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Polymer 44 (2003) 1287–1294

polymer

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Characterization of nano-structured poly(ε-caprolactone) nonwoven mats via electrospinning

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Received 11 June 2002; accepted 9 October 2002

Abstract

Nano-structured poly(ε-caprolactone) (PCL) nonwoven mats were prepared by electrospinning process. In this study, three types of solution were used. One dissolved in only methylene chloride (MC), the second dissolved in mixture of MC and *N*,*N*-dimethylformamide (DMF), the third dissolved in mixture of MC and toluene. MC, toluene and DMF are a good, poor, and nonsolvent for PCL, respectively. For the MC only, electrospun fibers had very regular diameter of about 5500 nm, but electrospinning is not facilitated. For the mixture of MC and DMF, electrospinning is certainly enhanced as well as fiber diameter decreased dramatically as increasing DMF volume fraction. It was due to high electric properties of solution such as dielectric constant and conductivity. Whereas, as increasing toluene volume fraction, electrospinning is strictly restricted due to very high viscosity and low conductivity. As the results, it has regarded that solution properties is one of the important parameter in electrospinning. Properties such as conductivity, surface tension, viscosity and dielectric constant of the PCL solutions prepared from three types of solvent system were studied. The morphology, crystallinity and mechanical properties of electrospun PCL nonwoven mats were characterized by scanning electron microscopy (SEM), wide angle X-ray diffraction (WAXD) and universal testing method (UTM), respectively.

Keywords: Poly(ε-caprolactone); Electrospinning; Nanofibers

1. Introduction

Aliphatic polyesters such as poly(lactic acid) (PLA), poly(glycolic acid) (PGA) and poly(ε-caprolactone) (PCL) and their copolymers are biodegradable polymers that have been used in biomedical and industrial application due to their biodegradability [1,2]. PCL has crystallizable rubbery properties so has been widely utilized for improving elasticity. MONOCRYL is commercial monofilament suture, it was formed from a segmented block coploymer of glycolide and caprolactone [3].

Fibers prepared from polymer solution or melt are applied in a wide variety of industrial fields. Fiber diameters made by conventional methods (melt, dry and wet spinning) have 5–500 μm [4]. Recently, development of electrospinning has been rapidly increasing in the past few years because it can prepare smaller than diameter of conventional fibers by 100 times. Electrospinning is a unique method that produces polymer fibers with diameter in the range of nano to a few microns using electirically driven jet of polymer solution or melt [5,6]. This technique has been developed since induced by Formhals in 1934 [7]. It is used to electrostatic force for making fibers. A high voltage power supply is required to create an electrically charged jet of polymer solution or melt. An electric field between capillary tip and a collector is created and induced a charge on the surface of the solution or melt. As increasing the electric field, the hemispherical shape of pendant drop at the end of capillary tip is charged a conical shape. It was known as the Tayler Cone [8]. If an electric field is induced above a critical value, it is ejected from the vertex of the Cone toward grounded collector. The charged jet comes out from the polymer liquid, it moves as a straight jet for some distance, and then travels a spiral path. It is triggered by the electrically driven bending instability [9], alternatively referred to as whipping instability [10]. The solvent will evaporate as the jet proceeds to the collector and accelerate

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PII: S0032-3861(02)00820-0

by electric field formed between capillary tip and grounded collector. The solidified fibers are collected on the grounded collector.

Electrospun nonwoven mats has small pore size, high porosity and high surface area, therefore, it can use in a wide variety of applications such as reinforcing fibers in composite materials [11,12] and for scaffolds in tissue engineering, etc. [11,13].

The morphology of electrospun fibers depends on the various parameters such as (i) solution parameters including viscosity, conductivity and surface tension, (ii) controlled variables including hydrostatic pressure in the capillary, electric potential at the tip and the tip-to-collector distance (TCD), (iii) ambient parameters including temperature, humidity and air velocity in the electrospinning chamber, etc. [14]. Therefore, optimal nanofibers can be prepared with controlling these parameters.

The object of this study is to prepare the poly(ε-caprolactone) (PCL) nonwoven mats and to characterize their physical and mechanical properties. Also, the effect of solvent on its electrospinning is investigated.

2. Experimental

2.1. Materials

PCL was purchased from Aldrich (Milwaukee, USA). The number average molecule weight (Mn) of PCL was 80,000 as determined by gel permission chromatography (GPC). This material was dissolved in three types of solvent. One is methylene chloride (MC) only, and the second is mixing solvent with MC/DMF ratios of 100/0, 85/15, 75/25, and 40/60 (v/v), the third is mixing solvent having MC/toluene ratios of 85/15 and 40/60 (v/v). PCL solutions were prepared with concentration ranging from 10 to 15 wt% using each three type of solvent. MC is a good solvent for PCL, and has a middle dielectric constant. Toluene is a poor solvent, has a low dielectric constant. While DMF is a nonsolvent for PCL, but it has high dielectric constant, also is polyelectrolyte. It was used for enhancing electrospinning. Fong et al. [15] have reported that DMF is a nonsolvent for nylon, but it helped during the electrospinning and the formation of electrospun fibers. At the results of preliminary experiments, the solvent properties have found to be affected in electrospinning. Solvent properties used in this study are given in Table 1 [16,17].

Table 1
Solvent properties

Solvent	Solubility	Bp (°C)	Dm[a] (μ), D	Diel.[b] (d)
MC	Good solvent	41	–	9.1
Toluene	Poor solvent	111	–	2.4
DMF	Nonsolvent	153	3.9	36.7

[a] Dipole moment in Debyes.
[b] Dielectric constant at 25 °C.

2.2. Methods

2.2.1. Surface tension, viscosity and conductivity of solution

Surface tensions for each solution were determined by the Wilhelmy plate method using tensiometer (K10ST, Krűss Co., Germany). Each experiment was performed at 20 °C. The platinum plate was cleaned with a butane torch.

Solution viscosities were determined by a Rheometer (DV III, Brookfield Co. USA) at 20 °C with a SH47 spindle at 80 rpm. Conductivity of each solution was measured by electric conductivity meter (G series, CM-40G, TOA Electronics Ltd, Japan).

2.2.2. Morphology

Morphology of electrospun PCL nonwoven mats was observed from scanning electron microscopy (SEM, X-650, Hitachi. Co., Japan) and the diameter of electrospun PCL nonwoven mats was measured from image analyzed (Image-proplus, Media Cyber netics Co., USA).

2.2.3. WAXD

Wide angle X-ray diffraction (WAXD) measurements were carried out with a fixed anode X-ray generator (Rigaku, Geigerflex; 40 kV and 30 mA) with Cu Kα radiation (λ = 1.5402 Å).

2.2.4. Tensile test

Mechanical properties of electrospun PCL nonwoven mats were determined with a universal testing machine (UTM, AG-5000G, Shimadzu, Japan) under a crosshead speed 10 mm/min at room temperature. All samples were prepared in the form of standard dumbbell-shaped according to ASTM D638 by die cutting from electrospun PCL nonwoven mats. Two directions were tested. One is along the machine direction (MD), the other is the cross direction (CD) (Fig. 1.).

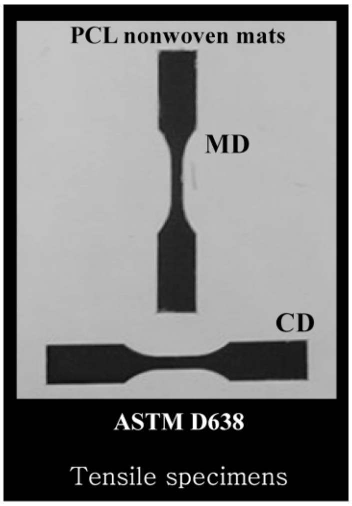

Fig. 1. Appearance of tensile specimens die cut from electrospun PCL nonwoven mats.

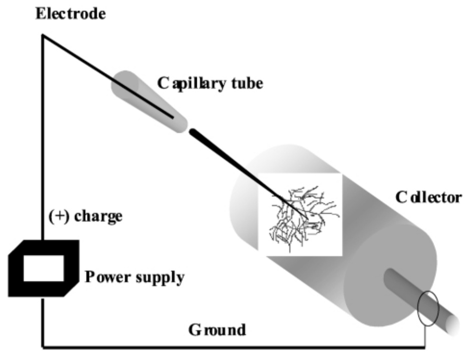

Fig. 2. Experimental set-up device for electrospinning process.

2.2.5. Electrospinning

Experimental set-up device used for electrospinning process is shown in Fig. 2. A variable high voltage power supply (CPS-60 K02v1, ChungpaEMT, Co., Korea) was used for the electrospinnings. It was used to produce voltages ranging from 3 to 50 kV. The polymer solution was poured in a 5 ml syringe attached with a capillary tip of 1 mm diameter. In order to minimize a falling drop at the capillary tip, the syringe was tilted at approximately 10° from horizontal, and was clamped to a stand. The positive electrode of a high voltage power supply was attached to a copper wire inserted into the polymer solution. The negative electrode was attached to grounded collector. Rotating drum wrapped with aluminum foil was used as collector. Rotating drum can be controlled speed ranging from 0 to 5.5 m/min.

3. Results and discussion

3.1. Solution properties

The surface tension of solution decreased as the DMF added (Fig. 3). Electrospun PCL nonwoven mats prepared well at surface tension of about 35.5 mN/m.

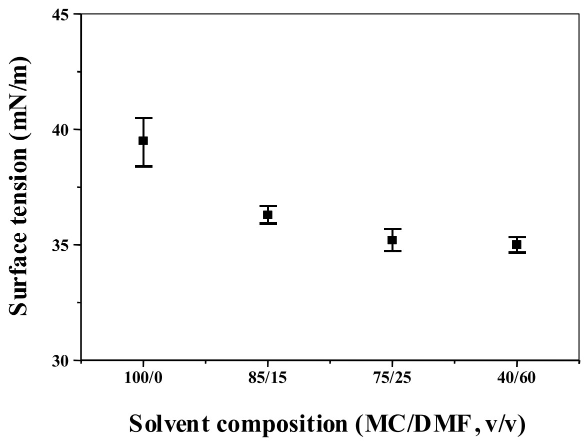

Fig. 3. Surface tension of 13 wt% solutions dissolved in the mixture of MC and DMF.

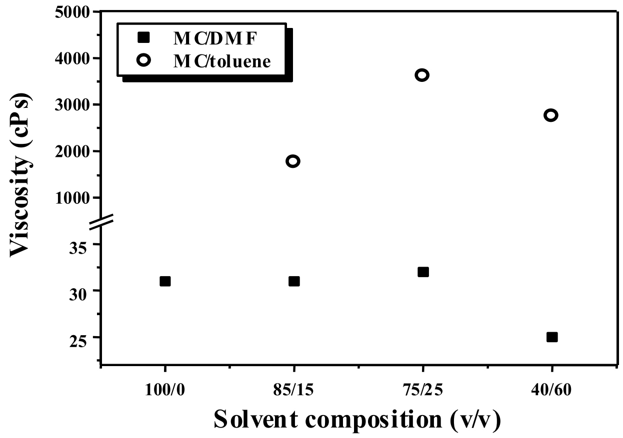

Fig. 4. Viscosity of 13 wt% solutions dissolved in the mixture of MC and DMF (■) and MC/toluene (○).

Spinning from solutions dissolved in only MC was often stopped due to low b.p. of MC solvent.

Fig. 4 shows the viscosity of solution for the MC/DMF and MC/toluene systems. For MC/DMF systems, viscosity retained by 25% DMF added and decreased slightly, whereas that of solution dissolved in MC/toluene systems increased dramatically. In these systems, electrospinning was restricted to their high viscosity.

Fig. 5 shows electric conductivity of each solution. For MC/toluene systems, solution conductivity did not change as toluene increased, whereas that of MC/DMF increased as DMF content increased.

Dielectric constant of solutions dissolved in the mixture of MC and DMF was increased significantly as the DMF added (Fig. 6). Dielectric constant of solution was strongly affected on spinning and diameter of electrospun PCL nonwoven mats. As increasing DMF content ranging from 0 to 60%, average diameter of electrospun PCL fibers decreased ranging 5500–200 nm.

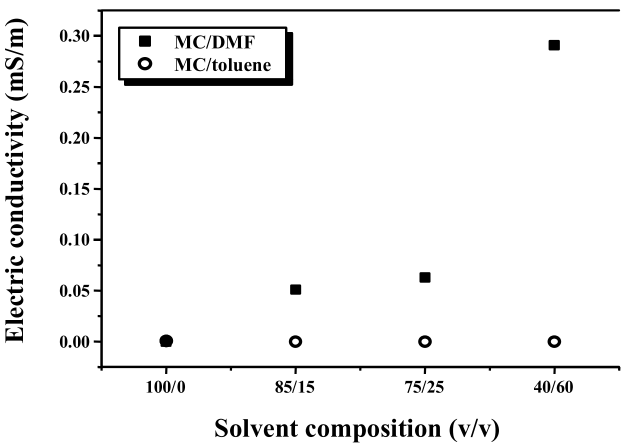

Fig. 5. Electric conductivity of 13 wt% solutions dissolved in the mixture of MC and DMF (■) and MC/toluene (○).

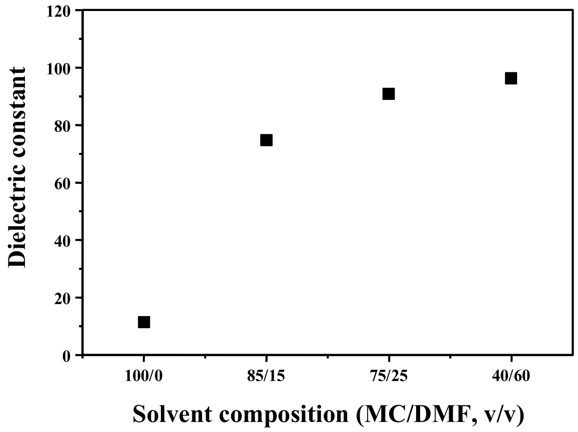

Fig. 6. Dielectric constant of 13 wt% solutions dissolved in the mixture of MC/DMF.

As the result, dielectric constant and conductivity of solution were key factor of electrospinning.

3.2. Morphology

Vollrath [18] has reported that beads regarding as 'by product' have been often formed in electrospinning. In our experimental, formed beads have been observed widely in electrospun PCL nonwoven mats prepared from all of these 10 wt% solutions (Fig. 7). Entov [19] has reported that the formation of beaded fibers is related to the instability of the jet of polymer solution and Fong [20] has reported about beaded PEO nanofibers. He explained that the viscosity, net charge density and surface tension of solution are key parameter of formed bead fibers. Also, many researchers reported about beaded fibers and beads during electrospinning [20–23].

As increasing DMF content, a number of beads

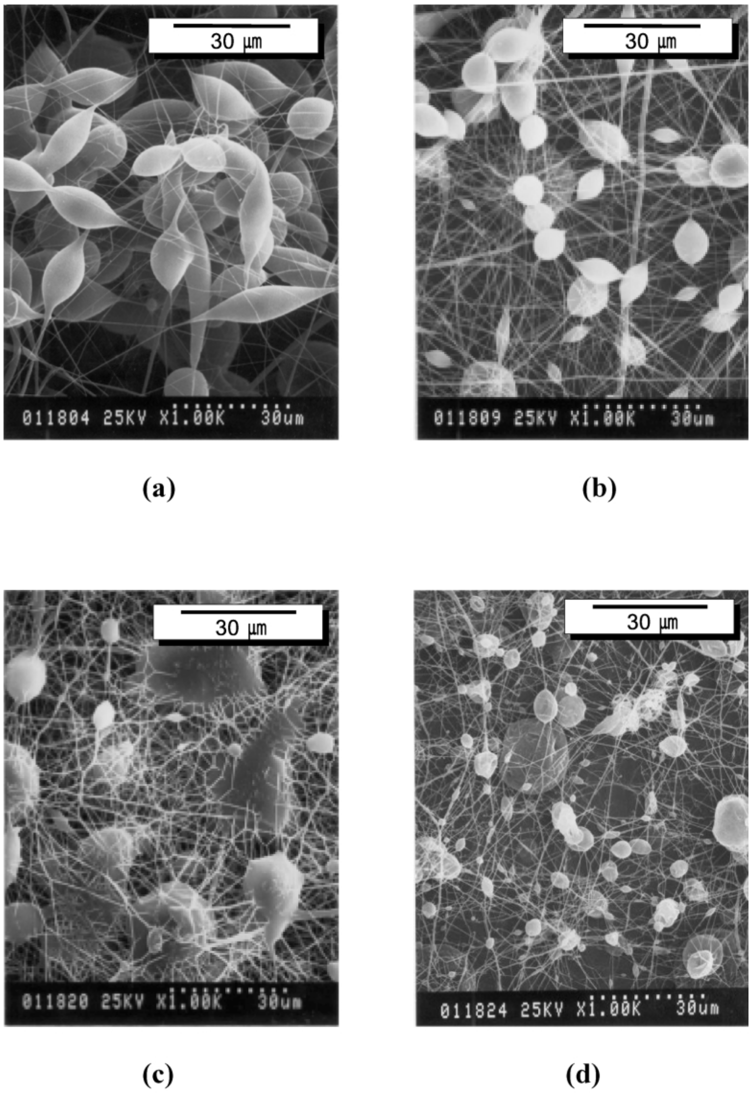

Fig. 7. SEM photographs of beads formed from a 10 wt% PCL solution dissolved in the mixture of MC/DMF (v/v), (a) 100/0 (b) 93/7 (c) 75/25 (d) 40/60.

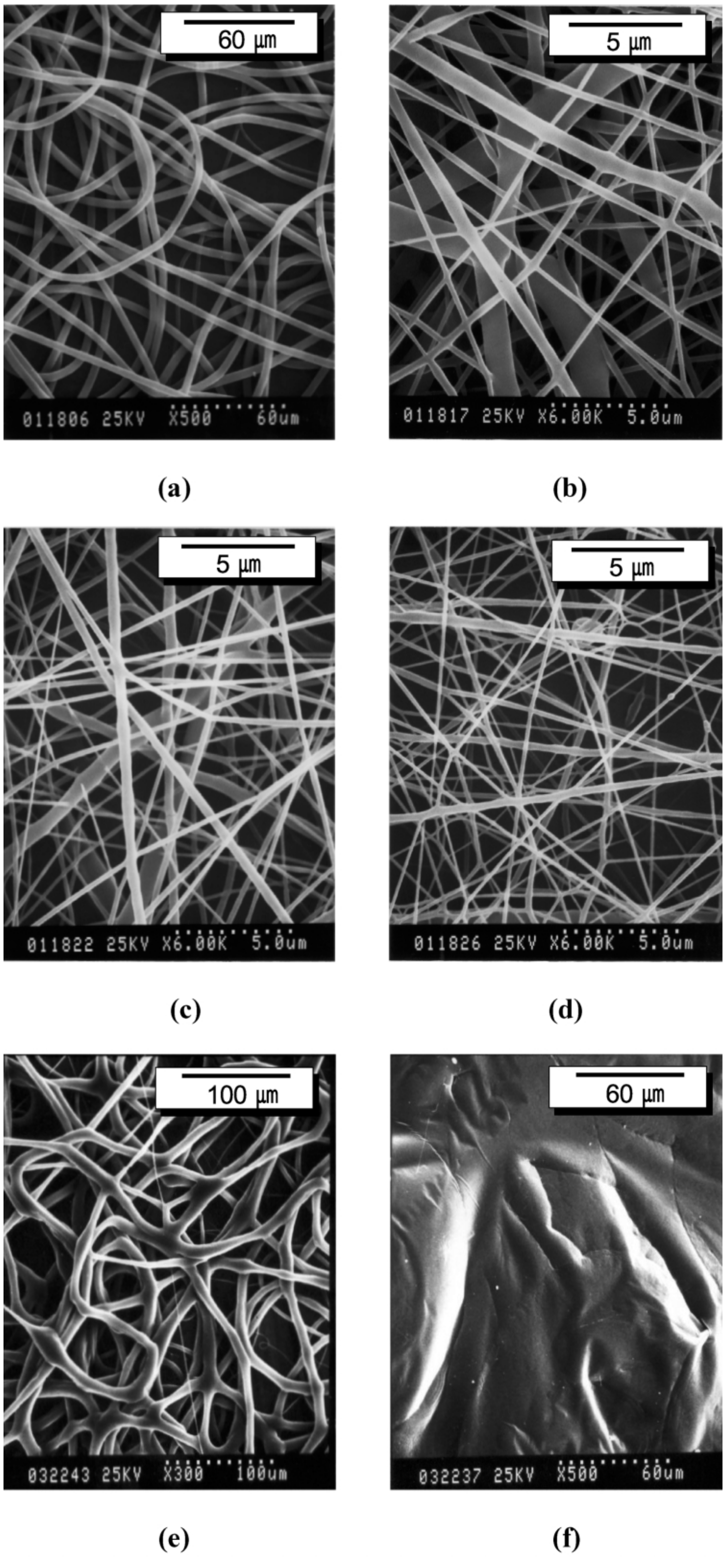

Fig. 8. SEM photographs of electrospun PCL nonwoven mats from three types of solvent system. (a) MC only, (b) MC/DMF, 85/15, (c) MC/DMF, 75/25, (d) MC/DMF, 40/60, (e) MC/toluene, 85/15, (f) MC/toluene, 40/60.

decreased, but increased again because of low viscosity at above 50% DMF content (Fig. 4).

The SEM photographs of electrospun PCL nonwoven mats prepared from three types of solvent systems shown in Fig. 8. For the MC only systems, it has showed that the jet was not splay and spilt. And it was observed a narrow distribution of an average diameter about 5500 nm (Figs. 8(a), 9 and 10), and surface of formed fibers was smooth.

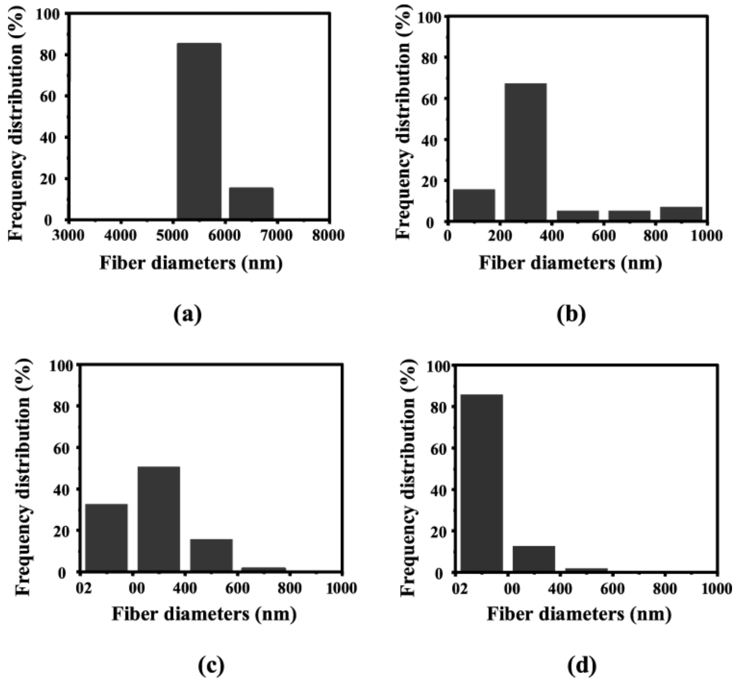

Fig. 9. Frequency distribution of electrospun fibers a 13 wt % solution dissolved in the mixture of MC/DMF (a) 100/0, (b) 85/15, (c) 75/25, (d) 40/60 (v/v).

The disadvantage of MC only system is large fiber diameter. For the MC/DMF systems, as increasing DMF volume fraction, spinning was dramatically enhanced, and splaying and splitting observed. Also the diameter of electrospun PCL fibers decreased conspicuously. It can be interpreted that as increasing DMF volume fraction, surface tension and viscosity decreased, while conductivity and dielectric constant increased. Therefore, it can be regarded that electric properties of polymer solution was one of key factors in electrospinning. Frequency distribution and average diameter of electrospun PCL fibers was shown in Figs. 8, 9 and 10, respectively.

For the PCL solutions dissolved in MC/toluene systems, spinning didn't facilitate. At MC/toluene 75/15 (v/v), fiber formation occurred, but fiber diameter was larger than that of electrospun from MC only system. The point bonding structures exhibited higher than that of electrospun from other systems. It conducts as factor to improve mechanical properties. At MC/toluene, 40/60 (v/v), fibers didn't form due to the high viscosity and low surface tension. Also low electric constant of toluene affected. In order to form fibers in electrospinning, a high enough viscosity and surface tension were required to maintain pendant drop at the end of capillary tip.

As the result of SEM photographs, the solvent composition and various solution properties conducted an important role in determining the fiber formation. And dramatic change in fiber diameter was observed in the effect of solvent.

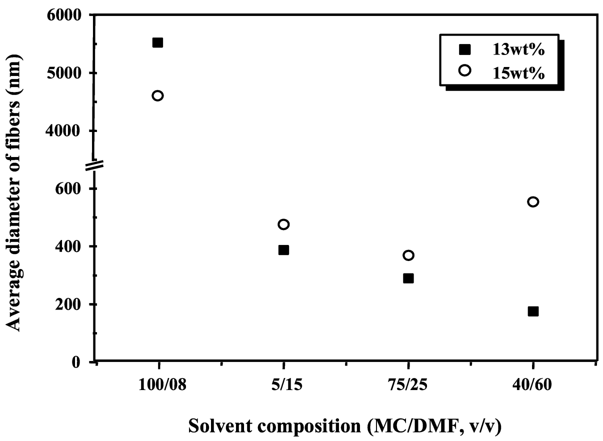

Fig. 10. Average diameter of electrospun fibers using solutions dissolved in the mixture of MC/DMF (■: 13 wt% and ○: 15 wt%).

3.3. Crystallinity

Fig. 11 shows the WAXD patterns for both a nonwoven mats electrospun from a 13 wt% solution dissolved in the

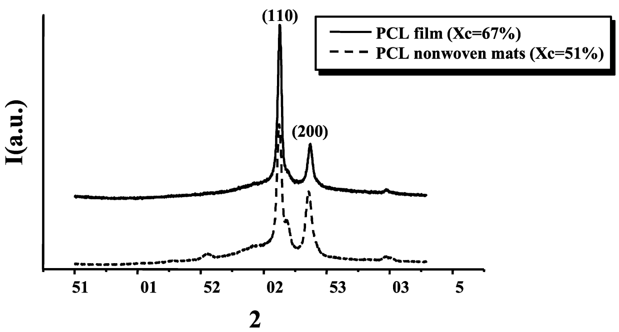

Fig. 11. WAXD patterns from melt crystallized PCL film and electrospun nonwoven mats from 13 wt% solution in the mixture of MC and DMF, 75/25(v/v).

Table 2
Mechanical properties of electrospuns PCL nonwoven mats

Linear velocity of drum surface (m/min)	Young's modulus (MPa)		Yield stress (MPa)		Tensile strength (MPa)		Elongation at break (%)	
	MD	CD	MD	CD	MD	CD	MD	CD
1.3	3.31	3.93	0.56	0.62	1.40	1.63	200	216
3.2	4.67	3.86	0.67	0.55	2.10	2.04	231	277
4.5	3.66	2.71	0.50	0.42	1.39	1.20	208	246

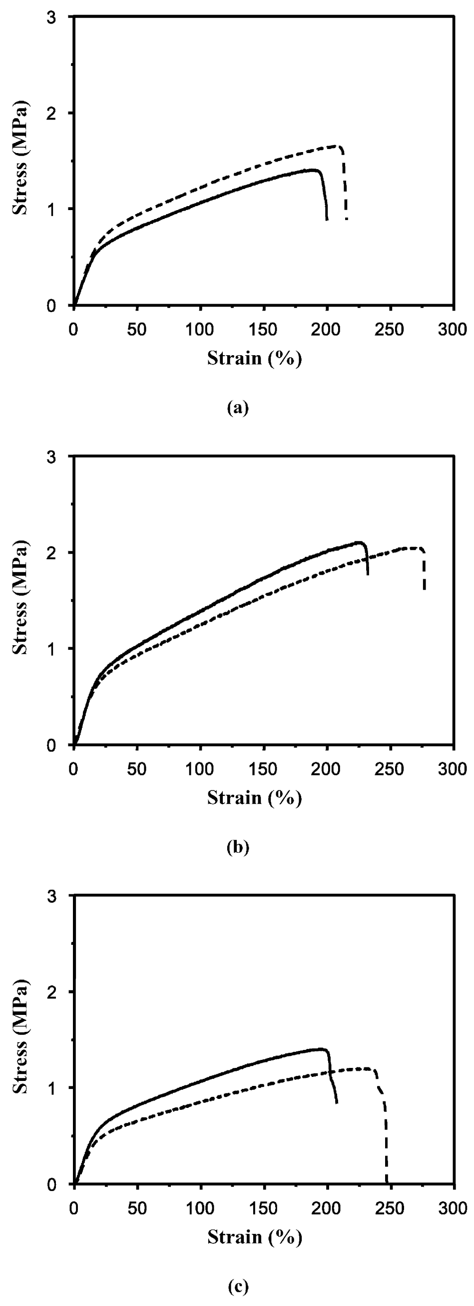

Fig. 12. Mechanical properties of PCL nonwoven mats prepared by electrospinning as a function of linear velocity of drum surface {(a) 1.3 m/min (b) 3.2 m/min (c) 4.5 m/min, (solid line: MD, dashed line: CD)}.

mixture of MC and DMF (MC/DMF, 75/25, v/v), and melt crystallized PCL film at equatorial direction. Even though the azimuthal distribution of the two crystalline reflection of electrospun PCL nonwovens mats was nearly isotropic, when comparing the electrospun PCL nonwoven mats with film, there was a significant decrease in intensity ratio (I_{110}/I_{200}) of two main peaks which can be seen during uni-axial tensile deformation process of orthorhombic semi-crystalline polymers. This implies that the chains and crystallites in nanofiber has some orientation to the same direction of fiber axis during electrospinning process. Also, the retardation of crystallization have been observed in electrospun PCL nonwoven mats and is commonly known.

As the results, the crystallinity of electrospun PCL nonwoven mats was lower than that of PCL film (Fig. 10). It can be explained that there is no drawing process in electrospinning.

3.4. Mechanical properties

If grounded collector can rotate with moving the right and the left, the phenomena between the pendant drop of the end at capillary tip and the grounded collector will very complex. Also, electrospun fibers collected on grounded collector may be conducted as an insulator. Reneker [9] explained such phenomenon with bending instability. He also reported that the expanding spiral structure taken by CCD camera is a simple example of some kinds of path.

Stress–strain curves of electrospun PCL nonwoven mats prepared as a function of linear velocity of drum surface shown in Fig. 12. Various mechanical properties can be evaluated from Fig. 12, as summarized in Table 2. In these experiments, linear velocity of drum surface was controlled ranging from 1.3 to 4.5 m/min. For electrospun PCL nonwoven mats prepared at 1.3 m/min, yield stress, tensile strength and modulus in the CD were higher those that in the MD (Fig. 12(a)). But for nonwoven mats prepared at 3.2 m/min, these in MD were higher than those in CD (Fig. 12(b)). But elongation at break was not changed. For linear velocity of drum surface higher (4.5 m/min), all of the properties decreased (Fig. 12(c)). Two methods can be introduced to prove these results. One is fiber orientation, and the other is bonding point between fibers. Electrospun fiber orientation can be described using a fiber orientation angle. Fiber orientation angle in nonwoven mats can be defined as the angle formed between the fiber axis and a

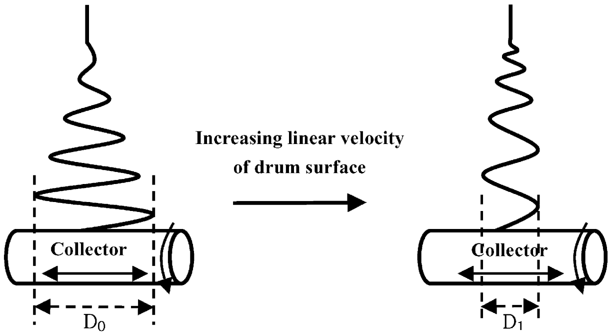

Fig. 13. Schematic diagram of the fiber spiral path on the PCL electrospinning.

line parallel to the web centerline (MD). Formation of point bonding structures affects physical and mechanical properties of nonwoven mats [24].

In general, electrospun fibers are distributed randomly in all directions. Also, it could be due to the spiral shape of electrified jet with increasing radial dimension. We had assumed that spiral shape was the unique path in electrospinning in our experimental.

The faster linear velocity of drum surface, the shorter is dimension of pitch ($D_0 \rightarrow D_1$, Fig. 13). Therefore, many fibers toward MD will be collected disordered structures as the linear velocity increasing. If the linear velocity is too fast, many of the electrospun fibers may be flown in the space. Also, the formation of pointed bond structure is not occurred because of the rapid linear velocity of drum surface.

4. Conclusions

In this study, we have evaluated that the three types of solutions was concerned with electrospinning. Also, the solution properties such as dielectric constant, viscosity, surface tension and conductivity have demonstrated to correlate strongly on the morphology of electrospun PCL nonwovens mats.

PCL solution dissolved in only MC, the fiber diameter electrospun at 13 wt% was 5500 nm having a narrow diameter distribution. For solutions dissolved in the mixture of MC and DMF, electrospinning became facilitate dramatically, the fiber diameter decreased by 200 nm. It can be interpreted that DMF has not only a high dielectric constant, but also polyelectrolyte behavior.

The most interesting of this study is the apparent change in the diameter and phenomenon of electrospinning observed in the electrospun PCL nonwoven mats. It strongly correlated to dielectric constant of solution. Crystallinity of electrospun PCL nonwovens mats decreased slightly in the WAXD. Electrospun PCL nonwoven mats exchanged mechanical properties of CD and MD as linear velocity of drum surface increasing.

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