutions during electrospinning, verifying the compound Taylor cone formation as monitored during the entire process of electrospinning via the visualization system of the device.

Both SEM and TEM results showed that by using the coaxial electrospinning process, it was possible to encapsulate fatty acid alkyl esters in a lyophilic or hydrophilic polymer shell and obtain form-stable nanoweb structures successfully, suggesting that the process could be further optimized in connection with the field of application.

3.3. TG results of PAN-FAAE and PMAE-FAAE nanowebs

The TG results of FAAEs, FAAE nanowebs and the control samples are summarized in Table 4. Their comparative TG curves, are given in

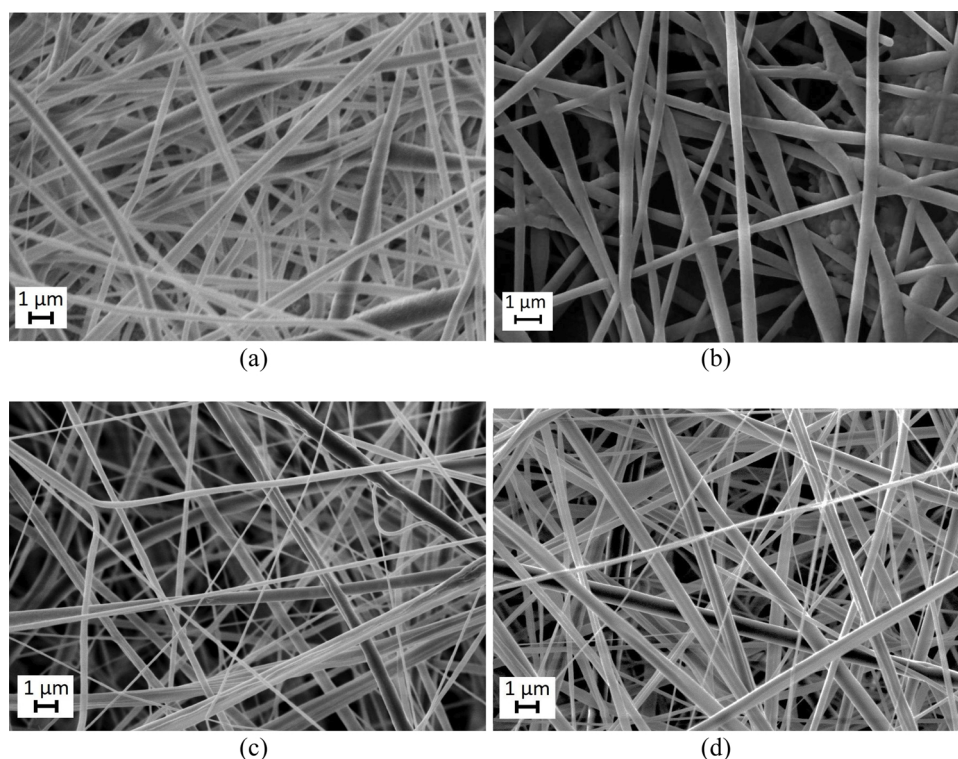


Fig. 3. SEM images showing the representative morphologies of: a) PAN-MP (10000x); b) PAN-IPP (15000x); c) PMAE-MP (10000x); d) PMAE-IPP (10000x).

Figs. 5 and 6. The thermal decompositions of FAAEs occurred in one step, starting at 169–175 °C and ending at 223–238 °C with almost no residue, attributed to the degradation the aliphatic chains and evolution of the methyl and isopropyl groups [7].

TG results of PAN (Control) nanowebs showed that the mass loss of 7 % up to 149 °C was most likely due to the volatilization of the solvent DMAc entrapped in the body of hollow fibers. The thermal decomposition of PAN (Control) nanofibers started at 292 °C, accelerated up to 312 °C and continued to 600 °C with a steady decrease, due to the bond breaking through the polymer chain of PAN and evolution of small molecules such as NH_3 , NO_2 , HCN and H_2O . The residue of PAN was 52 % at 600 °C in relation to the non-volatile hard segment of the polymer chains [43].

The PAN-MP and PAN-IPP nanowebs revealed a two-step thermal degradation behavior arisen from decompositions of the shell and core materials. The first steps in thermograms, say 181–215 °C for PAN-IPP and 177–215 °C for PAN-MP, mainly caused by the decomposition reactions of FAAEs. The mass losses at temperatures higher than 288–292 °C were related to the thermogravimetric behavior of PAN. The thermal decomposition reactions became more rapid at 310–326 °C and then steady between 500 and 600 °C due to complete evolution of the small molecules from the PAN chains. The residues of PAN-MP and PAN-IPP were 21–22 % related to the non-volatile hard segment of the polymer chains [19] and [43]. These results confirmed that both FAAEs and PAN-FAAE nanowebs were thermally stable, suitable for electro-spinning procedures, and suitable for different end-uses and applications considering the possible normal temperature ranges.

Fig. 6 shows the thermograms of FAAEs, PMAE-FAAE and PMAE (Control) nanowebs. PMAE(Control) decomposed in one distinguishable step, 5 % and 10 % mass losses corresponded to 185 °C and 257 °C, respectively. The thermal decomposition of PMAE (Control) speeded up at 351 °C and ended at 414 °C [31]. The TG analyses of PMAE-FAAE nanowebs revealed a two-step thermal decomposition behavior. The first step thermal degradation developed between 173 and 275 °C as a result of both FAAE and PMAE groups' evolutions and decompositions; however, the second step thermal degradation was governed by the

shell material thermal behavior. The thermal decomposition temperatures of PMAE-FAAE nanowebs at 10 % mass losses were 173–186 °C. The second step thermal decomposition reactions occurred between 361 and 417 °C and then became steady. The residues of PMAE-MP and PMAE-IPP were 2–3 %. In consequence, the TG results of PMAE-FAAEs indicated a considerable thermal stability and these nanowebs could be encouraging for many cold or ambient thermal energy storage applications.

3.4. DSC results of FAAEs, PAN-FAAE and PMAE-FAAE nanowebs

DSC analyses showed that phase change temperatures and corresponding enthalpies of FAAEs in their 2nd and 10th heating-cooling cycles did not change significantly and DSC graphs followed almost the same patterns. Table 5 summarizes the DSC results in terms of averages (AVE_{MP} and AVE_{IPP}) and standard deviations (SD_{MP} and SD_{IPP}) obtained from the measurements of six different MP samples and three different IPP samples. Fig. 7 a and b show typical DSC curves of MP and IPP samples obtained during 2nd and 10th heating-cooling cycles.

Methyl palmitate (MP) performed remarkable endothermic enthalpies, varied in a range of 208–237 J g^{-1} , between 28 and 38 °C during heating, and remarkable exothermic enthalpies, varied in a range of 208–237 J g^{-1} in between 22 and 16 °C during cooling, characterized by the curves with a single peak. The postponed crystallization during solidification, known as freezing point depression, was about 14–16 °C, and did not cause any difference in repeated solid-liquid phase change behavior of the material, thus, the amount of energies stored or retrieved by the PCM material during successive heating-cooling cycles remained almost the same. These results were found parallel to the well-defined thermal behavior of fatty acid methyl esters, characterized by good latent heats and sharp melting and freezing curves with minimal super-cooling in DSC analyses (the highest latent heats of methyl esters out of all the esters) due to their small alkyl chain and high polarity that results in a more stable crystal structure [44–46]. This implies a stable molecular structure in heating and cooling processes [36] and the thermal stability of this type of fatty

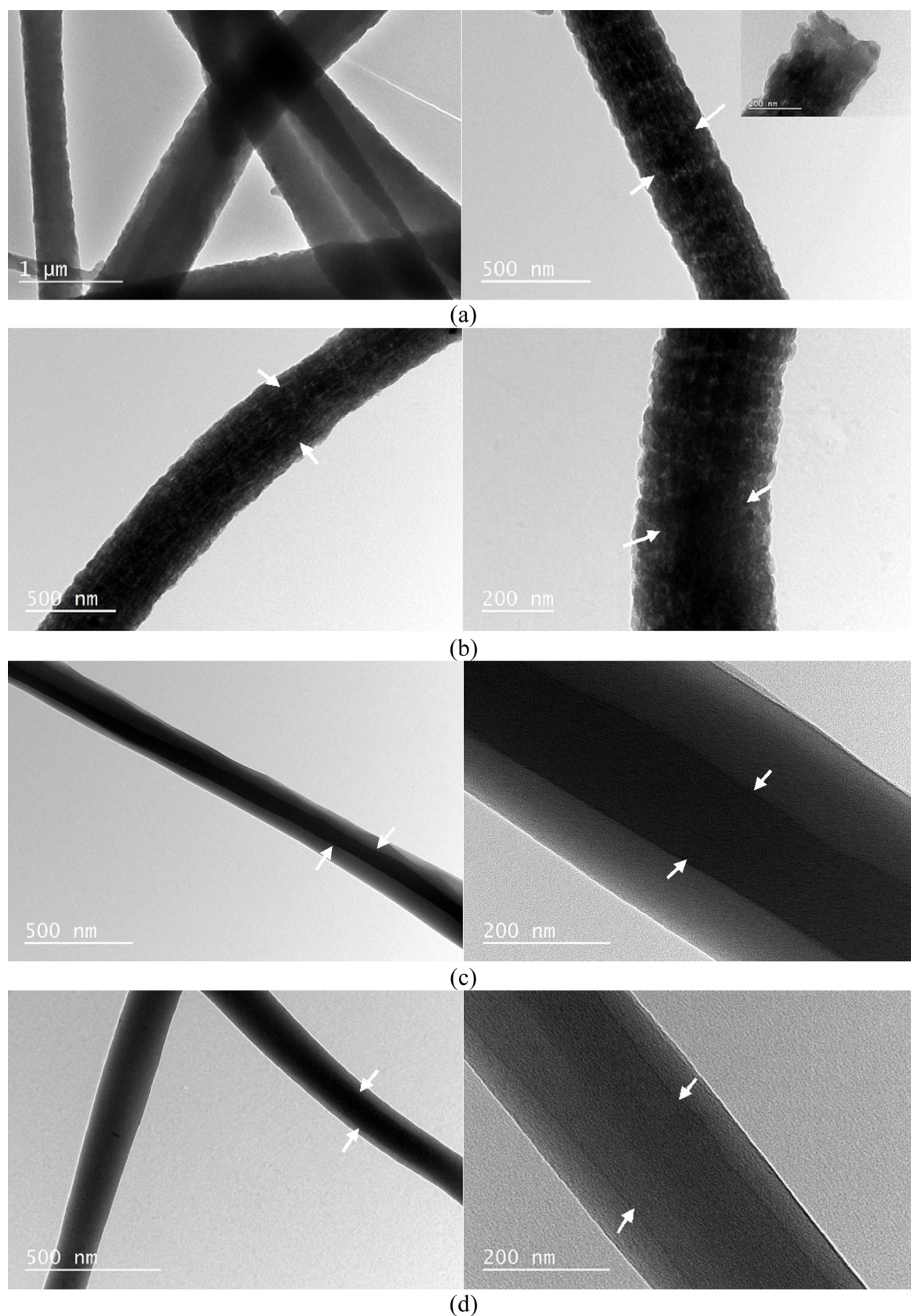


Fig. 4. TEM images representing sheath-core structures of: a) PAN-MP; b) PAN-IPP; c) PMAE-MP; d) PMAE-IP nanowebs.

acid ester.

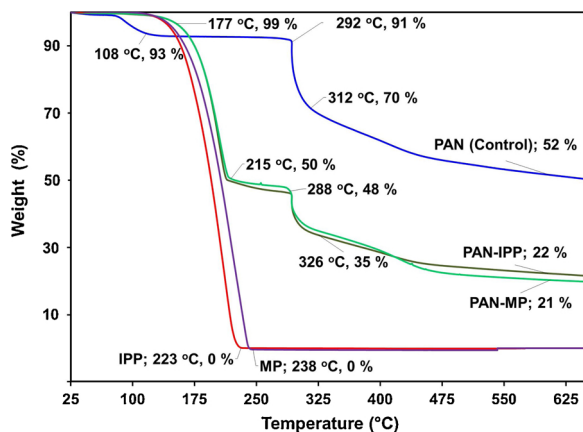
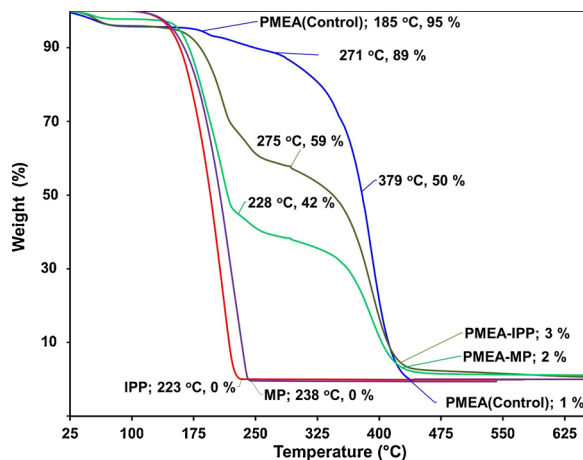
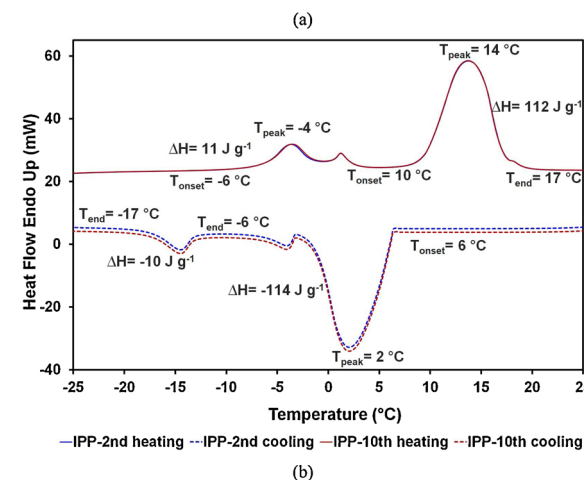
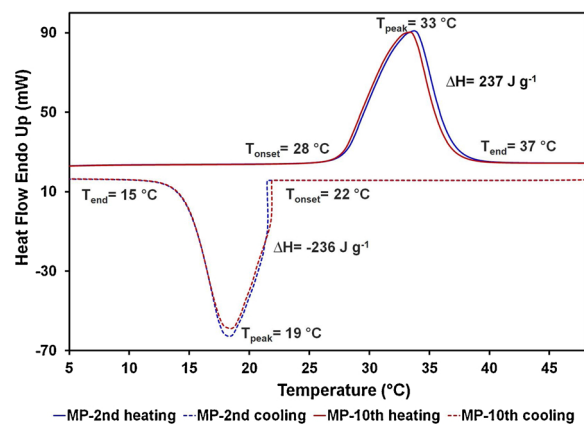
The DSC heating graphs of isopropyl palmitate (IPP) typically showed minor enthalpy peaks at around -5 to 4°C in addition to one

major enthalpy change at 11 – 19°C so that the total thermal energy absorbed was obtained as $121 \pm 2 \text{ J g}^{-1}$. Liquid to solid phase change mainly occurred at $8 - 0^{\circ}\text{C}$, followed by a minor exothermic enthalpy

Table 4

The TG results of PAN-FAAE and PMAE-FAAE nanowebs.

Sample	T(°C) at 5 % mass loss	T(°C) at 10 % mass loss	1 st step			2 nd step			
			T _{start} -T _{end} (°C)	Mass loss %	T _{peak} (°C)	T _{start} -T _{end} (°C)	Mass loss %	T _{peak} (°C)	Residue %
Methyl Palmitate (MP)	152	164	175–238	99	238	–	–	–	0
Isopropyl Palmitate (IPP)	148	158	169–223	99	210	–	–	–	0
PAN (Control)	108	293	53–149	7	88	292–312	30	297	52
PAN-MP	163	176	177–215	50	206	288–326	24	293	21
PAN-IPP	163	176	181–215	50	207	292–310	19	295	22
PMEA (Control)	185	257	351–414	95	391	–	–	–	0
PMEA-MP	161	173	173–228	58	217	364–417	33	394	2
PMEA-IPP	163	186	187–275	41	216	361–417	50	393	3

**Fig. 5.** The comparative TG decomposition graphs of FAAEs, PAN-FAAE and PAN (Control) nanowebs.**Fig. 6.** The comparative TG decomposition curves of FAAEs, PMAE-FAAE and PMEA (Control) nanowebs.**Fig. 7.** The DSC curve of a) MP and b) IPP during 2nd and 10th heating and subsequent cooling cycles.**Table 5**

Phase change characteristics of FAAEs in DSC analyses.

PCM	2 nd Heating				2 nd Cooling				10 th Heating				10 th Cooling			
	Phase Transition (°C)			ΔH (J g ⁻¹)	Phase Transition (°C)			ΔH (J g ⁻¹)	Phase Transition (°C)			ΔH (J g ⁻¹)	Phase Transition (°C)			ΔH (J g ⁻¹)
	T _{onset}	T _{peak}	T _{end}		T _{onset}	T _{peak}	T _{end}		T _{onset}	T _{peak}	T _{end}		T _{onset}	T _{peak}	T _{end}	
AVE _{MP}	28	35	38	220	24	19	16	222	28	35	38	219	24	19	16	219
SD _{MP}	± 1	± 1	± 1	± 10	± 2	± 2	± 1	± 11	± 1	± 1	± 1	± 12	± 2	± 2	± 2	± 12
AVE _{IPP}	-5/11	-2/16	4/19	122	8/-10	3/-13	0/-16	108	-5/11	-2/16	4/19	121	8/-10	3/-13	0/-16	108
SD _{IPP}	± 1	± 1	± 2	± 1	± 2	± 1	± 1	± 17	± 1	± 1	± 2	± 2	± 2	± 1	± 1	± 16

Table 6

The phase change characteristics of PAN-FAAE and PMAE-FAAE nanowebs in DSC analyses.

Sample	10 th Heating			10 th Cooling			$\Delta H_{\text{expected}}^1$ (J g ⁻¹)	Efficiency ² (%)
	Phase transition temperatures (°C)	Enthalpy ΔH (J g ⁻¹)		Phase transition temperatures (°C)	Enthalpy ΔH (J g ⁻¹)			
PAN-MP (n = 12)	T _{onset}	28–29	$\bar{x}$ 71	T _{onset}	24–25/13–14	$\bar{x}$ 68	168	E: 42; E _h : 54
	T _{peak}	31–32	s 8	T _{peak}	23/7–8	s 8		
	T _{end}	32–34	R 63–90	T _{end}	19–21/2–4	R 61–85		
PMAE-MP (n = 12)	T _{onset}	28	$\bar{x}$ 86	T _{onset}	24–25/4–5	$\bar{x}$ 85	125	E: 69; E _h : 82
	T _{peak}	30–33	s 13	T _{peak}	22–24/2–3	s 13		
	T _{end}	32–37	R 61–102	T _{end}	17–21/0 to –2	R 60–100		
PAN-IPP (n = 7)	T _{onset}	7–8	$\bar{x}$ 72	T _{onset}	9	$\bar{x}$ 72	93	E: 77; E _h : 84
	T _{peak}	13	s 3	T _{peak}	3–4	s 4		
	T _{end}	15–18	R 72–78	T _{end}	–1 to –4	R 70–77		
PMAE-IPP (n = 3)	T _{onset}	10–11	$\bar{x}$ 60	T _{onset}	9	$\bar{x}$ 62	69	E: 87; E _h : 91
	T _{peak}	13	s 3	T _{peak}	7	s 4		
	T _{end}	15–16	R 57–63	T _{end}	4–5	R 58–65		

¹ $\Delta H_{\text{expected}} = RW_{\text{core}} \times \Delta H$ of PCM in Table 5; $RW_{\text{core}} = 0.769$ for PAN-MP and PAN-IPP & 0.571 for PMAE-MP and PMAE-IPP.² Efficiency = (ΔH of NF sample/ $\Delta H_{\text{expected}}$) x100; E = mean efficiency; E_h = highest efficiency attained among the replicates.

change between -10 and -16 °C, which totally arrived 108 ± 16 J g⁻¹ energy. This multi-peak phase change behavior of IPP which occurred in a wide temperature range during heating-cooling cycles was attributed to the polymorphism displayed by alkyl esters with the bulkier alkyl groups, since these groups provide more interference between intermolecular ester bond interactions than the methyl group and this also tends to decrease latent heats during phase transitions [44–48]. Still, this phenomenon is not detrimental to the performance of FFAEs' as PCMs because the latent heats of these transitions are low [44]. The thermal stability and repeatability of the phase change behavior of IPP were assured as well with the repeated DSC analyses.

After all, the fatty acid alkyl esters of MP and IPP, were found quite suitable for use as PCM, considering their high latent heats of fusion in relation to the phase change temperatures, also presenting thermal and chemical stability.

Table 6 illustrates the phase change temperatures and enthalpies of PAN-FAAE and PMAE-FAAE samples obtained in 10th heating-cooling cycles in DSC analyses along with the expected heat enthalpies and the encapsulation efficiencies of nanowebs. The ratios of the core materials in sheath-core structures (RW_{core}) by weight were calculated as 0.769 and 0.571 for PAN-FAAE and PMAE-FAAE nanowebs, respectively, and then used as multiplier of the corresponding PCM's enthalpy in order to find the maximum attainable enthalpy of a particular nanoweb ($\Delta H_{\text{expected}}$). The encapsulation efficiencies (E %) were obtained as the ratio between actual and expected enthalpy values.

DSC results of twelve different PAN-MP samples are summarized in Table 6. Each test specimen performed two-way phase change behavior repeatedly during heating-cooling cycles at temperatures coinciding with those of MP. The heating enthalpy change was 71 ± 8 J g⁻¹ for PAN-MP nanowebs, indicating 42 % encapsulation efficiency on average in the electrospinning process with the applied process parameters. The enthalpy change in cooling was obtained as 68 ± 8 J g⁻¹ in total from 24 to 2 °C which split into two distinctive troughs as given in Table 6; thus, a two-step heat release occurred, say 65 % of the total between 25 and 19 °C and 35 % of it between 14 and 2 °C. The split thermal response of PAN-MP samples observed during freezing process was attributed to the impurity effect of DMAc solvent which was still entrapped in the sheath/core structure [19,47,49,50]. This was also verified by freezing point depressions from 35 ± 1 °C for MP to 31 – 32 °C for PAN-MPs due in part to incorporation of the solvent into the solid (core) matrix leading to a solid that has a lower melting point of PAN-MP samples.

DSC analyses of PMAE-MP nanowebs also yielded remarkable phase change enthalpies at similar temperature intervals of MP, say 86 ± 13 J g⁻¹ in heating and 85 ± 13 J g⁻¹ in cooling, obtained

based on the measurements of twelve different test specimen, indicating 69 % efficiency on average in electrospinning process with the applied process parameters. In this group, the phase change behavior of the sheath-core nano structures was quite similar to that of MP and 97 % of the heat release in cooling occurred in the range of 25 – 17 °C.

The summary of DSC results for seven different PAN-IPP samples given in Table 6 presents heating and cooling enthalpies of 72 ± 3 J g⁻¹ at 7 – 18 °C and 72 ± 4 J g⁻¹ at 9 to -4 °C, respectively, matching the major phase change intervals of IPP. The multi-peak phase transition of IPP core in the PAN shell during repeated heating-cooling cycles were observed as a diminished effect, not significantly changing the nanocomposite enhanced energy storage behavior. The electrospinning efficiency in this group of nanowebs arrived 77 % on average with the applied process parameters. Similarly, DSC analyses showed that all three PMAE-IPP nanowebs performed both endothermic and exothermic enthalpy changes of 60 ± 3 J g⁻¹ at 10 – 16 °C and 62 ± 4 J g⁻¹ at 9 – 4 °C, respectively, with the 87 % electrospinning efficiency.

All DSC results demonstrated that the developed PAN-FAAE and PMAE-FAAE nanowebs were provided with a significant heat absorption and heat release property functional at moderate specific temperature intervals which enabling different possible designs for energy management applications. Fig. 8 a and b show the DSC curves of PAN-MP and PAN-IPP for 10th and 100th heating and cooling cycles, verifying the maintained energy storage capacity and the possessed thermal and chemical stability of the sheath/core nano structures.

3.5. The thermo-physical properties and latent heat storage results of textile-based composite including PAN-MP nanoweb

To demonstrate the functionality of the shape stable FFAEs in the dynamic thermal response of the composite systems, two textile based multilayer structures were developed to observe their thermo-physical properties and latent heat storage behavior comparatively: one including PAN-MP nanoweb layer at the center (Composite B) and the other including PAN (Control) nanoweb layer at the center (Composite A), the latter was previously given in our study [19].

With this aim, a PAN-MP nanoweb, electrospun with 1.25 shell/core pump ratio, 6.8 kV/6.5 kV injector/collector voltages for 2 h, was inserted into the center of a multilayer structure to produce Composite B. The spun-bond nonwoven textile sheet (STS) was made of 100 % polyester microfibers (25 g m⁻²) and lining (L) sheet was 50.50 polyamide-polyester (36 g m⁻²). The matrix was then fixed under 2.5 bar at 132 °C for 24 s using a laboratory-type LaStar lining machine. Table 7 shows the composite compositions and sample weights.

The thermo-physical properties of composites were measured on a

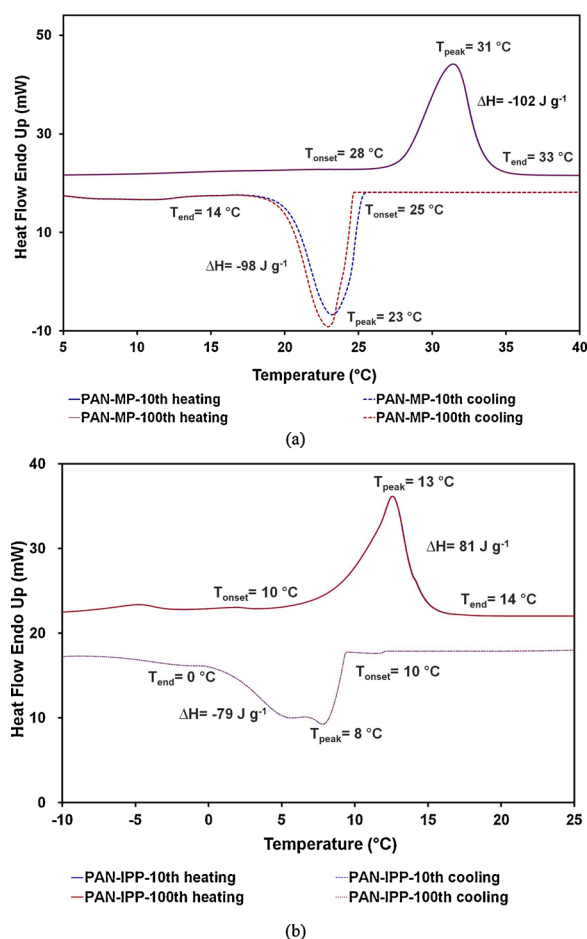


Fig. 8. The DSC curves of: a) PAN-MP:10th cycle and 100th cycle; b) PAN-IPP: 10th cycle and 100th cycle.

Hot Disc TPS 2500S to determine the thermal conductivity, specific heat capacity, thermal diffusivity and thermal effusivity [51] and [52]. During the experiment, the hot plate sensor with a diameter of 6.4 mm was placed between two layers of Composite B (0.5 mm $\times$ 2.0 mm $\times$ 7.0 mm). This ensures full contact of the sample with the sensor. Then, a small electrical power of 0.005 – 0.008 W was applied to the sensor having an initial temperature of 23.7 $^\circ\text{C}$, then the measurement was performed in a small-time interval (80–160 s). The data were evaluated with the software of the device (54 He 2005). The heat storage and release behavior of composites were also examined via DSC analysis. Table 8 summarizes the thermo-physical properties and latent heat storage behavior of the two textile-based composites, Composite B and Composite A.

The thermal conductivities, given in Table 8, indicate the heat transfer rates through the multi-layer structures. Composite B showed a slightly lower thermal conductivity than that of Composite A, most likely due to the presence of PCM and negligible changes in amount of still air entrapped between layers. Therefore, considering the thermal resistivity ratio between two composites was $R_B/R_A = 1.04$.

Table 7

The multilayer textile-based composites including PAN (Control) and PAN-MP nanoweb.

Composite Sample	Incorporated nanoweb type	Weight of textile layers in the sample (g)	Weight of nanoweb in the sample (g)	Total weight of the sample (g m^{-2})	Shape stabilized PCM ratio in the sample (w %)
Composite A*	PAN (Control)	0.00563	0.01914	244.0	–
Composite B	PAN-MP	0.00608	0.02040	337.0	77

* Composite A: STS/L/ PAN (Control)/L/STS, Noyan et al. [19]; Composite B : STS/L/PAN-MP/L/STS.

The specific heat capacity of Composite B was obtained as $452.1 \text{ J kg}^{-1} \text{ K}^{-1}$, which was 1.75 times greater than that of Composite A, a remarkable contribution to the total energy storage density of the system in addition to its latent heat storage capacity, needed for engineering approaches [53].

The thermal diffusivity (α), which is a characteristic of materials, is a measure of transient heat-flow through the material and describes the ability of a material to conduct thermal energy relative to its ability to store thermal energy [51] and [52]. The thermal diffusivity of Composite B was obtained $0.216 \text{ mm}^2 \text{ s}^{-1}$, 55 % of Composite A's thermal diffusivity ($0.393 \text{ mm}^2 \text{ s}^{-1}$). Thus, Composite B tended to transfer heat relatively slowly and store more thermal energy compare to its counterpart Composite A, and behaved like a barrier against temperature changes through the structure.

The thermal effusivity (ϵ) is a measure of material's ability to exchange thermal energy with its surroundings, sometimes defined as a comfort of contact which determines the interfacial temperature when two objects at different temperatures touch each other [54]. This is also a key performance metric of a PCM – a metric which is often referred to as “thermal inertia”, characterized by the thermal mass and thermal conductivity. In fact, with a higher thermal inertia, a given material can be thermally activated more rapidly and consequently more thermal load can be stored during the dynamic thermal process [55–57]. The thermal effusivity of Composite B was determined as $209.9 \text{ J m}^{-2} \text{ s}^{-1/2} \text{ K}^{-1}$, 30 % higher than that Composite A ($161.7 \text{ J m}^{-2} \text{ s}^{-1/2} \text{ K}^{-1}$), indicating that Composite B could more easily absorb and release heat at its surface [58] and [59].

The heat storage and release performance of Composite B during 2nd and 10th heating-cooling cycles of DSC analysis, given in Fig. 9, coincided with that of the PAN-MP nanoweb (see Fig. 8a). Composite B achieved 33 J g^{-1} latent heat energy storage between 13 and 32°C during heating period of DSC analysis; this was followed by 42 J g^{-1} heat release in its subsequent cooling cycle, indicating its suitability for dynamic heat management applications of such textile-based composite structures [19].

The heat release behavior of Composite B compared to that of Composite A was further analyzed near the phase transition region of $24.0\text{--}22.0^\circ\text{C}$ (See Table 9). 77 % by weight of Composite B constitutes PAN-MP nanoweb (260 g m^{-2} of 337 g m^{-2}). Composite B performed heat release of 32.8 J g^{-1} between 23 and 18°C (See Fig. 9); therefore, the latent heat released per square meter of the composite was estimated 8529.5 J m^{-2} . Considering the thickness of 0.005 m and phase change interval of $\Delta T = 5.2 \text{ K (}^\circ\text{C)}$, the volumetric latent heat capacity of Composite B was calculated as $328000.0 \text{ J m}^{-3} \text{ K}^{-1}$. On the other hand, volumetric sensible heat capacity of Composite B was obtained as $452342.0 \text{ J m}^{-3} \text{ K}^{-1}$ from the measured thermal effusivity and thermal conductivity values. Thus, a total of successive volumetric heat releases between 24.0 and 22.0°C attained $780342.0 \text{ J m}^{-3}$. The corresponding heat released from Composite A under the same conditions was $516226.8 \text{ J m}^{-3}$. Therefore, the transient heat release behavior of Composite B was 51 % higher than that of Composite A under similar conditions. These calculation results verify that the shape stabilized FAAEs, manufactured in this study in the form of nanoweb, are promising to enhance the thermal performance of many thermal energy conservation and management systems.

Table 8
Hot Disc TPS 2500S and DSC results of the textile-based composites.

Sample	Thermal conductivity	Thermal resistivity		Thermal diffusivity**		Specific heat capacity	Thermal effusivity***	Enthalpy change (10 th cycle)	
	k (W m ⁻¹ K ⁻¹)	R = 1/k (W ⁻¹ m K)	R _B /R _A	α (mm ² s ⁻¹)		c (J kg ⁻¹ K ⁻¹)	ε (J m ⁻² s ^{-1/2} K ⁻¹)	ΔH _{heating} (J g ⁻¹)	ΔH _{cooling} (J g ⁻¹)
Composite A*	0.1013 ± 0.0002	9.870	—	0.393 ± 0.006		257.9 ± 3.3	161.7 ± 0.9	—	—
Composite B	0.0974 ± 0.0002	10.267	1.04	0.216 ± 0.001		452.1 ± 1.9	209.9 ± 0.2	34(13 – 32 °C)	33 (23 to – 2 °C)

* Noyan et.al. [19]

** $\alpha = \frac{k}{\rho c}$.

*** $\epsilon = \sqrt{k\rho c}$; ρ = material density (kg m⁻³).

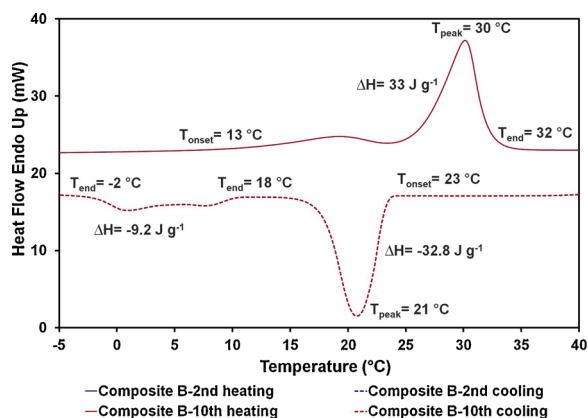


Fig. 9. The heat storage and release behavior of Composite B (including PAN-MP), obtained from 2nd and 10th heating-cooling cycles of DSC analyses.

4. Conclusion

In this study, two fatty acid alkyl esters (FAAEs), methyl palmitate (MP) and isopropyl palmitate (IPP) were investigated for their potential use as bio-based organic PCMs in nanofibrous web forms. With this aim, considering their non-reactivity, good mechanical and thermal properties and suitability for the fabrication of nanofibers, two copolymers, poly(acrylonitrile) (PAN) and poly(methacrylic acid-co-ethyl acrylate) (PMEA), were employed in coaxial electrospinning process as shell materials to envelope MP and IPP cores. Therefore, four form-stable fatty acid alkyl esters (FAAEs), say PAN-MP, PAN-IPP, PMAE-MP and PMAE-IPP, were produced as sheath/core nano structures. Based on core/shell solution characteristics and applied process parameters, specified for each type, nanofibrous web formations were achieved spontaneously without any chemical interaction between the materials and coaxial electrospinning could be repeated under the same conditions.

ATR-FTIR results showed that PAN-MP and PAN-IPP nanowebs demonstrated all distinctive bands of PAN and FAAE groups, and PMAE-MP and PMAE-IPP nanowebs presented all characteristic bands of PMAE and FAAE groups, also indicating no dissimilar transmission

bands and no new bond formation. SEM results confirmed that all four nanowebs were constituted as randomly oriented, morphologically uniform and mostly cylindrical overlaid nanofibers with the observed average fiber diameters of 287 ± 152 nm for PAN-MP, 270 ± 91 nm for PAN-IPP, 259 ± 81 nm for PMAE-MP and 289 ± 106 nm for PMAE-IPP. TEM results verified the sheath-core morphologies of the nanowebs. Therefore, the developed nanowebs structurally ensured to bring the advantages obtained through ultrafine fibrous layers, such as contributing to achieve good thermo-physical properties with large surface areas, being lightweight, holding good mechanical strength, and allowing direct use in various composites. Furthermore, the TG results confirmed that both core and shell materials and their nanowebs were thermally stable and the coaxial electrospinning process could be repeatedly and appropriately applied to the sheath/core nanoweb production without causing a thermal decomposition.

In repeated DSC analyses conducted for different samples, MP and IPP performed high enthalpy changes during their two-way phase transitions, in a route typically followed by fatty acid methyl esters or alkyl esters with the bulkier alkyl groups. MP absorbed 219 ± 12 J g⁻¹ between 28 and 38 °C and released the same amount of energy between 22 and 16 °C, so that the phase transitions were typically occurred as sharp melting and freezing curves with minimal super-cooling. IPP showed a multi-peak phase change behavior which occurred in a wide temperature range, say –5 to 19 °C during heating with 121 ± 2 J g⁻¹ and 8 to –16 °C during cooling with 108 ± 16 J g⁻¹. PAN-MP, PMAE-MP, PAN-IPP and PMAE-IPP nanowebs displayed corresponding phase transition characteristics to those of MP and IPP during heating-cooling cycles while performing remarkable enthalpies, say 71 ± 8 J g⁻¹, 86 ± 13 J g⁻¹, 72 ± 3 J g⁻¹ and 60 ± 3 J g⁻¹ during heating and 68 ± 8 J g⁻¹, 85 ± 13 J g⁻¹, 72 ± 4 J g⁻¹ and 62 ± 3 J g⁻¹ during cooling, respectively. Thus, the encapsulation efficiencies of PAN-MP, PMAE-MP, PAN-IPP and PMAE-IPP nanowebs were obtained as 42 %, 69 %, 77 % and 87 %, respectively. A hundred heating-cooling cycle DSC analyses, carried out for one PAN-MP and one PAN-IPP samples also verified the maintained heat storage capacities and the possessed thermal and chemical stabilities of the nanowebs for a longer term, which promising in energy management applications.

To demonstrate the contribution of the form stable FAAEs to the dynamic thermal response of a system, a textile based multilayer

Table 9
Comparative thermal energy release behavior of two composites in cooling period.

Heat Absorption / Heat Release Properties	Composite B	Composite A
Latent heat release per g of the composite (J g ⁻¹) (between 23.1 – 17.9 °C during heating)*	32.8	0
Latent heat release per m ² of the composite (J m ⁻²) ($m_{PAN-MP} \times \Delta H_{cooling}$)	260 × 32.8 = 8529.5	0
Thermal effusivity (ε; J m ⁻² s ^{-1/2} K ⁻¹)	209.9	161.7
Volumetric sensible heat capacity (J m ⁻³ K ⁻¹): $C = \rho c = \frac{\epsilon^2}{k}$	$\frac{209.9^2}{0.0974} = 452342.0$	$\frac{161.7^2}{0.1013} = 258113.4$
Volumetric latent heat capacity (J m ⁻³ K ⁻¹): $Q = \frac{(m_{PAN-MP} \times \Delta H_{cooling})}{\Delta T \times thickness}$	$\frac{(260 \times 32.8)}{(5.2 \times 0.005)} = 328000.0$	0
Total heat release per m ³ of the composite between 24 – 22 °C (J m ⁻³)	780342.0	516226.8

* See Fig. 9.

structure including the sheet of PAN-MP nanoweb (Composite B) and its counterpart consisting of hollow nanofibers without PCM (Composite A) were compared for their thermo-physical properties and energy storage behavior. Composite B with a lower thermal diffusivity ($0.216 \text{ mm}^2 \text{ s}^{-1}$) than that of Composite A ($0.393 \text{ mm}^2 \text{ s}^{-1}$) tended to perform a slower thermal diffusion through the structure like a barrier against temperature changes, and a higher thermal effusivity of Composite B ($209.9 \text{ J m}^{-2} \text{ s}^{-1/2} \text{ K}^{-1}$), 1.3 times that of Composite A ($161.7 \text{ J m}^{-2} \text{ s}^{-1/2} \text{ K}^{-1}$), indicated more easy thermal activation at its surface with surrounding. This was also presented with the analysis of the transient heat release performance of Composite B, which was 51 % higher than that of Composite A between 24.0 and 22.0 °C.

In conclusion, the coaxial electrospinning process given in this study is proposed as convenient and reproducible technique for encapsulating the fatty acid alkyl esters of MP and IPP in PAN and PMAE shells, for the first time, to achieve repeatable phase change and latent heat of fusion properties in nanofibrous structures with the enhanced thermo-physical properties. The developed PAN-FAAE and PMAE-FAAE nanoweb are promising to enhance the performance of many thermal energy storage (TES) and thermal management systems and suitable for ambient and cold energy storage applications in fields such as textile, packaging, medical, etc. Both the electrospinning efficiency of the nanoweb and their performances in composites or systems can be improved considering the requirements of any practice. The thermal responses of the products can be measured in more detail using real time monitoring systems in future studies.

CRedit authorship contribution statement

Emel Onder: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Writing - original draft, Writing - review & editing, Funding acquisition. **Nihal Sarier:** Conceptualization, Methodology, Investigation, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

This work was funded by the Scientific & Technological Research Council of Turkey (Grant No. 213M281). We thank Istanbul Kultur University (Turkey) and the R&D Department of Arçelik A.Ş. (Turkey) for their technical support. We also would like to thank Dr. Refik Arat for his supportive approach in the experimental work of this study.

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