Core-sheath Electrospinning of Shea Butter and Cellulose Acetate to Enhance Heat Transfer in Protective Clothing

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Research Article

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Abstract

Protective clothing for health workers requires heat transfer in hot and humid environments. To study the thermal conduction of phase-change materials and protect them from leakage, we selected skin-friendly shea-butter due to its suitable melting temperature, and the electrospinning processibility of biocompatible cellulose acetate. The shea-butter as a phase-change material was encapsulated in electrospun cellulose acetate fibres within a core/sheath structure, which was stabilised by two concentric Taylor cones during coaxial electrospinning. Transmission and scanning electron microscopy revealed a blood-in-tube vessel-like morphology. Next, differential scanning calorimetry and thermogravimetric analyses confirmed the heat capacity of shea-butter (latent heat of fusion: 42.73 J/g; thermal conductivity: 1.407 W/m·K). The flow rate of the core was proportional to the heat capacity of the shea-butter/cellulose acetate fibres. This was consistent with the finding that the electrospun fibres of the highest-ratio shea-butter (16.19%) had the highest thermal conductivity (0.421 J/g·K). The shea-butter:cellulose acetate ratio was approximately 15:80. The efficacy of heat transfer for the core/sheath fibres in human clothing was assessed by measuring skin temperatures at 13 sites in six males aged 25 to 35 under two conditions: wearing a mask and hood with attached cellulose acetate fibres in the presence and absence of shea-butter. The mean difference in skin temperatures (0.5 °C) between the two conditions was significant. Coaxial electrospinning of shea-butter/cellulose acetate fibres is therefore promising for protective clothing with efficient heat-transfer in the use of a large area.

Keywords

electrospinning·cellulose acetate·phase change material·heat transfer·skin temperature·protective clothing

Abbreviations

CA: cellulose acetate

PCM: phase change material

ShB: shea butter

CCN: coconut oil

C/S: CCN/ShB 1:1 (wt%)

A: acetone

D, DMF: dimethyl formamide

TiO_2: titanium oxide

ZnO: zinc oxide

T_m: melting temperature

T_c: solidifying (crystallising) temperature

ΔH: latent heat of fusion (enthalpy)

C_p: specific heat of at constant pressure

k: thermal conductivity

Introduction

Protective clothing for COVID-19 medical workers in hot-humid environments

Demand is growing for smart clothing and textiles that can protect wearers working in hot, humid environments by means of an integrated cooling mechanism. Due to the coronavirus disease 2019 (COVID-19) pandemic, protective clothing has become essential for both patients and medical personnel. Because the COVID-19 virus can be spread through inhalation of droplets and aerosols, healthcare workers are required to cover their respiratory organs. Unfortunately, wearing coveralls, medical gowns, N95 and filtering face masks, goggles, gloves, and powered air-purifying respirators for extended periods can result in heat strain and thermal discomfort (Park, 2020). For prolonged wear, virus-protective clothing should provide thermal comfort as well as intrinsic protective functions.

Electrospinning of cellulose acetate for protective clothing

Textiles and other materials used in protective clothing are required to provide high levels of functionality, which can cause thermal discomfort, leading in turn to a need for clothing that can offer enhanced heat-transfer abilities. Although cellulose is one of the most abundant and skin-friendly of biomaterials, it is relatively vulnerable to cell propagation and cannot be easily fabricated by electrospinning because it is insoluble in moderate acids and solvents (Khalf *et al.* 2015). Among cellulose derivatives, cellulose acetate (CA) is biodegradable and biocompatible and can be chemically processed with various solvents to fabricate electrospun fibres with a wide variety of applications, including separation membranes, tissue engineering, sensors, and catalysts (Aboamera *et al*. 2018; Liebert 2010; Wang *et al.* 2020; Zhang *et al.* 2018). Because electrospinning produces fibres with a high volume to specific-surface-area ratio, electrospun CA can intensify cell attachment, corresponding to an increase in pore number and sizes (Khalf *et al.* 2015). However, the microbial susceptibility of CA fabric needs to incorporate antibacterial nanoparticles. According to Anitha *et al*. (2013), Jatoi *et al.* (2020), and Phan *et al*. (2019), antimicrobial CA can be fabricated by inserting zinc oxide, copper, or silver nanoparticles in combination with thermo-conductive or thermo-regulative fillers, carbonaceous materials, or fatty oils. Table 1 lists previous reports that explore the functional results of electrospinning CA with nanoparticle additives. Electrospun CA with bactericidal additives appears to be suitable for protective and comfortable respiratory masks that can effectively transfer heat.

Thermal conductivity of phase-change materials

To enhance thermal comfort through thermal conductivity (k) mechanisms, phase-change materials (PCM) can be applied to the fabrication of protective face masks. The ideal PCM requires a melting point (T_m) range appropriate for its application; sufficient latent heat of fusion (ΔH); sufficient specific heat (C_p) capacity; a small change in phase volume; the absence of supercooling; chemical stability; high resistance to flammability, explosion, and toxicity; and high resistance to corrosion of the sheath materials. Such a material must also be easily processed and available at acceptable costs and quantities, according to Abhat 1983, Shchukina *et al.* 2018, Udangawa *et al.* 2019. Among the four types of PCMs (solid-liquid, solid-solid, solid-gas, and liquid-gas), solid-liquid PCMs offer higher ΔH and smaller changes in volume compared with solid-solid and solid-gas PCMs, making them suitable for thermal energy storage (Shchukina *et al.* 2018). Solid-liquid PCMs are available in organic, inorganic, and eutectic varieties. While an inorganic PCM of hydrated salts has a high ΔH per volume (250 to 400 $J \cdot dm^{-3}$) and k, organic PCMs of paraffin wax, fatty acids, and polyethylene glycol are favourable in terms of congruent melting without kinetically supercooling (Abhat 1983; Hemmatian *et al.* 2020; Oh *et al.* 2020). The *n*-alkane chains of paraffin wax affect the phase transition between an isotropic liquid and a well-ordered crystal. In this "metastable rotator phase", the number of carbon atoms (20 to 40) is related to the T_m of paraffin PCM and its ΔH (Sharma *et al.* 2015; Cholakova and Denkov, 2019). Meanwhile, fatty-acid PCMs consist of an aliphatic chain of 13 to 21 carbon atoms, the length of which is proportional to the weight percentage of the fatty acid and the number of carbon atoms, with a carboxyl group and a methyl group at each end (Wahyudi *et al.* 2018). Floros and Narine (2016) reported that diesters from fatty acids produced ΔH of 230 to 260 $J \cdot g^{-1}$, which were higher than ΔH of paraffins (150 to 200 $J \cdot g^{-1}$), with T_m of between 39 °C and 77 °C produced by reacting dialcohols with methyl esters.

A fatty-acid methyl ester from lipids is non-toxic, environmentally friendly, renewable, bactericidal, and safe for human skin, making it suitable for PCMs. Some fatty acids of PCMs exhibit phase transition near skin temperatures, ranging from 28 °C to 35 °C (Sharma *et al.* 2015). One such fatty acid, shea butter, has a T_m of 32 °C to 45 °C, which is higher than that of coconut oil (21 °C to 25 °C). This can be attributed to the longer chains of the main components of shea butter: stearic acid (41.8%) and oleic acid (46.5%) (Table 2), offsetting the higher T_m of stearic acid (69 °C) with that of oleic acid (16.3 °C), according to Udangawa *et al.* (2019), Eckey (1954) and Leakey (1999). The primary constituent of coconut oil, at 52.0% to 53.2%, is lauric acid ($C_{12}H_{24}O_2$), the T_m of which is 43.2 °C. Other components include 16.8% to 21.0% myristic acid ($C_{14}H_{28}O_2$), 7.5% to 10.2% palmitic acid ($C_{16}H_{32}O_2$), 5.0% to 10.0% oleic acid ($C_{18}H_{34}O_2$), and 2.0% to 4.0% stearic acid ($C_{18}H_{36}O_2$). The flash and solidifying points of the shea butter are also higher (> 200 °C and 17 °C to 27 °C, respectively) than those of coconut oil (113 °C and 9% to 16 °C, respectively). In short, shea butter (the eutectic of methyl stearate) offers a phase-change temperature closer to that of the human body temperature of 37.5 °C compared with coconut oil (the eutectic of methyl oleate).

Fabrication of core-sheath structural fibres using coaxial electrospinning

Numerous techniques for inserting the inorganic materials have been investigated to enhance the thermal transfer capacity of PCMs. These techniques include ultra-sonification of sol-gels, vacuum impregnation, hydrothermal processes, and carbonization. Among the techniques, electrospinning in a core-sheath (core-shell) structure is a promising method of expanding the surfaces of PCMs (Ali *et al.* 2019; Song *et al.* 2019). The nano-scaled PCM capsules also exhibit relatively efficient *k* due to a large surface-area-to-volume ratio during electrospinning. (Salunkhe and Shembeker 2012). Cai *et al.* (2013) used electrospinning to manufacture a composite of overlaid polyamide-6 nanofibres with the eutectics of capric-lauric-palmitic-stearic acids, and the inclusion of 10 wt% expanded graphite induced the nanofibrous composite to absorb the acid eutectics, increasing heat enthalpy and thermal capacity. Chen *et al.* (2013) manufactured composite PCM electrospun fibres of polyethylene glycol-cellulose acetate as a core-sheath and found that the content of polyethylene glycol affected the enthalpy of phase change. Pittarate *et al.* (2011) added 9 wt% polyethylene oxide (PEO) to an electrospun nanocomposite of cellulose acetate to enhance its elastic modulus, elongation at break, and tensile strength by 253%, 54%, and 446%, respectively. The low *k* of polymeric sheaths can be supplemented by the addition of inorganic materials such as expanded graphite, carbon nanotubes, GO, ZnO, or silica particles. Adding ZnO nanoparticles of 20 wt% of PEO maximised those values by 31%, 12%, and 47%, respectively, leading to a decrease in phase-change temperature by between −9 °C and 1 °C.

The design of protective textiles and clothing in hot, humid environments requires wearing trials from the design stage. In such environments, body temperature and sweat are unable to circulate out of the textiles and clothing, which activates heat dissipation by the human body to improve thermal comfort through evaporation, convection, conduction, and radiation. Between the skin and the textiles, the human body constantly transfers heat and moisture to keep a comfortable state by controlling body and skin temperature through vaso-venodilation-constriction of arterial flows to hands and feet, and evaporation of perspiration (Caldwell *et al.* 2014). Bedek *et al.* (2011) reported that, when skin temperature was predicted in simulations, the temperature was affected primarily by the *k* of underwear, and skin humidity was related to evaporation resistance, absorption rate, and drying time. Ghaffari *et al.* (2019) studied moisture resistance, air permeability, thermal insulation, and the resulting thermal comfort of electrospun polyacrylonitrile fibres sandwiched between a plain polyester fabric and a nylon-warp knitted fabric. Raccuglia *et al.* (2017) evaluated the subjective perception of skin wetness, thermal sensation, and thermal comfort produced by 24 samples by applying them to the upper backs of 12 male and female subjects. The study revealed that thickness affected the perception of cooling sensation and humidity, and the cooling capacity was proportional to the moisture content of the fibres.

This study was designed to develop a cooling-functional textile by electrospinning encapsulated PCMs in CA in a core-sheath structure. One objective was to fabricate the electrospun shea butter–CA with encapsulating additives in an attempt to intensify the *k* of the sheath and latent heat, leading to solidification of the core. The other was to evaluate the actual thermal regulation by suppressing the increase in skin temperature of six subjects. The results of a human-wearing assessment are compared with those of thermophysical tests to evaluate the

practical heat-transfer performance of functional clothing for healthcare workers treating patients with COVID-19.

Experimental methods

Materials

Cellulose acetate with a degree of acetylation of 55 ± 3% was obtained from Daejung Chemicals & Metals, Ltd and Kanto (Korea and Japan). Gel permeation chromatography revealed that CA had an average molecular weight (M_n) of 139,000, a mass average molecular weight (M_w) of 270,000, and a polydispersity index of 1.94. As solvents, acetone 99.8%, dimethylformamide (N,N-Dimethylformamide [DMF]) were purchased from Daejung Chemicals & Metals, Ltd (Korea). As a PCM for this study, shea butter (Butyrospermum parkii) consisting of 41.8% stearic acid and 46.5% oleic acid, along with coconut oil were purchased from Kerfoot (UK) and Ottogi Co., Ltd. (Korea). To provide the electrospun core and sheaths with *k*, radiation protection, and antibacterial activity, three additives were used: aqueous graphene oxide (GO) (Uni-Nanotech Corp, Korea) containing approximately 80% graphene flakes at a concentration of 6.2 g/L and a flake size of 0.5 to 5 μm, titanium dioxide (TiO_2), and zinc oxide (ZnO) (Guwall cakesoap Ltd., Korea).

Preparation and electrospinning

This study used a solvent system of acetone for electrospinning solutions: acetone with DMF at five different acetone:DMF (v/v) ratios (4:1, 2:1, 1:1, 1:2, 1:4). In the mixed solvents, electrospinning solutions of cellulose acetate were attempted at five concentrations between 17.5 wt% and 27.5 wt% at intervals of 2.5 wt%. As shown in Fig. 1, the CA powder was mixed physically with additives equivalent to 5% of the acetate weight. The mixture of prepared powder was then poured into an Erlenmeyer flask and dissolved in the mixed solvents at 55 ℃ to 60 ℃ while strongly stirred by a magnetic stirrer. Following completion of the dissolution reaction, the prepared solution was injected into a 10 cc syringe, and air bubbles in the syringe were removed.

The electrospinning device (ESR200, eS-robot, NanoNC Ltd., Korea) comprised two pumps, a robot that moves the pumps along the x and y axes, and a rotary drum collector. This device provided high voltage up to 30 kV in an acrylic box. The tips of the dual nozzle used in coaxial spinning had an inner diameter of 1.23 mm and an outer diameter of 1.50 mm in size, and the inner and outer diameters of a core needle were 0.33 mm and 0.63 mm, respectively. The sheath solution from another syringe was injected into the tube connecting to the dual nozzle with polyethylene and polytetrafluoroethylene tubes measuring 1/16 and 3/32 inches in diameter, respectively. For comparison with the core-sheath electrospun fibres, the needle of a single nozzle for electrospinning CA fibres with an inner/outer diameter of 0.5 mm/0.8 mm, which is similar to the area of the sheath, was used. The flow rate varied from 0.1 to 7.0 mL/h, the distance from the tip to the collector (TCD) ranged from 5.5 to 15.0 cm, and the applied voltage was from 13 to 25 kV. The final setting of core-sheath electrospinning was for the CA solution of 22.5 wt% to 25.0 wt%. Electrospun fibres of the PCM-CA were collected by aluminium foil wrapped around a drum rotating at 250 rpm. In Table 3, all 22 electrospun specimens are classified according to the

presence or absence of PCMs or additives, the type of PCMs, concentration, volume ratio of the binary solvent systems, and the flow rate of core and sheath.

Electrospun-fibre observations

Transmission electron microscopy (TEM), scanning electron microscopy (SEM), and optical microscopy of the electrospun fibres of core-sheath were used to confirm the presence of PCMs encapsulated in the CA sheath. During the experiments, the electrospun PCM-CA fibres were collected directly on 200-mesh copper grids coated with lacey carbon. Morphological images of the core-sheath fibres were taken using a field emission TEM (JEM-2100F, Joel Ltd.) at 200 kV. High-resolution SEM (SU8220, Hitachi Ltd.) at the Seoul Western Centre, Korea Institute of Basic Science, was also used to image the PCM-CA fibres at voltages of 10 to 15 kV. The electrospun fibres were examined directly through an optical microscope (Eclipse LV100ND, Nikon). The diameter of fibres and fibrils in a total of 60 to 90 per case were measured using ImageJ (National Institutes of Health, USA) and Gryphax software (Jenoptik, Japan), and frequency analyses of the fibre and histograms of fibre-size distribution were conducted in SPSS 19.0 (IBM SPSS Statistics).

Thermal characterization

The latent heat of fusion and thermal weight loss of the electrospun PCM-CA fibres were measured through differential scanning calorimetric analysis (DSC) and thermogravimetric analysis (TGA). To compare the thermal capacity of PCM-CA fibres and PCM itself, the enthalpies and melting-freezing peaks of each sample were analysed with a DSC (DSC 25, TA Instruments). The DSC measurement went through each stage at a nitrogen atmosphere as follows. First, 10 mg of each sample was placed in a Tzero aluminium pan. Next, the samples were stabilised at 25°C in an isothermal state for 1 min. They were then heated to 50°C at a rate of 10°C/min, isothermalised for 1 min, and then cooled to −10 °C at 20 °C/min, after which they stayed in an isothermal state for 1 min. For the second heating-cooling cycle, they were reheated and recooled to between −10 °C and 50 °C, and each stage was accompanied by isothermalising for 1 min. For TGA measurements, Q50 and Discovery (TA Instruments) devices were used. A platinum pan was weighed without any sample and after each sample was contained, and the samples were then heated from 25 °C to between 600 °C and 800 °C at a rate of 10 °C/min in a nitrogen atmosphere.

Application to facial mask hoods through 3D scanning and 3D printing

A face hood was fabricated to attach the PCM-CA electrospun fibres. The hood had to be stuck to the subjects' skin to increase the k of the PCM. To ensure an ergonomic design of the face hood, 3D scanning of a single adult male in his early 30s was performed from the head to the shoulder, and the left figure of the scanned face and head was symmetrically modelled in CAD software (Rhino 7, Robert McNeel & Associates) to create a human body model. This model was 3D-printed at full size with polylactic acid filaments using an FDM-type printer (Replicator+, MakerBot). The model was sliced into eight parts according to the size of the printer. The printing time for each part was 20 to 26 hours, with a total print time of eight days. The divided output was

finished by bonding with putty, bond, and carboxymethyl cellulose. The pattern of the face hood was draped with line-tape on the finished model. A 95%/5% polyester/polyurethane composition was used for the face hood fabricated by 3D draping on a model made by 3D scanning and 3D printing.

Human-wearing assessment

Six healthy male subjects aged 25 to 32 years were recruited by distributing recruitment documents at sports centres and health clubs for 10 weeks or through expert recommendations, with the approval of Ewha Womans University Institutional Review Board (No: ewha-202010-0014-03). After receiving sufficient explanation and signing the consent form, the subjects measured their height, weight, heart rate, and pulse rate (an average height of 175.01 ± 4.61 cm, an average weight of 76.93 ± 8.58 kg, and average body mass index of 25.12 ± 2.60). For each subject, 13 skin temperatures and left auditory canal temperatures were measured, including two facial body parts (left temple, left cheek), five upper-body parts (front neck, chest, upper left arm, lower left arm, and left hand), and five lower-body parts (abdomen, waist, left thigh, left calf, and left foot). A set of 8-channel thermistors (Gram LT-8A, Japan) were simultaneously used as skin-temperature sensors, and infrared thermography was taken with a thermal imaging camera (Flir C3, USA). An artificial climate room was set at 33.0 °C, 70 ± 2% relative humidity.

This study collected a total 13 skin-temperature records of the six subjects. To calculate the mean skin temperature of each subject, the Hardy and Dubois formula was used as follows:

$$\text{Mean skin temperatures (seven-point method)}$$

$$= 0.07*T_{forehead} + 0.35*T_{chest} + 0.14*T_{arm} + 0.19*T_{thigh} + 0.13*T_{calf} + 0.05*T_{hand} + 0.07*T_{foot} \quad \text{Eq.(1)}$$

Mean skin temperatures, auditory canal temperatures and subjective perception records were obtained from the human-wearing evaluation and analysed statistically using SPSS 19.0. The two experimental conditions of six subjects depended on the presence or absence of PCM: one conditioned for attaching the CA samples containing PCMs and the other for attaching the CA samples without PCMs. A paired-sample t-test was used to analyse the difference in the two conditions to confirm the effect of PCM fibres attached to the hoods on mean skin temperature ($p < 0.05$, two-way t-test).

Results and discussion

Monoaxially electrospun CA as a sheath and coaxially electrospun PCM as a core

The morphology of the electrospun cellulose acetate CA fibres was examined with a single nozzle and the PCM-encapsulating CA fibres were examined with a double nozzle through optical microscopy, SEM, and TEM. The diameters of the fibres and fibrils and the thickness and weight of the electrospun fibres were also measured. To select a suitable solvent for the CA solution, the solubility of CA and the solvents was considered with Hansen solubility parameters (HSPs). Water (δ_T: 48.18~47.90 $MPa^{0.5}$) is a non-solvent of CA (δt: 19.89 $MPa^{0.5}$; δ_h: 11.10 $MPa^{0.5}$) that does not enter within the radius of the HSPs. DMF (δ_h: 11.30 $MPa^{0.5}$) exhibit superior

solubility compared with acetone (δ_h: 6.97 $MPa^{0.5}$). The concentration of the solution dissolved with DMF wt% was much higher than that of the solution (below 15 wt%) when CA was dissolved with 100% acetone as a single solvent (Tungprapa *et al.* 2007). Mixing soluble solvents with CA resulted in higher critical-chain entanglement and improved the electrospinnability of CA. Mixing volatile solvents such as acetone is also necessary as the nano-scaled, rod-shaped CA electrospun fibres were neatly solidified when the solvent was sufficiently volatilised during jet ejection. When the solubility of a solvent is too high, the viscoelasticity of the solution may be insufficient for electrospinning (Lee *et al.* 2018).

The surfaces of the CA fibres varied from smooth surfaces resembling vinyl films to rough surfaces with paper-like fibre grains when electrospun in various solvent ratios. This pattern changed considerably depending on the acetone ratio. The lower the acetone ratio and the higher the DMF ratio, the more the fibres agglomerated like a smooth vinyl film, which is consistent with the literature (Aboamera *et al,* 2019; Crabbe-Mann *et al.* 2018). However, because other variables are involved in addition to the solvent ratio, dependence on the solvent ratio was not necessarily evident. In the A:D 4:1 solution, the acetone volatilised too quickly in a dry environment; it solidified before reaching the collector and was difficult to call an electrospun fibre. A mixed solvent ratio was therefore selected as A:D 1:1 instead of the high ratio of DMF at which the surface of the electrospun fibres had lost their cellulose properties and the low ratio of DMF when the surface was too dry and rough.

Electrospun CA fibres of 25 wt% at a ratio of A:D 1:1 had a tree-leaf shape and a diameter of 2.39 to 3.04 μm. In Fig. 2 (a), the CA fibres electrospun from the single nozzle are characterised by a few transparent microfibres shaped like midribs (approximately 100 μm) penetrating straight and numerous nanofibrils resembling side veins (approximately 500 nm) intertwining with each other. The diameter of the electrospun CA fibres was bisected at the micrometer scale (with a maximum value 28.25 to 28.45 μm) and the nanometer scale (with a minimum value of 270 to 970 nm), offsetting the average diameter. This can be attributed to the high flow rate, which widened the distribution due to the large volume of solution, which was demanded for the shell used in coaxial electrospinning to embrace the relatively large PCM core. We inferred that the acetone and DMF solvents did not mix homogeneously but combined separately with the CA polymers. Alternatively, insufficient voltage or too great inflow rate may have made it impossible for the solution jet flown to the collector to split, causing colloidal aggregation of the molecular chains. Some electrospun CA fibres may have failed to overcome the surface tension of the solution at the tip and Coulomb repulsion in the jet stretching due to the positive charge that was dispersed from its TiO_2 and ZnO.

In coaxial electrospinning using the dual nozzle, we investigated the morphological characteristics of the encapsulation of shea butter (ShB) inside the CA sheath. As shown in Fig. 3 (a), two concentric Taylor cones of each core and sheath solution were observed when the solutions were ejected from the tip of the dual nozzle. Due to Plateau-Rayleigh instability, the droplet of the spinning solution, originally spherical in shape due to surface tension, was stretched to an ellipse by jet stretching. Based on the TEM images in Fig. 3 (b) and (d), a cylindrical morphology with small beads characterised the core-sheath fibre, and ShB was inserted into the

CA fibres. However, when the flow rate of sheath did not correspond to that of core, some ShB leaked from the sheath, as shown in the left side the SEM image of Fig 3 (c). This may be attributable to the fact that the excessively high voltage applied to the dual nozzle split the ejected droplets.

Next, we investigated the effects of the core-sheath flow rate on the encapsulation of PCM in CA during core-sheath electrospinning. To determine the appropriate ratio for the sheath and the core, the inflow rate of the sheath was set from 1.0 mL/h to 8.0 mL/h, and the inflow rate of the core was set to 0.5 mL/h and 1.0 mL/h. In coaxial electrospinning, the viscosity of the core must be lower than that of the sheath, and the flow rate of the sheath must be sufficient to cover the core. The inflow rate set by the viscosity ratio between the core and the sheath is therefore critical (Khalf *et al.* 2015). For successful coaxial electrospinning, appropriate flow rates and voltage were required to keep two Taylor cones continuously stable and protect the core by the sheath against corrosion or fibre breakage. The encapsulated PCMs do not just protect the durability of the core and the stability of thermal cycling, but also augment multiple functions of its sheath by coating the surface of the PCM. The encapsulated PCM protects the core by avoiding leakage during thermal cycling and corrosion of or damage to its sheath (Alehosseini and Jafari 2020). The cellulose sheaths encapsulating the PCMs, octadecane, or linseed oil by coating with polysiloxane resins also control insulation, and ultraviolet protection, and play roles in self-cleaning, and self-healing to reinforce protective textiles or clothing (Li *et al*. 2019; Chen *et al.* 2020).

Heat transmittance of electro-spun fibres in DSC and TGA analysis

To study the effect of sheath flow rate on the *k* of the PCM-CA fibre, we analysed eight specimens, including ShB itself, with DSC and TGA. Table 4 and Fig. 4 illustrate the kinetic, thermophysical, thermodynamic characteristics of seven ShB-CA electrospun fibres, coconut oil, and ShB as revealed by DSC. As the main PCM in this study, ShB melted from 32.06 ℃ and reached its maximum at 37.86 ℃ with an enthalpy of 42.73 $J \cdot g^{-1}$. When crystallised, the phase change from liquid to solid began at 13.49 ℃, and its peak was reached at approximately 6.00 ℃ to 8.79 ℃. When the temperature increased in the second heating step, ShB began to melt at a temperature that was half that of the initial T_m (about 15 °C) to approximately half the enthalpy (21.368 $J \cdot g^{-1}$), and the temperature at the third heating-cooling cycle showed almost the same pattern as the second. This could be due to lack of crystallisation time, as it took at least 20 min to fulfil its own thermal function. Coconut oil had a T_m of 30.27 °C ($T_{m\ onset}$: 25.70 °C) and a solidification peak at 2.14 °C ($T_{c\ onset}$: 4.54 °C). This shows that, because ShB (at 37.86 ℃) was closer to body temperature than coconut oil (at 30.27 ℃), ShB could meet the first ideal PCM requirement, the proper range of T_m for its application (Abhat 1983, Shchukina *et al.* 2018, Udangawa *et al.* 2019).

Despite the ideal melting temperature, whether the thermophysical characteristics of ShB are adequate for the effective PCMs should be considered in association with the fatty-acid content and latent heat, as well as congruent behaviours of melting and crystallisation. Lawer-Yolar *et al*. (2019) pointed out that ShB was appropriate for thermal energy storage but inappropriate for a

PCM because its T_m (4.3 °C to 15.8 °C) was broader and its ΔH during freezing (29.9 to 41.6 J·g^{-1}) was lower than those of palm kernel oil and Allanblackia oil. Their result of the T_m was quite different from that of shown in Table 2 (Lawer-Yolar *et al.* 2019; Canale *et al.* 2005), because the ShB in their study comprised the different content of a lower stearic acid (least 20%) and a higher mono-unsaturated oleic acid (up to 60%). The feasibility of stearate in ShB for PCMs was confirmed in studies of methyl palmitate:methyl stearate at a 4:1 ratio, the synthesis of stearic acid into a porous carbonised-maize straw matrix by vacuum impregnating, and a eutectic mixture of stearic acid and benzamide s of 65.9 °C and ΔH of 200.15 J·g^{-1} due to added graphite that boosted k (Feldman *et al.* 1993; Suppes *et al*. 2003; Wen *et al*. 2021; Ma *et al*. 2019). We therefore adopted ShB despite its large volume change during phase changes that required encapsulation of its sheaths as a confined container.

When the results of Table 4 were scrutinised, ShB's absolute value of ΔH was found to be 42.73 J·g^{-1}, which is a quarter of a typical ΔH of PCMs (150 to 260 J·g^{-1}) in architectural applications yet is also similar to that of a fatty-acid mixture (40 to 100 J·g^{-1}), which was suitable for human comfort (18 °C to 25 °C) (Floros and Narine, 2016; Nazari *et al.* 2021). This can be attributed to different experimental conditions or methods, such as the heating and cooling rate or the isothermal duration required to keep ShB frozen for a certain crystallization period, as mentioned above. The DSC results for the absolute values of the ΔH of the PCMs and specimens were not significant. Nonetheless, the relative values used to rank the enthalpy were used to determine how the flow rate of the core/shell affected the ΔH, C_p, and k.

To compare the thermal behaviour of each sample, C_p, and k were calculated from the DSC results (Table 4). During the DSC cycles of heating and cooling, we assumed that the change in the internal energy of the system resulted from the only heat transfer rate ($\dot{Q}$) in a closed environment under constant pressure. The value for $\dot{Q}$ can be obtained from the first law of thermodynamics:

$$\Delta E_{\text{system}} = \Delta Q_{\text{in-out}} + E_{\text{generat}}\ (\text{J}) \qquad \text{Eq. (2)}$$

$$Q = {}_m C_v \Delta T\ (\text{kJ·s}^{-1}) \qquad \text{Eq. (3)}$$

$$\dot{Q} = \dot{m}\ C_p \Delta T\ (\text{kJ·s}^{-1}) \qquad \text{Eq. (4)}$$

where ${}_m$ is the mass of the specimen, $\dot{m}$ is the mass flow rate, C_v is the specific heat of constant volume, and C_p is the specific heat at constant pressure. One of the heat-transfer mechanisms, the heat transfer rate ($\dot{Q}_{\text{cond}}$), can be obtained from Fourier's law:

$$\dot{Q}_{\text{cond}} = -kA\frac{dT}{dx} \qquad \text{Eq. (5)}$$

where k is the heat conductivity of a substance, A is an area perpendicular to the heat transfer direction, and dT/dx is the temperature gradient.

We found that the higher flow rate of the core, the greater the ΔH, C_p, and k, which was the opposite to the effect of sheath flow rate. When the flow rate of the sheath increased from 2.0

mL/h to 4.0 mL/h, k of A-1T/A-2T at the same concentration (15.0 wt%) decreased from 0.524 $W \cdot m^{-1} \cdot k^{-1}$ to 0.242 $W \cdot m^{-1} \cdot k^{-1}$. This tendency was consistent with other cases, such as B-1T (4.0 mL/h) versus B-4T (3.0 mL/h) as well as B-2T (4.0 mL/h) versus B-3T (3.0 mL/h) at 17.5 wt% with different flow rates of the core (the former, 1.0 mL/h; the latter, 0.5 mL/h). In contrast to the shell, the flow rate of the core was proportional to the ΔH, C_p, and k, presumably contributing to the amount of PCM. However, in the DSC results, all samples were expected to improve the k of the CA shells, accompanied by other techniques detailed below.

The techniques involved in improving k in the fabrication of the porous PCM with carbon composites have been subjected to numerous studies. Liu *et al.* (2017) demonstrated the stability, reliability, and corrosion resistance of an expanded-graphite composite with adipic-succinic acid of a mass ratio of 7:3, a corresponding ΔH of 206 $J \cdot g^{-1}$ and a T_m of 135 ℃. An expanded-graphite composite of eutectic capric-palmitic-stearic acids with a mass ratio 79:15:6 also proved to be thermally stabile even after more than 500 thermal cycles despite a T_m of 21.3°C and a freezing point of 19.0°C with ΔH exceeding 127 $kJ \cdot kg^{-1}$ (Zhang *et al.* 2016). Expanded graphite with a porous structure and acid-treated, expanded-vermiculite-loading aluminium-oxide particles affects the adsorption of eutectic lauric-myristic-palmitic acids with a mass ratio of 55:30:15 and eutectic lauric-myristic-stearic acids with a mass ratio of 59.5:32.0:8.5 and results in an increase in k of the composite (Zhang *et al.* 2013; Wei and Li, 2017). In summary, the k of the shell can be supplemented when coated with carbonaceous solutions or covered with porous foams in or onto encapsulated PCM-CA fibres.

To measure the mass ratio of ShB and CA, TGA and DTG thermograms were made in a range of 300 ℃ to 500 ℃ as shown in Fig. 5 (a) and Table 5. ShB was thermally degraded from 423.97 ℃ to 477.35 ℃, peaking at 461.14 ℃. It consisted mainly of four components (C18:1, C18:2, C16:0, C18:0), with the boiling point of C16:0 overlapping the degradation temperature of the CA electrospun fibres (Table 2). However, the ratio of palmitic acid (C16:0, 3.3% to 3.9%) and TiO_2 and ZnO additives in ShB was nearly imperceptible and they were excluded from the TGA results presented in this study. The major component of stearic acid (C18:0) in ShB could be distinguished from other fatty acids as well as the CA fibres. The ratio of sheath to core was approximately 77.5–80.0 to 16.2–13.2. We therefore inferred that the B-1 sample had the largest amount of ShB core and the least ShB was contained in the C-2 or C-1 sample. The ratio obtained from the TGA results was in agreement with the DSC results that show the highest C_p were found in B-1T (0.421 $J \cdot g^{-1} \cdot K^{-1}$), and the lowest ones in C-1 (0.111 $J \cdot g^{-1} \cdot K^{-1}$). Fig. 5 (b) and (c) represent the ratio of C18:1 and C18:2 at 300 ℃ and that of C18:0 at 400 ℃ on the left side of the enlarged thermograms, consistent with Table 5.

Human-wearing tests through paired differences in skin temperature in contact with electrospun fibres with or without PCMs

Not only was the heat-transfer rate at the fibre level analysed in this study, we also attempted to verify the difference between the heat-transfer capacity of dual-structured PCM-CA electrospun fibres and that of single-structure CA fibres applied to the human body. To increase the k of PCM, the skin and the sample had to be in close contact. We therefore needed to design a

new hood and protective mask as the existing ones were not suitable for the thermal conduction of PCMs. Specifically, existing D-level protective clothing could not be used because PCM performance is realised only when it comes into direct contact with the skin. Fig. 6 (a) shows the new mask hood, which is divided into a head mask and a mask covering the face. The pieces of the mask hood were connected from the sideline of the ears, and heat could be easily dissipated by providing a large opening from the bottom of the back of the head. Velcro attached to the back functioned in two roles, not just opening but also adjusting in size. The electrospun fibre samples were then cut into 10×5 cm^2 pieces (total surface area: 200 cm^2) and attached to the inside of the face hood onto the skins of forehead, cheeks, neck, and left chest, as shown in Fig. 6 (a). This pattern for the mask hood was produced using a human face-head model that was 3D-scanned and -printed.

The electrospun CA samples and PCM-CA samples were attached to the inside of the forementioned face hood and worn by six subjects to evaluate the change in skin temperatures at 13 sites on their bodies. As shown in Fig. 6 (b), 75-min experiments were conducted twice per subject in a high-temperature and high-humidity environment (33 °C, 70% relative humidity). All the subjects sat to get accustomed to the environment for 35 minutes, then changed their hood. Next, after walking at 5 km/h on the treadmill for 20 min, they sat again and rested for 15 minutes. With the collected data of skin temperature and sweat, we found a significant difference in the effect of PCM cooling performance by comparing the skin temperature at the 13 sites, including the inner ear, with a paired t-test using SPSS.

Table 6 and Fig. 7 show the results of the paired t-test of the six subjects and the changes in skin temperature in the presence and absence of PCM in electrospun CA samples in the face hood. In Table 6, the mean skin temperature of individual subjects and the mean skin temperature of all six subjects were calculated by Eq. (1) from Hardy and Dubois, for comparison purposes. The mean skin temperature was lower when wearing a hood with PCM-CA electrospun fibres, except for subject B, whose mean skin temperature when wearing a hood without PCM in CA fibres was higher (34.650 °C) compared with a hood with PCM in CA fibres (34.157 °C).

Fig. 7 illustrates the differences in the average mean skin temperature of all six wearers in the presence and the absence of PCM in CA fibres of the mask hoods. The difference in skin temperature for each of the four sections at 1–20 min, 20–35 min, 40–60 min, and 60–75 min was analysed according to the experimental protocol. In Fig. 7, the black dotted line is the temperature when the hood without PCM was worn, and the red dotted line is the temperature when the hood with PCM was worn. Regardless of the presence or absence of PCM, the auditory canal temperature was approximately 2 °C higher than the mean skin temperature, and it increased at a moderate rate. In the first recovery period at the beginning of the experiment, the temperature showed a constant or slight drop at 30 to 35 min during the initial stage of walking. This phenomenon could be a result of temporary cardiovascular contraction caused by sitting and walking. After changing to the second hood with the new PCM-CA samples, most subjects experienced a more gradual ascent in mean skin temperatures, and the difference between the hoods with and without PCMs had increased. The average skin temperature of all subjects was higher when wearing the hood with the PCM-CA fibres (emerald dotted line) by about 0.20 °C,

compared with the PCM in CA fibres (orange solid line). The average of mean skin temperatures was further delayed toward the second half of the experiment by increasing the gap to 0.25 °C at 70–75 min compared with wearing a hood with the no PCM-CA fibres. This is in agreement with previous research that clothing made of the PCM-microcapsules and PCM-yarns dropped microclimate and humidity within the clothing (Bartkowiak *et al.* 2013). It was therefore concluded that PCM-CA fibres can help prevent skin temperature from increasing.

Another notable finding was the superior effectiveness of heat transfer as measured by the human-wearing assessment compared with the DSC results. The heating system in humans, metabolism, is different from the furnaces used in DSC and TGA and is associated with different thermoregulating mechanisms of homoiotherms or isovelocities. The furnace was required to be set for a constant rate of heating and cooling, which meant more heat was available, to the point that it exceeded the latent heat of ShB, which then tried to react endothermically. This explains why the results of DSC and the human-wearing assessments were incongruent. Hou *et al.* (2019) contended that the most effective technique for evaluating protective clothing of PCMs is human-wearing assessment despite its high cost and time commitment. Mechanical techniques aided by software are designed to control process parameters based on mathematically simplified modelling but can cause difficulties when applied to human heat transfer, which organically intertwines the exchange of thermal conduction and convection from metabolic production to respiration, tissues, and blood (Hou *et al.* 2019). The basal metabolic rate (84.0 to 86.6 $J \cdot s^{-1}$) for the average male adult (30-year-old, 70 kg in weight, 173 cm in height, with a body surface area of 1.8 m^2) increased by 15 $kcal \cdot min^{-1}$ during exercising compared to 0.5 $kcal \cdot min^{-1}$ while sleeping, and lost 244 kJ of heat, corresponding to a decrease in body temperature of 1 °C as the C_p of human body is 3.49 $kJ \cdot kg^{-1} \cdot °C^{-1}$ (Kenny *et al.* 2017; Yunus 2003).

Another difference between the DSC results and those of the human-wearing assessment was the change in k of the CA fibres by sweating. During the experiments, the subjects expressed considerable amounts of perspiration, which countered the increasing skin temperatures, consistent with other literature suggesting that releasing sweat or moisture increases heat capacity and storage by expanding the gap of k between materials and sweat (Raccuglia *et al*. 2017; Guan *et al.* 2020). Sweating could provoke evaporative cooling through the difference in water vapor pressures between the skin and the air. However, this study excluded the effect of convection by manipulating the ventilation and humidity of the experimental environment to make it windless-damp (relatively humidity 70%).

To take advantage of complex mechanisms of heat transfer in humans, some researchers have attempted human-wearing trials of an innovative hybrid cooling system by means of the combination of thermal conduction, convection and irradiation. Hybrid cooling applications with PCMs, through wearing tests for eight subjects, were suggested with insulation layers, four fans in a cooling vest containing ice packs through heat convection and conduction (Chaen *et al.* 2019; Udayraj *et al.* 2019). Using ventilation fans lowered body core temperatures by 0.2°C and decreased rectum temperature by 0.13 °C and mean skin temperature near the neck by 5 °C. In sum, the cooling performance of PCM-CA electrospun fibres can be enhanced by adding an extra cooling apparatus in combination with thermal convection and irradiation.

Conclusions

Protective clothing for COVID-19 medical workers in hot, humid environments should incorporate thermoregulating mechanisms of heat transfer. To control heat transmittance of skin temperature, ShB composed of stearic and oleic acids was chosen for the PCM because of its appropriate T_m of 28 °C to 35 °C, bactericidal activity, and non-toxicity on human skin.

This research focused on the formation of electrospun CA fibres and PCM-CA fibres and their characterisation, heat capacity at measured by DSC and TGA analyses, and heat transfer through human body assessment. First, to fabricate the PCM encapsulation of a core-sheath structure, CA solutions of 17.5 wt% to 25.0 wt% were coaxially electrospun at a solvent ratio of A:D 1:1 from a TCD of 12 cm at the flow rate of 2.0 to 4.0 mL/h (sheath) and 0.5 to 1.0 mL/h (core). The morphology of PCM-CA electrospun fibres were characterised by the insertion of the core in sheath-like blood in tubular vessels with a few spherical beads as observed through TEM, SEM, and optical microscopy.

Second, DSC results revealed that the heat capacity of electrospun PCM-CA fibres was a half to a quarter of that of ShB, with a ΔH of 42.73 $J \cdot g^{-1}$, a C_p of 1.90 $J \cdot g^{-1} \cdot K^{-1}$ and k of 1.407 $W \cdot m \cdot K^{-1}$. The sheath flow rate was inversely proportional to the heat capacity of the PCM-CA fibres, as measured by ΔH, C_p, and k. This can be attributed to the thickness of the sheath wall, which corresponded to the flow rate of the sheath. In contrast to the flow rate of the sheath, the relationship between the flow rate of the core and the heat capacity was proportional. In TGA results, the thermal degradation peak of ShB was 461.14 °C (due to its major component of steric acid) and that of CA was 389.61 °C a result of mixing with the palmitic acid. The ratio of CA to ShB was inferred to be as high as 78% to 80% and as low as 16% to 13%. The electrospun PCM-CA fibres with the highest ratio of ShB as shown in TGA coincided with the fibres with the largest k of 0.421 $J \cdot g^{-1} \cdot K^{-1}$ in the DSC results.

Finally, in the human-wearing assessment, wearing a hood with PCM-CA fibres (the experimental condition) decreased mean skin temperature in five of six subjects by 0.5 °C, compared to attaching only CA fibres (the control). During the walking exercise, the difference in the two conditions gradually rose to 0.25 °C. At 70–75 min during the second sitting-rest after walking, the average mean skin temperatures sharply dropped, resulting in the biggest gap between the two conditions, as supported by the paired t-test ($p < 0.05$). In conclusion, the effectiveness of PCM-CA fibres was validated as it delayed the increase of skin temperatures.

This study successfully encapsulated PCM by coaxially electrospinning a core-sheath structure. It was also confirmed the potential of the technique for thermoregulating protective clothing. We found it is necessary for the core to increase latent heat as well as for the sheath to enhance k. For this, future research should address the fabrication of PCM composites by coating them with carbonaceous materials to improve heat transfer through the combination of thermal conduction and convection.

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Author's Contributions

Conceptualisation, experiments, analyses, investigation, data curation, writing, review and editing, visualization, Hye Jin Kim; supervision, funding acquisition, Changsang Yun; consultation, Ji Hun Park; preparation of human wearing tests, Syifa Salsabila.

Conflict of interest

We are pleased to declare no conflict of interest.

Figures

Figure 1

Schematic diagram of total experiments in this research

Figure 2

SEM and optical microscopic images of 25.0 wt% electrospun CA fibers in A:D 1:1 (v/v) solvents (a) a histogram and optical microscopic image of the CA fibre (magnification: 4x), (b) SEM image of the CA fibre (magnification: 200x, SE), (c) optical microscopic image of the CA fibre (magnification: 10x), (d) SEM image of the CA fibre (magnification: 5x, SE)

Figure 3

TEM images of encapsulation of PCM as a core in CA electrospun fibers as sheaths (a) two concentric Taylor cons of core-sheath solutions, (b) enlarged TEM image of ShB core encapsulated in sheath CA fibre, (c) SEM image of the ShB encapsulated in CA fibres, (d) enlarged TEM image of the ShB-CA fibre

Figure 4

DSC results for shea-butter, coconut oil and PCM-CA fibers in (a) heating and (b) cooling

Figure 5

TGA results for shea-butter and PCM-CA fibers in a range of (a) 300□ to 500 □, (b) 300 □ to 400 □ and (c) 380 □ to 480 □

Figure 6

(a) Schematic designs of face-hoods for human wearing assessment and attachment sites for electrospun fibers with and without PCM, (b) experimental protocols and (c) IR thermal and photographic images during the human wearing assessment

Figure 7

Changes in mean skin temperature and auditory canal temperature of all subjects according to the presence of PCM or absence of the PCM (control condition) in CA fibers of face-hoods

Supplementary Files

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- groupimage1.png