

EFFECT OF ZINC OXIDE CONTENT ON MORPHOLOGY TRANSITION AND SHAPE MEMORY BEHAVIOR OF ELECTROSPUN POLY(L-LACTIDE-CO-GLYCOLIDE-CO-CAPROLACTONE) MATERIALS FOR SKIN-RELATED APPLICATIONS

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Abstract

Shape memory polymers (SMPs) represent a class of smart materials of increasing importance in biomaterials engineering and dermatological applications. Their ability to undergo reversible shape changes in response to physiological stimuli enables the design of materials capable of conforming to the skin surface and enhancing the performance of delivery systems. The aim of this study was to evaluate the effect of zinc oxide (ZnO) addition on the electrospinning process and the properties of electrospun fibrous mats based on a poly(L-lactide-co-glycolide-co-caprolactone) (PLGC) exhibiting shape memory behavior. The fibrous mats were fabricated by electrospinning using a chloroform/methanol solvent system (1:1 v/v). It was demonstrated that ZnO content significantly influences the morphology of the material — at 0.5 wt% a fibrous structure was obtained, whereas higher concentrations (2.5 and 5 wt%) resulted in the loss of fibrous morphology and the formation of more compact structures. FTIR analysis confirmed the presence of ZnO without significant changes in the chemical structure of the polymer. All samples retained shape memory properties at a temperature close to human body temperature, indicating their potential applicability under physiological conditions. The obtained results demonstrate that ZnO content governs the morphology transition from fibrous mats to compact film-like structures, which in turn significantly affects shape memory behavior; low ZnO concentrations favor the formation of uniform fibrous materials suitable for skin-related applications, whereas higher concentrations lead to dense, film-like structures that may serve as protective or occlusive layers, while still retaining functional shape memory properties.

Keywords: *shape memory polymers, electrospinning, polymeric fibrous mats, zinc oxide, dermatological applications, PLGC*

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Introduction

In recent years, there has been a dynamic development of biomaterials intended for regenerative medicine and tissue engineering applications, including materials designed for contact with the skin [1–4]. Particular attention has been paid to smart materials capable of responding to environmental stimuli such as temperature, pH, or humidity. This group includes shape memory polymers (SMPs), which are able to reversibly change their shape in response to specific stimuli and have found application in biomedical materials, including drug delivery systems and materials intended for contact with tissues. The shape memory effect in polymers is typically associated with the presence of two distinct structural domains: a permanent phase responsible for fixing the original shape and a switching phase that enables temporary shape fixation and recovery. The activation of the shape recovery process is most commonly triggered by temperature, particularly when the material is heated above its glass transition temperature (T_g) or melting temperature (T_m), allowing the polymer chains to regain mobility and return to their original configuration [5,6]. This mechanism enables precise control over shape transformation and makes SMPs particularly attractive for biomedical applications requiring stimulus-responsive behavior.

These features make them promising candidates for dermatological applications, where conformity to the skin surface and functionality under physiological conditions are of key importance.

One of the techniques enabling the production of materials with a highly developed specific surface area is electrospinning. This method allows the fabrication of porous fibrous structures with a high surface-to-volume ratio, which promotes cell interaction and the transport of active substances. Owing to these properties, electrospun nonwovens are widely used, among others, as wound dressing materials and carriers for bioactive compounds. In recent years, increasing attention has been devoted to electrospun fibrous materials exhibiting shape memory properties. The combination of electrospinning and SMPs enables the fabrication of highly porous, flexible structures that can conform to complex surfaces and respond to external stimuli. However, the electrospinning of shape memory polymers remains challenging due to the need to balance solution properties, such as viscosity and conductivity, with the preservation of functional behavior. Additionally, the incorporation of additives may further influence both fiber formation and the shape memory performance of the resulting materials [1,2,7,8].

To impart additional functional properties, polymeric materials are increasingly modified with inorganic particles. Zinc oxide (ZnO) is one of the most extensively studied additives due to its antibacterial, anti-inflammatory, and tissue-regenerative properties [3,10,11]. Therefore, the incorporation of ZnO into polymeric materials may enhance their application potential in dermatological contexts. It has been demonstrated that the presence of ZnO in electrospun polymer systems may affect not only their bioactive properties, but also the electrospinning process itself and the structure of the resulting materials [3,10]. ZnO is also widely used as an active ingredient in cosmetology and dermatology, particularly in preparations intended for the care of acne-prone skin [12,13]. It exhibits antibacterial, anti-inflammatory, and sebum-regulating activity, which makes it effective in reducing acne lesions. Its mechanism of action involves, among others, inhibition of *Cutibacterium acnes* growth through the generation of reactive oxygen species and the release of Zn^{2+} ions, as well as reduction of pro-inflammatory cytokine production and regulation of sebaceous gland activity [12,13]. In sheet masks, ZnO primarily

serves a soothing and regenerative function. Due to the occlusive effect characteristic of this form of application, the penetration of active ingredients is enhanced and a moist environment favorable for skin recovery is maintained. ZnO is particularly used in formulations intended for irritated skin or skin following cosmetic procedures, where it helps to reduce erythema and accelerate epidermal regeneration [14]. It is also frequently combined with moisturizing substances such as hyaluronic acid or panthenol [12].

In the case of anti-acne sheet masks designed for the back, ZnO plays an important role due to the greater activity of sebaceous glands in this area and the tendency for more severe inflammatory lesions to develop. The sheet form enables uniform coverage of a large skin surface area and prolonged contact of the active substance with the epidermis. As a result, ZnO can effectively inhibit bacterial growth, reduce inflammation, and decrease sebum secretion, while also representing a potential alternative to topically applied antibiotics [13,14].

Despite its numerous advantages, the use of ZnO requires an appropriate concentration to be selected, since excessive amounts may lead to skin dryness and disruption of the skin barrier [15]. In topical formulations, ZnO is typically used at concentrations below 5% to balance efficacy and skin compatibility. Consequently, it is often combined with moisturizing and soothing agents. In this context, fibrous materials exhibiting a shape memory effect may represent a particularly promising solution, enabling effective therapeutic action at low ZnO loadings while minimizing the risk of damage to the skin hydrolipid barrier. Despite the growing interest in both ZnO-modified polymer systems and shape memory materials, there is still a limited understanding of how inorganic additives affect the electrospinning process and functional properties of fibrous materials exhibiting shape memory behavior. In particular, the combined effect of ZnO incorporation and shape memory functionality in electrospun systems intended for skin-related applications has not been sufficiently explored. In addition, the effect of ZnO concentration on the spinnability and properties of fibrous mats based on shape memory systems has not yet been fully elucidated.

Therefore, the aim of this study was to investigate the effect of ZnO addition on the electrospinning process and on the structural, chemical, and functional properties of electrospun fibrous mats based on a shape memory

poly(L-lactide-co-glycolide-co-caprolactone) (PLGC), with particular emphasis on their potential use in skin-related applications [3,4].

Materials and Methods

Materials

A poly(L-lactide-co-glycolide-co-caprolactone) (PLGC) was used for the fabrication of fibrous mats. The terpolymer, composed of L-lactide, glycolide, and ϵ -caprolactone (L-LA/GL/ ϵ -CL 69/16/15), was synthesized at the Centre for Polymer Materials of the Polish Academy of Sciences, via solvent-free ring-opening polymerization (ROP) using zirconium acetylacetonate as a low-toxicity, biocompatible initiator. The synthesis approach was based on the methodology described by Smola et al. [16], although the terpolymer composition investigated in the present study differs from that reported therein. Polymer blends were prepared by melting the terpolymer granules at approximately 185 °C, followed by the incorporation of ZnO, (Merck Life Science Sp.z.o.o.; Poznań, Poland). During ZnO addition, the temperature was reduced to approximately 180 °C. The mixture was then manually homogenized in a surgical steel vessel. A chloroform/methanol mixture (1:1 v/v) (POCH - Avantor, Poland) was used as the solvent system for further processing. ZnO was introduced as an inorganic additive at different concentrations. For the sample containing 0.5 wt% ZnO, the additive was incorporated in powder form, whereas for higher concentrations (2.5 and 5 wt%), ZnO was added in the form of a pre-prepared blend (granulate).

Electrospinning process

PLGC was dissolved in a chloroform/methanol mixture (1:1 v/v) at a concentration of 10% (w/v) at room temperature under continuous magnetic stirring until a homogeneous solution was obtained. After complete dissolution, an appropriate amount of ZnO was added, and the mixture was subjected to ultrasonic homogenization for approximately 3 min (20 kHz, pulse mode) to improve particle dispersion within the polymer solution. The prepared solutions were loaded into syringes, ensuring the elimination of air bubbles. Each syringe was equipped with a needle of 0.22 mm inner diameter and mounted in an electrospinning apparatus (TIC 1092012, UBB, Bielsko-Biała, Poland). The electrospinning setup used in this study is schematically presented in Fig. 1.

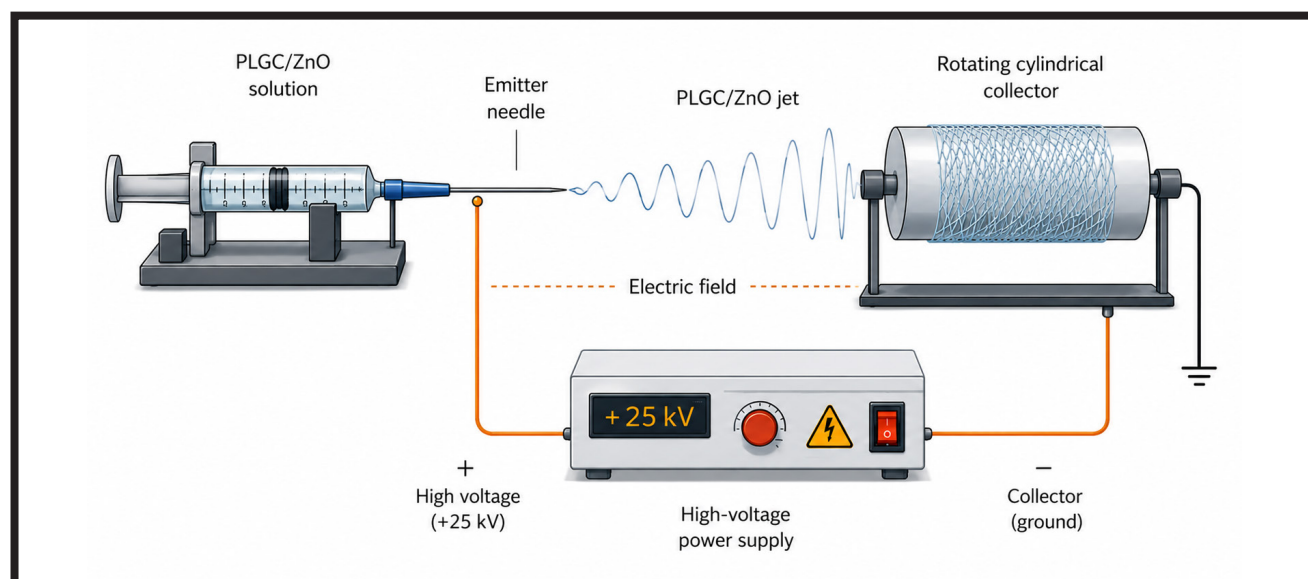


FIG. 1. Schematic illustration of the electrospinning process

TABLE 1. Electrospinning parameters for PLGC and PLGC/ZnO mats

Electrospinning parameters	TER_ES	TER_ZnO_5%	TER_ZnO_2.5%	TER_ZnO_0.5%
Needle diameter [mm]	0.22	0.22	0.22	0.22
Collector diameter [mm]	40	40	40	40
Collector rotational speed [rpm]	330	330	360	230
Applied voltage [kV]	25.1	25.0	25.0	25.0
Flow rate [mL/h]	1.5	1.5	1.5	4
Needle-to-collector distance [cm]	20	20	20	20
Temperature [°C]	21.9	20.7	19.8	21.1
Relative humidity [%]	22	28	27	31
Electrospinning time [min]	165	240	130	64

Electrospinning was carried out at an applied voltage of approximately 25 kV and a needle-to-collector distance of 20 cm under ambient conditions (temperature 20–22 °C, relative humidity 22–31%). Environmental conditions were continuously monitored and maintained within these narrow ranges throughout all experiments to ensure process reproducibility. Detailed process parameters for individual samples are summarized in Table 1. A higher solution flow rate was applied for the sample containing 0.5 wt% ZnO compared to the other samples.

As a result of the electrospinning process, four types of materials were obtained. The morphology and structural integrity of the materials depended on ZnO content. The reference sample and the sample containing 0.5 wt% ZnO formed flexible fibrous mats, whereas samples with higher ZnO content (2.5 and 5 wt%) exhibited more compact, film-like structures.

Methods

Thickness measurements

Sample thickness was measured using a Mitutoyo thickness gauge (model 7301). At least five measurements were taken at different locations for each sample. The mean value and standard deviation were then calculated.

Scanning Electron Microscopy (SEM)

The morphology of the fibrous mats was examined using scanning electron microscopy (SEM) with a JEOL JSM-5500LV microscope. Prior to analysis, samples (1 cm × 1 cm) were mounted on SEM stubs and sputter-coated with a thin layer of gold. Observations were carried out at magnifications

ranging from 100× to 5000×. Approximately 10 micrographs were acquired for each sample from different representative regions. Fiber diameter analysis was performed based on measurements of 70 fibers for the reference TER_ES sample and 55 fibers for the TER_ZnO_0.5% sample, and the results are reported as mean values ± standard deviation.

Fourier Transform Infrared Spectroscopy (FTIR)

The chemical structure of the materials was analyzed using Fourier Transform Infrared Spectroscopy (FTIR). Measurements were performed using a Thermo Scientific Nicolet iS5 spectrometer (Thermo Fisher Scientific, Warsaw, Poland) equipped with an ATR accessory with a diamond crystal. Spectra were recorded in the wavenumber range of 4000–500 cm⁻¹ with a resolution of 4 cm⁻¹. Spectra were collected for each sample from both sides.

Shape Memory Evaluation

Samples with dimensions of 5 mm × 50 mm were prepared to evaluate shape memory properties. Shape memory testing was performed using five specimens per sample type (n = 5), prepared according to DIN EN ISO 527-3. Prior to testing, specimen thickness was measured, and results were reported as mean values ± standard deviation. The samples were heated and shaped on a pre-designed mold (Fig. 2) to obtain a temporary shape. Subsequently, they were cooled in a chamber at 5 °C to fix the imposed geometry. After cooling, the samples were placed on a heating plate at approximately 37 °C, and recovery to the original shape was observed. The recovery process was recorded using a camera and analyzed frame by frame, enabling assessment of recovery behavior and kinetics, including recovery time.

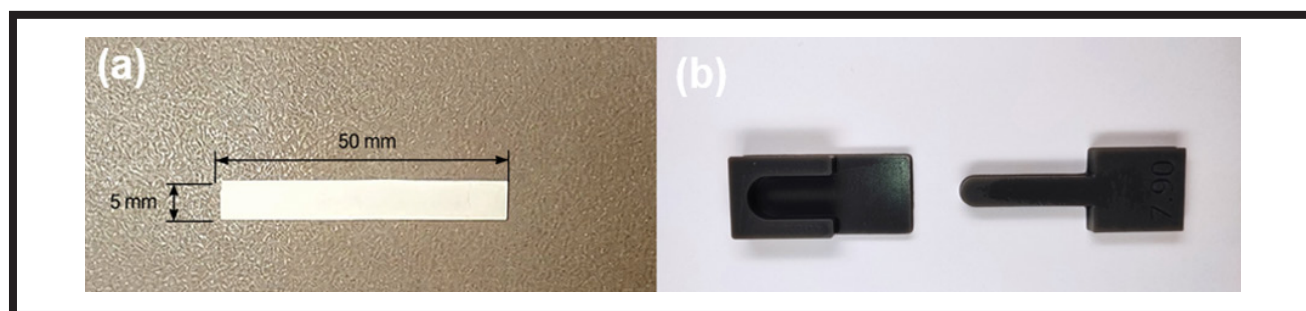


FIG. 2. Specimen used for shape memory testing (5 mm × 50 mm) and the mold applied for inducing and fixing the temporary shape

Calorimetric Investigations

Differential scanning calorimetry (DSC) measurements were performed using a MDSC 2920 calorimeter (TA Instruments, USA) equipped with a refrigerated cooling system. Samples weighing approximately 5 mg were placed in standard aluminum pans and analyzed under a nitrogen atmosphere with a purge gas flow rate of 40 mL/min. The samples were heated from -30°C to 220°C at a rate of $20^{\circ}\text{C}/\text{min}$, followed by cooling at the same rate. The calorimeter sensitivity was better than $0.2\ \mu\text{W}$. Characteristic transition temperatures and enthalpy values were determined from the DSC thermograms using Universal Analysis software (version 4.5A, TA Instruments, USA).

Results and Discussions

During electrospinning, increasing ZnO content introduced noticeable processing difficulties, particularly related to solution stability and particle sedimentation. For solutions containing higher ZnO concentrations ($\geq 2.5\ \text{wt}\%$), particle sedimentation and precipitate formation within the syringe were observed, indicating limited system stability. These effects became more pronounced with increasing ZnO content and likely contributed to the observed changes in material morphology. As a result of the electrospinning process, four samples were obtained. Macroscopically, the materials differed in appearance and physical characteristics. Samples with a well-developed fibrous structure were soft and flexible, whereas materials with higher ZnO content were more rigid, brittle, and less uniform. Variations in thickness were also observed, reflecting structural differences between the samples.

The thickness of the obtained materials was analyzed to quantitatively evaluate these differences (Table 2). Significant variations were observed depending on both electrospinning parameters and ZnO content. The reference sample (TER_ES) exhibited the highest thickness (0.35 mm), which can be attributed to stable electrospinning conditions and a moderate process duration (165 min). In contrast, the sample containing 2.5 wt% ZnO (TER_ZnO_2.5%) showed the lowest thickness (0.06 mm), likely due to the highest collector rotational speed (360 rpm), which promotes fiber stretching and reduces material accumulation. The sample containing 0.5 wt% ZnO (TER_ZnO_0.5%), despite the shortest electrospinning time (64 min), exhibited a relatively higher thickness (0.12 mm). This can be explained by the increased flow rate (4 mL/h) and lower collector rotational speed (230 rpm), which favor rapid material deposition. The sample containing 5 wt% ZnO (TER_ZnO_5%) showed an intermediate thickness (0.10 mm), despite the longest electrospinning time (240 min), suggesting that higher ZnO content adversely affects process stability and limits the formation of thicker layers. Overall, these results indicate that mat thickness is not determined solely by

TABLE 2. Mean thickness and standard deviation of electrospun PLGC mats with varying ZnO content

Sample	Thickness [mm]
TER_ES	0.35 ± 0.01
TER_ZnO_0.5%	0.12 ± 0.01
TER_ZnO_2.5%	0.06 ± 0.01
TER_ZnO_5%	0.10 ± 0.01

electrospinning time but is strongly influenced by process parameters (flow rate, collector speed) and ZnO content, which affects the physicochemical properties of the spinning solution.

SEM images (Fig. 3) revealed a significant influence of ZnO content on material morphology. The pure PLGC sample (TER_ES) exhibited a well-developed fibrous structure typical of electrospun materials (Fig. 3a,c). The fibers formed a dense, randomly oriented, and interconnected network with relatively uniform diameters, and the structure was continuous and free of major defects, indicating stable electrospinning conditions.

Quantitative analysis of fiber diameters for the TER_ES sample (Fig. 4a) showed values in the range of approximately $0.7 - 1.1\ \mu\text{m}$, with an average diameter of $0.92 \pm 0.18\ \mu\text{m}$. The relatively narrow distribution confirms the uniformity of the process and the stability of the polymer jet.

The sample containing 0.5 wt% ZnO retained a fibrous morphology (Fig. 3b,d), although with reduced uniformity. Local structural disturbances were observed in the form

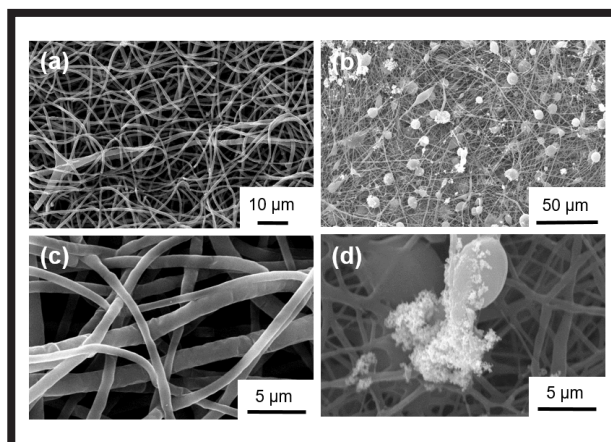


FIG. 3. SEM micrographs of electrospun mats: (a, c) Pure PLGC (TER_ES), (b, d) TER_ZnO_0.5%

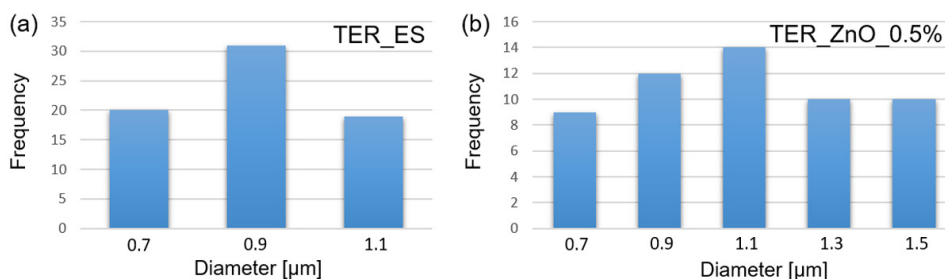


FIG. 4. Fiber diameter distribution for the electrospun samples: (a) TER_ES, (b) TER_ZnO_0.5%

of bead-like features, spherical particles, and agglomerates associated with ZnO. The fiber diameter distribution was broader ($0.7 - 1.5 \mu\text{m}$), with a higher average value of $1.05 \pm 0.30 \mu\text{m}$. The increased standard deviation indicates greater structural heterogeneity, likely resulting from disturbances in jet stability caused by ZnO particles. These observations suggest that even a low ZnO content affects the electrospinning process, leading to increased heterogeneity while still preserving the fibrous character.

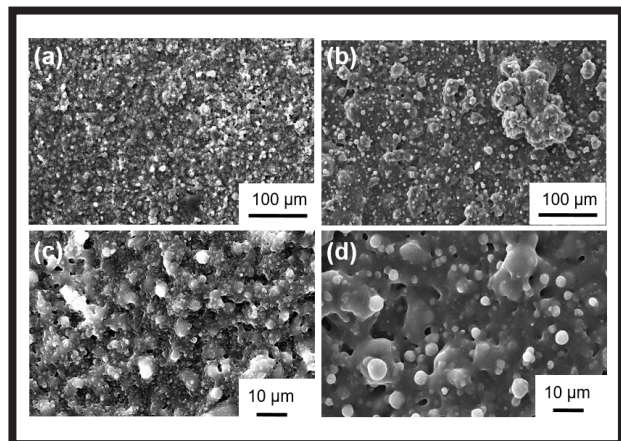


FIG. 5. SEM micrographs of electrospun mats: (a, c) TER_ZnO_2.5%, (b, d) TER_ZnO_5%

Increasing ZnO content to 2.5 and 5 wt% resulted in pronounced morphological changes (Fig. 5). In these samples, the typical fibrous structure was no longer observed, and the materials exhibited compact, film-like morphologies. The absence of distinguishable fibers prevented fiber diameter analysis, confirming a transition from fibrous to non-fibrous structures. This transformation indicates that higher ZnO concentrations destabilize the electrospinning process and hinder the formation of a continuous polymer jet. This effect can be attributed to ZnO particle agglomeration as well as changes in solution properties, such as viscosity, electrical conductivity, and phase homogeneity, which are critical for jet stability. At low concentrations (e.g., 0.5 wt%), the distance between nanoparticles is relatively large, and the polymer present in the solution provides steric stabilization, reducing particle–particle interactions and preventing aggregation. At higher concentrations (2.5–5 wt%), the interparticle distance decreases and the frequency of particle collisions increases. Under these conditions, steric stabilization becomes insufficient, allowing attractive van der Waals forces to dominate and leading

to irreversible nanoparticle agglomeration. Additionally, processing difficulties related to solution instability and sedimentation at higher ZnO contents likely contributed to reduced system homogeneity and poorer material quality. The observed transition from a fibrous morphology to a compact film-like structure can be attributed to changes in solution properties and electrospinning jet stability. Higher concentrations of ZnO nanoparticles are likely to increase flow disturbances and affect key parameters, including electrical conductivity, viscosity, and solvent evaporation behavior. As a result, the jet may not undergo sufficient stretching and solidification before reaching the collector. Consequently, the deposited material remains partially fluid, promoting the coalescence of adjacent deposits and leading to the formation of a continuous film rather than discrete fibers. The transition from a porous fibrous network to a dense film-like structure is a key finding, as it significantly affects both mechanical and functional properties of the materials.

FTIR spectra of all samples exhibited similar profiles, indicating that the chemical structure of the PLGC terpolymer was preserved after electrospinning (Fig. 6).

Characteristic absorption bands corresponding to the polymer structure were observed in all samples. The most intense band at approximately 1750 cm^{-1} is attributed to C=O stretching vibrations of ester groups. Bands in the range of $1180\text{--}1080 \text{ cm}^{-1}$ correspond to C–O–C and C–O stretching vibrations, while bands at $2990\text{--}2940 \text{ cm}^{-1}$ are associated with C–H stretching in aliphatic chains. The addition of ZnO did not cause significant shifts in the main polymer bands, indicating the absence of major chemical changes in the polymer matrix [2,3]. However, variations in band intensity were observed, likely due to the presence of ZnO and morphological differences.

In ZnO-containing samples, an additional band in the low wavenumber region (approximately at 500 cm^{-1}) was observed, with intensity increasing with ZnO content. This band is attributed to Zn–O vibrations. Overall, FTIR analysis confirms that ZnO incorporation does not significantly alter the chemical structure of the terpolymer. The observed differences in material properties are therefore mainly related to physical and structural effects rather than chemical modification. The assignment of characteristic bands is summarized in Table 3.

The shape memory behavior of the materials was evaluated at temperatures close to physiological conditions ($\sim 37^\circ\text{C}$). All samples exhibited shape memory properties, confirming the functional stability of the PLGC terpolymer regardless of ZnO content and morphology. However, significant differences in recovery kinetics were observed (Fig. 7), strongly correlated with material morphology. The pure PLGC

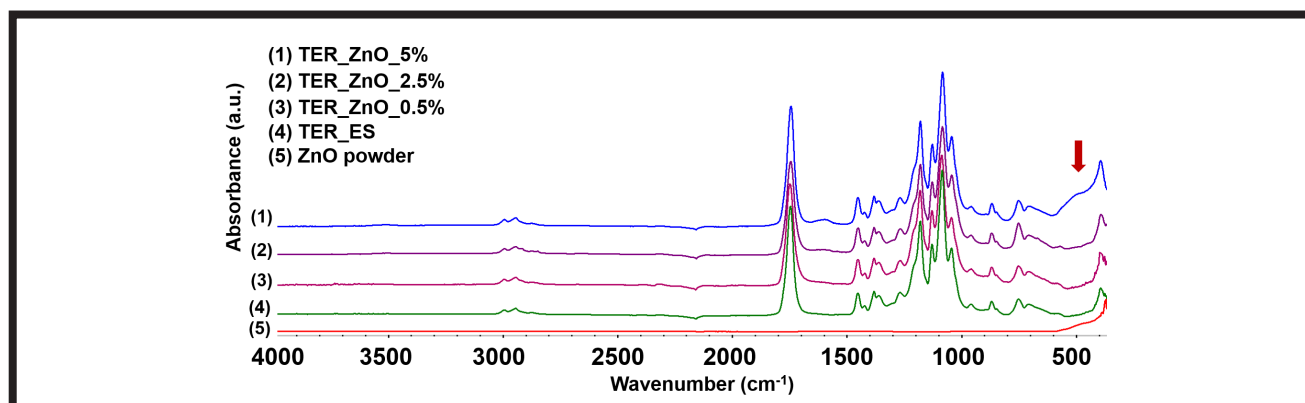
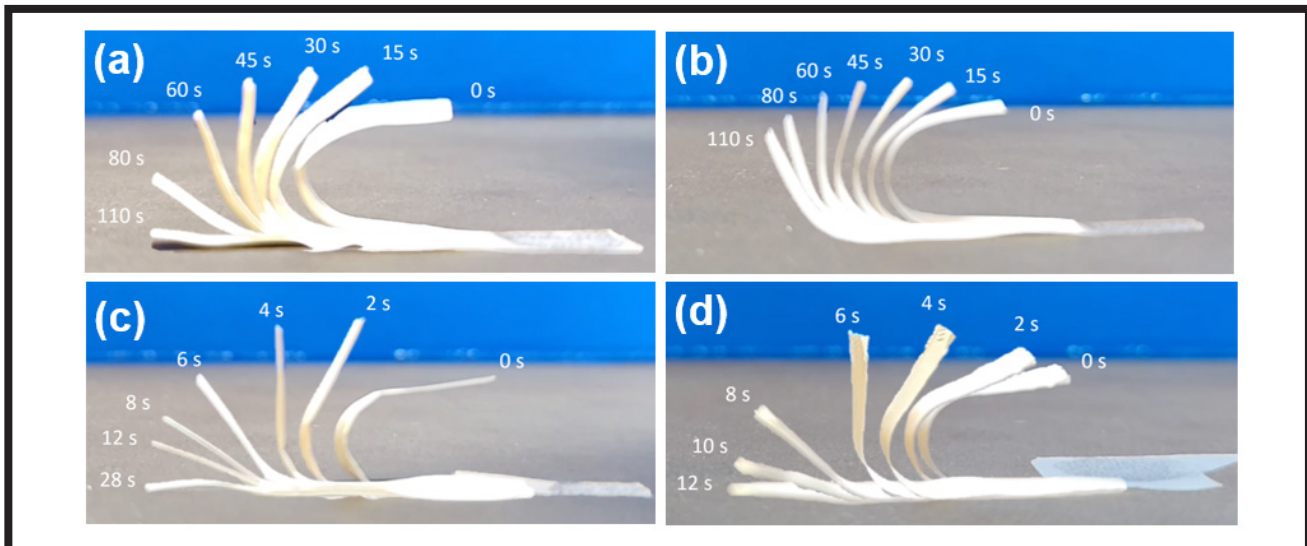


FIG. 6. FTIR spectra of electrospun PLGC fibrous mats and PLGC mats modified with ZnO

TABLE 1. Electrospinning parameters for PLGC and PLGC/ZnO mats

Wavenumber [cm ⁻¹]	Band assignment	Interpretation
2990–2940	C–H stretching vibrations	aliphatic chains of PLGC terpolymer
~1750	C=O stretching vibrations	ester groups in PLGC structure
1450–1360	C–H bending vibrations	aliphatic fragments
1180–1080	C–O–C / C–O stretching vibrations	ester functional groups
~500	Zn–O vibrations	presence of zinc oxide (ZnO)

**FIG. 7. Shape memory behavior of electrospun PLGC and PLGC/ZnO fibrous mats: (a) TER_ES, (b) TER_ZnO_0.5%, (c) TER_ZnO_2.5%, (d) TER_ZnO_5%**

sample exhibited uniform and gradual recovery, returning to its original shape within approximately 110 s, which is characteristic of homogeneous fibrous networks.

The sample containing 0.5 wt% ZnO showed slower and incomplete recovery, despite retaining a fibrous structure. This behavior is attributed to structural defects (beads, agglomerates), which restrict polymer chain mobility and disrupt stress distribution. In contrast, samples with higher ZnO content (2.5 and 5 wt%), exhibiting film-like structures, demonstrated faster recovery kinetics. This can be explained by improved heat transfer within the dense structure and more uniform activation of switching segments. Additionally, higher stiffness of the films may contribute to more efficient stress recovery. Importantly, all samples retained shape memory functionality, indicating that this effect is an inherent property of the PLGC terpolymer and is not suppressed by ZnO addition or morphological changes.

The results demonstrate that ZnO significantly influences both the electrospinning process and the final material properties. The main limitation at higher ZnO contents is the difficulty in achieving uniform dispersion, leading to instability, sedimentation, and morphological transformation. A key finding is the morphology-dependent shape memory behavior. Fibrous structures with defects (0.5 wt% ZnO) exhibit slower and less complete recovery, whereas dense film-like materials (2.5 and 5 wt% ZnO) show faster shape recovery due to differences in heat transfer efficiency and activation of the switching segments. From an application perspective, both morphologies offer distinct advantages. Fibrous mats provide high surface area and porosity, which are beneficial for cell interaction and gas exchange. In con-

trast, dense films may function as occlusive dressings, offering improved protection while maintaining conformability due to shape memory properties. Thus, by controlling ZnO content, it is possible to tailor both the functional properties and morphology of the material, which is particularly advantageous for dermatological applications.

Figure 8 compares the DSC curves of the unmodified shape-memory PLGC terpolymer in granular form (curve 1) and the fibrous mat obtained by electrospinning (curve 3), together with the corresponding second heating runs after controlled cooling from the melt (curves 2 and 4, respectively). The DSC curve of the granular terpolymer recorded between –30 and 220 °C indicates a low degree of crystallinity, evidenced by a small endothermic melting peak of the PLA crystalline phase ($T_m = 140.3$ °C, $\Delta H_m = 22$ J/g). This effect disappears during the second heating cycle, suggesting that the residual crystalline fraction present in the as-prepared material is not regenerated after melting and controlled cooling.

The main thermal transition observed in all samples is the glass transition, accompanied by enthalpy relaxation. For the electrospun PLGC fibrous mat, the enthalpy relaxation effect ($\Delta H_r = 4.87$ J/g) is more than 180 times higher than for the PLGC granules, indicating a significant nonequilibrium state and chain orientation induced by the electrospinning process. A slight increase in the glass transition temperature of the fibrous mat further suggests partial alignment of terpolymer chains in the electrostatic field during electrospinning. The second heating curves exhibit nearly identical profiles, indicating similar thermal behavior after erasing the processing history.

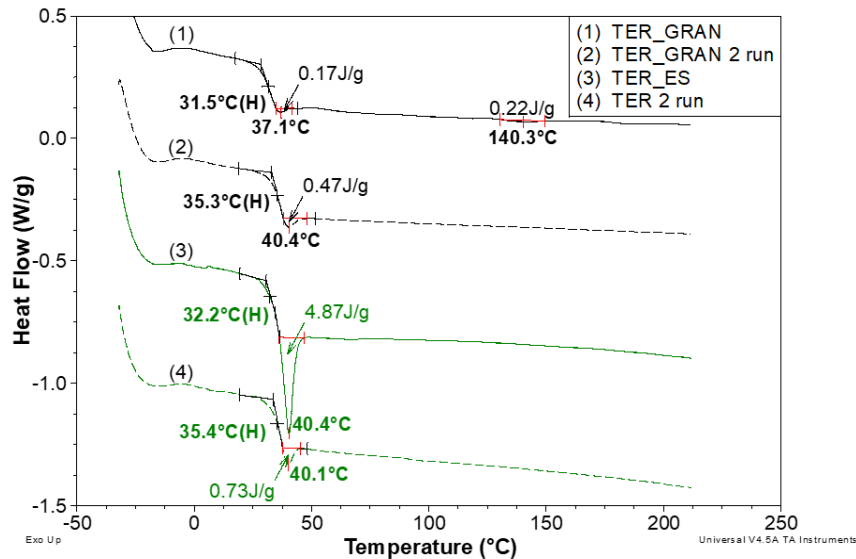


FIG. 8. DSC curves of PLGC in granular form (TER_GRAN) and as an electrospun fibrous mat (TER_ES), obtained during the first and second heating runs over the temperature range of -30 to 220 °C at a heating rate of 20 °C/min and a nitrogen flow rate of 40 mL/min

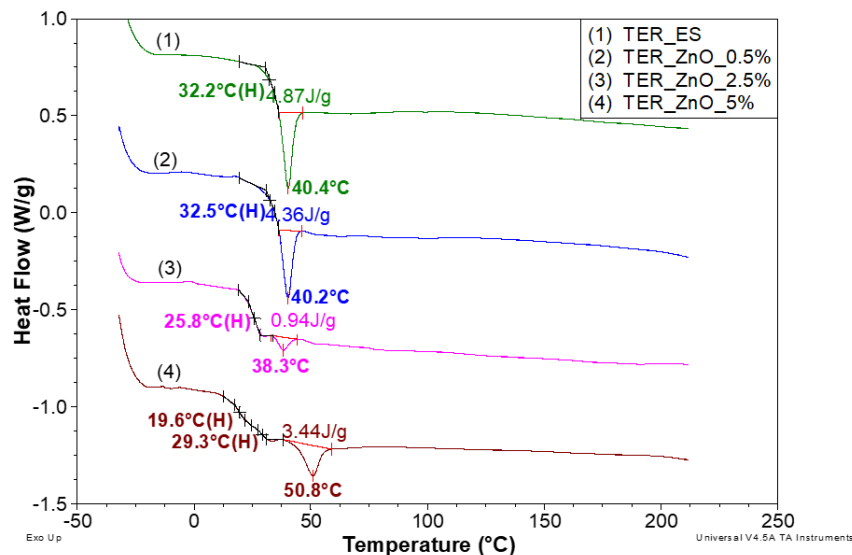


FIG. 9. DSC curves of electrospun PLGC mats containing different ZnO concentrations. Measurement conditions as described in Figure 8

Figure 9 compares the DSC curves of electrospun PLGC mats containing different amounts of ZnO.

Increasing ZnO content resulted in a noticeable shift of the glass transition region toward lower temperatures. For the TER_ZnO_5% sample, the glass transition appeared to split into two stages, indicating increased structural heterogeneity of the material. In addition, the DSC curves of the TER_ZnO_2.5% and TER_ZnO_5% samples exhibited an endothermic effect above the glass transition region that differed from the enthalpy relaxation observed for the unmodified TER_ES and TER_ZnO_0.5% samples. The intensity of this effect increased and shifted toward higher temperatures with increasing ZnO content. These changes may be associated with structural reorganization of the polymer matrix induced by ZnO incorporation. This interpretation is supported by the

corresponding morphological changes observed by SEM (Figs. 3 and 5), including the transition from a fibrous to a film-like structure, as well as by differences in shape memory recovery behavior (Fig. 7). However, a detailed identification of this thermal event would require additional investigations, such as small-angle X-ray scattering or diffraction analyses, which were beyond the scope of the present study.

Conclusions

The conducted study demonstrated that electrospinning enables the fabrication of PLGC terpolymer-based materials exhibiting shape memory properties and tunable morphology. The addition of zinc oxide significantly influences both the electrospinning process and the structure of the obtained

materials. A low ZnO concentration (0.5 wt%) allows the preservation of fibrous morphology while introducing structural heterogeneity and potential bioactive properties. Increasing ZnO content leads to destabilization of the electrospinning process, reduced system homogeneity, and a transition from a fibrous network to a dense film-like structure. The primary limiting factor for higher ZnO concentrations is the difficulty in achieving uniform particle dispersion, resulting in sedimentation, process instability, and deterioration of material quality. Quantitative analysis of fiber diameters confirmed that ZnO addition leads to increased average fiber diameter and broader diameter distribution, indicating reduced process stability and increased heterogeneity of the fibrous structure. FTIR analysis confirmed that ZnO incorporation does not significantly affect the chemical structure of the polymer, indicating that the observed changes are primarily physical and structural in nature. All materials retained their ability to recover shape at a temperature close to human body temperature, confirming their potential applicability in skin-related applications. Importantly, the kinetics of the shape memory effect were strongly dependent on material morphology. Fibrous structures exhibited slower and less efficient recovery, whereas dense film-like materials showed faster and more uniform shape recovery. From an application standpoint, fibrous mats are particularly attractive for applications requiring high porosity, breathability, and interaction with biological tissues, while film-like materials may serve as protective or occlusive systems with improved barrier properties.

These findings demonstrate that ZnO content can be used as a key parameter to control both the morphology and functional behavior of PLGC-based materials. Future studies should focus on optimizing ZnO dispersion within the PLGC matrix to improve electrospinning stability and achieve controlled morphology across a wider range of compositions. Further investigations are needed to quantitatively evaluate shape memory performance, including recovery ratio, cyclic stability, and long-term behavior under physiological conditions. In addition, comprehensive biological assessments, such as cytocompatibility, skin interaction, and antimicrobial activity, should be conducted to validate the suitability of these materials for dermatological applications. DSC analysis demonstrated that the PLGC terpolymer was thermally stable up to 220 °C and was not adversely affected by the electrospinning process. Furthermore, ZnO incorporation significantly influenced the thermal behavior of the material, particularly within and above the glass transition region. The observed effects may be related to structural changes in the polymer matrix, although further studies are required to confirm this hypothesis.

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