

## Phase-change core/shell structured nanofibers based on eicosane/poly(vinylidene fluoride) for thermal storage applications

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**Abstract**—We fabricated eicosane/poly(vinylidene fluoride) (PVDF) core/shell nanofibers by melt coaxial electrospinning as potential heat-storage applications. Eicosane, a hydrocarbon with melting point near the human body temperature and high latent heat, was chosen as the core material. Melted eicosane and PVDF solutions were coaxially electrospun using a double spinneret, in which melted eicosane was fed at 0.090-0.210 mL/h while the feeding rate of PVDF solution was maintained constant at 1.500 mL/h. The applied voltage and working distance were maintained constant at 12 kV and 17 cm, respectively. Good core/shell structure of nanofibers was observed at core feed rates of 0.090-0.180 mL/h by transmission electron microscopy. Differential scanning calorimetry and thermogravimetric analysis values indicated good thermal stability and high energy-storage capacity of the obtained nanofibers. The highest amount of eicosane encapsulated in the electrospun core/shell nanofibers reached 32.5 wt% at core feed rate 0.180 mL/h and had a latent heat of 77 J/g at melting point 39.2 °C. These shape-stabilized core/shell composite nanofibers showed good thermoregulating properties and had sufficiently high tensile strength for potential energy-storage applications, especially in smart textiles.

Key words: Melt Electrospinning, Coaxial Electrospinning, Phase-change Material, Eicosane, Nanofiber, Energy Storage

### INTRODUCTION

Phase-change materials (PCMs) are highly attractive because of their high performance in thermal-energy storage [1,2]. They can absorb, store, and release a large amount of heat at a constant phase-transition temperature. PCMs include linear-chain hydrocarbons known as paraffin waxes (or *n*-alkanes), hydrated salts, poly(ethylene glycols), fatty acids, and mixtures or eutectics of organic and inorganic compounds [1-3]. Compared to other PCMs, paraffin has high latent heats, high chemical and thermal stability, noncorrosiveness, and, in particular, low cost. It is widely used in textiles because its phase-transition temperature is close to the human body temperature [4]. However, like other solid-liquid PCMs, paraffin repeatedly melts and solidifies during phase changes; therefore, its leakage into the surrounding environment is unavoidable, which shortens its usable lifetime [5]. The fabrication of microcapsules, in which a PCM is encapsulated in a polymer shell, is an efficient method for preventing the leakage of PCMs. Sol-gel processes [6] and different polymerization methods such as emulsion polymerization [7], in situ polymerization [8,9], suspension polymerization [10,11], and interfacial polymerization [12] were used to fabricate microcapsules comprising *n*-octacosane, tetradecane, nonadecane, and paraffin wax, which have high latent heats and good encapsulation efficiencies. Nevertheless, most of the microcapsules cannot be directly used in some applications. In particular, for textile applications they

must be incorporated with supporting materials. For example, paraffin microcapsules could be embedded in a matrix of acrylic and polyurethane using coating methods such as knife-over-roll, knife-over-air, screen-printing, gravure printing, and dip coating [13-15]. Electrospinning is another one-step technique for incorporating paraffin as well as other PCMs into electrospun fibers, which can be directly used in textile applications. Several PCM/polymer composite electrospun nanofibers such as lauric acid/polyethylene terephthalate (PET) [16], stearyl stearate/PET [17], and polyethylene glycol (PEG)/cellulose acetate [18] have been prepared by solution electrospinning. However, the fabrication of paraffin/polymer composite nanofibers by this method is limited because of the lack of solvents for paraffin and polymers. To overcome this limitation, Alay et al. [19] used a two-step method to fabricate paraffin/polymer composite nanofibers. First, nanocapsules of poly(methyl methacrylate-co-glycidyl methacrylate)/*n*-hexadecane were prepared by emulsion polymerization, which were then introduced into polyacrylonitrile nanofibers by electrospinning. As shown later, melt electrospinning is the most suitable technique for fabricating paraffin/polymer composite nanofibers. However, only few studies on these materials have been reported.

Coaxial electrospinning, a new technique to fabricate core/shell nanofibers, has recently received increasing attention. This method places PCM in the core of a nanofiber, which is protected by a polymeric shell layer from the environment. Therefore, during the phase-change processes, the shape of the electrospun nanofibers is maintained, which prevents the leakage of PCM. In our previous study [20], core/shell poly(ethylene glycol) (PEG)/poly(vinylidene fluo-

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ride) (PVDF) nanofibers fabricated by solution coaxial electrospinning exhibited good tensile strength with an energy-storage capacity of up to 34.8 J/g. However, this system has the following limitations. First, only PEG with a molecular weight of 1,000 g/mol (PEG1000) and a heat of fusion of 171.9 J/g is a suitable core PCM for the electrospinning of PEG/PVDF core/shell nanofibers. Second, the PEG encapsulation capacity is relatively low (20 wt%) because of the dilution of PEG in solution, leading to lower heat storage. Although PEGs with higher molecular weight have higher heat of fusion, they have lower critical concentration, resulting in lesser encapsulated polymer in the core of the nanofibers. To overcome this problem, we employed melted PEG in the core to successfully fabricate PEG/PVDF core/shell nanofibers by coaxial electrospinning [21]. Because of the elimination of the solvent, PEGs with a molecular weight of 1,000, 2,000, and 4,000 g/mol were well encapsulated in the core of the nanofibers, exhibiting relatively high latent heats of fusion of 22, 36, and 68 J/g, respectively. However, PEGs with molecular weights below 8,000 g/mol exhibit lower fusion enthalpy and higher supercooling compared to paraffin with 10-20 carbon atoms [4]. The melting temperature of PEG significantly depends on its molecular weight; PEG1000 with melting temperature near the human body temperature is suitable for applications in smart textiles. McCane et al. [21] developed a melt coaxial electrospinning method to fabricate PCM-containing composite nanofibers using octadecane, hexadecane, and eicosane as core materials and poly(vinyl pyrrolidone) as shell material. The obtained nanofibers could load 31, 37, and 45 wt% of hexadecane, eicosane, and octadecane, respectively, corresponding to the melting enthalpies of 71, 88, and 114 J/g. However, this procedure has a drawback: it reduces encapsulation efficiency caused by the hydrophilic poly(vinyl pyrrolidone), leading to incomplete core-shell structures of the obtained nanofibers. In addition, the usage of poly(vinyl pyrrolidone), a strong hydrophilic polymer, as a shell material decreases the efficiency of PCM encapsulation during the exposure of the nanofibers to water/moisture.

We fabricated eicosane/PVDF core/shell composite nanofibers using a melt coaxial electrospinning procedure. Eicosane is widely used as a PCM in textiles for its high heat of fusion, good chemical stability, and ability to freeze without supercooling. Because its melting temperature is near the human body temperature, it can adapt to maintain the body temperature [23-26]. PVDF, a hydrophobic and semicrystalline polymer with high mechanical strength and good thermal properties, is a suitable shell material for encapsulating eicosane in composite nanofibers. The morphology and size of the electrospun composite nanofibers were investigated using field-emission scanning-electron microscopy (FE-SEM). The core/shell structure of the electrospun eicosane/PVDF composite nanofibers was observed by transmission electron microscopy (TEM). We used differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to investigate the thermal properties and thermal reliability of the eicosane/PVDF composite nanofibers. In addition, we evaluated the tensile and thermoregulating properties of nonwoven mats of eicosane/PVDF core/shell composite nanofibers.

## EXPERIMENTAL

### 1. Materials

Kynar 761, a commercial product of PVDF, was obtained from

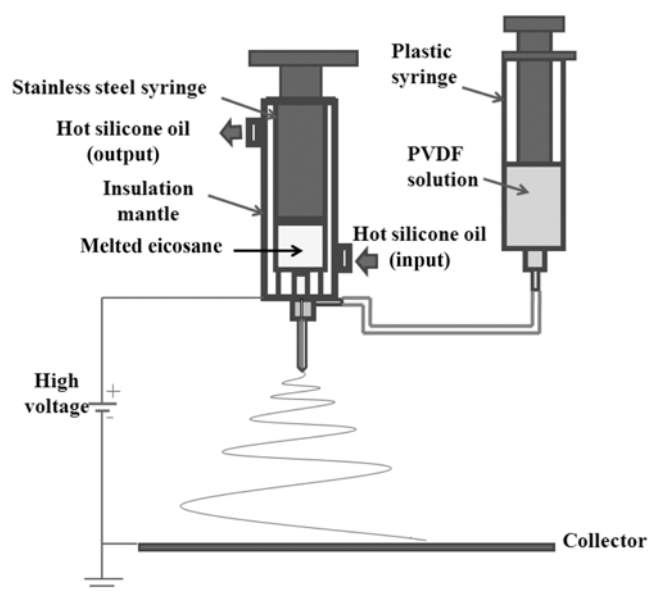


Fig. 1. Schematic of melt coaxial electrospinning.

Elf Atochem of North America Inc. Eicosane was supplied by Sigma-Aldrich (St Louis, MO, USA). *N,N*-dimethylformamide was purchased from Samchun Co. (South Korea). All the chemicals were used without further purification.

### 2. Coaxial Electrospinning

Fig. 1 illustrates the melt coaxial electrospinning process. Eicosane was put into a stainless-steel syringe preheated to 55 °C. PVDF (16 wt%) dissolved in *N,N*-dimethylformamide was placed into a plastic syringe. The melted eicosane and the PVDF solution were injected into the coaxial composite spinneret, which consisted of two concentric capillaries. The inner and outer capillary had the inner and outer diameters of 0.35 and 1.05 mm and of 0.65 and 1.20 mm, respectively. The feed rates of the core and shell materials to the capillaries were controlled by two separate pumps (Nano NC, Seoul, Korea). Both capillaries were connected to the same high-voltage power supply. The electrospun composite nanofibers were collected on aluminum foil placed above a flat and grounded metal plate. The applied voltage and the distance between the tip of the spinneret and the collector were maintained at 12 kV and 17 cm, respectively. The constant shell flow rate was 1.500 mL/h, and the core flow rate was varied from 0.090 to 0.210 mL/h.

### 3. Characterization

The morphology of the nonwoven mats was observed using an FE-SEM (HITACHI S-4700, Tokyo, Japan) with a coating system (BAL-TEC MED020). The average diameter of the electrospun nanofibers was determined from the FE-SEM images using visualization software TOMORO Scope Eye 3.6. The structure of the coaxially electrospun core/shell nanofibers was determined by TEM observations (Tecnai™ G2, USA), which were obtained by using carbon-coated copper grids comprised of electrospun coaxial fibers.

The transition temperatures and latent heats of the electrospun eicosane/PVDF composite nanofibers were analyzed via DSC (SH IN2920, TA Instruments, New Castle, DE, USA) with a heating/cooling rate of 10 °C/min under constant nitrogen flow. To determine the thermal reliability of the eicosane/PVDF composite nano-

fibers, a thermal cycling test involving 100 consecutive melting and cooling cycles was conducted. To determine the PCM content in the coaxially electrospun composite nanofibers, a TGA was performed using a thermal analyzer (EXSTAR 6000, Seiko Instruments Inc., Chiba, Japan) in the temperature range 25–650 °C with a heating rate of 20 °C/min under nitrogen flow.

The mechanical properties of the nonwoven mats of the electrospun core/shell nanofibers were characterized by tensile tester (LR 5K, Lloyd Instruments Ltd., Bognor Regis, UK). The nonwoven webs of the composite nanofibers were tested with a 0.1-N preload at a crosshead speed of 5 mm/min according to American Society for Testing and Materials (ASTM) D638. The length, width, and depth of the nonwoven web test sheets was ~30 mm, 10 mm, and 50  $\mu\text{m}$ , respectively. Tensile strength and elongation at break results of the non-woven mats were average values from five repetitions

of testing.

The thermoregulating capacity of the obtained nonwoven mats was tested by using thermocouple thermometers (SE 309, Taiwan, China), in which a glass tube filled with 1.0 mL water was rolled with a 3-mm-thick insulation jacket made from different coaxially electrospun nonwoven mats and then covered with aluminum foil. The control tube was covered with aluminum foil only. All the tubes were immersed in a water bath at controlled temperatures of 15–60 °C. The temporal temperature evolution was recorded to evaluate the thermal insulating capacity of the obtained PCMs.

## RESULTS AND DISCUSSION

### 1. Morphology of Coaxially Electrospun Composite Nanofibers

In the melt coaxial electrospinning process, several factors deter-

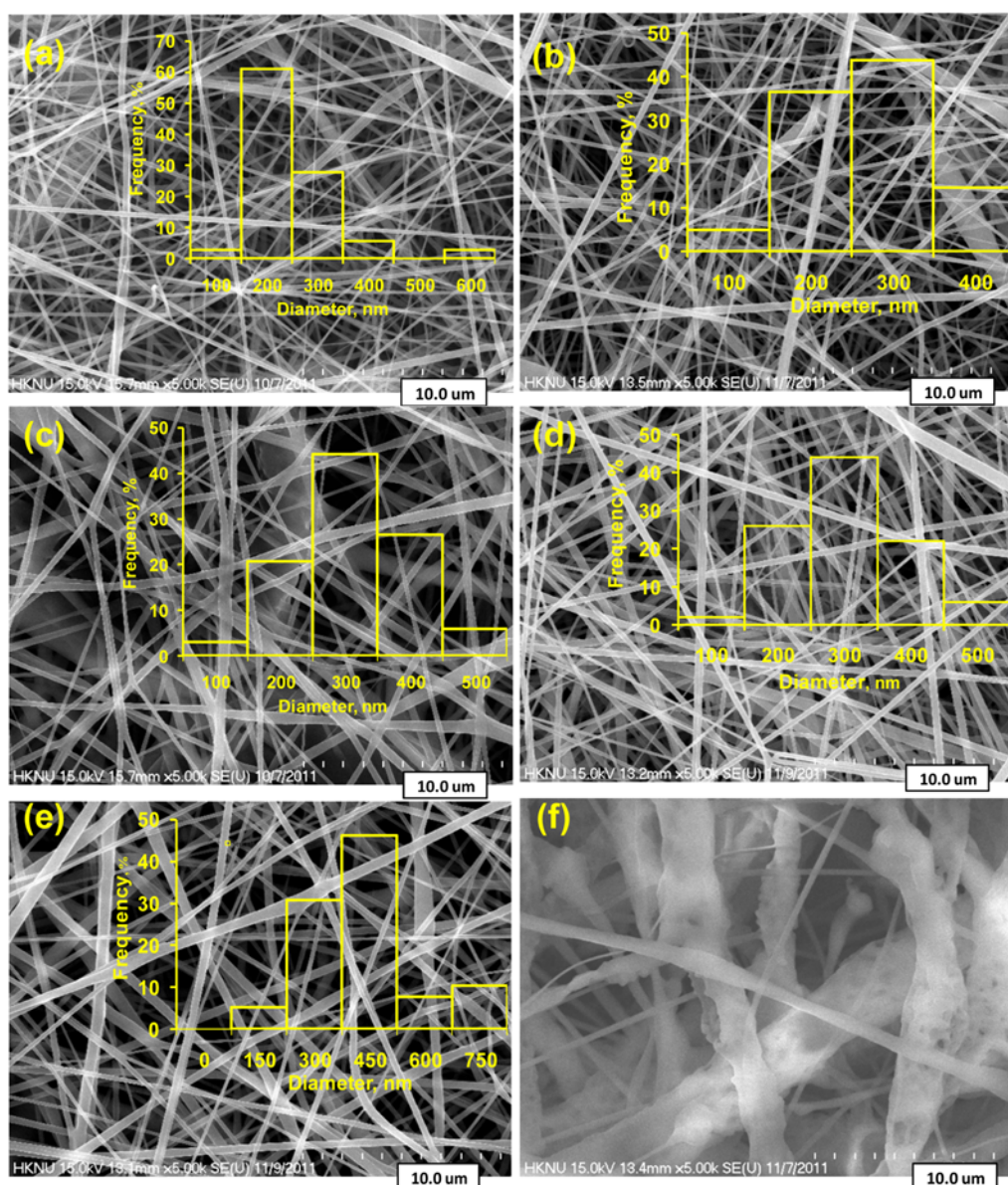


Fig. 2. FE-SEM images of electrospun nanofibers and diameter distributions (inserted diagrams) of PVDF (a) and electrospun eicosane/PVDF composite nanofibers fabricated at core feed rates of (b) 0.108 mL/h, (c) 0.126 mL/h, (d) 0.150 mL/h, (e) 0.180 mL/h, and (f) 0.210 mL/h. The shell feed rate was fixed at 1.500 mL/h.

mine the success of the formation of the core/shell-structured composite nanofibers. During coaxial electrospinning, a double Taylor cone, in which the shell fluid forms a sheath around the core fluid, develops at the tip of the coaxial spinneret. With sufficient values of viscosity, feeding rates, and interface tension of inner and outer liquids, the shell fluid can stabilize the core and protect it against breaking up into droplets. To overcome surface tension, the shell component stretches, exerting a viscous drag on the core fluid, resulting in a stable compound jet [20,27]. To evaluate the dependence of the stability of coaxially electrospun core/shell-structured nanofibers with the highest eicosane encapsulation efficiency on the core-to-shell feed rate ratios, the shell feed rate was maintained constant at 1.500 mL/h while the core feed rate was varied from 0.090 to 0.210 mL/h. Fig. 2 shows the FE-SEM images of nonwoven mats of PVDF nanofibers and eicosane/PVDF composite nanofibers fabricated at different core feed rates. At core feed rates  $\leq 0.180$  mL/h, fine fibers were produced with few hundreds of nanometers in diameter. When the core feed rate became 0.210 mL/h, the nonwoven mat exhibited rod-like fibers of diameter 3–7  $\mu\text{m}$ , which may contribute to the breakdown of the coaxial Taylor cone at high core feed rates. At core feed rates  $\geq 0.210$  mL/h, the shell fluid could not completely encapsulate the core fluid. Furthermore, because of the poor compatibility between melted eicosane and PVDF solution, eicosane adhered to the fiber surface.

The core/shell structures of the electrospun eicosane/PVDF composite nanofibers fabricated at different core feed rates were elucidated using TEM (see Fig. 3). All the composite nanofibers fabricated at the core feed rates from 0.108 to 0.180 mL/h showed a good core/shell structure, with a clear boundary between the core and shell. The diameters of the coaxially electrospun eicosane/PVDF composite nanofibers were larger than those of PVDF nanofibers and

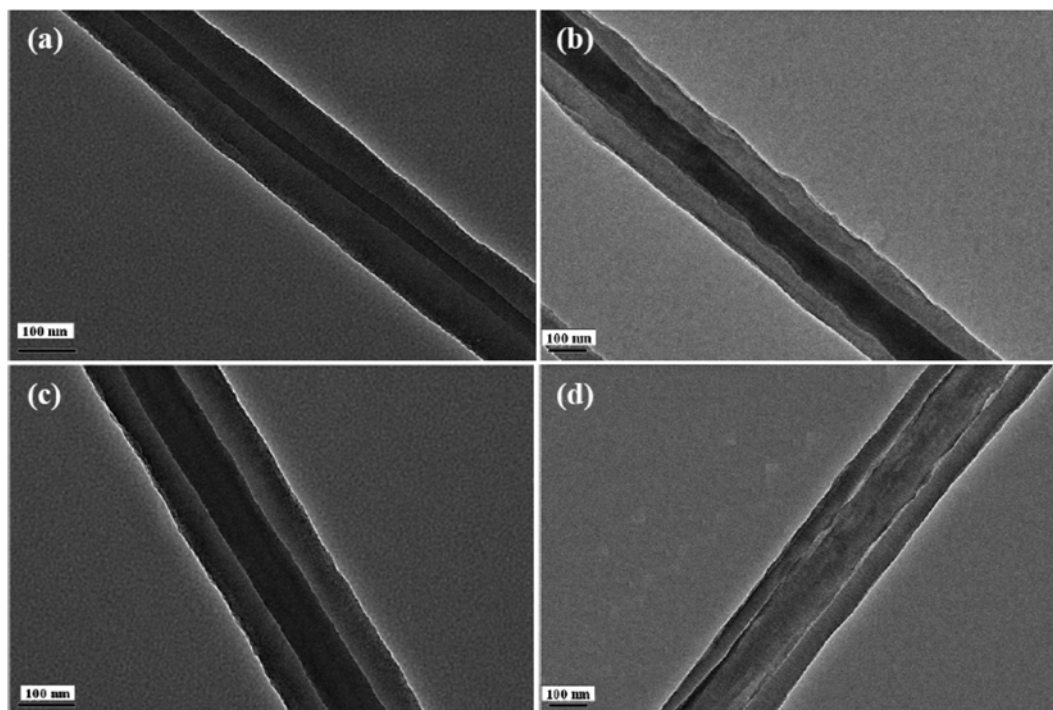
**Table 1. Average diameters of electrospun eicosane/PVDF composite nanofibers and their cores as a function of core feed rate. The shell feed rate was fixed at 1.500 mL/h**

Core feed rate (mL/h)	Average diameter of fibers (nm)	Average diameter of the core (nm)
0.108	241	35
0.126	256	85
0.150	263	103
0.180	280	172

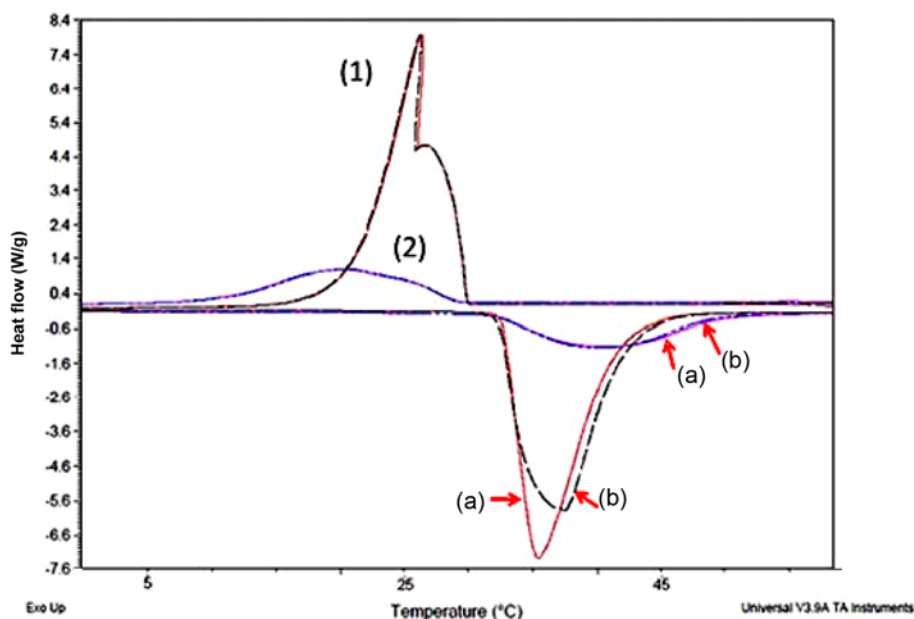
slightly increased when the core feed rate was increased. However, a large increase in core diameter and a decrease in shell thickness were observed with increasing core feed rate (Table 1), indicating a concomitant increasing eicosane loading of the core in the composite nanofibers.

## 2. Thermal Properties

Paraffin is good PCM because of its high heat of fusion, good chemical stability, availability over a wide range of temperature, and ability to freeze without supercooling, as shown below. We used paraffin eicosane as the PCM in coaxially electrospun eicosane/PVDF composite nanofibers. Thermal properties of eicosane and nonwoven mats of eicosane/PVDF composite nanofibers are shown in Fig. 4 and Table 2. The melting and crystallization points of eicosane were 36.52  $^{\circ}\text{C}$  and 26.06  $^{\circ}\text{C}$ , respectively, which were in the range of the body-comfort temperature. Therefore, eicosane is a good candidate as PCM in smart textiles. Broadening of both the fusion and crystallization peaks of eicosane in the eicosane/PVDF composite nanofibers was observed. In particular, the melting point increased while the crystallization point decreased. This observation might be because of the encapsulation of eicosane, which would slow down



**Fig. 3. TEM images of electrospun eicosane/PVDF composite nanofibers fabricated at core feed rates of (a) 0.108 mL/h, (b) 0.126 mL/h, (c) 0.150 mL/h, and (d) 0.180 mL/h. The shell feed rate was fixed at 1.500 mL/h.**



**Fig. 4.** DSC curves of (1) eicosane and (2) electrospun eicosane/PVDF composite nanofibers after (a) 5 and (b) 100 thermal cycles. The composite nanofibers were prepared at a core feed rate of 0.180 mL/h and a shell feed rate of 1.500 mL/h.

**Table 2.** Thermal properties of eicosane and nonwoven mats of eicosane/PVDF composite nanofibers

Type of sample	Number of cycles	Melting point (°C)	Heat of fusion (J/g)	Crystallization temperature (°C)	Heat of crystallization (J/g)
Eicosane	5	36.52	237	26.06	234
	100	37.28	236	26.04	234
Eicosane/PVDF core/shell nanofibers	5	39.20	77	21.18	75
	100	39.20	77	21.18	75

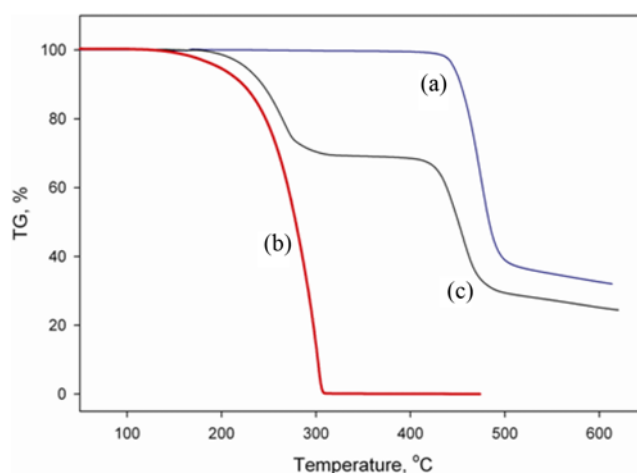
heat transfer from the environment to the core, thereby disturbing the melting and crystallization processes of eicosane. The following equation is used to calculate the content of eicosane encapsulated in the eicosane/PVDF composite nanofibers [18,28]:

$$EI(\%) = \frac{\Delta H_{Ei/PVDF}}{\Delta H_{Ei}} \times 100 \quad (1)$$

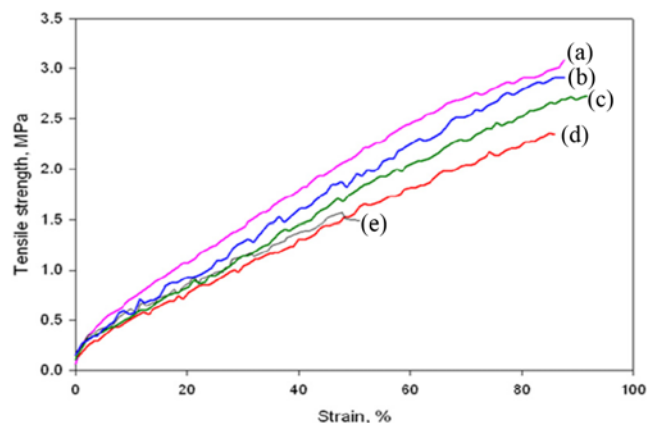
where  $\Delta H_{Ei/PVDF}$  and  $\Delta H_{Ei}$  are the measured latent heats of fusion of the eicosane/PVDF composite nanofibers and pure eicosane, respectively. At a core feed rate of 0.180 mL/h,  $\Delta H_{Ei/PVDF}$  and  $\Delta H_{Ei}$  were 237 and 77 J/g, respectively. Therefore, the calculated amount of eicosane encapsulated in the composite nanofibers was 32.49 wt%, which is comparable to the encapsulation ratio of other paraffin in either paraffin/polymer microcapsules or paraffin/polymer composite nanofibers. Sari et al. [7] and Alkan et al. [28] reported microencapsulation ratios of *n*-octacosane and docosane in poly(methyl methacrylate) PMMA/paraffin of 43 wt% and 28 wt%, respectively. For comparison, coaxial nanofibers of paraffin/TiO<sub>2</sub>-poly(vinyl pyrrolidone) containing 31 wt% hexadecane and 45 wt% octadecane, respectively, were successfully fabricated by McCann et al. [22].

The DSC curves of electrospun eicosane/PVDF composite nanofibers after 5 and 100 thermal cycles were indistinguishable, whereas the melting point of pure eicosane changed slightly with increasing thermal cycles. This might be caused by the history-dependent ther-

mal properties of the samples. In particular, eicosane in eicosane/PVDF composite nanofibers probably underwent melting-solidifying processes during electrospinning. There were no changes in the curve shapes or the positions and sharpness of the melting points



**Fig. 5.** TGA curves of (a) PVDF, (b) eicosane, and (c) electrospun eicosane/PVDF composite nanofibers. The composite nanofibers were prepared at a core feed rate of 0.180 mL/h and a shell feed rate of 1.500 mL/h.



**Fig. 6. Tensile strength vs. strain of nonwoven mats of (a) electrospun PVDF nanofibers and electrospun eicosane/PVDF composite nanofibers fabricated at core feed rates of (b) 0.108 mL/h, (c) 0.150 mL/h, (d) 0.180 mL/h, and (e) 0.210 mL/h. The shell feed rate was fixed at 1.500 mL/h.**

and crystallization points of a nonwoven mat of electrospun eicosane/PVDF composite nanofibers after 5 and 100 thermal cycles, indicating the thermal stability of the obtained electrospun composite nanofibers.

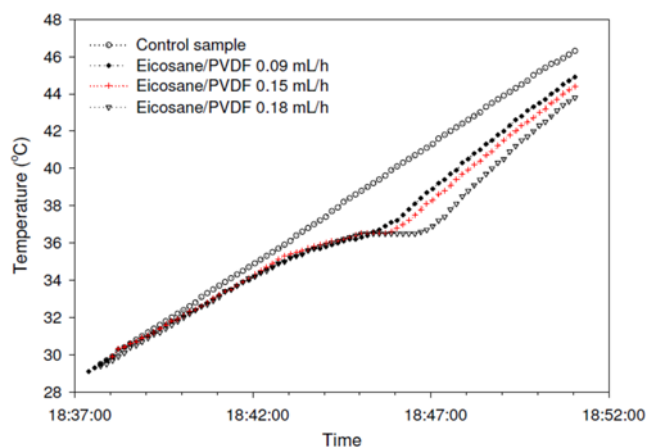
Fig. 5 shows the TGA diagrams of eicosane, electrospun PVDF composite nanofibers, and electrospun eicosane/PVDF composite nanofibers. Eicosane was completely decomposed at 300 °C whereas PVDF was thermally stable up to 470 °C. The weight loss of the electrospun eicosane/PVDF composite nanofibers in the temperature range 25–400 °C was attributed to the loss of eicosane encapsulated in the composite nanofibers, which amounted to 33.2 wt%. This value could be the loading weight of eicosane, which is consistent with the value calculated based on the heat of fusion.

### 3. Mechanical Properties

Fig. 6 shows the tensile strength versus strain curves of nonwoven mats of electrospun PVDF nanofibers and eicosane/PVDF composite nanofibers fabricated at different core feed rates. The tensile strengths and strains of the nonwoven mats of eicosane/PVDF composite nanofibers fabricated at core feed rates up to 0.180 mL/h were slightly lower than those of the nonwoven mat of PVDF nanofibers because of the encapsulation of a mechanically weak component (eicosane) in the composite nanofibers. At a core feed rate of 0.210 mL/h, the tensile strength and strain of the nonwoven mat of the eicosane/PVDF composite nanofibers decreased significantly. This might be attributed to two factors: (i) the significant increase in the eicosane fraction, and (ii) an incomplete core/shell structure of the composite nanofibers. Because of the poor compatibility between eicosane and PVDF, a phase separation in which eicosane is heterogeneously dispersed on the surface of PVDF nanofibers (observed in the FE-SEM images) may occur, significantly decreasing the mechanical strength of the composite nanofibers.

### 4. Thermoregulating Properties

The most important properties of PCMs for applications are their heat-storage and thermoregulating properties. The thermoregulating abilities of electrospun eicosane/PVDF composite nanofibers are shown in Fig. 7. When a water bath containing test tubes covered with the nonwoven mats of electrospun eicosane/PVDF composite



**Fig. 7. Thermoregulation curves of a control sample and nonwoven mats of eicosane/PVDF composite nanofibers fabricated at core feed rates of 0.108 mL/h, 0.150 mL/h, and 0.180 mL/h. The shell feed rate was fixed at 1.500 mL/h.**

nanofibers was gradually heated, the temperatures of the test tubes first continuously increased to 35 °C and then remained constant in the range 35–37 °C, close to the melting point of eicosane. This is probably because of the absorption of heat energy during the melting of eicosane, slowing the increase in the temperatures of the test tubes. When a nonwoven mat fabricated at a core feed rate of 0.180 mL/h was used, the temperature of covered test tube remained almost constant for 3 min from 35–37 °C. The temperatures of the test tubes covered with the nonwoven mats of eicosane/PVDF composite nanofibers fabricated at lower core feed rate (0.108 and 0.150 mL/h) increased faster. The value of fusion latent heat of eicosane in the eicosane/PVDF composite nanofibers was attributed to this phenomenon. The increase in the core feed rate leads to increase in the eicosane encapsulation ratio and fusion latent heat, resulting in higher efficient energy storage. These results show that nonwoven mats of eicosane/PVDF composite nanofibers fabricated by melt coaxial electrospinning could be used as thermoregulating materials.

## CONCLUSION

Core/shell eicosane/PVDF composite nanofibers were successfully fabricated via melt coaxial electrospinning at controlled core feed rates. The core/shell structure of the composite nanofibers fabricated at feed rates  $\leq 0.180$  mL/h was confirmed by TEM observations. Nonwoven mats of electrospun eicosane/PVDF composite nanofibers with eicosane content up to 32.5 wt% had a relatively high latent heat of 77 J/g at melting point 39.2 °C, which is close to the human body temperature. These core/shell nonwoven mats exhibited effective thermoregulating ability, which allowed for a stable temperature in the covered test tube for 3 min. They also showed high mechanical strength and good thermal stability. Therefore, these core/shell nanofibers are potential heat-energy-storage materials in thermoregulated textiles.

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