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Form-stable phase change electrospun nanofibers mat with thermal regulation and biomedical multi-functionalities

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ABSTRACT

This study aimed to introduce a smart multifunctional textile composed of a phase change material, i.e., polyethylene glycol (PEG), with a potential for thermo-regulative biomedical application. PEG was efficiently form-stabilized with polycaprolactone, and the nanofibers mats were developed by electrospinning to overcome the PEG leakage issue during the phase change process. Gelatin and curcumin were also incorporated to enable the biomedical performance of the textiles. The results revealed that the electrospun nanofibers possessed randomly oriented morphology, sufficient water absorption capability, good mechanical properties, and excellent phase change performance. The fibers’ diameter varied from 220 nm to 370 nm, with a tensile strength ranging from 10 to 30 MPa. Furthermore, the fabricated mats possessed a latent heat of 61.7 J/g and reliable energy absorption-release cyclability over 100 heating-cooling cycles. The curcumin-loaded textiles revealed an initial burst release followed by a sustained release over one week. They further presented a significant antioxidant activity of 81.23 ± 3.08 % after 24 h, introducing a great potential application as a biomedical dressing to diminish inflammation with a cooling effect.

1. Introduction

Medical textiles have been used widely in various biomedical applications, from face masks and wound dressings to tissue-engineered scaffolds and implants. The design and fabrication of an appropriate medical textile involve multidisciplinary research in medical, chemical, polymer, and textile engineering sciences. Medical textiles have been fabricated with various manufacturing methodologies, such as hand spinning, pressure spinning, rotary jet spinning, melt-blowing, template synthesis, self-assembly, phase separation, and electrospinning. Out of these techniques, electrospinning has raised significant attention due to the unique properties of the developed electrospun textiles, including a high surface area, porosity with suitable dimensions, air permeability, ability to release active substance, effective exudate absorption, mechanical stability, moisture balance, ability to mimic the extracellular matrix, and providing conditions for cell adhesion and growth factors [1–4].

Many characteristics are reported in the literature on the requirements of an ideal biomedical dressing. They include biocompatibility without originating toxicity or inflammation, adequate hemostatic functionality, antibacterial and antioxidant performance, sufficient exudate absorption/water vapor transmission, capacity to keep a moist environment, proper healing, pain-relieving capabilities, suitable mechanical strength to prevent breakage, easily changing and removing without trauma, architected microstructure enabling drugs loading and promoting cell proliferation/differentiation [5,6]. However, a less-considered characteristic, which might significantly affect biomedical properties, e.g., face mask or wound healing, especially burn wounds, could be temperature regulation and cooling. In hot environmental conditions, for example hot summertime, thermal-regulated dressings are urgently needed to protect the skin/wound from heat and mitigate harm caused by high temperature. This new category of medical textiles could be prepared by integrating functional materials into dressings, which can regulate the microenvironment temperature around a certain point. For instance, smart thermo-regulating medical textiles can be developed by embedding phase change materials (PCMs)
in medical textiles. As a kind of smart material, PCMs, can absorb and store thermal energy as latent heat and then release it at the critical phase transition temperature \([7,8]\). Accordingly, PCM-based biomedical textiles exhibit a buffering effect in response to the environment and thereby can keep the wound/skin at a comfortable temperature \([9–11]\).

The most commonly used PCMs for fabricating smart textiles with thermo-regulation ability include organic compounds with a phase change point ranging from 20 to 40 \( ^{\circ}C \). These organic compounds could be found as solid paraffin, most fatty acids, and polyethylene glycols (PEGs), resulting in the final fabrics that actually cannot absorb solar power or other thermal energy in practice since most of our ambient temperature is \(< 30 ^{\circ}C \). Thanks to the advantages of high storage capacity, chemical stability, non-toxicity, biocompatibility, and small volume change during the phase change progress, PEGs have been widely adopted for electronic equipment, thermal recovery, and smart textiles \([9]\). Likewise, PEGs have been applied widely for dressings with biocompatible, hydrophilic, flexible ether-based, and non-immunogenic properties. It has been reported that PEG-based wound dressings accelerate wound closure through the growing up and proliferation of skin cells achieved by collagen deposition \([14]\). The Food and drug administration (FDA) has approved PEG for internal consumption and drug delivery systems \([15]\). Nevertheless, for thermo-regulating applications, the leakage issue has restricted the implementation of PEGs. Fortunately, the encapsulating or supporting PEG by polymer matrixes can efficiently address this drawback \([16–19]\). Here, the selection of a suitable polymer for encapsulating PEG is key. On the one hand, the polymer must be compatible with PEG to provide high encapsulation efficiency without any phase separation. On the other hand, due to the target application, e.g., biomedical dressing, it must pass the criteria such as biocompatibility, non-toxicity, etc.

Here, we hypothesized that polycaprolactone (PCL) could support PEG in developing a leakage-free temperature-responsive dressing textile. PCL is an FDA-approved biomaterial known for its biocompatibility and biodegradability with various applications, such as cardiovascular grafts, drug delivery, dental splints, bone scaffolds, and wound dressings \([20–23]\). However, analogous to most synthetic polymers, the biological properties of PCL and PEG are significantly inferior to those of natural biopolymers. As such, we further hypothesized that adding a third natural polymer compound, such as gelatin, can effectively address this drawback. Gelatin is a tasteless, colloidal protein that is widely used in biomedicine due to its biocompatibility, biodegradability, nontoxic properties, and bioactivity. Gelatin can promote cell attachment thanks to its collagen sequences and numerous motifs \([24–26]\). Furthermore, incorporating active agents with therapeutic validity for treating wounds is one of the promising approaches for accelerating the healing process and minimizing the appearance of scars \([27]\). One of the well-established bioactive agents widely used for wound dressing development is curcumin. Curcumin is a phenolic compound with a considerable effect on wound healing thanks to its anti-inflammatory, antifungal, antioxidant, and antimicrobial properties, especially against the most abundant microorganism on the skin, i.e., \(Staphylococcus aureus\) \([27–29]\). To the best of our knowledge, such a PCM-polymERIC system created via electrospinning with multifunctionalities has not been reported elsewhere.

As such, this study reports the design, fabrication, and characterization of smart multicomponent nanofibers as temperature-regulative wound dressings. Our results confirmed the fabrication of nano-sized random-oriented fibers with excellent spinnability, high PEG-encapsulation efficiency, significant mechanical properties, and effective antioxidant performance. The developed thermo-regulating medical textiles also revealed excellent repeatable phase change properties with a room-temperature phase change point, making them exciting smart medical textiles for biomedical applications, e.g., mats for skin masks or wound dressings.

2. Experimental

2.1. Materials

Polyethylene glycol (PEG, \(M_n = 1000\) g/mol), polycaprolactone (PCL, \(M_n = 80,000\) g/mol), gelatin from bovine skin (Type B), and curcumin (for synthesis) were purchased from Sigma-Aldrich. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) and 1,1-Diphenyl-2-picrylhydrazyl Free Radical (DPPH) were provided by Tokyo Chemical Industry (TCI). Absolute ethanol (Etax Aa \( \geq 99.7\% \)) was obtained from Anora, Finland. PBS solution (pH 7.4) was obtained from Oy FF-Chemicals Ab.

2.2. Electrospinning

Electrospinning was performed on a homemade electrospinning setup. The setup comprised a high-voltage power supply (maximum capacity of 30 kV), a rotating aluminum collector (adjustable from 10 to 1000 rpm), and a syringe pump. To prepare the spinning solution, a 10 wt\% PCL suspension was prepared by dissolving PCL in HFIP under a gentle mixing at 55 \( ^{\circ}C \). This solution was used to optimize the electrospinning conditions. Various spinning conditions were employed to find the optimum ones regarding the quality of the spun fibers. The applied voltage, collector speed, flow rate, gauge needle, and needle distance to the collector were found to be 20 kV, 300 rpm, 25 \( \mu \)l/min, 20 G, and 11 cm, respectively, to obtain bead-free fibers. The hybrid mats, including PP (PCL + PEG), PG (PCL + Gelatin), PPG (PCL + PEG + Gelatin), and Cur@PPG (PCL + PEG + Gelatin + Curcumin), were then electrospun with the same spinning conditions. To make the electrospinning solutions, the components, i.e., PEG (10 and 20 wt%), PCL (10 and 20 wt%), and gelatin (10 wt%), were dissolved in HFIP separately, then mixed together and stirred for 4 h at 55 \( ^{\circ}C \). The final homogeneous solution was then used for electrospinning. The curcumin-loaded mat, i.e., Cur@PPG, was prepared with the same method, except that the curcumin was first dissolved in a minor amount of absolute ethanol, and then the volume was adjusted by adding HFIP. The concentration of the curcumin was 5 wt% of the total mass of the dried polymers, i.e., PCL, PEG, and gelatin. The Cur@PCL mat was also fabricated to investigate the effect of PEG and gelatin on the drug release rate.

2.3. Characterisation

2.3.1. Fourier transform infrared spectroscopy (FTIR)

The fabricated mats were subjected to FTIR spectroscopy PerkinElmer model to investigate their chemical structure. The wavenumber range, number of scans, and resolution were set at 4000 to 500 cm\(^{-1}\), 16, and 4 cm\(^{-1}\), respectively.

2.3.2. Scanning electron microscopy (SEM)

The morphology of the electrospun mats was examined by the SEM images captured from the sample’s surface using a Zeiss Sigma VP scanning electron microscope. The sample was first coated with a thin layer of gold–palladium (4 nm) prior to the subjection of imaging at 3 kV. ImageJ Fiji software was used to measure the diameter of the fibers by measuring at least 80 random fibers.

2.3.3. PCM Leak test

To investigate any possible leakage of PEG from the developed mats, the mat and pure PEG were put on the surface of a clean white paper and kept in an oven at 40 \( ^{\circ}C \), which is above the melting temperature of the PCM, for 3 h. The photographs of the PEG and mats before and after the leak test were used to monitor PEG leakage. Furthermore, the samples were also examined with DSC before and after the leakage test.

2.3.4. Swelling ratio and weight loss

The amount of water uptake capacity of the fabricated mats was measured at 37 \( ^{\circ}C \) in PBS with a pH of 7.4, simulating the physiological conditions.
microenvironment. The sample was first dried in a vacuum oven at 40 °C for 48 h. It was weighted \((m_0)\) and then immersed in the PBS solution. Its weight after 24 h \((m_f)\) was used to calculate the swelling ratio (SR) through Eq. (1).

\[
SR(\%) = \frac{m_f - m_0}{m_0} \times 100
\]

The swelled sample (after a week) was thoroughly dried in a vacuum oven and weighed \((m_0)\). The sample weight loss (WL) was then calculated by Eq. (2).

\[
WL(\%) = \frac{m_0 - m_d}{m_0} \times 100
\]

### 2.3.5. Water contact angle

The water contact angle measurement was used to investigate the surface properties of the developed mats. Approximately a 5 µl water droplet was deposited on the sample’s surface using a Theta Flex Optical Tensiometer. The contact angle was measured immediately and 60 s after droplet deposition. Five measurements were performed, and the average value ± standard deviation was reported.

### 2.3.6. Mechanical properties

The mechanical properties of the developed mats were measured by a dynamic mechanical analysis (DMA) machine (TA Instruments DMA Q800) at a controlled force mode. The strip-shaped sample was stretched under a pre-load of 0.1 N and a stretching rate of 0.2 N/min. The test was performed at 25 °C and 40 °C (higher than the melting point of PEG) to investigate the effect of temperature on the mechanical properties of the sample. In this case, the sample was kept for 15 min at 40 °C prior to stretching.

### 2.3.7. Phase change performance

DSC (Differential scanning calorimetry) thermograms were used to investigate the phase change properties of the fabricated mats. The tests were performed under a nitrogen atmosphere on a TA Instruments model Discovery DSC 250 Auto from −10 °C to 50 °C. The cooling/heating rate was fixed at 5 °C/min. The sample was exposed to two heating-cooling cycles. The first was conducted to remove the thermal history of the sample, and the second one was used to extract the phase change properties, including the melting point (\(T_{m}\)), melting enthalpy (\(\Delta H_m\)), crystallization temperature (\(T_c\)), and crystallization enthalpy (\(\Delta H_c\)).

The theoretical load \((L)\) and actual coverage \((C_a)\) of phase change material (PEG) in the fiber were calculated based on Eq. (3) and Eq. (4) [30], where \(m_{PEG}\) and \(m_{mat}\) are the mass of the PEG and the mat, respectively. Furthermore, \(\Delta H_{m,PEG}\) and \(\Delta H_{m,mat}\) are melting enthalpy of PEG and the mat, respectively.

\[
L_i(\%) = \frac{m_{PEG}}{m_{mat}} \times 100
\]

\[
C_a(\%) = \frac{\Delta H_{m,mat}}{\Delta H_{m,PEG}} \times 100
\]

The measurement was also performed for 100 cycles to study the cycling stability of the fabricated textiles. Besides, the pre-heated sample (from the leak test) was subjected to the DSC test to evaluate phase transition stability. To quantitatively measure the changes in the latent heat of melting and crystallization before and after heat treatment as well as 100 heating and cooling cycles, the loss of melting enthalpy \((\Delta H_m)\) and crystallization enthalpy \((\Delta H_c)\) of the PPG mat were calculated according to Eq. (5) and Eq. (6).

\[
|\Delta H_m| = \frac{|\Delta H_m - \Delta H_{m,b}|}{\Delta H_{m,b}} \times 100
\]

2.3.8. In vitro curcumin release assay

The standard curcumin curve was first plotted by measuring the absorbance of the release medium containing different concentrations of curcumin. Due to the poor solubility of curcumin in aqueous media, the release medium was 1 % absolute ethanol in PBS, pH 7.4. To evaluate the amount of drug release from Cur@PPG and Cur@PCL, the sample \((2 \times 2 \mathrm{~cm}^2)\) was immersed into the release medium under constant stirring at 37 °C. At certain time points, the UV absorbance of curcumin in release media was measured at the wavelength of 429 nm. After that, the concentration of the released curcumin was obtained from the standard curve (Fig. S1) and used to determine the cumulative release at selected time intervals (1, 2, 4, and 8 h, then every 24 h till one week) through Eq. (7) [31]. Three samples were tested, and the mean ± standard deviation was reported.

\[
\text{Cumulative release}(\%) = \frac{C_i V_i + \sum_{i=1}^{n} C_{i-1} V_i}{m_t} \times 100
\]

where \(C_i\) is the curcumin concentration in the released medium at the time \(i\), \(V_i\) is the total volume of the released solution, \(V_t\) is the sample solution volume \((3 \mathrm{ml})\), and \(m_t\) is the total amount of curcumin in the sample.

2.3.9. Antioxidant activity

A 1,1-diphenyl-2-picrylhydrazide (DPPH) assay was used to study the antioxidant activity (AOA) of the fabricated mats. Namely, a 10 µg/ml DPPH ethanolic solution with initial absorbance \((A_0)\) at a wavelength of 517 nm was prepared. Then the mat was immersed in 3.0 ml of the above-mentioned DPPH solution. After that, the system was incubated in the dark at room temperature for specific periods, including 30 min, 1, 2, 3, and 24 h. Finally, the absorbance of the DPPH solution \((A_j)\) was again measured at 517 nm. The AOA of the mats was calculated using Eq. (8).

\[
\text{AOA}(\%) = \frac{A_0 - A_j}{A_0} \times 100
\]

3. Results and discussion

3.1. Nanofibers topology and microstructure

The structure, shape, and diameters of the electrospun mats were monitored by SEM images. All samples were produced under similar ambient conditions optimized experimentally. The SEM images are provided in Fig. 1 and Fig. S2a. PEG lacked spinning possibility, as poor fibers containing considerable amounts of beads were observed in the SEM image (Fig. S2b). Continuous, smooth fibers without aggregation and other particulate structures were formed in the rest of the samples, indicating no phase separation for PCL, PEG, and gelatin occurred during the electrospinning process. Furthermore, they exhibited a typical nonwoven nanofibrous structure, with a layer-by-layer deposition of nanofibers and a high surface area-to-volume ratio with high porosity. Although most of the fibers had tubular-like morphology,
irregular fibers, such as flat ribbon-like, bead-like, and capillary, could be found, leading to the non-uniform fiber diameters distribution [32]. The average diameter was determined as $330 \pm 150$ nm for plain PCL mat, which was in the range reported in the literature, e.g., 227 nm [33] and 412 nm [2]. The average diameter decreased to $220 \pm 140$ nm in the PP mat, while it increased to $370 \pm 170$ nm in PPG. The change in the viscosity and viscoelasticity of the electrospun solution could explain this behavior. It has been reported that the higher solution viscosity results in a higher viscoelasticity force due to excess entanglement of networks in a polymeric matrix, which competes with Rayleigh instability, leading to bigger fibers with less homogeneity [34,35]. Moreover, at higher viscosities, dense fibers are stretched in various shapes and

![Fig. 1. SEM images of electrospun mats and the fiber diameter distribution. a) and b) PCL, c) and d) PP, e) and f) PPG, and g) and h) Cur@PPG. The SEM imaging was performed at 3 kV with a 500 X magnification. The diameter of at least 80 fibers was extracted using ImageJ software.](image-url)
directed in different patterns, as not all their surfaces are exposed to the electrostatic force simultaneously under high electrical force, leading to a wide range of size distribution [36]. In the PP sample, the viscosity was lower than the neat PCL solution due to the presence of a very low viscosity PEG component, while the viscosity increased in the PPG sample after blending a relatively high viscous gelatin component. The average diameter was then decreased to 330 ± 150 nm in the Cur@PPG mat, which could be explained by an increase in the solution conductivity after adding curcumin [28].

3.2. Water interactions

Hydrophilicity is one of the important parameters that significantly affect retaining wound moisture and the ability to absorb wound exudates. It also influences cell adhesion and proliferative properties and helps oxygen and cell nutrients transport toward the wound bed [37–39]. In this study, the hydrophilicity of the fabricated samples was evaluated by their swelling behavior as well as water contact angle measurement. The results are provided in Fig. 2a. All nanofibers revealed a good swelling ratio ascribing to the infiltration of water molecules within the nanofibrous network. Namely, the porous and interconnected structure of nanofibers facilitated water molecules' infiltration [40]. For the PCL mat, water uptake capacity was 260 ± 25 %, consistent with the value reported by Hashemi et al. [41], while it was 330 ± 20 % in the PP sample. In other words, adding PEG boosted the water uptake capacity by approximately 25 %. This improvement could be due to the considerably higher hydrophilic nature of PEG than PCL [42] as well as the smaller fiber diameter in the PP mat than PCL, which led to an increase in the pore sizes and, thereby, an enhancement in the swelling ratio [3]. Although the average fiber diameter was higher in the PPG mat than in PP, PPG presented moderately a higher swelling ratio (360 ± 30 %), which could be explained by gelatin's high water uptake capacity, thanks to the abundant hydroxyl and amino ester groups [40]. Our assessment revealed that the incorporation of curcumin into the PPG mat did not significantly affect the swelling capacity, agreeing with previous observations on the swelling behavior of the curcumin-loaded PCL/gelatin mat [43]. The WL of all the samples was obtained by immersing the fabricated mats in PBS and measuring their mass change after one week at 37 °C to evaluate the possible degradation/release of the components. The plain PCL mat presented a minor WL of 2 %, suggesting a slight loss of structural integration upon one-week immersion, as previously reported by Zhou et al. [44]. As expected, the rest of the mats, i.e., PP, PPG, and Cur@PPG, revealed significantly higher weight loss due to dissolving hydrophilic PEG and gelatin. It could also be due to the relatively high swelling ability of the mats, causing a freer movement of the amorphous chains; thereby, the fibers were ruptured from the structure and accelerated the weight loss [14].

The wettability of the fabricated mats was evaluated by a water contact angle measurement. This is an important feature that plays a crucial role in the surface interaction with the biological environment, in particular, cell adhesion, distribution, and proliferation, as well as drug release [2,45]. The pure PCL mat presented a contact angle of 134.5 ± 2.1° (Fig. 2b), indicating an obvious hydrophobic surface [32]. After blending PEG and gelatin, the contact angle dropped to <15° (Fig. 2c and Fig. 2d), indicating a significant wettability compared to pure PCL owing to the presence of hydrophilic amino groups of gelatin and hydroxyl groups of PEG that reacted with water and reduced angle. Notably, the water droplet was completely absorbed in 10 s (Video S1). The contact angle was slightly higher in Cur@PPG (35.1 ± 1.7°), in which the absorption of the water droplet was marginally slower (Video S2). This behavior could be explained by the fact that the presence of the highly water-insoluble nature of curcumin on the surface of the mat changed the free surface energy and hydrophilicity, as also observed by Lv et al. [28]. Altogether, the swelling capacity measurement results, along with water contact angle observations, suggest that the fabricated PPG and Cur@PPG mats might be considered efficient wound dressings in the suction of wound exudation fluid, transferring nutrients and oxygen, and moisturizing the wound bed.

3.3. Drug release

A sustained drug-release property would definitely be an added value for a biomedical dressing [43]. The cumulative drug release profiles from Cur@PCL and Cur@PPG mats within one week are provided in Fig. 2f. As depicted, the release profile of curcumin was significantly different in the Cur@PPG and Cur@PPG mats. Although both mats exhibited a rapid release in the first 24, the amount of released drug was considerably higher in the Cur@PPG mat. Furthermore, after 24 h, the Cur@PPG mat provided a steady release for up to 7 days, while the amount of released curcumin did not change considerably in the Cur@PCL sample. The early-stage rapid release of curcumin in both mats could be attributed to the high specific surface area of nanofibers, which facilitated the diffusion of the surface-loaded drug into the medium [46]. After this stage, one possible drug release mechanism from a polymer matrix can be obtained by polymer degradation, which leads to drug diffusion [47]. Thus, the minor release of curcumin from the Cur@PCL mat after 24 h could be due to the very low degradation rate of PCL within 7 days in the PBS solution, as previously observed in the weight loss results. Likewise, the relatively high initial burst release in the Cur@PPG mat (44.2 ± 3.1 %) could be due to the hydrolytic degradation of PEG and gelatin fibers (see weight loss results). It is noteworthy that the drug release was prolonged for 7 days in the Cur@PPG mat with a maximum release rate of 84.4 ± 4.2, indicating

Fig. 2. a) Swelling ratio (after 24 h) and weight loss (after 7 days) of the fabricated mats in the PBS solution (pH 7.4) at 37 °C. The water contact angle of b) PCL, c) PP, d) PPG, and e) Cur@PPG at room temperature. f) Cumulative release of curcumin from Cur@PCL and Cur@PPG mats within 7 days at 37 °C in a PBS solution (pH 7.4) containing 1 vol% absolute ethanol.
that the electrospinning of hydrophobic PCL fibers, along with hydrophilic PEG and gelatin, to some extent, reduced water penetration to the structure and resulted in a sustained curcumin release. The difference between the loaded and the released curcumin could be due to the fact that some amounts of the loaded drug were fully covered by the hydrophobic PCL matrix, which hindered the curcumin release even after 7 days. Noticeable that the relatively high release rate of hydrophobic curcumin into an aqueous medium could be attributed to its higher contact area with water after loading into the nanofibers. Besides, its transformation from the crystalline to the amorphous state in the electrospun nanofibers, causing an increase in curcumin energy increases, could also significantly affect a high dissolution rate [28].

3.4. Mechanical properties

The tensile measurements were performed on the electrospun mats to monitor their mechanical properties. The typical stress-strain curves are provided in Fig. S3. The mechanical properties, including tensile modulus, tensile strength, and elongation at break, were therefore determined from their corresponding stress-strain curves for comparison. The results are summarized in Table 1. The obtained results closely correlated with previously published data on PCL electrospun mats. For instance, the tensile strength and elongation at break of electrospun PCL mat were respectively reported as 1.74 ± 0.14 MPa and 110 ± 11 % in the research work performed by Hashemi et al. [41]. Likewise, Elamparithi et al. [48] reported a relatively low tensile strength of 2.7 MPa for a plain electrospun PCL scaffold. However, Neppalli et al. [49] observed a tensile strength of 15.9 MPa with a relatively high tensile strain of 467 % for a PCL nonwoven mat. The plain PCL mat had relatively high flexibility, attributed to the methylene groups [50]. Its stiffness significantly increased upon the incorporation of PEG and gelatin. Namely, the tensile modulus of the spun PCL was 10.81 ± 0.51 MPa, while it increased to 2100 ± 100 MPa and 40.96 ± 1.95 MPa in PCL containing gelatin (PG) and PEG (PP), respectively. Likewise, the tensile modulus of the spun sample containing both PEG and gelatin, i.e., PPG, was significantly higher than the plain PCL. Although the tensile strength enhanced considerably after compounding PEG into PCL, the addition of gelatin reduced the tensile strength, which could be attributed to the weaker mechanical properties of natural polymers than the synthetic ones [50].

As expected, the elongation at break was reduced in both mats containing PEG and gelatin. In other words, the individual addition of PEG and gelatin led to the fabrication of a stronger and stiffer mat with less flexibility performance. Nevertheless, the tensile strength of the PPG mat, containing both PEG and gelatin, was lower than the plain PCL, which could be explained by the contrasting impact of PEG and gelatin on the tensile strength. Surprisingly, although the PPG had higher stiffness than plain PCL, its elongation at break was significantly higher, which could be attributed to the synergistic effect of the interfacial adhesion between the three components and the damping effect of the voids in the sample [51]. As Fawal et al. [52] suggested, it might also be attributed to the thicker nanofibers in PPG than PCL, which could make further junction points among themselves (keeping together the adjacent fibers), thus, showing higher mechanical properties. It is noticeable that the incorporation of curcumin did not compromise the tensile strength and elongation values, indicating that it was appropriately blended in the system and provided sufficient adhesion [50]. This might be due to intermolecular interaction through hydrogen bonding. We also performed tensile testing at a temperature higher than the PCM (PEG melting point, e.g., at 40 °C, to investigate the possible effect of PEG's melting on the mechanical properties. The stress-strain curve of the Cur@PPG mat at 40 is provided in Fig. S3 as well. For comparison, the plot of plain PCL is also included. In both cases, the curve's trend was similar to that of measurements conducted at room temperature, proving the lack of any PEG release. Nevertheless, the tensile modulus and tensile strength decreased significantly at 40 °C, which could be explained by the softening of the polymer chains at the higher temperature.

A proper biomedical dressing/textiles must possess acceptable mechanical strength to be adapted to skin tissue as well as to body movements. Fortunately, one of the advantages of the nanofibers membranes application is that their mechanical properties can fulfill the requirements of wound dressings [28,53]. Although the mechanical properties of human skin are affected by age, gender, skin region, and test methods, the tensile strength, elongation at break, and Young's modulus have been reported between 2.5–16 MPa, 35–115 %, and 4.6–20 MPa, respectively [2]. Thus, the mechanical properties of the developed mats meet the requirements of dressings to provide excellent mechanical support and protection without any harm to adjacent skin tissue.

3.5. In vitro antioxidant activity

The reactive oxygen species formed after an injury can affect the adherence and proliferation properties of fibroblast cells, thereby causing tissue damage in the wound area and retard the healing process. Therefore, they should be eradicated from wound sites to promote healing. The release of antioxidant particles is one of the effective methods in this sense [28,54]. Studies have indeed shown that curcumin exhibits significant defensive properties against oxidative stress by scavenging reactive free radicals [27]. Thus, the DPPH radical scavenging test was performed to investigate the antioxidant activity (AOA) of the fabricated mats. The photographs of the DPPH solutions 24 h after incubation with the fabricated mats are presented in Fig. 3a. In the presence of an H-donating antioxidant, DPPH radicals in ethanol solution could be transformed from purple to yellow [55]. Hence, the curcumin-free mats, including pure PCL, PP, and PPG, did not have any significant antioxidant activities over time, while the Cur@PPG mat possessed good antioxidant activity, as the color change of the solution from purple to yellow was pronounced.

The absorbance of the solution was measured by utilizing a UV–vis spectrophotometer to quantify the antioxidant activity of the fabricated mats. The UV–vis spectra of the DPPH solution before immersion and 30 min after incubation with the Cur@PPG mat are depicted in Fig. 3b. Furthermore, the AOA of the mats at different incubation times is represented in Fig. 3c. The DPPH solution presented a strong absorption peak at 517 nm. The peak intensity significantly decreased after 30 min immersion of the Cur@PPG mat, indicating a strong ability to scavenge free radicals [46]. The calculation results showed that the curcumin-free mats presented very low antioxidant activity, which might be attributed to the occurrence of DPPH absorption by the membrane during the contact or the existence of the terminal hydroxyl group in PCL [56]. Unlike the curcumin-free mats, the AOA of the Cur@PPG mat was significantly high; it was 81.23 ± 3.08 % after 24 h. Similarly, Motasaddizadeh et al. [29] observed an AOA of 82 % after 40 min in curcumin-loaded polyvinyl alcohol/chitosan nanofibers. Furthermore, an AOA of 80 % has been reported for nanofibers composed of chitosan, gelatin, PCL, and curcumin [46]. Likewise, up to 85 % AOA was reported for the gelatin-based nanofiber membranes loaded with curcumin [28].

Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Tensile modulus (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation at break (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>10.81 ± 0.51</td>
<td>6.63 ± 0.28</td>
<td>111 ± 5</td>
</tr>
<tr>
<td>PG</td>
<td>2100 ± 100</td>
<td>4.08 ± 0.18</td>
<td>27.2 ± 0.2</td>
</tr>
<tr>
<td>PP</td>
<td>40.96 ± 1.95</td>
<td>9.58 ± 0.39</td>
<td>58 ± 2</td>
</tr>
<tr>
<td>PPG</td>
<td>25.81 ± 1.12</td>
<td>4.68 ± 0.21</td>
<td>154 ± 5</td>
</tr>
<tr>
<td>Cur@PPG</td>
<td>29.74 ± 1.32</td>
<td>5.54 ± 0.23</td>
<td>177 ± 6</td>
</tr>
<tr>
<td>PCL*</td>
<td>3.79 ± 0.14</td>
<td>4.57 ± 0.19</td>
<td>109 ± 5</td>
</tr>
<tr>
<td>Cur@PPG*</td>
<td>7.86 ± 0.40</td>
<td>3.60 ± 0.15</td>
<td>187 ± 9</td>
</tr>
</tbody>
</table>

* At 40 °C.
Altogether, our results strongly confirmed that the antioxidant activity of the mats was completely attributed to curcumin, not the other components, i.e., PCL, PEG, and gelatin. The AOA of the Cur@PPG mat significantly enhanced over time ($P < 0.05$), which could be attributed to the sustained release of curcumin from the mats, as previously proved in the drug release study. To conclude, the Cur@PPG mat might have an active effect on wound repair and shortening the wound healing cycle because antioxidants can regulate the overproduction of reactive oxygen species, reduce the inflammatory response, and promote the formation of granulation tissue [55]. However, complementary assessments like in vitro and in vivo cell studies must be performed to prove further the benefit of these newly developed PCM-based textiles for the claimed application.

3.6. Temperature regulation and phase change performance

The practical applications of thermal-regulated materials are generally governed by thermal properties [57]. Thus, the DSC
thermograms were used to identify the phase-change temperatures as well as the thermal storage capacity of the fabricated mats, i.e., PPG and Cur@PPG. Plain PCL, PEG, and gelatin were also examined for comparison. The results are shown in Fig. 4. Besides, the corresponding phase change properties extracted from DSC thermograms are summarized in Table 2. As provided, the pure PEG exhibited an obvious melting endothermic peak and a pronounced crystallization exothermic peak, respectively, at 33.8 °C and 27.2 °C, indicating a reversible phase transition. Such a phenomenon is attributed to the coexistence of amorphous and crystalline phases during the crystal transformation of most PEGs [57,58]. Neither an endothermic nor exothermic peak appeared in the pure PCL and gelatin thermograms under the studied temperature range, meaning they did not show phase change performance within −10−50 °C. Particularly, PCL and gelatin had no contribution to the enthalpy of the phase change fibers. The DSC thermograms of fabricated PPG and Cur@PPG mats presented similar thermal storage and released characteristics as PEG did during the melting and crystallization progress. Evidently, the phase change temperatures did not change significantly, i.e., the interior PEG inside the fibers experienced phase transitions at the same temperatures as the plain PEG did. This phenomenon suggests that the regular alignment of PEG molecules was not affected by the surrounding PCL and gelatin chains. In contrast to our results, Karimi et al. [59] reported a reduction in the phase change temperatures after the encapsulation of PCM inside a zein shell, possibly due to a slower heat conduction rate in zein as well as more imperfect and smaller crystals formed in zein fibers hindering the crystallization of the PCM. We also noticed that the phase change enthalpies of PCM-based mats were lower than those of pure PEG, indicating that a load of PCM dramatically governed the heat storage capacity of the phase change fiber. It is of note that the Cₚ values were in agreement with Lᵣ values, suggesting the complete phase transition of PCM in the fiber. It further specifies the excellent compatibility between components as well as the uniform dispersion of the PEG molecules. The values of phase change enthalpies were slightly lower in the drug-loaded mat, i.e., Cur@PPG compared to the PPG mat, which could be explained by the lower amount of loaded PEG.

A big advantage of PEG as a PCM is the adjustability of its melting temperature with its molecular weight without changing its compatible nature with the support matrix. This enables the PEG usage in a wide temperature range needed in different target applications. The model PEG used in this research was a PEG with molecular weight 1000 g/mol that shows melting at around 30 °C. By increasing the molecular weight, e.g. 8000 g/mol, the melting will increase to above 60 °C. PEGs with relatively higher molecular weight and latent heat capacity could be easily incorporated into the developed PCL/gelatin fibers. However, since in this work, the aim was to buffer temperature around the body temperature, PEG1000 with a melting point of ~30 °C was selected as the model PCM. Notably, the observed phase change enthalpies in the current study were in the range reported in the literature for PEG1000-based PCM composites, indicating the excellent compatibility between the selected components resulted in efficient loading of PEG1000 inside the PCL/gelatin substrate. For instance, Wang et al. [9] reported fabrication and characterization of smart textiles composed of PEG1000, polyamide 6, and titanium dioxide which possessed a maximum latent heat of 51.14 J/g. Likewise, a melting enthalpy of 100 J/g has been reported for the polypropylene/PEG1000 PCM textiles, while the latent enthalpy of the plain PEG1000 was reported as 135 J/g [60]. Employing PEG with higher molecular weight in developing thermal buffering textiles would make it possible to get higher phase change enthalpies, as reported by Ji et al. [57] or Noyan et al. [61]. However, the higher molecular weight PEGs show higher melting points far from the body temperature, which make them ineffective for cooling purpose of wearables.

In practice, the thermal reliability and reusability of the fabricated PCM mats are important. Hence, as an example, the thermal energy storage capacity of the fabricated PPG mat was examined under 100 consecutive heating-cooling cycles. Besides, the thermal energy storage capacity was evaluated after thermal treatment of the mat at 40 °C to investigate any possible PEG leakage at a higher temperature. The DSC thermograms are presented in Fig. 4. The corresponding data are also tabulated in Table 2. There were no remarkable differences in the DSC curves and enthalpies before and after heat treatment, as both ΔHₘ and ΔHᵣ were <2 %, revealing that PEG was effectively embedded inside PCL/gelatin matrix and no leakage happened during melting. The photograph of the mats before and after 3 h thermal treatment at 40 °C (Fig. 5) also clearly illustrated that the pure PEG melted with heating while no PEG was released from the mats. Furthermore, the phase change performance had little difference after multiple thermal cycle tests. Namely, ΔHₘ decreased from 64.5 J/g to 63.7 J/g. This minor change indicated that no PEG leaked from the fibers after the thermal cycle tests, in line with the previous results reported on PEG-based mats [9]. Although the melting point and crystallization temperatures did not change considerably after heat treatment, they shifted slightly to higher temperatures after cycling. This behavior revealed the influence of PCL and gelatin molecular structure on the distribution and state of PEG. The melting point of the employed PEG is around 30 °C. After incorporation in the polymeric matrices, the melting point typically tends to shift to a lower temperature due to the restriction of PEG chain mobility and intermolecular interactions such as hydrogen bonding (initial cycles). However, after many consecutive heating/cooling cycles, this restriction effect is eliminated to some extent, and PEG’s melting point and enthalpy in the composite gets closer to its original value (100th cycle). In summary, the DSC results confirmed that the fabricated PCM mats experienced phase change at a temperature close to the human skin temperature (34−37 °C) [11], which is beneficial to accelerate practical applications such as smart wound dressings. Besides, DSC findings proved that the developed mats possessed excellent heat storage or heat release performance with remarkable cyclic stability, enabling them to buffer temperature around the body temperature; thus, they could be favorable smart materials for thermo-regulation.

The pure PCL and PPG mats were placed on a pre-heated plate at 60 °C to further evaluate the thermal regulation performance. The infrared thermal images were used to monitor the temperature variation of mats visually. To measure the temperature more precisely, a
thermocouple was inserted into the surface of the mat. The results are illustrated in Fig. 5c and Fig. 5d. In both mats, the temperature rose continuously to a maximum temperature, i.e., 43 °C in the plain PCL mat and around 40 °C in the PCM one. The lower maximum temperature in the PCM mat was possibly due to its high latent heat value [62]. In the cooling step, the temperature was reduced to room temperature in both mats; however, the PPG mat presented a gradual reduction around the phase change temperature, indicating the crystallization of PEG. It is worth mentioning that the phase change step was not seen during the heating step, which might be due to the high rate of temperature increase resulting from the relatively low thickness of the mat.

4. Conclusions

Herein, a series of PCM-based medical textiles as the multifunctional biomedical dressing was fabricated successfully via electrospinning. A phase change polyethylene glycol material with low melting temperature was efficiently embedded into the polycaprolactone matrix to bring a thermo-regulating property. Besides, gelatin and curcumin were added to the compound to improve the biomedical performance of the fabricated textiles. A randomly oriented morphology was achieved, in which the fibers presented tubular-like as well as flat ribbon-like and capillary morphology with an average diameter ranging from 220 nm to 370 nm. Our results confirmed that the presence of PCM polyethylene glycol not only established excellent phase change and thermo-regulating performance in the fabricated mats but also significantly improved their interaction with water, which is an essential feature in medical design. Namely, the water absorption improved from 260 ± 25 % in the PCL mat to 330 ± 20 % in the PCM-based one. Likewise, the contact angle dropped dramatically from 135° to <20°, indicating a pronounced change from a hydrophobic surface to a hydrophilic one. As confirmed in the in vitro release study, a sustained release of hydrophobic curcumin in an aqueous medium was achieved over one week with an up to 85 % release rate attributing to the curcumin’s higher contact area with water after loading into the nanofibers. The curcumin-loaded dressing also presented a high antioxidant activity of 81.23±3.08 % after 24 h, which might be a helpful feature in shortening the wound/skin healing process. The fabricated mats also possessed significant mechanical properties suitable for biomedical dressing applications and skin tissue. Finally, well-established phase change properties, even after 100 times cycling, as well as thermal treatment at a higher melting point of the trapped PEG, were proved entirely by DSC thermograms. To conclude, the developed thermo-regulating textiles with antioxidant properties point toward future medical textiles for biomedical dressing applications.

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CRediT authorship contribution statement

Hossein Baniasadi: Conceptualization, Investigation, Methodology, Formal analysis, Visualization, Writing – original draft. Maryam Madani: Methodology, Writing – review & editing. Jukka Seppälä: Resources, Writing – review & editing, Funding acquisition. Julie B. Zimmerman: Resources, Writing – review & editing. Maryam Roza Yazdani: Conceptualization, Investigation, Methodology, Formal analysis, Visualization, Resources, Writing – original draft, Funding acquisition.

Declaration of competing interest

The authors declare that there is no conflict of interest.

Data availability

Data will be made available on request.

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