

Smart composite nanofibers based on PLA/PEG with the addition of clove oil as thermal regulators

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Abstract: Smart nanofibers based on PLA and PEG with the addition of clove oil (*Eugenia caryophyllus*) (EO) were obtained using the electrospinning technique. The nanofibers were characterized by SEM, FT-IR, TGA and DSC. For the PLA/PEG/EO composite (mass ratio 2/1/0.25), the temperature of the maximum decomposition rate was approximately 370°C. This composite exhibited good latent heat energy storage (melting enthalpy 77.5 J/g at 34.7°C). Smart nanofibers can be used as thermal regulators in medicine, electronics, and food and textile industries.

Keywords: energy storage, latent heat, phase change materials.

Inteligentne nanowłókna kompozytowe na bazie PLA/PEG z dodatkiem olejku goździkowego jako regulatory termiczne

Streszczenie: Metodą elektroprzędzenia otrzymano inteligentne nanowłókna na bazie PLA i PEG z dodatkiem olejku goździkowego (*Eugenia caryophyllus*) (EO). Nanowłókna scharakteryzowano metodą SEM, FT-IR, TGA i DSC. Dla kompozytu PLA/PEG/EO (2/1/0,25) temperatura maksymalnej szybkości rozkładu wynosiła około 370°C. Kompozyt ten wykazywał dużą zdolność magazynowania energii cieplnej w postaci ciepła utajonego (entalpia topnienia 77,5 J/g w temperaturze 34,7°C). Dzięki tym właściwościom inteligentne nanowłókna mogą znaleźć zastosowanie jako termiczne regulatory w medycynie, elektronice oraz przemyśle spożywczym i tekstylnym.

Słowa kluczowe: magazynowanie energii, ciepło utajone, materiały zmiennofazowe.

The use of phase change material (PCM) has become the focus of much attention since there has been an increase in energy consumption. When ambient temperature increases or decreases, PCMs can store high latent heat at melting point, which can be salt hydrates, paraffins, fatty acids, fatty acid esters, or a mixture of all three [1, 2]. Latent heat energy storage allows a high rate of energy storage and release per unit weight of PCM during phase change [1, 3]. Considering a 5 mm thick plate containing PCM, it can return stored latent heat energy to the environment over to 8 hours [4]. With application of different methods, technology used in storing heat energy can increase efficiency, and energy resources can be used effectively [5].

Polyethylene glycol (PEG) is a polymer used in the development of biocompatible and biodegradable tissue engineering scaffolds [6]. PEGs have a wide molecular weight range from 200 g/mol to 35,000 g/mol [7]. Synthetic polymers are preferred as support materials in the production of PCM compounds, and natural polymers are

used less. In addition, PEGs are considered environmentally safe materials for latent heat energy storage [8].

Some pain relievers may have side effects, but herbal treatments have fewer negative aspects [9]. The highest concentrations of constituents in clove essential oil were eugenol (88.58%), eugenyl acetate (5.62%) and β -caryophyllene (1.38%) and showed antibacterial activity against the *Staphylococcus epidermidis* strain [10]. In addition, eugenol can show antifungal, antiallergic and antioxidant properties [11–13] and has local numbing and pain-relieving effect, especially against tooth and gingival pain [14]. Clove and thyme oils are also known to be highly effective repellent agents against insects [10, 15]. In addition, composites loaded with 15% pine needle oil provided an antibacterial effect against *E. coli* and *S. aureus* bacteria [16].

Poly(lactic acid) (PLA) is a linear polyester with biocompatibility that can be obtained by catalytic ring opening and condensation polymerization of lactic acid produced from corn, beet, and cane sugar [17]. In electrospinning ultrafine phase-change fibers, much effort is required to improve thermophysical properties [18]. Also, flattened PLA macromolecules containing additives can form a semi-crystalline phase, increasing mechanical strength [19].

The electrospinning method used by Formhals in 1934 to spin synthetic fibers using electric charges, was imple-

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mented to spin small diameter fibers. Cellulose acetate fibers also were spun using an acetone/alcohol solution [20]. On the other hand, when PLA-based nanomaterials form composites with antibiotic compounds by the electrospinning method, they can produce a controlled release [21]. In addition, a *Cupressus sempervirens L.* loaded nanofiber release study was developed for drug design [22].

Short-term thermal protection reactions are known as vasodilation, vasoconstriction and shivering in humans and is associated with a change in body temperature from 36.5°C (average 33.0°C for the skin), which is the ideal temperature. When body temperature changes, people begin to feel uncomfortable [23]. Providing thermal comfort can be of vital importance during a regional body temperature decrease or increase even for a certain period. Similarity and functionality of polymer nanofibers to an extracellular matrix is recommended in wound dressings and applications such as tissue engineering scaffolds [24].

Although production of PCM-containing materials has become the focus of attention in recent years, target temperature range should be specific according to the usage area. In this study, PLA/PEG/EO composite nanofibers (mass ratios 1/1/0.25, 1.5/1/0.25, 2/1/0.25) were obtained by the electrospinning method, and nanofiber morphology, chemical composition, thermal reliability, and heat storage/release performances of composite fibers were investigated.

EXPERIMENTAL PART

Materials

Analytical grade *N,N*-dimethylformamide (DMF) (99.8%), PEG ($M_w = 1000$ g/mol), poly(lactic acid) (PLA) was purchased from NatureWorks LLC (4043 D Nebraska, USA) ($M_w = 160,000$ g/mol) and was used as received. 100% pure *Eugenia caryophyllus* essential oil (EO) was purchased from BAÇEM Balıkesir Metropolitan Municipality Rural Services, Turkey.

Methods

Preparation of nanofibers

For sample PCM1, PLA concentration was fixed considering a 44% w/v solvent, and the ratios of nanofibers containing PLA, PEG and EO were 1:1:0.25, respectively. PCM2 ratios were 1.5:1:0.25 for PLA, PEG and EO, respectively while PCM3 ratios were 2:1:0.25 (Table 1). Blend solution dissolved in 5 mL DMF was stirred continuously at room temperature for 12 hours to ensure a homogeneous mixture. The prepared solutions were placed in a 5 mL syringe that was attached horizontally to a pump section of an electrospin device that was a NE 100 electrospinning system (Inovenso LLC, Istanbul, Turkey) at 17.5 kV, 25°C and a solution flow rate of 0.65 mL/h. The distance between the needles and collector was 16.5 cm adjusted and applied, and the collector was covered with aluminium foil [25, 26].

Table 1. The components of PCM nanofibers

| Sample | PLA/PEG/EO mass ratio | PEG content wt% |
|--------|-----------------------|-----------------|
| PCM1 | 100/100/25 | 44.4 |
| PCM2 | 150/100/25 | 53.6 |
| PCM3 | 200/100/25 | 60.6 |

FT-IR

FT-IR spectra were recorded on a Perkin–Elmer FT-IR Spectrum One B spectrometer (Waltham, Massachusetts, USA). Pure PLA and PCM nanofibers were determined with a spectrum 100 FT-IR spectrometer in transmission mode at a resolution of 4 cm⁻¹ and nanofibers were scanned at wavelengths between 4000 cm⁻¹ and 650 cm⁻¹ [25, 27].

TGA

Thermal degradation of PCMs and pure PLA nanofibers was determined with TA Instruments SDT Q600 simultaneous thermogravimetric analyser and differential scanning calorimeter (TGA-STD) (New Castle, Delaware, USA) between 0–650°C under a nitrogen atmosphere at a heating rate of 10°C/min [23, 25].

DSC

Thermal properties of PCM composite nanofibers were determined with a DSC Q2000 V24.11 Build 124 (TA Instruments, New Castle, Delaware, USA). Approximately 10 mg of dried sample was prepared. Heating and cooling rate was 2°C/min in a range of -20°C to 100°C and in a nitrogen atmosphere [25, 28]. The melting point (T_m) and crystallization temperature (T_c) were taken as the value of the peak extreme of a given phase transition.

SEM

Surface properties and morphology of PLA-based composite nanofibers with PEG and essential oil differing in content were investigated using a ZEISS Sigma 300 Gemini Carl Zeiss 300VP (Jena, Germany) scanning electron microscope operating at an accelerating voltage of 5 kV. Gold coating with QUORUM Q150 RES (Laughton, Great Britain) was applied to nanofiber samples to increase conductivity before imaging [29, 30].

RESULTS AND DISCUSSION

Morphology

Average fiber diameters of PCM1, PCM2 and PCM3 nanofibers and pure PLA were investigated by SEM. The pure PLA fibre diameter was 113.8 nm (Fig. 1a). PCM1 nanofibers had spheroidal structures of PEG that stood out clearly (Fig. 1b) and fibre diameters varied between

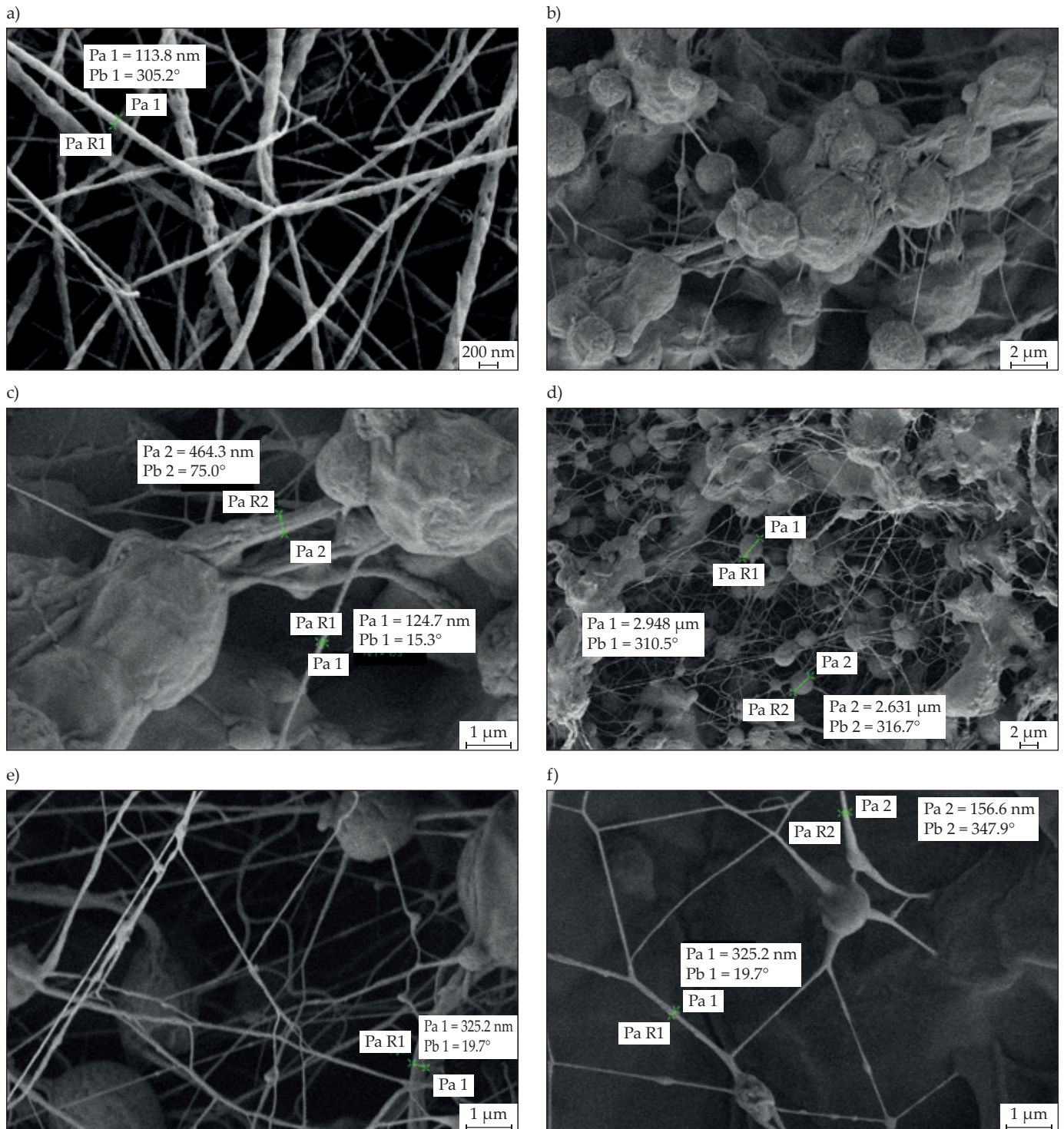


Fig. 1. SEM images of nanofibers: a) pure PLA, b–c) PCM1, d–e) PCM2, f) PCM3

464.3 nm and 124.7 nm (Fig. 1c). In the PCM2 nanofiber, it was possible to see PEG spheres at approximately 2.948 μm (Fig. 1d) and fibre diameter was approximately 325.2 nm thick (Fig. 1e). Fiber diameters of PCM3 were 156.6 nm and 170.8 nm and spheres were observed that were PEG and essential oil. Droplets of essential oil molecules presented as smaller drop spheres on fibres (Fig. 1b–f). PCM nanofibers were determined to be thicker than pure PLA fibers, and this may be associated with an increase in PEG content in composite fibres [25, 31, 32].

Fig. 2 shows images of PCM1, PCM2 and PCM3 nanofibers on aluminium film.

FT-IR analysis

Chemical structure of nanofibers was investigated by FT-IR. According to the FT-IR absorption spectra of pure PLA, PEG, and essential oil-containing nanofibers (Fig. 3), C=O band stretching vibration of PLA at 1758 cm^{-1} is seen as a strong peak. A large peak observed at 3480 cm^{-1} is

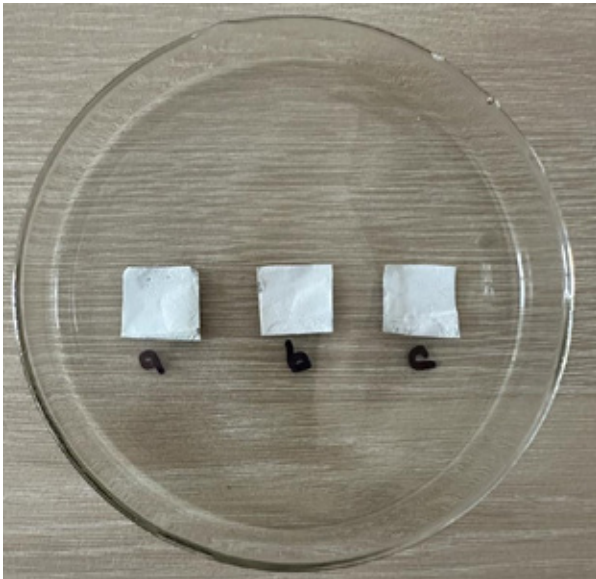


Fig. 2. Nanofiber pieces fixed on aluminium film: a) PCM1, b) PCM2, c) PCM3

stretching vibration of O–H groups of PLA. Peaks at 1058 cm^{-1} and 1172 cm^{-1} originate from C–O stretching vibration, and a peak around 2960 cm^{-1} and about 1432 cm^{-1} and 1752 cm^{-1} are characteristic absorption of C–H bending and stretching vibration. A large peak observed at 3480 cm^{-1} is stretching vibration of PLA O–H groups. Peaks at 1058 cm^{-1} and 1172 cm^{-1} originate from C–O stretching vibrations, and peaks at 2960 cm^{-1} , 1432 cm^{-1} and 1752 cm^{-1} are stretching vibrations of C–H bond. A peak observed at 3486 cm^{-1} is assigned to O–H stretching vibration of the PEG, and peaks at 2798 cm^{-1} and 1464 cm^{-1} can be attributed to C–H and essential oil in the nanofiber structure [25].

Thermal properties

The samples were heated, cooled, and reheated at a heating rate of $2^\circ\text{C}/\text{min}$ over a temperature range of -20 to 100°C . DSC curves are shown in Fig. 4. Thermal property data obtained from DSC curves and melting transition enthalpy, crystallization transition enthalpy, phase transition temperatures during heating/cooling are summarized in Table 2.

According to DSC data of PLA/PEG/EO composites, latent heat storage melting enthalpies range from 35.3 J/g to 77.5 J/g . PCM3, which starts to phase change at 12.7°C ,

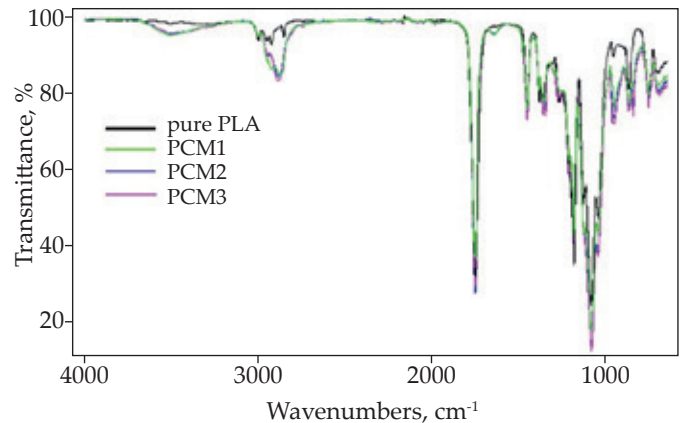


Fig. 3. FT-IR spectra of pure PLA [33], PCM1, PCM2 and PCM3

stores approximately 78 J/g of latent heat energy at 34.7°C with a significant energy storage at 25.7°C . Maximum heat energy storage temperature is 32.4°C for PCM1 and 34.7°C for PCM2. Pure PEG enthalpy is about 120 J/g and melting temperature (T_m) is about 36°C (Fig. 4a) additionally melting enthalpy of pure PLA is quite low (Fig. 4e). The variation in the PEG content can originate different enthalpies and different transition temperatures [36].

TGA curves of PLA/PEG/EO composite fibers with different mass ratios are given in Fig. 5. Pure PLA decomposes in one step (Fig. 5a), while PLA/PEG/EO composites decompose in 2 steps according to the changing maximum rate of decomposition temperature (T_{max}) (Figs. 5b–d). Pure PLA degraded at 318.7°C (Fig. 5a), while PCM1 nanofibers degraded at approximately 237°C and 346°C (Fig. 5b). On the other hand, PCM2 decomposed at an average of 248°C and 377°C (Fig. 5c), and PCM3 nanofibers degraded at approximately 246°C and 374°C . Pure PEG maximum rate of decomposition temperature was 372.3°C (Fig. 5e). TGA data of pure PLA, PEG and PLA/PEG/EO composite nanofibers were summarized in Table 3. Thermostability of PCM nanofiber materials appears to be suitable for applications up to 200°C . Morphology and thermal properties of composite fibers can change significantly with adjustment of PEG content. [25, 34, 35].

CONCLUSIONS

In this study, PLA-based composite nanofibers with different clove and PEG contents were successfully fabricated. According to DSC results, the nanofibers stored latent thermal energy from about 12°C to 36°C , and espe-

Table 2. DSC data of PEG, PLA, and PCM nanofibers

| PCM | $T_m, ^\circ\text{C}$ | $\Delta H_m, \text{J/g}$ | $T_c, ^\circ\text{C}$ | $\Delta H_c, \text{J/g}$ |
|------|-----------------------|--------------------------|-----------------------|--------------------------|
| PEG | 35.7 | 120.10 | 22.7 | 135.90 |
| PLA | 60.2 | 1.96 | – | – |
| PCM1 | 32.4 | 35.26 | 15.6 | 46.59 |
| PCM2 | 34.7 | 59.94 | 12.7 | 65.74 |
| PCM3 | 34.7 | 77.48 | 18.5 | 77.79 |

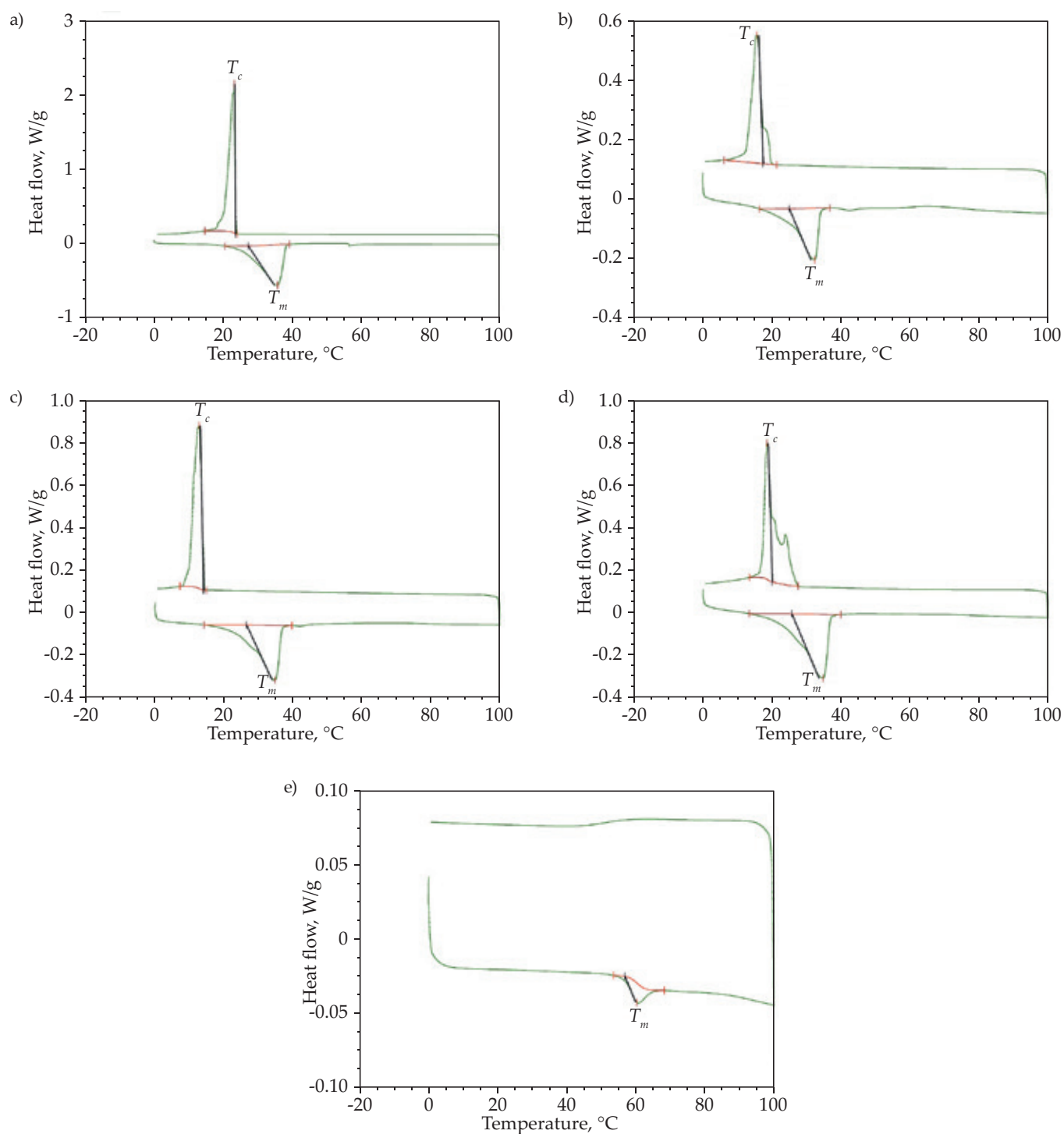


Fig. 4. DSC curves: a) PEG, b) PCM1, c) PCM2, d) PCM3, and e) PLA

Table 3. TGA data of PLA, PEG, and PCM nanofibers

| Samples | Degradation temperature range, °C | | T_{max} , °C |
|---------|-----------------------------------|-------------|----------------|
| PLA | 174.8–367.1 | | 318.7 |
| PEG | – | 292.2–420.5 | 372.4 |
| PCM1 | Step 1 | 220.2–328.1 | 237.0 |
| | Step 2 | 325.0–402.7 | 345.8 |
| PCM2 | Step 1 | 224.1–305.1 | 248.2 |
| | Step 2 | 355.2–420.9 | 377.2 |
| PCM3 | Step 1 | 234.8–279.9 | 246.2 |
| | Step 2 | 324.9–430.1 | 374.6 |

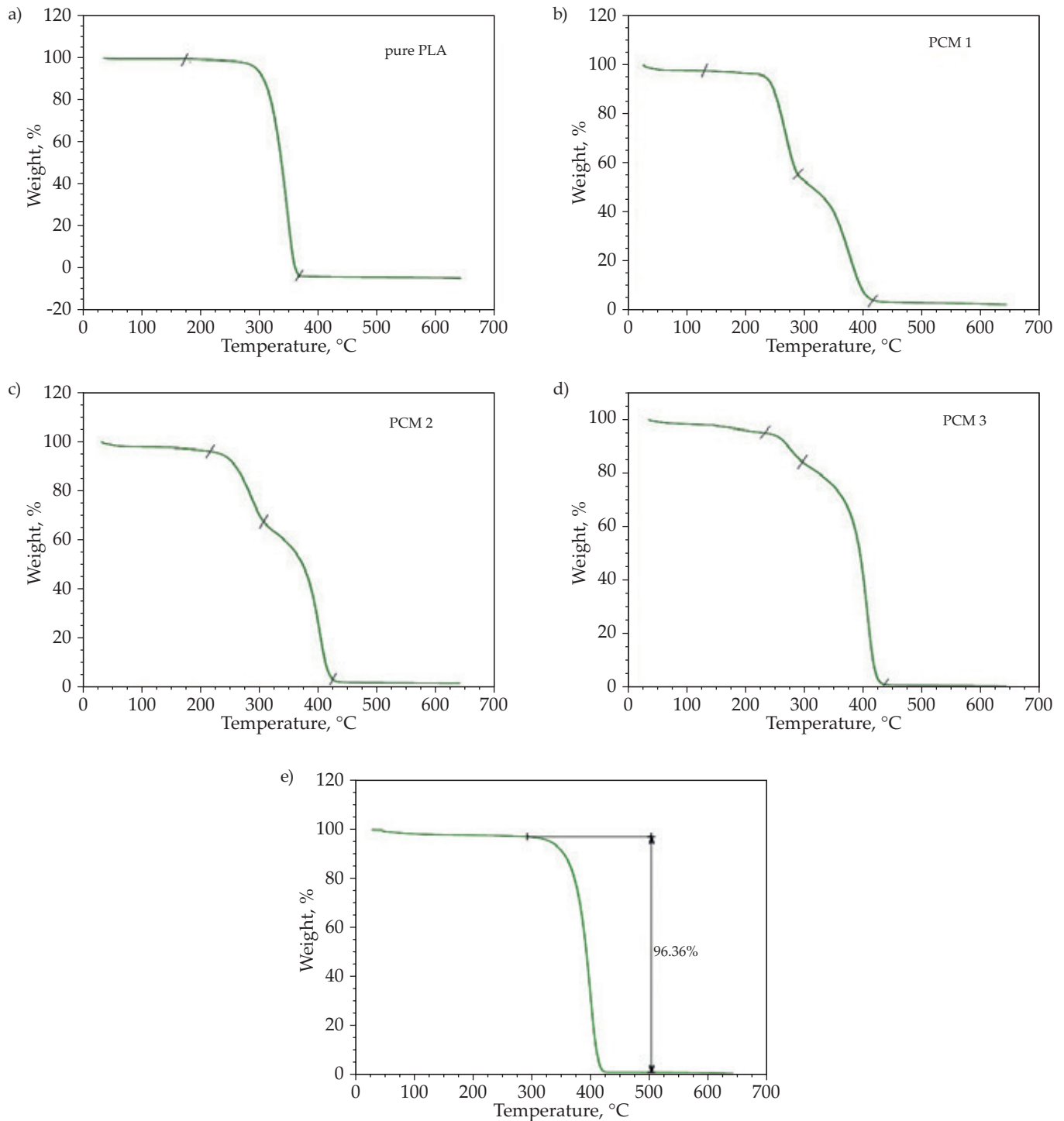


Fig. 5. TGA curves: a) PLA, b) PCM1, c) PCM2, d) PCM3, e) PEG

cially PCM3 nanofibers have useful latent thermal energy with a melting enthalpy of 77.5 J/g at melting temperature of about 35°C. The ideal human body temperature of 36.5°C (average for skin 33°C) [23] is a source of thermal energy for nanofibers, and with the local use of PCM nanofibers, in the event of a drop in body temperature, the latent thermal energy store can be returned into the environment and maintain body temperature for a specified period of time. Moreover, the above-mentioned properties of the essential oil in the nanofiber structure,

such as local numbing, pain-relieving effect, and insect repellent effect [10, 14], suggest that the obtained composite nanofibers can make significant contributions in the fields of medicine, textiles, and food as economical, functional, and smart material.

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