eXPRESS Polymer Letters Vol.9, No.1 (2015) 49–65
Available online at www.expresspolymlett.com
DOI: 10.3144/expresspolymlett.2015.6

Enhancing the mechanical properties of electrospun polyester mats by heat treatment

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Received 31 May 2014; accepted in revised form 9 August 2014

Abstract. Microfibrous materials with a targeted design based on poly(L-lactic acid) (PLA) and poly(ε-caprolactone) (PCL) were prepared by electrospinning and by combining electrospinning and electrospraying. Several approaches were used: (*i*) electrospinning of a common solution of the two polymers, (*ii*) simultaneous electrospinning of two separate solutions of PLA and PCL, (*iii*) electrospinning of PLA solution in conjunction with electrospraying of PCL solution, and (*iv*) alternating layer-by-layer deposition by electrospinning of separate PLA and PCL solutions. The mats were heated at the melting temperature of PCL (60°C), thus achieving melting of PCL fibers/particles and thermal sealing of the fibers. The mats subjected to thermal treatment were characterized by greater mean fiber diameters and reduced values of the water contact angle compared to the pristine mats. Heat treatment of the mats affected their thermal stability and led to an increase in the crystallinity degree of PLA incorporated in the mats, whereas that of PCL was reduced. All mats were characterized by enhanced mechanical properties after thermal treatment as compared to the non-treated fibrous materials.

Keywords: *nanomaterials, electrospinning, poly(L-lactic acid), poly(ε-caprolactone), thermal sealing*

1. Introduction

During the last decade nanotechnologies have made a remarkable progress in the development of novel materials with a design and properties which have been unknown until now. Electrospinning and electrospraying are two particularly attractive processes for the preparation of micro- and nano-structured polymeric materials. Electrospinning is a technology used for the preparation of micro- and nanofibers with a length of up to several tens of meters. Because of the various morphologies, large specific surface area and porous structure, mats find application in medicine (mats with antitumor, antibacterial or hemostatic activity), pharmacy (drug carriers), for immobilization of enzymes for water purification or for the preparation of fibrous materials with magnetic properties [1–6]. Electrospraying allows the fabrication of micro- and nanoparticles, which can serve as drug carriers for the preparation of micro- and nanofilms for electroencapsulation, in direct electrowriting, etc. [7–9]. The possibility for combining the two processes with the purpose of creating a novel generation of fibrous materials decorated with micro- or nanoparticles is particularly attractive [10, 11]. The combination of the two methods is still scarcely reported.

Despite the above-described advantages of the fibrous materials it is known that they are characterized by poor mechanical properties. One of the possible routes for enhancement of the strength of the mats is based on heating them at temperatures close to and above the melting temperature (T_m) of the polymer(s) they are composed of. In the majority of cases the thermal treatment of the mats enables the

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preparation of polymeric materials, in which the fibrous structure is partially or completely lost, and the pristine fibers are interconnected forming a network. A limited number of studies on the enhancement of the mechanical properties of fibrous materials by thermal treatment exist in the literature. Improvement of the mechanical properties of polysulfonic fibers [12], poly(L-lactic acid) (PLA) fibers [13] or fibers from PLA with incorporated multiwall carbon nanotubes [14] has been achieved by heat treatment. Lee *et al*. [15] have prepared poly(ε-caprolactone) (PCL)/Pluronic F127 scaffolds with enhanced mechanical properties after heat treatment suitable for tissue engineering applications. Based on the literature review it can be concluded that up to date no data is available about the preparation of mats from two or more polymers with enhanced mechanical parameters after heat treatment and by combining the electrospinning and electrospraying techniques.

In the present study the preparation of mats with a desired structural hierarchy on a micro- and nano-level by combining the electrospinning and electrospraying processes has been discussed. Two biodegradable and biocompatible polymers with versatile medical applications: PLA with a high melting temperature (T_m = 165°C) and PCL with a lower melting temperature (T_m = 60°C) were used. It was the difference in the thermal behavior of the polymers that allowed the preparation of fibrous materials with an original design and desired mechanical characteristics. Fibrous materials were fabricated by: (*i*) electrospinning of a common solution of the two polymers, (*ii*) simultaneous electrospinning of two separate solutions of PLA and PCL, (*iii*) simultaneous electrospinning (PLA) and electrospraying (PCL) of two separate solutions, and (*iv*) alternating, layer-by-layer deposition by electrospinning of PLA and PCL solutions. The obtained materials are further designated as PLA/PCL mats, PLA_{elspin}/PCL_{elspin} mats, PLA_{elspin}/$PCL_{elspray}$ mats, and 'sandwich'-type mats. The electrospun mats were heated at T_m of PCL (60°C), thus enabling the thermal sealing of the fibers by molten PCL fibers/particles. Special attention has been paid to the structure-properties relationship of the fibrous material before and after heat treatment. The morphology and topology of the mats was assessed by scanning electron microscopy (SEM) and fluorescence microscopy. The hydrophilic/hydrophobic properties of the mats were evaluated by measuring the water contact angle. The crystallinity degree of the polymers and the thermal stability of the mats before and after heat treatment were determined by differential scanning calorimentry (DSC) and thermogravimetric analysis (TGA). The tensile behavior of the mats was also assessed.

2. Experimental section

2.1. Materials

Poly(L-lactic acid) (PLA, Sigma-Aldrich, Germany) with a $\bar{M}_w$ = 96 000 g/mol and $\bar{M}_w/\bar{M}_n$ = 1.75; poly (ε-caprolactone) (PCL, CAPA 6800, Perstorp, Sweden) of mean molecular weight 80 000 g/mol; and fluorescein (F-free acid, Sigma-Aldrich, Germany) were used. Dichloromethane (DCM) and dimethylformamide (DMF) were supplied by Merck, Germany and dimethylsulfoxide (DMSO) was purchased from Sigma-Aldrich, Germany.

2.2. Preparation of fibrous materials

2.2.1. Preparation of fibrous materials by electrospinning of a single solution

In the present study PLA, PCL mats and mats composed of fibers containing PLA and PCL in various weight ratios – 75/25, 60/40 or 50/50 wt/wt (PLA_{75}/PCL_{25}, PLA_{60}/PCL_{40} and PLA_{50}/PCL_{50} mats) were fabricated by electrospinning a single spinning solution using one syringe. Fibrous materials with a 'sandwich' type structure were prepared, as well. This was achieved by consecutive electrospinning of PLA or PCL solutions onto one and the same collector followed by electrospinning of a PCL or PLA solution, respectively. The 'sandwich' type mats composed of initially deposited PLA fibers and a PCL fiber layer on top are denoted as 'sandwich' PLA+PCL. In the case when PLA fibers are deposited on top of PCL fibers the mats are designated as 'sandwich' PCL+PLA. A schematic of the electrospinning setup used for preparation of the described fibrous materials is presented in Figure 1a.

PLA and PCL fibers, as well as 'sandwich' type mats were prepared from 9 wt% polymer solutions of PLA in DCM/DMSO (75/25 wt/wt) and of PCL in DCM/DMF (93/7 wt/wt). PLA/PCL fibers were obtained after dissolving the respective amounts of polymers in the required volume of DCM/DMSO (75/25 wt/wt) with a total polymer concentration of 9 wt%.

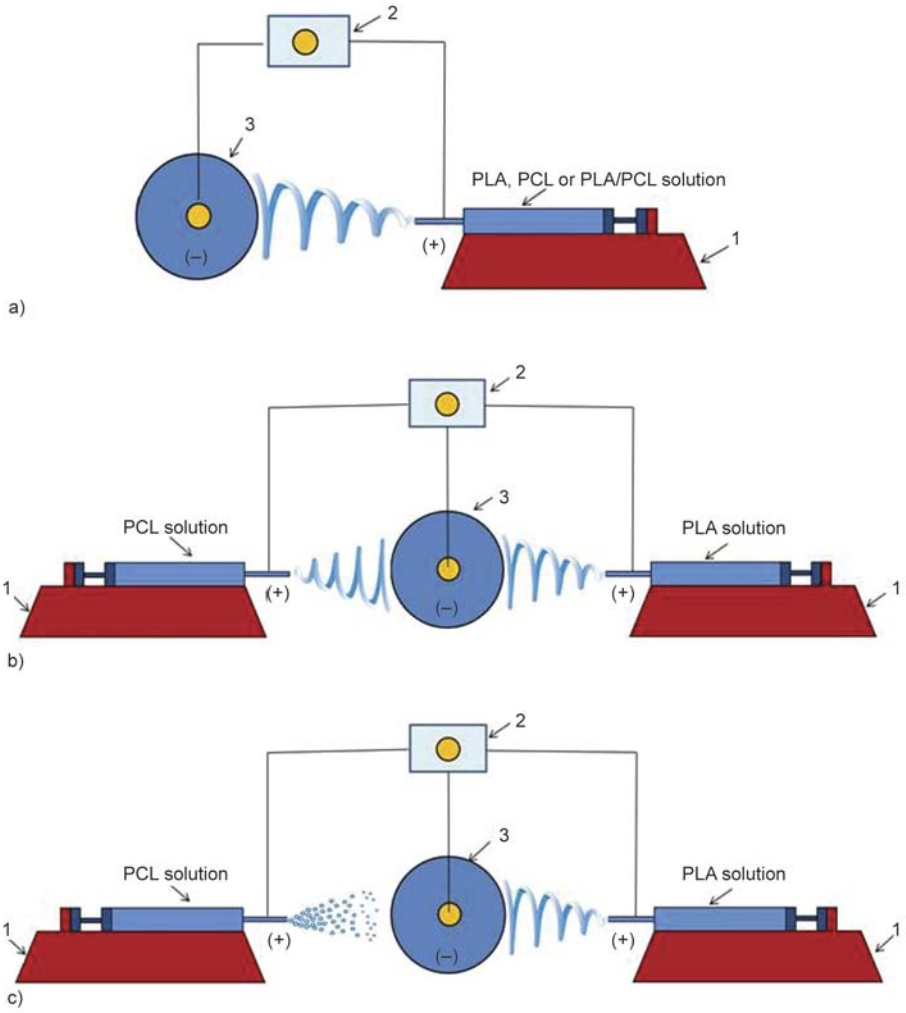

Figure 1. Schematic representation of the setup used for electrospinning of a single solution [PLA, PCL, PLA/PCL or 'sandwich' type (PLA+PCL or PCL+PLA) mats] (a); for simultaneous electrospinning of two separate solutions (PLA_{elspin}/PCL_{elspin} mats) (b) or for simultaneous electrospinning and electrospraying of two separate solutions (PLA_{elspin}/$PCL_{elspray}$ mats) (c); 1 – pump, 2 – high voltage power supply and 3 – rotating collector

2.2.2. Preparation of fibrous materials by simultaneous electrospinning of two separate solutions

Microfibrous materials were prepared by simultaneous electrospinning of two separate PLA and PCL spinning solutions using two separate syringes (Figure 1b). The mats are denoted as PLA_{elspin}/PCL_{elspin} and depending on the flow rate of the solutions they are designated as: $PLA_{elspin(3)}$/$PCL_{elspin(1)}$ (3 mL/h for PLA solution and 1 mL/h for PCL solution), $PLA_{elspin(3)}$/$PCL_{elspin(2)}$ (3 mL/h and 2 mL/h) and $PLA_{elspin(3)}$/$PCL_{elspin(3)}$ (3 mL/h and 3 mL/h). The polymer concentration of the PLA and PCL spinning solutions was 9 wt% and DCM/DMSO (75/25 wt/wt) and DCM/DMF (93/7 wt/wt) solvent systems were used, respectively.

2.2.3. Preparation of fibrous materials by simultaneous electrospinning and electrospraying of two separate solutions

Mats were prepared by simultaneous electrospinning of a PLA solution and electrospraying of a PCL solution using two separate syringes (Figure 1c). The fibrous materials are denoted as PLA_{elspin}/$PCL_{elspray}$. Depending on the flow rate of the solutions the mats are marked as: $PLA_{elspin(3)}$/$PCL_{elspray(1)}$ (3 mL/h for PLA solution and 1 mL/h for PCL solution), $PLA_{elspin(3)}$/$PCL_{elspray(2)}$ (3 mL/h and 2 mL/h) and $PLA_{elspin(3)}$/$PCL_{elspray(3)}$ (3 mL/h and 3 mL/h). In this case the concentration of the PLA solution was 9 wt% (DCM/DMSO = 75/25 wt/wt), and that of PCL – 0.4 wt% (DCM/DMF = 93/7 wt/wt).

Regardless of the method used for preparation of the mats (electrospinning or electrospraying) the

collector rotation rate was 600 rpm. The conditions employed for preparation of PLA and PLA/PCL mats were: applied voltage of 17 kV, tip-to-collector distance – 10 cm and solution feed rate of 3 mL/h. In the case of the PCL mat the applied voltage was 20 kV, the distance from the capillary tip to the collector – 15 cm and the solution feed rate – 1 mL/h. The PLA+PCL and PCL+PLA 'sandwich' type mats were prepared by electrospinning a PLA solution at a voltage of 17 kV, tip-to-collector distance of 10 cm and a solution feed rate of 3 mL/h, and a PCL solution at a voltage of 20 kV, distance from the capillary tip to the collector – 15 cm and a solution feed rate of 1 mL/h. For the preparation of a PLA_{elspin}/PCL_{elspin} mat a PLA solution was electrospun at a voltage of 17 kV, tip-to-collector distance of 10 cm and a solution feed rate of 3 mL/h, and a PCL solution – at a voltage of 20 kV, a working distance of 15 cm and a feed rate of 1, 2 or 3 mL/h. In the case of PLA_{elspin}/$PCL_{elspray}$ non-woven textile a PLA solution was electrospun under the same conditions used for preparation of the PLA_{elspin}/PCL_{elspin} mats, whereas the PCL solution was subjected to electrospraying at a voltage of 20 kV, tip-to-collector distance of 10 cm and a solution flow rate of 1, 2 or 3 mL/h.

2.3. Heat treatment of the fibrous materials

The electrospun mats were placed in a vacuum oven (Laboratory vacuum oven Binder, Germany) and heated at 60±0.1°C for 15 min with the purpose of achieving thermal sealing of the fibers by the molten PCL fibers/particles. The fibrous materials were heated without removing the aluminum foil onto which they were electrospun in order to prevent folding of the mats during their thermal treatment.

2.4. Characterization of the electrospun materials

The morphology of the mats before and after heat treatment was assessed by scanning electron microscopy (SEM). The samples were vacuum-coated with gold and subsequently observed by SEM (Jeol JSM-5510, Jeol Ltd., Tokyo, Japan and Philips SEM 515, Netherlands). The mean fiber diameter was determined by measuring at least 20 fibers from a SEM micrograph using Image J software [16].

Further evidence for the melting of the PCL fibers/particles was provided by incorporation of fluorescein (F) in the PCL solution (PCL^F) and subsequent observation of the fibrous materials by fluorescence microscopy (NU-2, Carl Zeiss Jena, Germany). Micrographs of one and the same sample fragment were taken before and after turning a fluorescence light source on. For the sake of comparison the mats were observed prior to heating them at 60°C, as well.

The thermal behavior of the obtained fibrous materials was evaluated by differential scanning calorimetry (DSC). The samples were heated in the temperature range from –80 to 250°C at heating rate of 10°C/min under nitrogen (TA Instruments, DSC Q2000, USA). The crystallinity degree (χ_c) of the polymers χ_c^{PLA} for PLA and χ_c^{PCL} for PCL in the fibrous materials was calculated using Equations (1) and (2):

$$\chi_c^{PLA}\,[\,\%\,] = \frac{\Delta H_m^{PLA} - \Delta H_{cc}^{PLA}}{\Delta H_m^{PLA,0} \cdot W^{PLA}} \cdot 100 \qquad (1)$$

$$\chi_c^{PCL}\,[\,\%\,] = \frac{\Delta H_m^{PCL} - \Delta H_{cc}^{PCL}}{\Delta H_m^{PCL,0} \cdot W^{PCL}} \cdot 100 \qquad (2)$$

where W^{PLA} is the weight fraction of PLA, and W^{PCL} – the weight fraction of PCL; ΔH_m^0 is the melting enthalpy when the respective polymer is in a 100% crystalline state: $\Delta H_m^{PLA,0}$ = 93.0 J/g [17]; $\Delta H_m^{PCL,0}$ = 139.5 J/g [18]; ΔH_{cc}^{PLA} and ΔH_{cc}^{PCL} is the enthalpy at the temperature of cold crystallization of the respective polymer. Thermogravimetric analysis (TGA, TA Instruments TGA Q5000, USA) of the mats was performed by heating the samples up to 800°C.

The water contact angles of the fibrous materials were measured using an Easy Drop DSA20E KRÜSS GmbH apparatus, Germany. Drops of distilled water with a volume of 10 μL were deposited on the surface of the test specimens (cut in the direction of the collector rotation). The mean contact angle value was determined after averaging at least 10 measurements for each specimen.

2.5. Mechanical behaviour of the fibrous materials

The tensile characteristics of the fibers were evaluated using a Zwick/Roell Z 2.5 apparatus, Germany load cell 2 mV/V, type Xforce P, nominal force 2.5 kN, test Xpert II. Strain rate – 20 mm/min and room temperature – 21°C. All samples were cut in the direction of collector rotation with dimensions of 20×60 mm and a thickness of ca. 200 μm. For the

sake of statistical significance 10 specimens of each sample were tested, after which the average values of Young's modulus, the ultimate stress and maximum deformation at break were determined.

3. Results and discussion

3.1. Morphology and topological alterations in the electrospun mats before and after heat treatment

3.1.1. Morphology and topology of the fibers prepared by electrospinning of a single solution

The electrospinning of the solutions resulted in the preparation of randomly deposited defect-free fibers, and in the case of electrospraying – of particles. SEM micrographs of the fibrous materials (before and after heat treatment) are shown in Figure 2. The mean diameter of the PLA fibers was ca. 1170±220 nm, and that of PCL fibers before heating was twice as small (515±125 nm). The smaller average diameter of the PCL fibers can be attributed to the lower feed rate of the spinning solution (1 mL/h) as compared to the PLA solution – 3 mL/h. The heat treatment of the PCL mat led to substantial alterations in the fiber morphology and the mat topology (Figure 2), whereat the fibers lost their cylindrical shape. The single melted PCL fibers were connected by zones of PCL fusion. The size of the sites of merging and the voids in the material can be controlled by heating of mats with a different thickness.

SEM micrographs of mats prepared by electrospinning of common PLA/PCL solutions are presented in Figure 2. In these cases interconnecting of the PLA fibers was attained by thermal sealing in the intersections, whereat a continuous network was formed (Figure 2, after heating). It was found that on increasing the PCL content in the pristine PLA/PCL mats, a denser network of interconnected fibers was formed after thermal treatment. The mean fiber diameter

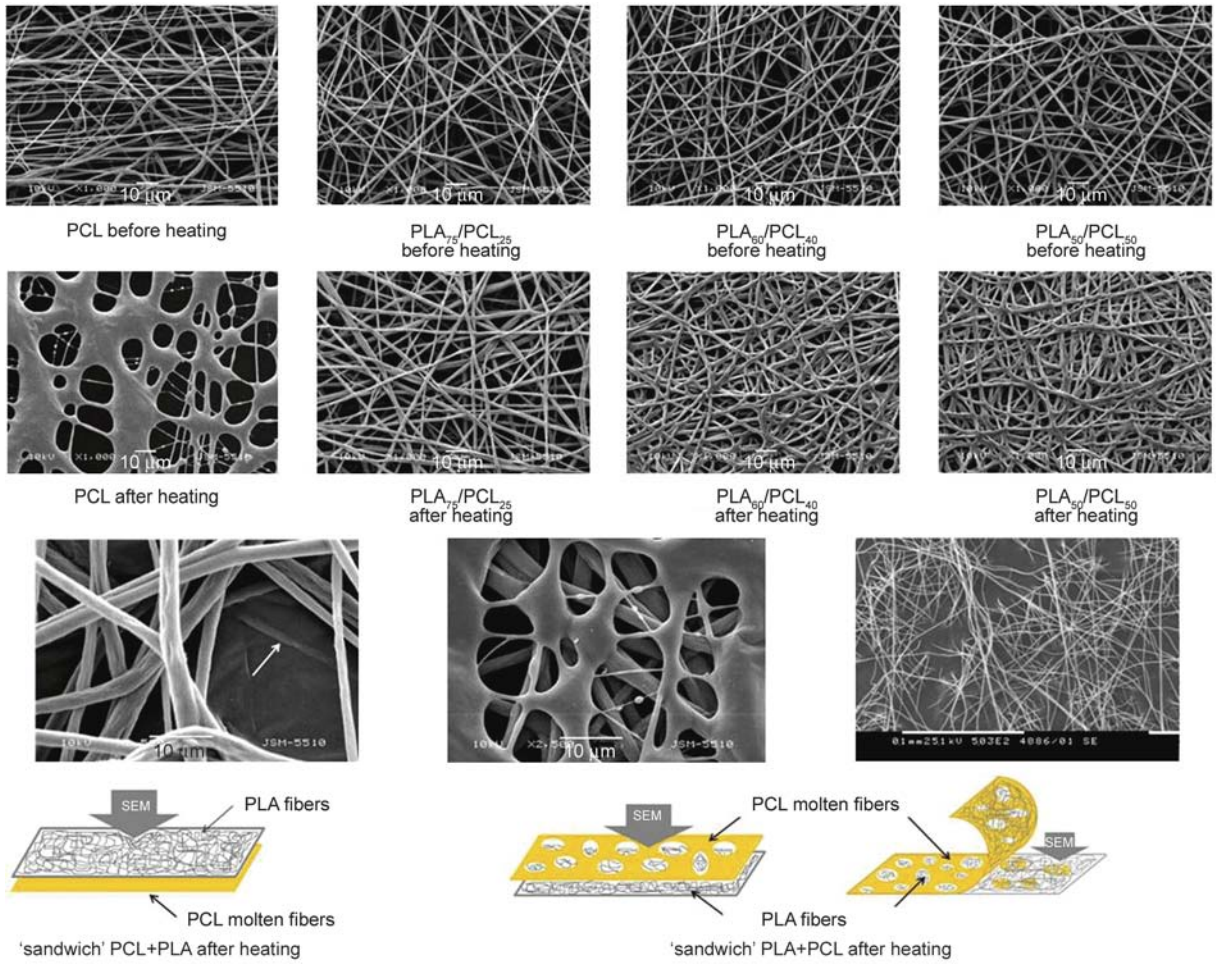

Figure 2. SEM micrographs of PCL, PLA/PCL and 'sandwich' type PCL+PLA and PLA+PCL mats before and after heating at 60°C; magnification ×1000. For 'sandwich' type fibrous materials the position of taking the micrographs (the surface or the bulk of the mat) is schematically presented. The arrow in the SEM micrograph of the 'sandwich' PCL+PLA after heating indicates a PLA fiber submerged in the molten PCL fibers.

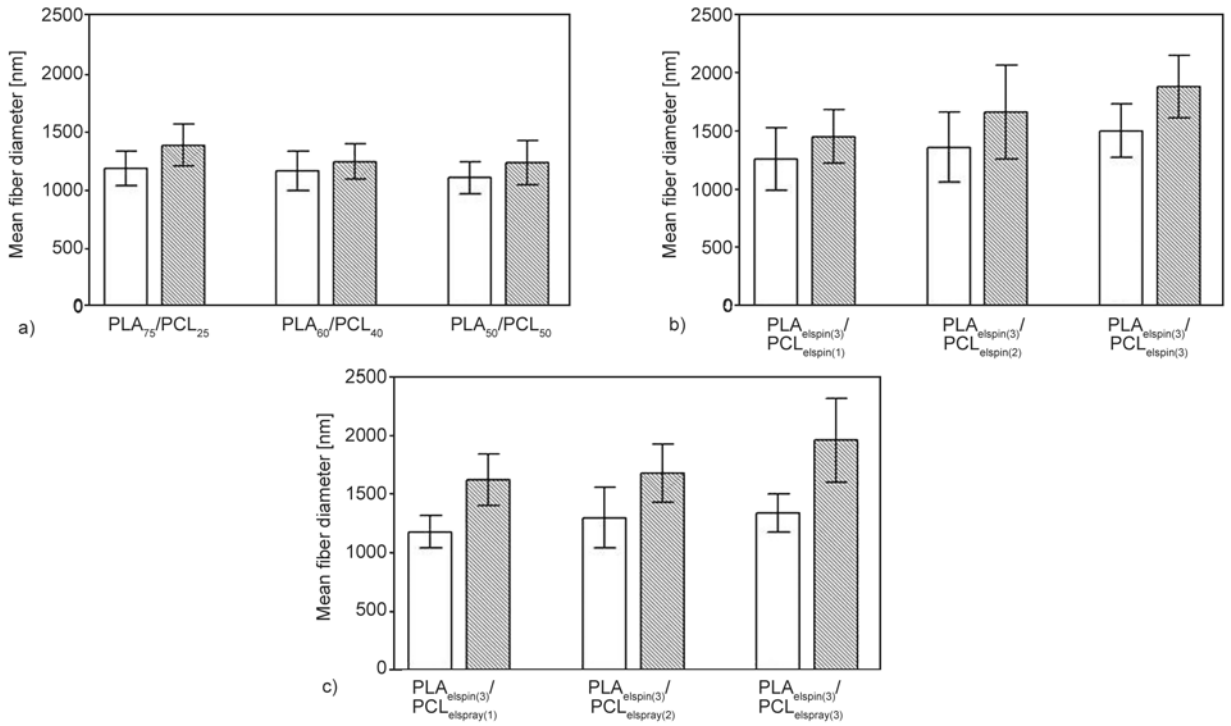

Figure 3. Mean fiber diameters of: PLA/PCL (a), $PLA_{elspin}/PCL_{elspin}$ (b) and $PLA_{elspin}/PCL_{elspray}$ (c); empty bars – before heating, hatched bars – after heating

before heat treatment did not vary significantly for PLA_{75}/PCL_{25}, PLA_{60}/PCL_{40} and PLA_{50}/PCL_{50} fibers and it was ca. 1150 nm, and after heating its value was 1300 nm (Figure 3a). The increase in the mean fiber diameter was attributed to the interconnection of the fibers.

The possibility for preparation of mats with a 'sandwich'-type design was studied. These novel materials were prepared by alternating electrospinning of a PCL and a PLA solution, terminating by deposition of PLA or PCL fibers on top of the prepared mats. The two 'sandwich'-type mats are schematically represented in Figure 2. The morphological alterations in the mats after heating indicate that in the case of 'sandwich' PCL+PLA the PLA fibers are submerged in the molten PCL fibers. A more interesting phenomenon was observed in the case of 'sandwich' PLA+PCL mats, where after melting of PCL fibers a filter-like structure was obtained.

3.1.2. Morphology and topology of fibers prepared by simultaneous electrospinning of two separate solutions

The simultaneous electrospinning of PLA and PCL solutions resulted in the preparation of $PLA_{elspin}/PCL_{elspin}$ mats composed also of defect-free fibers. It was found that with increase in the flow rate of the PCL solution the average fiber diameter in the mats increased: 1260±270 nm for $PLA_{elspin(3)}/PCL_{elspin(1)}$, 1360±300 nm for $PLA_{elspin(3)}/PCL_{elspin(2)}$ and 1500±230 nm for $PLA_{elspin(3)}/PCL_{elspin(3)}$. After heating the diameter of PLA fibers in the $PLA_{elspin}/PCL_{elspin}$ mats was larger than that in PLA mats: 1450±230, 1660±400 and 1880±270 nm for $PLA_{elspin(3)}/PCL_{elspin(1)}$, $PLA_{elspin(3)}/PCL_{elspin(2)}$ and $PLA_{elspin(3)}/PCL_{elspin(3)}$, respectively. The larger diameter may be attributed to coating of the PLA fibers with molten PCL. As seen from the SEM micrographs shown in Figure 4, after heating the PLA fibers were thermally sealed through molten PCL. The $PLA_{elspin(3)}/PCL_{elspin(3)}$ fibers were sealed to the greatest extent because in this case the amount of the melting polymer was the highest.

3.1.3. Morphology and topology of fibers fabricated by simultaneous electrospinning and electrospraying of two separate solutions

$PLA_{elspin}/PCL_{elspray}$ mats have been fabricated by simultaneous electrospinning of a PLA solution and electrospraying of a PCL solution. It is evident from the SEM micrographs of the fibrous materials (Figure 5) that the defect-free and cylindrical PLA fibers are decorated with PCL particles. It was found that

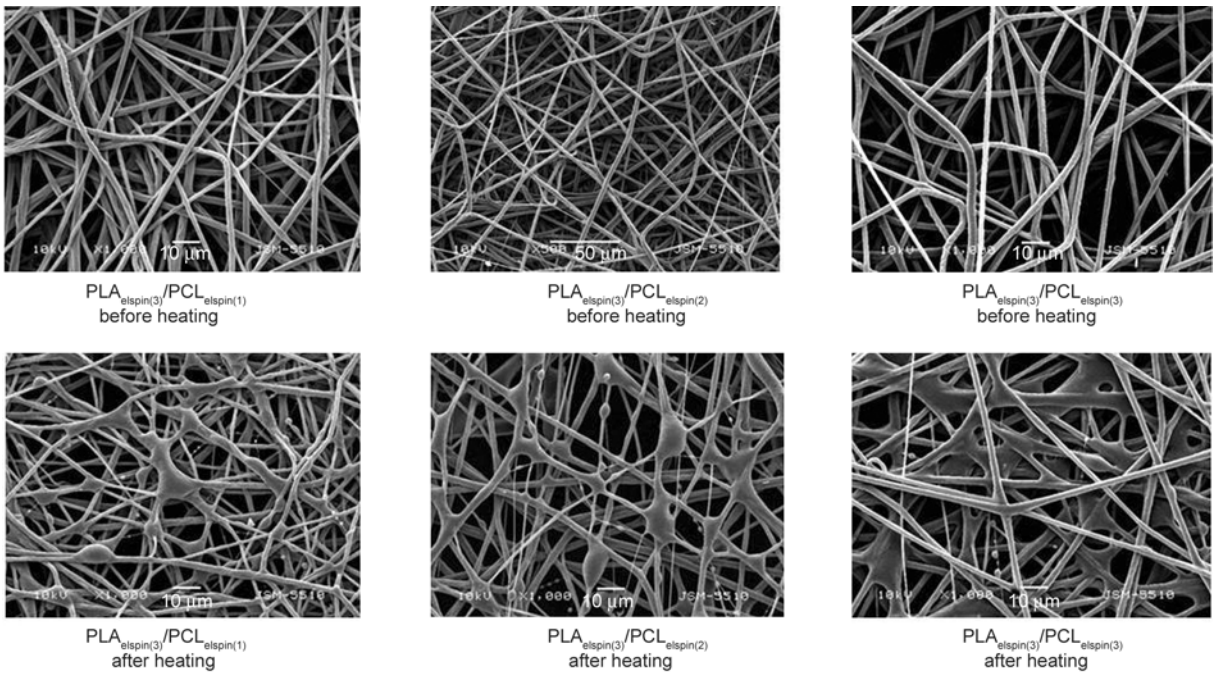

Figure 4. SEM micrographs before and after heating (60°C) of PLA$_{elspin}$/PCL$_{elspin}$ fibers prepared at various feed rates of the PCL$_{elspin}$ solution – 1, 2, or 3 mL/h; magnification ×1000

with the increase in the feed rate of the PCL solution the mean diameter of the particles increased. It was ca. 900±180, 1150±170 and 1300±170 nm at an electrospraying rate of the solution of 1, 2 and 3 mL/h, respectively.

The heat treatment of the mats led to melting of PCL particles, whereupon the PLA fibers were sealed in the sites where the particles were located. It was found that with the increase in the feed rate during electrospraying a greater number of particles were deposited on the PLA fibers. This explains why the greatest number of sealed fibers are observed in the case of the PLA$_{elspin(3)}$/PCL$_{elspray(3)}$ system. The diameter of the PLA fibers in the PLA$_{elspin}$/PCL$_{elspray}$ mats before heating was close to that of the fibers of a PLA mat – ca. 1250 nm.

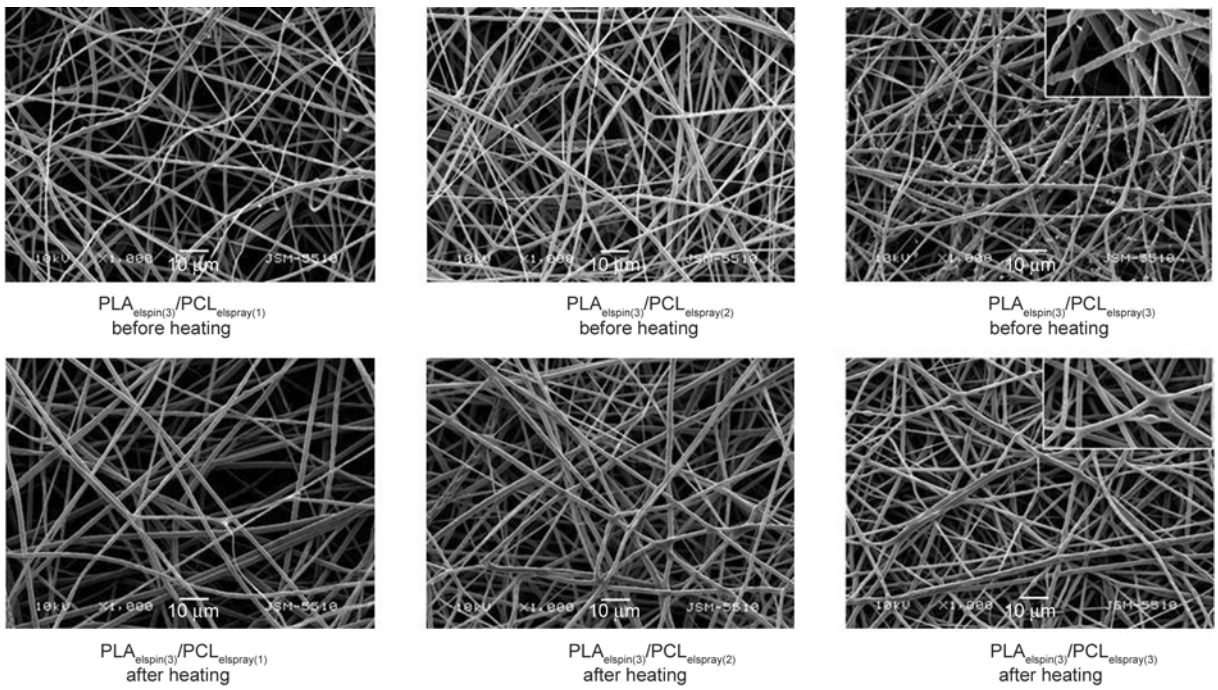

Figure 5. SEM micrographs of PLA$_{elspin}$/PCL$_{elspray}$ fibers prepared at various feed rates of the PCL$_{elspray}$ solution – 1, 2 and 3 mL/h before and after heat treatment (60°C); magnification ×1000, insets – ×1400

After heating it increased to 1700 nm as a result of coating of the fibers with the molten PCL particles (Figure 3).

The obtained results indicate that after heating the mats at the melting temperature of PCL, only the part of the material which is composed of PCL melts (PLA melting temperature – ca. 165°C). As already discussed and as evident from Figures 2, 4 and 5, after thermal treatment the fibrous structure of the mats is preserved but the PLA fibers are thermally sealed by the molten PCL fibers/particles. A different case is observed when the polymer scaffold is composed of one polymer and after heat treatment the individual fibers do not retain their initial morphology and the material obtains film-like morphology [13, 14]. It is evident from the obtained results that the porous structure of the mats (the voids between the fibers) depends both on the architecture of the fibrous materials and on their thermal treatment. It was found that after heating the porosity of the PLA_{50}/PCL_{50} mats was reduced as compared to the pristine mats. This finding held true for $PLA_{elspin(3)}/PCL_{elspin(3)}$ fibers, as well, but the tendency was expressed to a smaller extent. In contrast, in the case of $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats the voids between the fibers after melting the PCL particles increased. This indicates that fibrous materials with desired porous structure can be prepared after heating depending both on the mat architecture (mats composed of fibers only or fibers and particles) and on the PCL content in the pristine material. In the case of all types of mats no shrinking of the fibrous structure was observed after heat treatment. Supplementary information about the distribution of the sites and the manner of sealing of the fibers with the molten PCL fibers/particles was obtained after incorporation of fluorescein (F) in the PCL spinning/spraying solution. The fluorescein-loaded PCL fibers or particles participating in mat formation are further denoted as PCL^F. In Figure 6 micrographs taken of one and the same fragment of the fibrous materials before and after turning a fluorescence light source on are presented. This juxtaposition allowed us to take into account the morphological changes occurring in the the fibrous materials after heating them at 60°C. As seen from Figure 6, the PCL^F fibers before heating were characterized by an intensive fluorescence signal along their length, thus indicating that F was well dispersed in the fibers. After thermal treatment of the PCL^F mat, a layer composed of molten fibers was observed and the fluorescence signal was emitted by the entire material (image not shown). Formation of such a molten fibers layer was observed in the case of 'sandwich' type PLA+PCL^F mats after heating, as well (Figure 6). Comparing the images of the $PLA_{elspin(3)}$/ $PCL^F_{elspin(3)}$ and $PLA_{elspin(3)}/PCL^F_{elspray(3)}$ mats (Figure 6) before and after turning a fluorescence

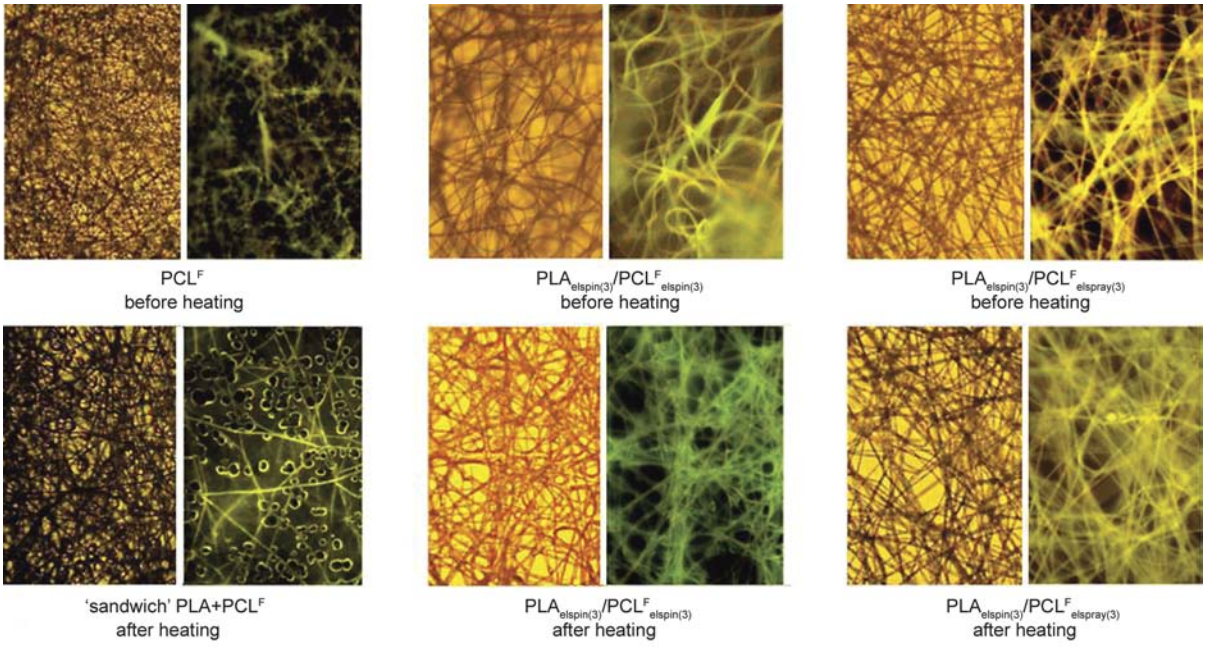

Figure 6. Optical micrographs of one and the same fragment of PCL^F, 'sandwich' type PLA+PCL^F mat, $PLA_{elspin(3)}/PCL^F_{elspin(3)}$ and $PLA_{elspin(3)}/PCL^F_{elspray(3)}$ fibrous materials before and after turning a fluorescence light source on; magnification ×25

light source on allowed to distinguish clearly the PLA fibers from the PCL^F fibers/particles. After heat treatment in these mats a change in the distribution of the fluorescence signal, corresponding to sealing of the fibers by means of molten PCL^F fibers/particles (Figure 6) was observed.

3.2. Degree of crystallinity and thermal stability of the mats

The PLA, PCL, PLA_{50}/PCL_{50}, $PLA_{elspin(3)}/PCL_{elspin(3)}$ and $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats were subjected to DSC analysis. It was found that the crystallinity degree of PLA was affected both by the composition and the thermal treatment of the fibrous material (Table 1). For the PLA, PLA_{50}/PCL_{50} and $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats before heating the crystallinity degree of the polyester was ca. 30%, and for $PLA_{elspin(3)}/PCL_{elspin(3)}$ mats – ca. 20% (Table 1). After heat treatment of the fibrous materials it increased, its values being 43, 22 and 45% for PLA_{50}/PCL_{50}, $PLA_{elspin(3)}/PCL_{elspin(3)}$ and $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats, respectively (Table 1). This result can be explained by the formation of an additional PLA crystalline phase in the fibers after heating the mats. This is evidenced by the absence of a cold crystallization peak in the thermograms of the mats subjected to thermal treatment. The results we have obtained are consistent with the literature data for increase in the crystallinity degree of PLA after thermal treatment [19]. Unlike the case of PLA, the crystallinity degree of PCL was found to decrease after heating the mats, which was observed for the PLA_{50}/PCL_{50}, and $PLA_{elspin(3)}/PCL_{elspray(3)}$ systems (Table 1). In the fibrous matrials before or after their heating cold crystallization for PCL was not detectd.

The thermal stability of the fibrous materials was estimated by TGA analysis.The thermograms of PLA, PCL, PLA_{50}/PCL_{50}, $PLA_{elspin(3)}/PCL_{elspin(3)}$ and $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats before and after heating are shown in Figure 7 and the degradation temperature (T_d) of PLA and PCL in the mats is presented in the Table 2. As seen, the PLA mats were characterized by a degradation temperature (T_d) of approximately 355°C. PCL fibers before heating degraded at 405°C. The results indicate that the PCL fibers possess greater thermal stability.

It was found that the material obtained from the PCL fibers molten at 60°C degraded at a temperature close to that for a PCL mat – 402°C. Melting of PCL in the PLA_{50}/PCL_{50} and $PLA_{elspin(3)}/PCL_{elspin(3)}$ mats led to the obtaining of materials with greater thermal stability (as compared to the non-heated mats), which were characterized by 50% weight loss at around 350–360°C. The presence of the particles in $PLA_{elspin(3)}/PCL_{elspray(3)}$ when not preliminarily heat-treated had no impact on the thermal sta-

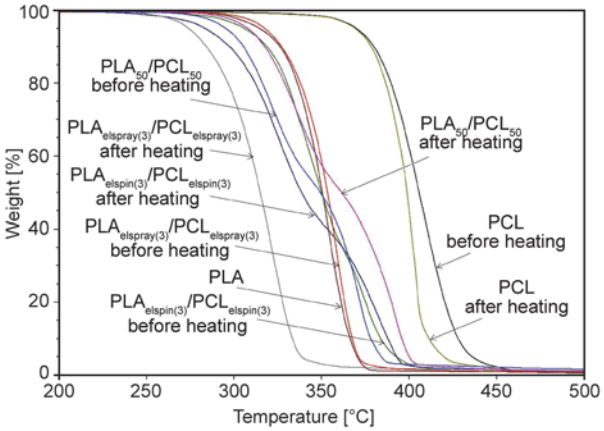

Figure 7. TGA thermograms of PLA, PCL, PLA_{50}/PCL_{50}, $PLA_{elspin(3)}/PCL_{elspin(3)}$, $PLA_{elspin(3)}/PCL_{elspray(3)}$ fibers before and after heating at 60°C

Table 1. Values of ΔH_{cc}^*, ΔH_m, χ_c for PLA and χ_c for PCL in the PLA, PLA_{50}/PCL_{50}, $PLA_{elspin(3)}/PCL_{elspin(3)}$, $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats before and after heating them at 60°C

Mat	ΔH_{cc}^{PLA} [J/g]	ΔH_m^{PLA} [J/g]	ΔH_m^{PCL} [J/g]	χ_c^{PLA} [%]	χ_c^{PCL} [%]
PCL before heating			78.7		56.4
PCL after heating			78.1		56.0
PLA	14.9	44.2		31.5	
PLA_{50}/PCL_{50} before heating	5.0	20.8	41.6	33.9	59.6
PLA_{50}/PCL_{50} after heating	*	19.9	37.8	42.8	54.3
$PLA_{elspin(3)}/PCL_{elspin(3)}$ before heating	10.1	28.1	18.0	19.4	12.9
$PLA_{elspin(3)}/PCL_{elspin(3)}$ after heating	*	20.6	37.8	22.2	27.1
$PLA_{elspin(3)}/PCL_{elspray(3)}$ before heating	14.0	42.8	0.8	30.9	0.6
$PLA_{elspin(3)}/PCL_{elspray(3)}$ after heating	*	41.7	0.5	44.8	0.4

*no cold crystallization was detected

Table 2. Degradation temperature (T_d) of PLA and PCL in the electrospun fibrous materials

Sample	T_d of PCL [°C]	T_d of PLA [°C]
PCL before heating	405	
PCL after heating	402	
PLA		355
PLA_{50}/PCL_{50} before heating	372	322
PLA_{50}/PCL_{50} after heating	392	336
$PLA_{elspin(3)}/PCL_{elspin(3)}$ before heating	375	345
$PLA_{elspin(3)}/PCL_{elspin(3)}$ after heating	383	325
$PLA_{elspin(3)}/PCL_{elspray(3)}$ before heating	*	358
$PLA_{elspin(3)}/PCL_{elspray(3)}$ after heating	*	322

*T_d not observed

bility of the fibrous materials as compared to those composed of PLA, whereas the degradation temperature of the mats after heating was lower (322°C). This result might be attributed to the difference in the concentrations of the starting PCL solutions subjected to electrospraying (0.4 wt%) and electrospinning (9 wt%), thus indicating that the PCL amount in $PLA_{elspin(3)}/PCL_{elspray(3)}$ was not sufficient to improve the thermal stability of this material.

3.3. Water contact angle of the fibrous materials

During recent years an increasing interest has been paid to the development of superhydrophobic self-cleaning surfaces with properties similar to those of the lotus leaves which surface is uniformly covered with micro-sized protrusions and recesses decorated with nano-sized particles of a wax-like material. By combining the biomimetic approaches and modern nanotechnologies such as electrospinning and electrospraying the development of surfaces with specific hydrophobic behavior can be achieved. A 3D architecture with micro- and nanohierarchical arrangement lies in the basis of these properties. In the present study a relationship was found between the 3D micro- and nanoarchitecture of the mats and their hydrophobic behaviour. The average value of the water contact angle of a PCL mat before heating was ca. 121°, and that of a PLA mat – 125°. These values for a PLA and PCL mat were in conformity with already reported data [20, 21]. The thermal treatment of the PCL fibrous material led to a significant decrease in the water contact angle values – 68° (Figure 8). This result is also consistent with the data obtained from water contact angle studies of a PCL film conducted by other authors [22]. Before heat treatment the contact angle of PLA_{50}/PCL_{50} and $PLA_{elspin(3)}/PCL_{elspin(3)}$ mats remained close to that of a PCL mat, but after heating it was reduced to 88 and 79° (Figure 8). The $PLA_{elspin(3)}/PCL_{elspray(3)}$ fibrous materials represented some peculiarities. In that case the melting of the PCL particles did not exert any effect on the hydrophobic character of the mats: the contact angle values were ca. 120° after and ca. 124° before heating for a $PLA_{elspin(3)}/PCL_{elspray(3)}$ mat (Figure 8).

It is noteworthy that in the determination of the hydrophobic characteristics of the fibrous materials apart from the polymer nature, a key part is played by the micro- and nanohierarchy in architectural aspect similarly to superhydrophobic structures occurring in nature. For that reason the mats characterized by a higher number of hierarchic levels (fibers – PCL, fibers/fibers – $PLA_{elspin}/PCL_{elspin}$ or fibers/particles – $PLA_{elspin}/PCL_{elspray}$) before heat treatment showed higher water contact angle values than the materials obtained after heat treatment regardless of the fact that the polymer composition was one and the same (fibers – PCL, partially molten fibers – $PLA_{elspin}/PCL_{elspin}$ or fibers thermally sealed by molten PCL particles – $PLA_{elspin}/PCL_{elspray}$).

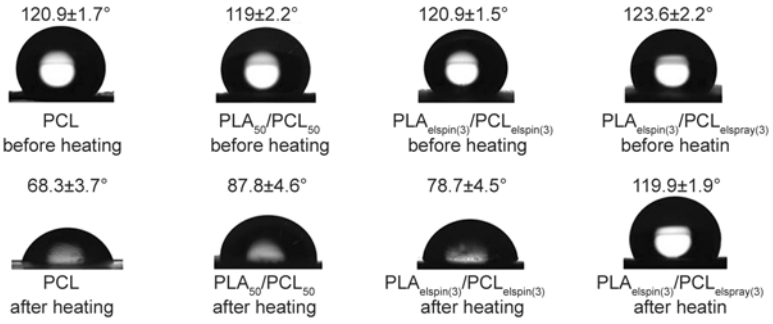

Figure 8. Digital photographs of water droplets deposited onto PCL, PLA_{50}/PCL_{50}, $PLA_{elspin(3)}/PCL_{elspin(3)}$ and $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats before and after heat treatment at 60°. The fibrous materials were cut in the collector rotation direction.

This also accounted for the small difference in the water contact angle of the $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats after heating, where the fibrous structure of the mat was preserved and only thermal sealing of the fibers by melting of PCL particles occurred. This impact of the surface topology of the mats indicates that the hydrophobic characteristics of the fibrous materials can be influenced more easily after heat treatment of the fibrous materials prepared by electrospinning of a common PLA/PCL solution or by simultaneous electrospinning of two separate solutions of PLA and PCL.

On the other hand it was found that the polymer scaffold composition also affects the hydrophobic characteristics of the fibrous materials. The trend for a decrease in the water contact angle value of thermally sealed mats is observed in the case of fibers prepared by electrospinning of a common PLA/PCL solution (Figure 9). It was found that with increase in the PCL content in the fibers the water contact angle values decreased after thermal sealing: 107.5±2.3° for PLA_{75}/PCL_{25}, 91.9±3.3° for PLA_{60}/PCL_{40} and 87.8±4.6° for PLA_{50}/PCL_{50} (Figure 9). In this case this was also attributed to the PCL melting part which was accompanied by reduction in the levels of architectural hierarchy. Before the thermal sealing the PLA/PCL materials were hydrophobic and no considerable difference in the water contact angle values of the mats – 120°, was observed (Figure 9).

For the $PLA_{elspin}/PCL_{elspin}$ systems a relationship was found indicating that with the increase in the amount of the deposited PCL fibers (i.e. higher flow rate of the PCL spinning solution) the contact angle values were lower after thermal sealing (113.8±3.6°, 91.3±5.8 and 78.7±4.5° for $PLA_{elspin(3)}/PCL_{elspin(1)}$, $PLA_{elspin(3)}/PCL_{elspin(2)}$ and $PLA_{elspin(3)}/PCL_{elspin(3)}$, respectively) compared to those before the thermal treatment of the mats: 122° (Figure 9). The decrease in the water contact angle values after thermal sealing might be attributed to melting of the PCL fibers. In the case of the 'sandwich' type PLA+PCL mats before heat treatment the contact angle acquired values characteristic of PCL – 121°, since these fibers were deposited on the mat surface, and after heating – ca. 94°. 'Sandwich' PCL+PLA mats represented a different case where no significant difference in the values of the contact angle before and after heating the mat (125°) was observed. These values were close to those of the PLA fibers and this could be explained by the fact that the PCL fibers are located beneath those of PLA and upon melting they do not affect significantly the topology of the mat surface.

3.4. Mechanical testing of the fibrous materials

The mechanical properties of the fibrous materials obtained by electrospinning depend on a number of parameters, such as: fiber diameter [23], presence of defects (bead-like, spindle-like defects) along the fiber length [24] or on the crystallinity degree of the polymer constituting the fibers [the amorphous phase of the fibers accounts for their elastic properties (elastomeric properties)], and the crystalline phase imparts strength (dimensional stability to the array of molecules) [25]. Some electrospinning conditions, such as the air humidity also have an impact on the mechanical properties of the mats [26]. The architecture of the micro- and nanoscale fibrous materials is of importance, as well: when they are composed of oriented fibers the mat is stronger compared to mats composed of randomly deposited fibers [27, 28]. It is possible to prepare fibrous materials possessing desired strength by varying the weight ratios of the two polymers [29]. Interconnected fibers also improve the mechanical proper-

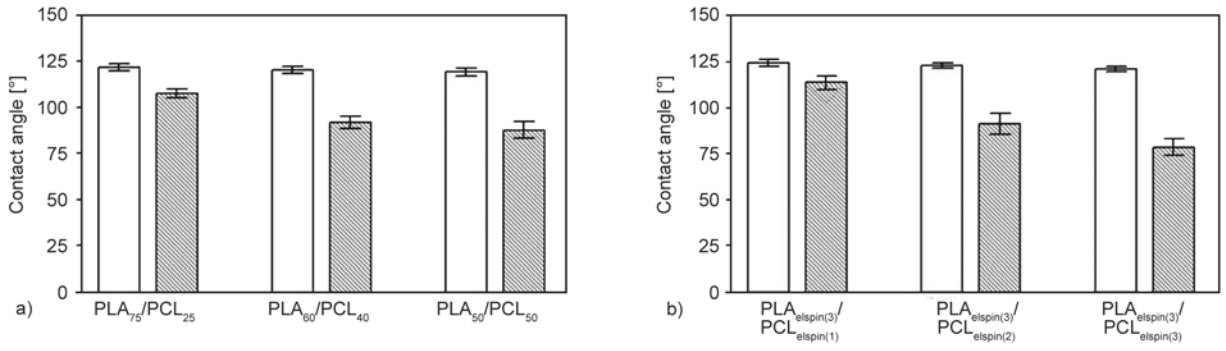

Figure 9. Contact angle values measured upon water droplet deposition onto PLA/PCL (a) and $PLA_{elspin}/PCL_{elspin}$ (b) mats; empty bars – before heating, hatched bars – after heating. The mats were cut in the collector rotation direction.

ties of the fibrous materials [30], which are influenced by the structure of the fibers and the interactions between them, as well [31]. Enhancement of the mechanical parameters (tensile strength, yield stress, and Young's modulus) can be achieved in the presence of finer fibers (a nano-network) among the main fibers [32].

A major problem regarding the mechanical testing of electrospun micro-and nanofibrous materials is the lack of reliable standards for the performance of these tests. An issue of great significance which has been barely discussed in scientific literature is the determination of the mechanical characteristics of micro- and nanofibrous non-woven textile and the direction in which the test specimens should be cut: parallel (0°) or at a definite angle with respect to the collector rotation direction (45, 90° or others). In the process of cutting the test specimens from the electrospun mats mechanical disruption of the fibers takes place. In the majority of cases the fibers have a tendency to wind around the collector in the direction of its rotation. Depending on the manner in which the fibers are deposited, mats composed of fibers aligned along the collector rotation axis or randomly deposited fibers are prepared. The experiments we have performed have demonstrated that the mats cut in the collector rotation direction (0°) display better mechanical properties compared to those cut at an angle of 90°. Intermediate mechanical properties are manifested by test specimens cut at an angle of 45° (Figure 10). These results can be explained by the amount of fibers caught by the grips of the tensile testing apparatus. That is why for samples cut in the collector rotation direction it is more probable that a greater number of fibers will be clamped by their both extremities between the grips as compared to samples cut at angle of 45 or 90°. This leads to the manifestation of better mechanical parameters in the case of fibers cut at an angle of 0° as compared to those cut at angle of 45 or 90°.

The possibility for enhacement of the mechanical characteristics of the mats (PLA/PCL, 'sandwich' type (PLA+PCL and PCL+PLA), $PLA_{elspin}/PCL_{elspin}$ and $PLA_{elspin}/PCL_{elspray}$) by subjecting them to thermal treatment was studied. All mats were cut along the rotational direction of the collector and heated at the melting temperature of PCL (60°C). The purpose was to achieve thermal sealing of the fibers by the molten PCL fibers or particles. The results from the performed mechanical tests of the fibrous materials before and after heating are presented in Figure 11.

3.4.1. Mechanical assays of mats prepared by electrospinning of a single solution or by simultaneous electrospinning of two separate solutions

The determination of the mechanical characteristics of the control samples (before thermal sealing) revealed that PLA fibers had higher values of Young's

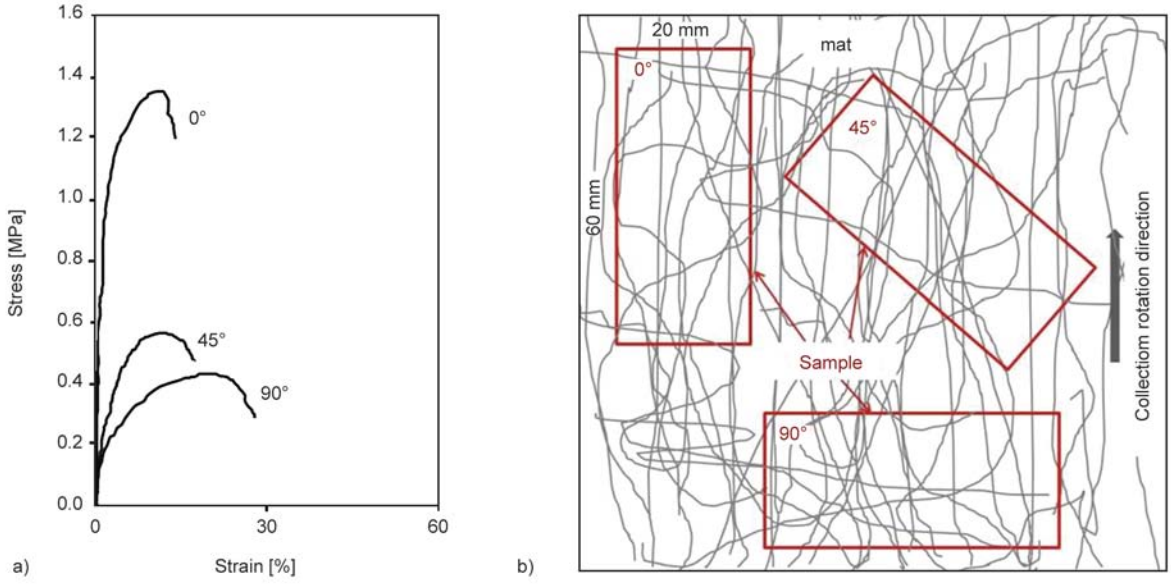

Figure 10. Impact of the direction of cutting of mats (0, 45 or 90°) with respect to the collector rotation direction on the mechanical behavior of the $PLA_{elspin(3)}/PCL_{elspin(3)}$ mat after heating (a) and schematic representation of the different directions of cutting (b)

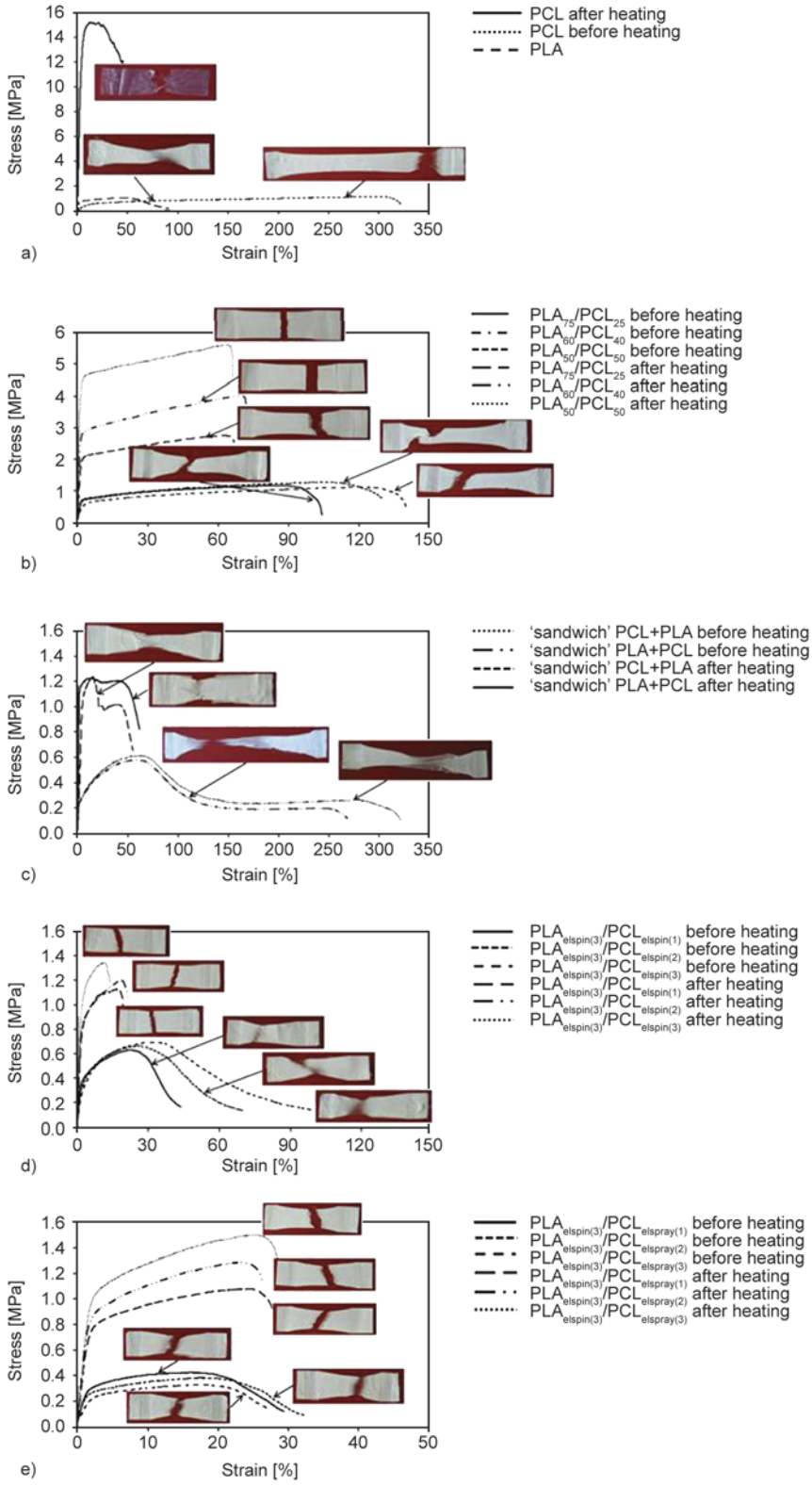

Figure 11. Mechanical stress/strain curves of PLA and PCL mats (a), PLA/PCL (b), 'sandwich' type mats (PLA+PCL or PCL+PLA) (c), $PLA_{elspin}/PCL_{elspin}$ mats (d) and $PLA_{elspin}/PCL_{elspray}$ (e) before and after heat treatment

modulus – 46 MPa as compared to PCL fibers – 5 MPa (Figure 11a). It was found that the difference in the strength of the mats exerted an effect on the degree of their deformation before breaking. It was smaller for a PLA mat (100%) as compared to that for a PCL mat before heat treatment (330%). The ultimate stress values of the two mats prior to heat treatment did not show any significant difference: ca. 0.19 and 0.52 MPa, for PLA and PCL, respectively (Figure 11a). Melting of the PCL fibers at

60°C led to a substantial change in the mechanical behavior of the obtained PCL material. A considerable increase in the strength; Young's modulus values – ca. 330 MPa, and ultimate stress – 12 MPa (Figure 11a) was recorded. The material composed of molten PCL fibers demonstrated poorer plastic properties as compared to the PCL fibrous materials and breaking occurred at a smaller deformation of 50%. This is an indication that melting of the polyester fibers results in the obtaining of PCL material with enhanced mechanical characteristics.

In Figure 11b the results obtained from the tensile tests of PLA/PCL mats before and after thermal sealing are displayed. It is noteworthy that before heat treatment the fibrous materials manifested similar behaviour with regard to the elastic deformations: the value of Young's modulus for all fibers was ca. 30 MPa. It was found that with the increase in the PCL content the materials underwent greater deformation before breaking. It was ca. 98% for PLA_{75}/PCL_{25}, 125% for PLA_{60}/PCL_{40} and 135% for PLA_{50}/PCL_{50} (Figure 11b). These results were in accordance with the results obtained from the tensile tests for PLA and PCL mats (before heat treatment), showing that the deformation of PCL before breaking was greater than that of PLA. The ultimate stress of the mats before heat treatment was ca. 0.6 MPa. Heating of the PLA/PCL materials resulting in PCL melting led to the obtaining of more robust fibrous materials. The PLA_{50}/PCL_{50} mats which were characterized by the highest degree of fiber interconnectivity exhibited the greatest strength (Young's modulus – 325 MPa and ultimate stress – 4.8 MPa, Figure 11b). In contrast to them the PLA_{60}/PCL_{40} had Young's modulus of ca. 185 MPa and ultimate stress of ca. 3.5 MPa, and the PLA_{75}/PCL_{25} fibers were the most brittle ones (Young's modulus – 100 MPa and ultimate stress – 2.6 MPa), characterized by the lowest degree of interconnectivity of the fibers (Figure 11b). After thermal treatment breaking of the PLA/PCL mats took place at a smaller deformation degree (70%) as compared to non-heated fibers, and this phenomenon occurred regardless of the PCL content (Figure 11b).

The curve profiles of the 'sandwich' type PLA+PCL and PCL+PLA mats before heat treatment indicated a behavior of the mats characteristic of each of the polymers. In the case of these materials regardless of the mat design (deposition of the layer of PCL fibers beneath or on top of that of PLA fibers) when tensile tests were performed with the specimens breaking occurred in the PLA fibers first (deformation ca. 100%) followed by breaking of PCL fibers (deformation ca. 300%). These changes in the length of the mats were consistent with the results for the deformational changes in the PLA and PCL fibrous materials before heating (Figure 11c). Young's modulus was ca. 22 MPa and the ultimate stress of the fibrous materials – ca. 0.13 MPa. In this case the thermal sealing of the mats resulted in enhancement of the mechanical properties, as well. When breaking thermally treated mats, first the layer of molten PCL fibers broke, and then followed by breaking of the PLA fibers. As shown in Figure 3, in the case of 'sandwich' type PLA+PCL mats submerging of the PLA fibers in the molten PCL fibers was observed, whereas in the case of the 'sandwich' PCL+PLA mats the PCL molten fibers penetrate in the bulk of the layer of PLA fibers. This new distribution of the polymers in the bulk of the mats after heating exerts an effect on the mechanical behavior of the mats. As evident from Figure 11c, in the course of breaking of 'sandwich' PCL+PLA mats two well defined maxima were observed. The first one corresponded to breaking of the PCL molten fibers (maximum deformation of 20%), and the second one – to breaking of the PLA fibers (50%). The two peaks characteristic of each of the polyesters are less clearly distinguished in the course of the stress/strain curves of the heated 'sandwich' PLA+PCL mats. The values of the deformation at break of the two polymers were close to those recorded after heating of 'sandwich' PCL+PLA mats. After heat treatment the two types of fibrous materials ('sandwich' PLA+PCL and PCL+PLA) were characterized by values of Young's modulus of ca. 68 MPa and ultimate stress of ca. 0.7 MPa.

3.4.2. Mechanical testing of mats prepared by simultaneous electrospinning of two separate solutions

PLA_{elspin}/PCL_{elspin} mats before heat treatment were characterized by values of Young's modulus and ultimate stress, of ca. 15 and 0.10 MPa, respectively (Figure 11d). A relationship was found according to which with the increase in the amount of deposited PCL fibers in the mat (i.e with the increase in the feed rate of the PCL spinning solution), the maximum deformation before breaking of the material increased. The $PLA_{elspin(3)}$/$PCL_{elspin(3)}$ mats (100%)

underwent the greatest deformation followed by $PLA_{elspin(3)}/PCL_{elspin(2)}$ (70%) and $PLA_{elspin(3)}/PCL_{elspin(1)}$ mats (40%, Figure 11d). After heat treatment the fibrous $PLA_{elspin}/PCL_{elspin}$ materials became stronger and higher values for Young's modulus (50 MPa) and ultimate stress (1.0 MPa, Figure 11d) were recorded. The greater strength of the mats after heat treatment was attributed to thermal sealing of the fibers with the molten PCL fibers. The greatest strength was demonstrated by the $PLA_{elspin(3)}/PCL_{elspin(3)}$ mats which contained the highest PCL content and thus thermal sealing occurred to the highest degree.

3.4.3. Mechanical testing of mats prepared by simultaneous electrospinning and electrospraying of two separate solutions

The results for PLAelspin/PCLelspray fibers indicated that in this case heat treatment led to the obtaining of materials with enhanced strength. That was attributed to thermal sealing of the PLA fibers with the molten PCL particles. It was found that the greatest strength was manifested by $PLA_{elspin(3)}/PCL_{elspray(3)}$ mats where sealing took place to the greatest extent, because the material before heat treatment contained the greatest amount of particles. The values of Young's modulus (38 MPa) and the ultimate stress (1.00 MPa) for the mats after heat treatment were twice as high as the values obtained for these parameters prior to heat treatment of the mats – ca. 17 MPa for Young's modulus and 0.13 MPa – for the ultimate stress (Figure 11d). Another characteristic feature of the $PLA_{elspin}/PCL_{elspray}$ materials was breaking at one and the same degree of deformation – 30% before and after heat treatment (Figure 11d).

To summarize, in the present study we used two biodegradable and biocompatible polymers with different thermal behavior: PLA with melting temperature of 165°C and PCL with lower melting temperature (T_m = 60°C). The thermal treatment of the mats at the T_m of PCL led to improvement of their mechanical properties. The heating of the PLA/PCL, $PLA_{elspin}/PCL_{elspin}$ and $PLA_{elspin}/PCL_{elspray}$ mats, at the T_m of PCL, allowed us to obtain fibrous materials of interconnected fibers (PLA/PCL mats) or PLA fibers thermally sealed by molten PCL fibers or particles ($PLA_{elspin}/PCL_{elspin}$, $PLA_{elspin}/PCL_{elspray}$). In the case of the 'sandwich'-type mats we observed PLA fibers submerged in molten PCL fibers ('sandwich' PCL+PLA after heating) or filter-like structure ('sandwich' PLA+PCL after heating). This morphological change of the fibrous materials was the primary cause of their mechanical properties improvement. The most durable heat treated fibrous materials were obtained in the case of the PLA/PCL mats produced by electrospinning of a single solution. The obtained results indicate that depending on the architecture of the fibrous materials after heat treatment mats with various degrees of sealing of the fibers, with enhanced strength and deformability before breaking can be fabricated.

4. Conclusions

In the present study new fibrous materials of various composition and architecture were prepared from PLA and PCL using electrospinning and electrospraying. Mats were obtained by electrospinning of a common solution, or using two separate solutions for concurrent electrospinning, or for layer-by-layer deposition on the collector, as well as for using electrospinning in conjunction with electrospraying. Thermal treatment at the melting temperature of PCL enabled the sealing of the fibers thus enhacing the mechanical properties of the mats. The fibrous materials are of interest for a variety of applications such as drug delivery systems, tissue engineering scaffolds, wound dressings or filter membranes.

Acknowledgements

AT thanks Prof. Ph. Dubois (University of Mons – UMONS, Belgium) for providing the possibility to perform internship at the Laboratory of Polymeric and Composite Materials and Dr. R. Mincheva for assistance in performing mechanical tests – carried out during the internship. The internship of AT is financially supported by the POLINNOVA project FP7-REGPOT-2012-2013-1, Grant 316086.

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