

Yao Lu,
Yan-Chun Chen,
*Pei-Hua Zhang

Key Laboratory of Textile Science and Technology,
Ministry of Education,
Donghua University,
Shanghai 201620, China,
*E-mail: phzh@dhu.edu.cn

Preparation and Characterisation of Polylactic Acid (PLA)/Polycaprolactone (PCL) Composite Microfibre Membranes

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Abstract

Biodegradable polymers like PLA and PCL have wide application in tissue engineering because of their biocompatibility, degradation and mechanical properties. In this study, the optimised electrospinning parameters of PLA/PCL composite membranes were determined with scanning electron microscopy to obtain smooth and relatively fine microfibre. The properties and structure of electrospinning PLA, PCL and PLA/PCL(70/30) membranes were investigated by scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray diffraction (XRD), the water contact angle, water absorption degree and tensile strength. The results revealed that PLA/PCL composite membranes possessed better mechanical and hydrophilic properties when compared to single component microfibre membranes like PLA and PCL. The improvements above are conducive to microfibre membrane application in the biomedical sector.

Key words: PLA/PCL, electrospinning, microfibre membrane, property.

Introduction

Poly(lactic acid) (PLA) and polycaprolactone (PCL) are biomedical materials approved by the USA Food and Drug Administration (FDA) for their non-toxic and good biological compatibility. They are often used in tissue engineering or imitating extracellular matrix as functional materials for cell growth [1, 2]. PCL has excellent biological compatibility and toughness mainly applied in a controlled releasing carrier, such as drug loading, etc. However, PCL needs 2 - 4 years to degrade completely [3]. PLA is the most used biodegradable material by far because it has good biological compatibility and significantly high strength and modulus. PLA's final products of degradation are CO₂ and H₂O, and the intermediate products are lactic acid and hydroxy acid, which are all accepted by the body [4]. Although PLA's strength is high, there still exist problems such as low elongation, poor toughness and weak impact-resistance strength. Aiming at improving the slow degradation rate, poor hydrophilicity, weak strength and cell-attached force of PCL, introducing other biodegradable components to make up for the poor aspects of PCL performances has encouraged more research into materials such as PCL/PHBV, PCL/Collegen and PCL/Polyethylene glycol [5 - 8].

The earliest origin of electrospinning is the electrostatic spray phenomenon found by Rayleigh in the late 19th century [9], and later Formales started to study electrospinning technology. Several researches have demonstrated electrospinning is an effective method which can prepare superfine fibres with diameters from 5nm to 1µm that possess high a specific surface area and porosity [10 - 12] using different materials like PLA, PEO & PLGA. These features enable electrospinning to have wide application in biological engineering. Kwon et al. [13] found that umbilical cord vascular endothelial cells had good proliferation and adhesion on finer fibre (0.3 and 1.2 µm). Boland [14] prepared PLA/PCL electrospinning membranes with different diameters and morphology to expand its application in biological engineering. Yang et al. [15] found that smooth muscle cells grew better on a PLA/PCL blend stent than on a single component of PLA stent. Papers studying PLA/PCL electrospinning fibres can be classified into two categories: the preparation technology of PLA/PCL and application of PLA/PCL. Most papers place emphasis only on one aspect. Our research combined both technological parameters and properties of PLA/PCL electrospinning fibres, and compared them to PLA and PCL single component fibres. However, the methods we used are more comprehensive.

Electrospinning technology is well suited to process synthetic biocompatible poly-

mers for biomedical application. Potential applications include drug-loading, intravascular stent and medical implant mesh. PLA/PCL composite membranes were prepared and compared to PLA and PCL samples to demonstrate the superiority of multi-component electrospinning membranes. The reduction of the crystallinity degree can significantly accelerate the degradation rate, and the increase in the tensile strength and elongation can improve the supporting capacity. This paper discusses the electrospinning process parameters of PLA/PCL composite membranes. Scanning electron microscopy (SEM), differential scanning calorimetry (DSC), X-ray diffraction (XRD), the water contact angle, water absorption and tensile strength techniques were used to investigate the structure, morphology and properties of electrospun PLA, PCL and PLA/PCL microfibres.

Experimental

Materials

Poly(D,L-lactic acid) and PCL polymers were purchased from Yisheng New Materials Co., LTD (Shengzhen, China). The molecular weight of PLA is 10⁵ and that of PCL's - 8×10⁴. Methylene dichloride (DCM) and N,N-dimethyl formamide (DMF) were obtained from the Damao Chemical reagent factory (Tianjing, China). All of the chemicals were analytical reagent grade and were used with no further purification.

Preparation of the spinning solution and electrospinning process

PLA and PCL polymers were dissolved at different ratios with DCM and DMF mixed solvents. The solution was stirred until completely dissolved using a magnetic blender. For the electrospinning process, the solution was sucked into a 5 ml-syringe pump. The syringe was then put on an iron support. The receiving device was aluminum foil connected to the ground. The solution was stretched under the action of the electrostatic field force upon the opening of high voltage, eventually forming disorderly microfibre membranes along with the evaporation of the solvent. The machine adopted in the research was an 85-2A Magnetic stirrer (Huanyu Technology Instrument Factory, China), LSP01-1A micro-injection pump (Longer Precision Pump Co., Ltd, China) and JG 50-1 Dc high voltage transmitter (Shanghai Shenfa Detecting Instrument Factory, China).

Characterisation of the structure and performance

Scanning electron microscopy (SEM)

The surface structure of the microfibre membranes was characterised by a HITACHI S - 3000 scanning electron microscope (HITACHI Co., Ltd., Japan). The average fibre diameter was calculated using 100 individual diameters for each sample with Photoshop CS3 software. The pore diameter of the membranes' surface was analyzed by an American contador automatic membrane pore measuring instrument.

Differential scanning calorimetry (DSC)

Thermal analysis of the microfibre membranes was conducted by DSC. Dry samples (5 mg) were heated from 20 to 200 °C at a scanning rate of 10 °C/min using Phrisl differential scanning calorimetry (USA) under nitrogen atmosphere.

X-ray diffraction (XRD)

The crystallisation property was obtained by XRD measurements, which were recorded using a Shimadzu XRD-6000 diffractometer (Germany). XRD measurements of the microfibre samples prepared were made at 40 kV and 200 mA. A Cu-K α radiation source was used to scan the samples in a 2 θ range from 0° to 60° at a scan rate of 0.06°/s. The d-spacing was determined from Bragg's law ($n\lambda = 2d \sin \theta$), where θ is the diffraction angle, and λ is the wave-length ($\lambda = 1.54056 \text{ \AA}$ for a Cu

target). The degree of crystallinity was determined by implementing the area integration method from XRD intensity data over the range of 2 θ from 0° to 60°. The calculation of the degree of crystallinity was according to *Equation 1*.

$$\chi = \frac{\sum I_c}{\sum I_c + \sum I_a} \quad (1)$$

where, I_c is the intensity of the crystallisation peak, and I_a is the intensity of the amorphous peak.

Hydrophilic evaluation

The hydrophilic contact angle is an important indicator characterising the material's hydrophilic performance, measured by a OCA15EC Contact Angle Meter (Beijing North Defei Co., Ltd., Beijing). The experiment was conducted at room temperature using a yellow-light source, with a water volume of around 4 μ l. Each sample was tested in 5 different positions. The final average contact angle was calculated from these 5 data.

Water absorption

Water absorption was characterized by the water absorption degree. Samples were cut into 4 \times 4 cm pieces and immersed in PBS solution for 24 hours. The degree of water absorption was according to *Equation 2*

$$R = (W_1 - W_0) / W_0 \times 100\% \quad (2)$$

R is the water absorption degree, W_0 the initial weight of samples, and W_1 is the weight of immersed samples that were drip-dried by filter paper.

Mechanical performance

Membranes were cut into 40 \times 5 mm rectangle samples, and their effective tensile length samples was 20 mm. The uniaxial tensile test was carried out at a tensile rate of 10 mm/min. The average tensile strength and elongation was calculated from 5 samples. The thickness, which was controlled at about 0.05 mm, was measured by a micrometer caliper accurate to 0.01 mm.

■ Results and discussion

Electrospinning process parameters

The experiment discussed the effect of parameters on the electrospinning membranes' surface structure, including the solvent ratio (DCM: DMF), PLA/PCL blending ratio, solution concentration, voltage, and receiving distance (distance between the needle tip and target).

Solvent ratio (DCM:DMF)

DCM and DMF were chosen as solvents for producing PLA/PCL electrospinning fibres. The ratio of DCM:DMF is one of the most controlling parameters of the morphologies. Five ratios of DCM:DMF ranging from 100:0, 80:20, 70:30 & 60:40 were studied in this stage. *Figure 1* shows SEM photos of electrospinning PLA/PCL fibres at different solvent ratios of DCM/DMF. PLA/PCL solutions were prepared at a concentration of 8%. The positive voltage applied was 14 kV, the receiving distance - 15 cm, the flow rate of the polymer solution - 0.6 ml/h, and the PLA/PCL blending ratio was 70/30. Without DMF or little DMF, the dominant morphologies (*Figures 1.a & 1.b*) are those that have fibres with relatively large diameters or fibres with uneven diameters. With too much DMF, there was a serious adhesion phenomenon (*Figures 1.d & 1.e*) throughout the microfibrinous samples. In this case, the reason was the incomplete evaporation during the movement of the polymer jet toward the collector. Therefore the ratio of DCM: DMF of 80:20 maybe the most suitable choice for gaining relatively fine fibre with smooth morphology.

Solution concentration

The concentration also has an important effect on microfibre morphologies. Three concentrations of solution ranging from 8, 10 & 12% were studied in this stage. These parameters were chosen based on a pre-experiment where we found that the concentration was smaller than 8%, for example 6% of the liquid drop was received instead of microfibrines. And when the concentration was bigger than 12%, the electrospinning process could not last for a long time, and the needle may occlude after about 30 minutes. *Figure 2* presents the fibre-diameter distribution of PLA/PCL microfibrines at different solution concentrations. Fibres prepared by electrospinning had a solvent ratio of DCM:DMF = 80:20. The positive voltage applied was 14 kV, the receiving distance - 15 cm, the flow rate of the polymer solution - 0.6 ml/h, and the PLA/PCL blending ratio was 70/30. For lower concentrations of solutions in the electrospinning process, the average fibre diameter rose with a wider distribution range.

To enhance the application of microfibre in tissue engineering, fibrous membranes should acquire the following parameters according to Zeinab Karami et al.[16]: The absence of beads allows to prevent

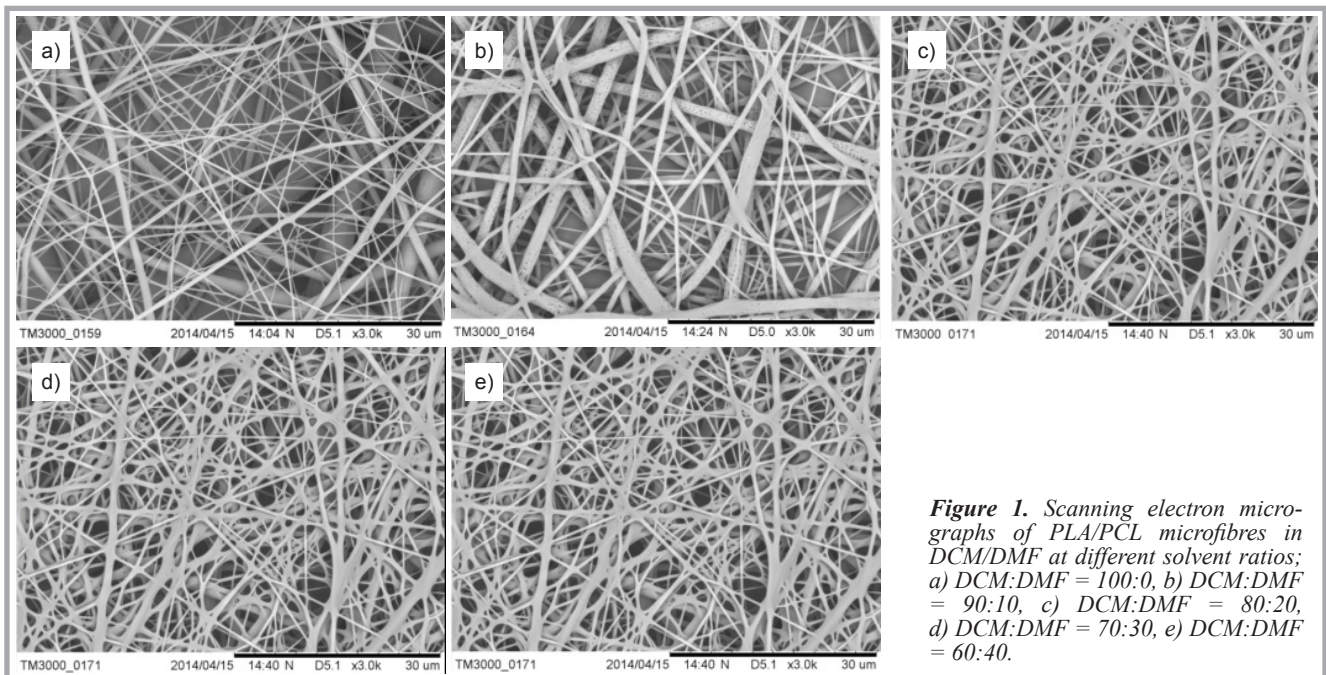


Figure 1. Scanning electron micrographs of PLA/PCL microfibres in DCM/DMF at different solvent ratios; a) DCM:DMF = 100:0, b) DCM:DMF = 90:10, c) DCM:DMF = 80:20, d) DCM:DMF = 70:30, e) DCM:DMF = 60:40.

trapped portions of the drug and ensure drug-release. What is more, the minimum average diameter and concentrated fibre distribution result in the surface-area-volume ratio of the microfibres, which is good for cell adhesion, proliferation and, remarkably, the drug molecule tendency. On the basis of the requirements above, the best sample selected were PLA/PCL

microfibres at a concentration of 8% (**Figure 2.a**), with an average diameter of 312.6 nm and concentration distributed between 200 to 400 nm.

Voltage

It has been observed that the shape of the initiating droplet can be changed by several electrospinning parameters, such

as the voltage applied. The principle of the voltage's action can be understood as follows [17]: The surface of the polymer solution at the tip of the spinneret becomes charged along with the movement of ions. When the electric force is high enough to overcome the surface tension's force, a straight and quasi-stable charged jet is formed. Therefore a suitable effect

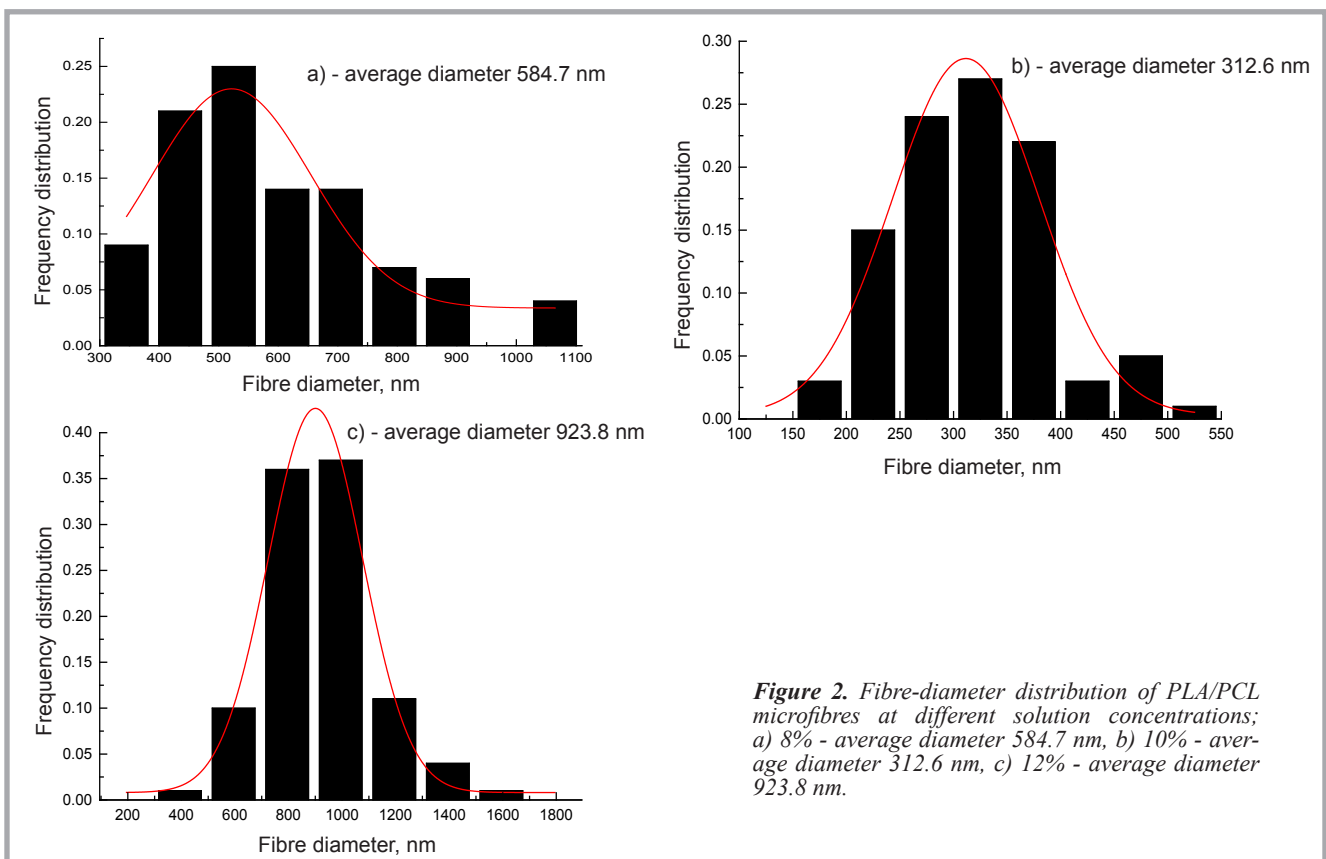


Figure 2. Fibre-diameter distribution of PLA/PCL microfibres at different solution concentrations; a) 8% - average diameter 584.7 nm, b) 10% - average diameter 312.6 nm, c) 12% - average diameter 923.8 nm.

Table 1. Fibre diameter and deviation of PLA/PCL microfibrils collected under different voltages.

Voltage, kV	Fibre diameter, nm
12	384.3±14.8
14	312.6±16.1
16	576.3±27.3
18	528.0±31.6
20	517.4±30.7

of the voltage is actually the balance between the electric force and surface tension, which is critical to determine the initial cone shape of the polymer solution at the tip of the spinneret. Moreover the effective voltage is associated with the solution's features, such as concentration. **Table 1** shows the fibre's average diameter and deviation of PLA/PCL microfibrils collected under different voltages. The ratio of DCM:DMF was 80:20, the solution concentration - 8%, the receiving distance - 15 cm, the flow rate of the polymer solution - 0.6 ml/h, and the PLA/PCL blending ratio was 70/30. The initiating jet was formed when the voltage exceeded 8 kV, but the jet was not stable at a voltage below 12 kV. The jet suspended at the tip of the spinneret and formed a conical-shaped solution (Taylor Cone). By increasing the voltage, the solution was removed from the tip more quickly and uniform fibre formed. When the voltage was increased to 18 kV, the Taylor cone shape oscillated and became asymmetrical, resulting in a large diameter irregularity of fibres. As **Table 1** shows, both fibre diameters were relatively small at a voltage of 12 kV and 14 kV. But the diameter deviation was the smallest when the voltage was 12 kV, which means more uniform fibrous morphologies.

Receiving distance

The receiving distance refers to that between the needle tip and the target. **Table 2** presents the fibre's average diameter and deviation of PLA/PCL microfibrils

collected at different receiving distances ranging from 15 to 27 cm (when the distance was 27 cm, there were very few fibres deposited on the aluminum foil, which made it impossible for us to calculate its average diameter). The other electrospinning parameters were as follows: a ratio of DCM:DMF of 4:1, a solution concentration of 8%, and voltage of 12 kV. Compared with other parameters, the receiving distance had little effect on the fibre diameter, but an increase in distance may lead to fewer fibres deposited on the aluminum foil. **Figure 3** shows SEM photos of microfibrils collected at the same time at two different receiving distances. When the distance was increased to 27 cm (**Figure 3.b**), there were very few fibres collected. Therefore the receiving distance of 15 cm seemed suitable for PLA/PCL electrospinning.

PLA/PCL blending ratio

Figure 4 shows SEM photos of PLA/PCL membranes at different blending ratios. **Figure 5** shows the fibre diameter distribution of PLA/PCL = 70/30, as well as PLA and PCL single component membranes using the same electrospinning parameters. From **Figure 4**, we can see that adding PCL to PLA leads to the unevenness of the fibre from the SEM photos. It can be seen that the sample of PLA/PCL 90/10 had the most obvious fibre unevenness phenomenon (**Figure 4.a**). The PLA/PCL ratio of 70/30 selected has the best morphology compared to the others, and was thought of as the most suitable ratio. When the PLA and PCL ratio was 70:30, the fibre diameter was distributed well from 300 to 400 nm (**Figure 5.b**).

Overall a group of suitable processing parameters for preparing PLA/PCL microfibrils was decided by observing the electrospinning membranes' surface. The SEM technique and statistical method were used to evaluate the fibres'

Table 2. Fibre diameter and deviation of PLA/PCL microfibrils collected under different receiving distances.

Receiving distance, cm	Fibre diameter, nm
15	384.3±18.3
18	433.5±24.5
21	428.5±21.2
24	419.3±22.9

homogeneity and calculate their average diameter. Some researches also obtained the solvents' volatility as an evaluation index by using the Fourier Transform Infrared Spectroscopy (FTIR) technique. However, the paper did not test the samples' FTIR, the reasons for which can be explained as follows: First the solvents we used in the experiment were DCM and DMF, in which DCM has good volatility and can be volatilised completely in air in a short time, while DMF cannot be volatilised as its boiling point is 152.8 °C. Therefore we can state that there must be some DMF remaining in the membrane even without the FTIR test. However, the paper was aimed at comparing PLA/PCL to PLA and the PCL single component electrospinning membrane, which were all prepared under the same conditions that will not be affected by DMF remains. Another important reason is that the parameters we chose in the paper was a group of relatively suitable parameters instead of the best one for PLA/PCL electrospinning fibres under the conditions we mentioned herein. This means that even if another person also prepared PLA/PCL membranes using the parameters we mentioned, he or she may not get samples with the best morphology, because even same materials can have different properties, such as the molecular weight; and the environment condition, including temperature or humidity, is also very important to form an electrospinning membrane.

Structure and property characterisations of microfibre membranes

As a result of experimental studies, the following parameters were selected: a PLA/PCL blending ratio of 70/30, DCM: DMF ratio of 4:1, a solution concentration of 8%, voltage of 12 kV, receiving distance of 15cm, and feed rate of 0.6ml/h. PLA, PCL and PLA/PCL microfibre membranes were prepared using the parameters above and their structure and performance were tested.

Surface structure and pore-diameter

Scanning electron micrographs of PLA, PCL and PLA/PCL microfibrils are pre-

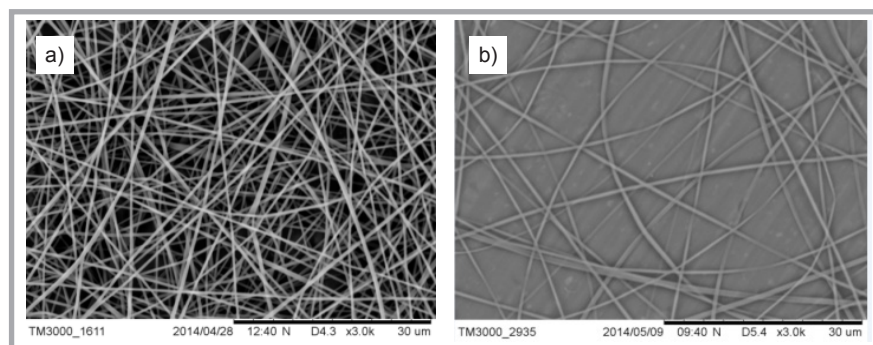


Figure 3. Scanning electron micrographs of PLA/PCL microfibre membranes at different receiving distances (collected for 30 min), receiving distance: a) 15 cm, b) 27 cm.

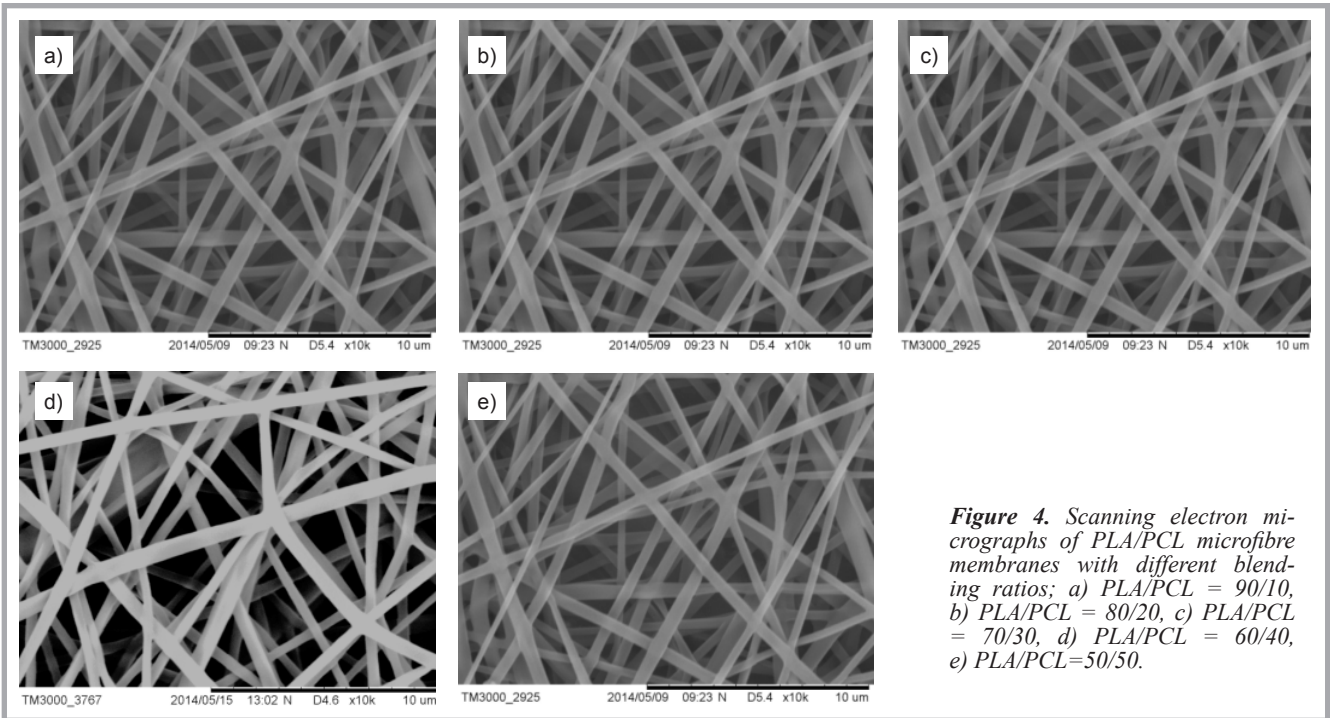


Figure 4. Scanning electron micrographs of PLA/PCL microfibre membranes with different blending ratios; a) PLA/PCL = 90/10, b) PLA/PCL = 80/20, c) PLA/PCL = 70/30, d) PLA/PCL = 60/40, e) PLA/PCL=50/50.

sented in **Figure 6**. Their pore-diameter distribution histograms are shown in **Figure 7**. As **Figure 6** shows, three samples possess similar morphologies.

However, PLA fibres (**Figure 6.a**) had larger variations and presented a more irregular structure when compared with the other two samples (**Figure 6.b** &

6.c). However, PCL and PLA/PCL fibres were observed as more regular structures. PLA, PCL and PLA/PCL polymers were electrospun as a film-like surface

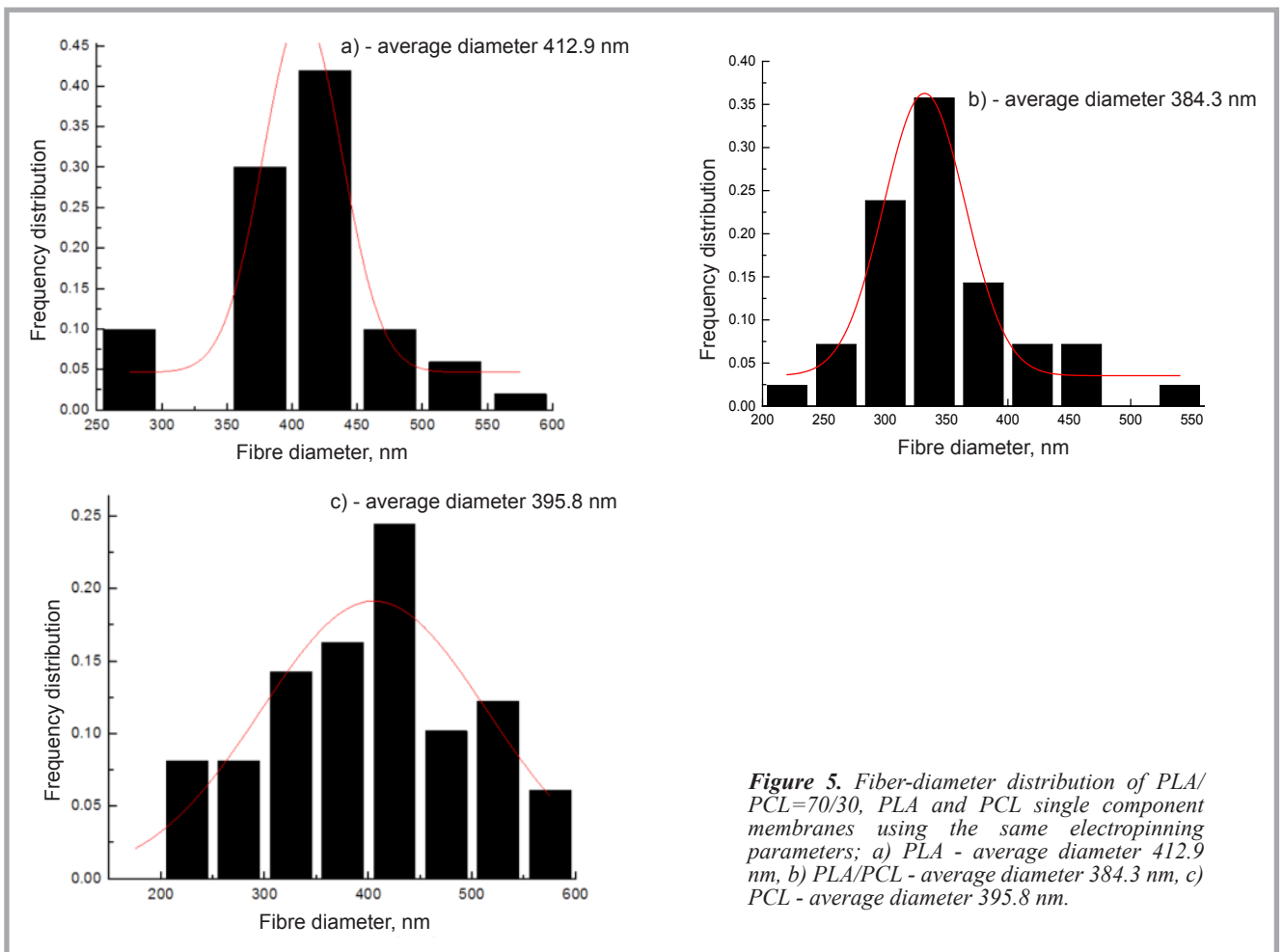


Figure 5. Fiber-diameter distribution of PLA/PCL=70/30, PLA and PCL single component membranes using the same electrospinning parameters; a) PLA - average diameter 412.9 nm, b) PLA/PCL - average diameter 384.3 nm, c) PCL - average diameter 395.8 nm.

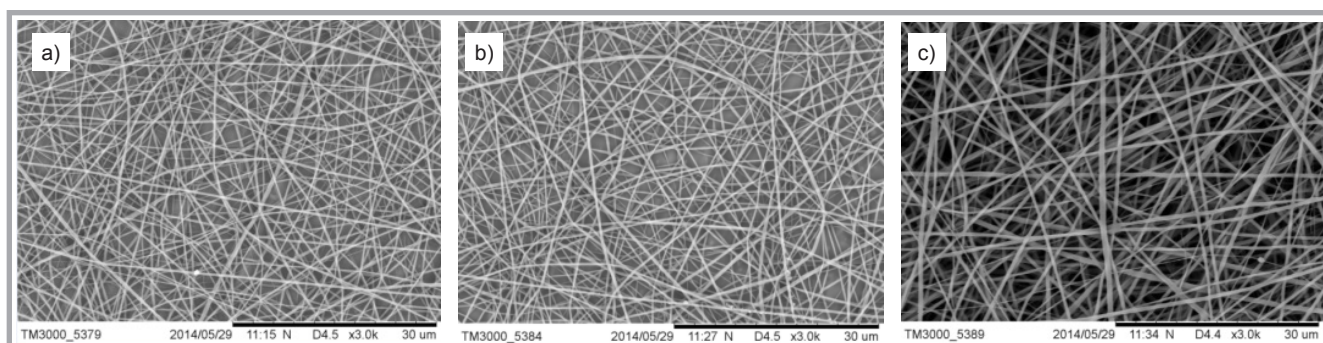


Figure 6. Scanning electron micrographs of PLA, PCL & PLA/PCL microfibre membranes; a) PLA, b) PCL, c) PLA/PCL.

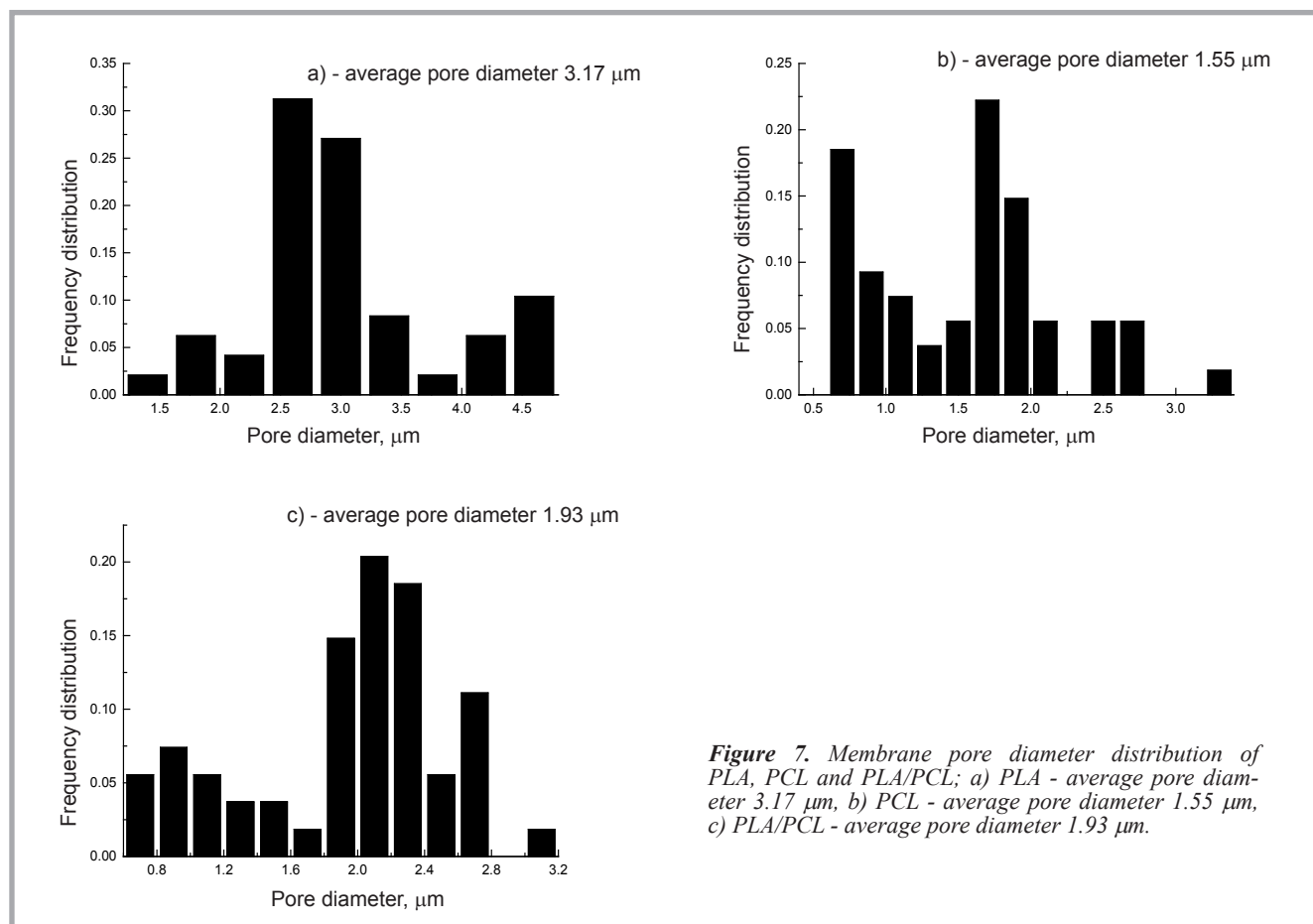


Figure 7. Membrane pore diameter distribution of PLA, PCL and PLA/PCL; a) PLA - average pore diameter 3.17 μm , b) PCL - average pore diameter 1.55 μm , c) PLA/PCL - average pore diameter 1.93 μm .

with numerous micropores. As *Figure 7* shows, PLA membranes possessed the widest pore-diameter distribution, ranging from 1 to 5 μm , with a larger average pore diameter (*Figure 7.a*). PCL's pore-diameter concentration was distributed from 0.5 to 3 μm (*Figure 7.b*). PLA/PCL's pore diameter changed from 0.6 to 3.2 μm , but was more focused

between 2 and 3 μm (*Figure 7.c*). Several maximum values are presented in *Figures 7* histograms, which is because microfibrils were deposited in a disorderly fashion, which led the pore size to be distributed in a relatively wide range, with more than one peak obtained as a result. The final conclusion was that PCL and PLA/PCL microfibrils show similar

morphologies of regular structure, while PLA had a larger irregular structure with a larger pore diameter. PLA was difficult to be made into microfibrils, as there always existed large fibres of relative high irregularity. On the other hand, PCL is more suitable to be made into microfibrils. Adding PCL to PLA can improve its spinnability and own membranes with irregular fibres.

Hydrophilicity and water absorption

Table 3 provides the contact angle and water absorption degree of three samples in a PBS environment for 24 hours. PBS is a kind of buffer solution which is used to maintain the PH value around

Table 3. Water absorption and contact angle of PLA, PCL, PLA/PCL electrospun membranes.

Sample	Water absorption, %	CV _{wa} , %	Contact angle, deg	CV _{ca} , %
PLA	2.68	2.68	139	1.09
PCL	62.96	4.67	133	0.56
PLA/PCL	101.90	5.02	125	0.60

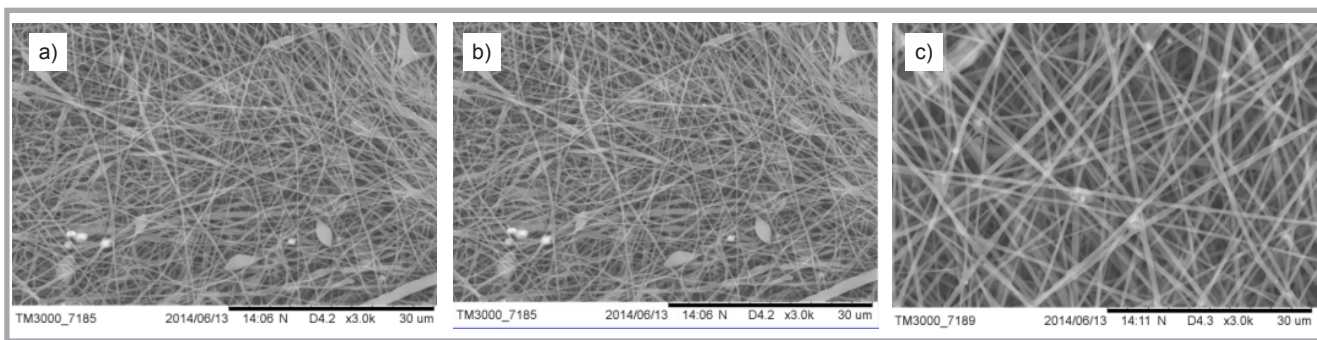


Figure 7. Scanning electron micrographs of PLA, PCL and PLA/PCL membranes after immersed in PBS solution for 24 hours; a) PLA, b) PCL, c) PLA/PCL.

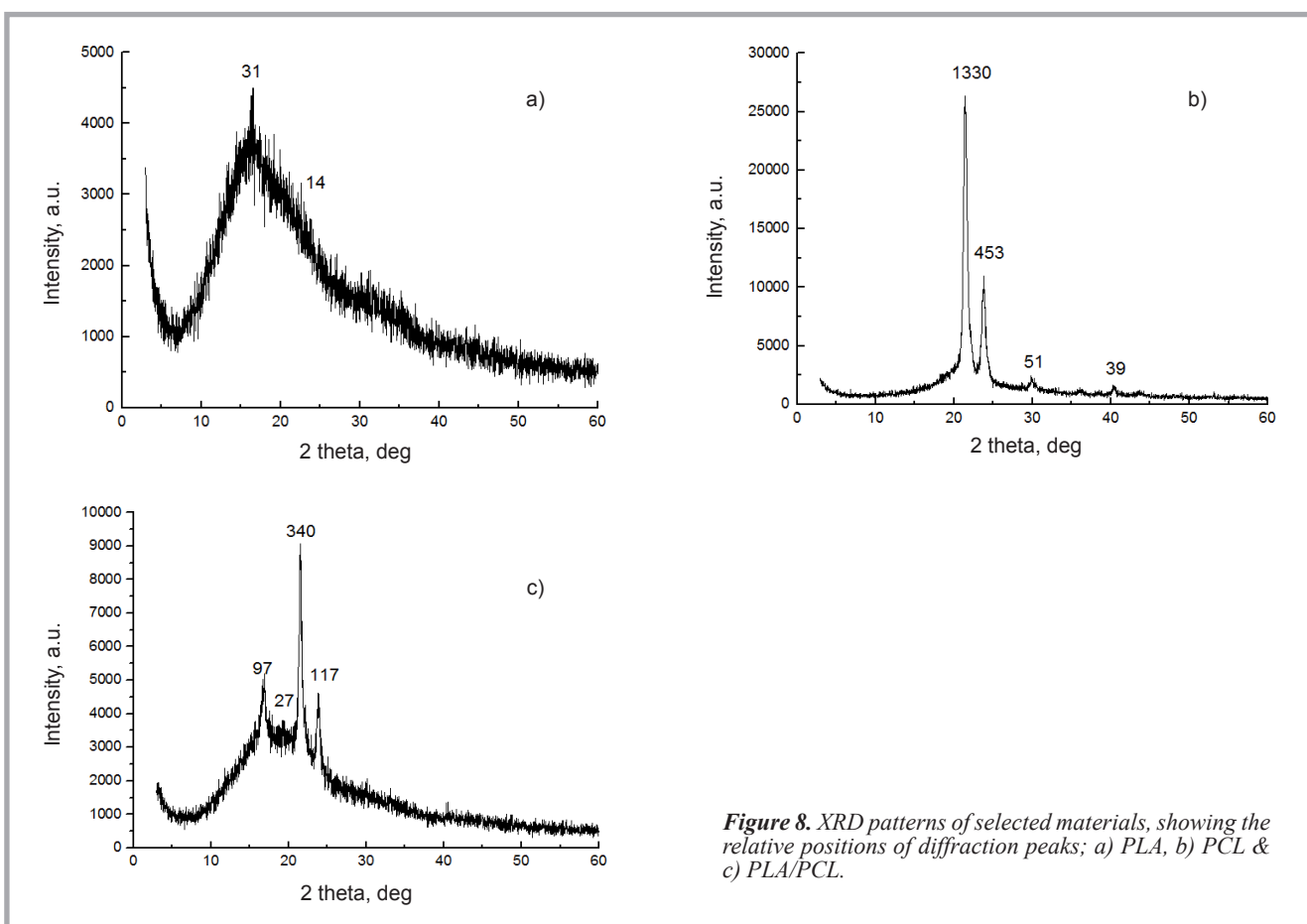


Figure 8. XRD patterns of selected materials, showing the relative positions of diffraction peaks; a) PLA, b) PCL & c) PLA/PCL.

the samples. CV listed in **Table 3** means the coefficient of variation, which was used to measure the variation degree of data. PLA, PCL and PLA/PCL composite membranes are all hydrophobic materials; the contact angles 3 samples were as follows: PLA > PCL > PLA/PCL. Blending two materials together leads to a small decrease in the contact angle.

Figure 7 shows the morphology of PLA, PCL and PLA/PCL membranes after being immersed in PBS for 24 hours. On the basis of **Table 3**, PLA had the lowest water absorption degree, which is due to the higher crystallinity. It is difficult for

the PBS environment to enter into the inner layers of the electrospun PLA microfibrils in a short time. The water absorption of fibres lead to a little swelling, which may have effect on morphologies. The fibrous surface feather with no beads and regular structure is suitable for application in tissue engineering. Hence little or entirely no differences were expected after immersion in the PBS environment. PLA membranes absorbed almost no water and the fibre remained the same compared to before immersion. PCL's water absorption rate was much bigger than that of PLA, which was 62.96%, but there was a slight swelling and adhesion

between fibres. While PLA/PCL membranes had the highest water absorption and almost maintained fibrous characteristics in the membranes.

Crystallinity and thermal performance
Figure 8 shows the X-ray diffraction pattern of three samples. The degree of crystallinity of PLA, PCL & PLA/PCL samples were 31.43%, 54.65% and 17.34%, respectively. PLA/PCL composite membranes possessed the smallest degree of crystallinity, and PLA had 2 diffraction peaks (31, 14) detected at $2\theta = 16.4^\circ$ and 22.6° , respectively. Their corresponding d-spacing values were determined

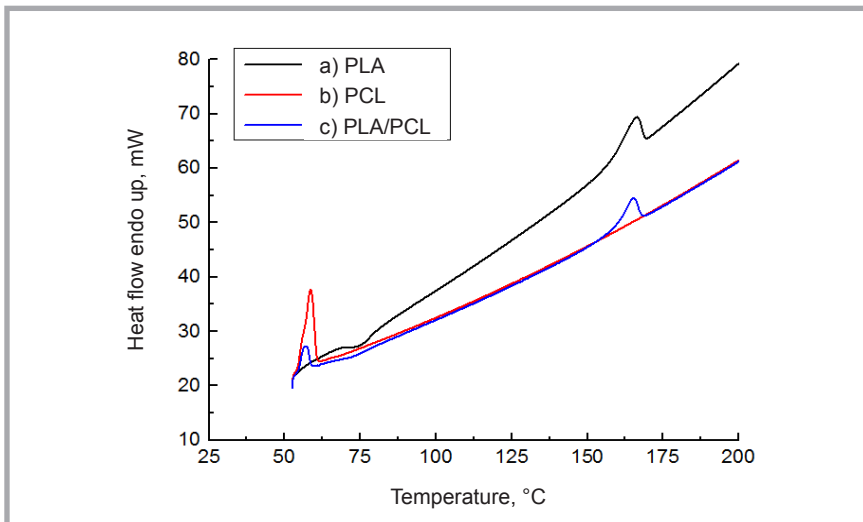


Figure 9. DSC curves of PLA, PCL, PLA/PCL.

Table 4. Tensile strength and elongation of PLA, PCL, PLA/PCL membranes.

Sample	Tensile strength, MPa	CV _{ts} , %	Elongation at break, %	CV _{eb} , %
PLA	2.01	14.47	82.20	13.31
PCL	1.54	14.77	108.72	18.12
PLA/PCL	7.22	13.68	109.22	12.28

as 0.54 and 0.39 nm (Figure 8.a). As for PCL samples, there are different diffraction peaks (1330, 453, 51, 39) detected at $2\theta = 21.4, 23.8, 29.9, 40.3^\circ$. The d-spacing of PCL samples are 0.41, 0.37, 0.30 and 0.40 nm (Figure 8.b). PLA/PCL samples have 4 diffraction peaks (97, 27, 340, 117) with corresponding $2\theta = 16.9, 19.3, 21.5, 23.8^\circ$ (Figure 8.c). The crystal peaks of PLA were less obvious with a low absorption intensity, showing more amorphous scattering. This may be due to the different degrees of molecule deformation during the electrospinning process [14]. PCL had two sharp crystal peaks with strong absorption intensity, which lead to a high degree of crystallinity. The PLA/PCL materials' diffraction pattern had features of both PLA and PCL i.e., wide amorphous scattering and an obvious peak, but the absorption intensity of the three peaks were not high.

By adding low molecular-weight PCL polymers to PLA, the membranes' degree of crystallinity decreased sharply, and the relatively high amorphous morphology was suitable for improving drug loading efficiency and promoting drug release [18]. Moreover the low degree of crystallinity can shorten the degradation time, which solved the problem of PLA and PCL's long degradation.

Figure 9 shows DSC curves of PLA, PCL and PLA/PCL microfibre membranes. For PLA and PCL samples only

one melting peak existed. The peak values in the PLA and PCL curves were 166.29 °C and 58.57 °C, corresponding to the melting points of these two materials, respectively. There were two peak values existing in the PLA/PCL curve which equal the melting points of PLA and PCL polymers, thus the two materials were distributed evenly in the composite membranes.

Mechanical properties

Table 4 presents the tensile performance of PLA, PCL and PLA/PCL. It is generally believed that PLA possesses a high tensile strength but low toughness, while PCL has excellent elongation but poor strength. The results show that PLA's strength was superior to that of PCL; but PLA's elongation was low. PLA/PCL composite membranes showed the highest tensile strength, with an elongation similar to PCL's. As is well noted in the literature [19 - 21], there existed relative slippage between the PLA and PCL polymers during the process of fibre stretching, which effectively prevented the fibre tensile effect. In addition, there existed forces between PLA and PCL materials such as the van der Waals force and so on, which also prevented fibre stretching and enhanced the effect of the composite membranes' mechanical properties.

Conclusions

In this study, PLA/PCL microfibre membranes were prepared by the electrospinning process. In order to obtain nonwoven fabric with a distribution of diameters from 200-400 nm, the following parameters of formation were selected: a ratio of PLA/PCL of 70/30, solvent ratio of DCM:DMF of 80/20, a solution concentration of 8%, voltage of 12 kV, receiving distance of 15 cm, and feed rate of 0.6 ml/h. In the above condition, the PLA/PCL membranes had fibres with an average diameter of 384.3 nm and a concentration distribution between 200 to 400 nm.

To demonstrate that the addition of PCL to PLA polymer can improve the microfibre membranes' properties and structure, several experiments including the SEM, DSC, XRD, water contact angle, water absorption degree and tensile strength were carried out. The results obtained from morphology and pore-size evaluation revealed that PCL and PLA/PCL samples had a smaller pore size (1.55 and 1.93 μm) and average fibre diameter. Water contact angle and absorption degree data showed that PCL's addition to PLA contributed to improving the samples' hydrophilicity. From the thermal evaluation, two melting peaks in the PLA/PCL DSC's curve were found corresponding to the two components' melting points. The PLA/PCL's degree of crystallinity was found to be much lower than that of PLA and PCL from the XRD test. The tensile test showed that PLA had a high tensile strength but with low elongation, and that PCL possessed excellent elongation with poor strength, while the PLA/PCL composite membranes' strength was much larger than that of PLA, with an elongation similar to PCL. Therefore the PLA/PCL microfibre membrane was a composite material with high strength and high elongation. Finally, in obtaining smooth and relatively fine PLA/PCL microfibre of small fibre diameter and regular structure, the addition of PCL to PLA polymer had significant effects on the morphology structure, hydrophilicity, crystallinity and mechanical property.

Acknowledgements

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INSTITUTE OF BIOPOLYMERS AND CHEMICAL FIBRES LABORATORY OF METROLOGY

Contact: Beata Palys M.Sc. Eng.
ul. M. Skłodowskiej-Curie 19/27, 90-570 Łódź, Poland
tel. (+48 42) 638 03 41, e-mail: metrologia@ibwch.lodz.pl



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The **Laboratory** is active in testing fibres, yarns, textiles and medical products. The usability and physico-mechanical properties of textiles and medical products are tested in accordance with European EN, International ISO and Polish PN standards.

Tests within the accreditation procedure:

- linear density of fibres and yarns, ■ mass per unit area using small samples, ■ elasticity of yarns, ■ breaking force and elongation of fibres, yarns and medical products, ■ loop tenacity of fibres and yarns, ■ bending length and specific flexural rigidity of textile and medical products

Other tests:

- **for fibres:** ■ diameter of fibres, ■ staple length and its distribution of fibres, ■ linear shrinkage of fibres, ■ elasticity and initial modulus of drawn fibres, ■ crimp index, ■ tenacity
- **for yarn:** ■ yarn twist, ■ contractility of multifilament yarns, ■ tenacity,
- **for textiles:** ■ mass per unit area using small samples, ■ thickness
- **for films:** ■ thickness-mechanical scanning method, ■ mechanical properties under static tension
- **for medical products:** ■ determination of the compressive strength of skull bones, ■ determination of breaking strength and elongation at break, ■ suture retention strength of medical products, ■ perforation strength and dislocation at perforation

The Laboratory of Metrology carries out analyses for:

- research and development work, ■ consultancy and expertise

Main equipment:

- Instron tensile testing machines, ■ electrical capacitance tester for the determination of linear density unevenness - Uster type C, ■ lanometer