



# Nanofibrous mats of poly(trimethylene terephthalate) via electrospinning

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## Abstract

Nanofibrous mats were prepared by electrospinning of poly(trimethylene terephthalate) (PTT) with diameter ranging from 200 to 600 nm. Morphology of electrospun nanofiber obtained by changing processing parameters such as solution concentration and their deposition time, was investigated with scanning electron microscope (SEM). Especially, periodic feature of surface roughness, such as diamond-shaped structure, was exhibited as the deposition time increased. In this work, it was shown that this phenomenon might result from polymer chain mobility, which was induced by solvent properties, and point bonding structure. In addition, schematic diagram was introduced to identify the formation of diamond-shape structure in PTT electrospun nanofibrous mats.

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## 1. Introduction

Poly(trimethylene terephthalate) (PTT) has become one of the most important polymer materials recently because PTT is a promising material for engineering plastic and textile fiber. Many studies based on synthetic technique, spinning technology, morphological structure and properties of fiber, as well as crystallization behaviors, have been widely investigated [1–5]. It is well known that conditions occurring during the spinning determine the structure and properties of as-spun fibers, and their behavior in further technological operation [6].

Electrospinning method has attracted a great deal of attention to produce nanofibrous membranes ranging from sub micron to nano size in diameter. More than 30 different types of polymer fibers have been prepared by electrospinning in our laboratory. Reneker [7] has discussed about their possible uses in different technologies, their history, patent received, and the mechanisms of formation. In earlier work, fibers from acrylic resins dissolved in dimethyl formamide were obtained by electrospinning [8]. Bulk polyethylene and polyethylene dissolved in paraffin were electrospun by Larrondo and Manley [9]. In addition, Kim et al. carried out electrospinning of poly(ethylene terephthalate) in molten

state [10]. Zacharides and Porter [11] prepared high modulus fibers from Kevlar and poly(*p*-phenylene terephthalamide). Poly(ethylene oxide) was used for determining the optimum conditions and characterization of fibers [12–14]. Conductive electrospun nanofibers were obtained from polyaniline/poly(ethylene oxide) blends [15]. Nylon, poly(vinyl alcohol) and cellulose acetate fibers were electrospun in solution [16,17]. Although many reports have examined the morphology of various polymers during electrospinning, little has been done to understand the characteristics and morphology of specific material.

Nonwoven behavior significantly affected by the topography, such as pore size, deposition density and surface roughness. Physical Sciences Inc. (PSI) demonstrates the application of the electrospinning technique for fabrication and reinforcement of Gossamer structure (thin, lightweight membranes for space application). Whereof, PSI has shown a newly developed technique referred to as *Patterned Electrospinning*, which is based on traditional melt electrospinning techniques [18]. *Patterned Electrospinning* utilizes a grounded template, in a user specified pattern, which promotes selective electrospinning deposition under proper condition. Furthermore, the nonwoven deposits are optimized for area density, reflectivity, and strength via manipulation of fiber diameter, and deposition time.

In this study, PTT nanofibrous mats are prepared by electrospinning method on rotating drum. PTT nanofibrous

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mats with different surface roughness are intentionally prepared as the function of the deposition time. Morphological and mechanical properties are examined by scanning electron microscopy (SEM) and universal testing machine (UTM). Moreover, the other goal of this study is aimed to understand the effects of electrospinning parameters on the macroscopic surface structure of PTT nanofibrous mats.

## 2. Experimental

### 2.1. Materials

PTT (inherent viscosity = 0.92, Shell Co., UK) was used in the form of a pellet. Trifluoroacetic acid (TFA) and methylene chloride (MC) were purchased from Showa Chemical Ltd (Japan) and used without further purification. Both were well mixed with the volume ratio of 50/50. TFA/MC was used as solvent of PTT to prepare the polymer solutions at different concentrations ranging from 5 to 16 wt% for electrospinning. Surface tension and viscosity of polymer solution were determined by tensiometer of the Wilhelmy plate type (K10ST, Krüss Co., Germany) and rheometer (DV III, Brookfield Co., USA) at 25 °C, respectively.

### 2.2. Electrospinning setup

Polymer solution was supplied in a syringe by micro tube pump (MP-3N, Tokyo Rikakikai Co. Ltd, Japan) continuously. The syringe used in these experiments had a capillary tip diameter of 0.5 mm. The electric field was provided by a high voltage power supply (CPS-60 K02v1, Chungpa EMT Co., South Korea), which can generate voltage of up to 50 kV. The copper probe of the generator was inserted into the syringe and electricity was conducted through the solution. A grounded rotating drum was positioned

perpendicular to the tip of the syringe on which were deposited by the electrospun fibers. PTT nanofibrous mats were prepared in traverse direction (TD) and machine direction (MD) with 200 mm width and 400 mm length, respectively. After solvent evaporating, fibers were ready for morphological study. To determine the mechanical property, the samples were dried under vacuum at 25 °C for 24 h.

### 2.3. Measurements and characterization

The morphology of the electrospun PTT nanofibers is investigated with optical microscopy and SEM (GSM-5900, Jeol Co., Japan). Optical micrographs were taken with a Nikon Eclipse ME600 model to investigate the presence of electrospun nanofibrous mats on the aluminum foil. The tensile strength and elongation at break were determined with a UTM (AG-5000G, Shimadzu, Japan) under the crosshead speed of 10 mm/min at room temperature. ASTM Standard D 638 method was observed for preparing the sample as shown in Fig. 1.

## 3. Results and discussion

The electrospinning for PTT was conducted at both tip-to-collector distance, 13 cm and solvent volume ratio of TFA and MC, 50/50 (v/v). These conditions were an optimal to prepare the nanofibrous mats.

One of major determinant of fiber morphology was solution concentration. Fig. 2 shows the concentration dependence of surface tension and corresponding viscosities of PTT dissolved in TFA/MC. The surface tension and viscosity were increased with increasing of solution concentration. The SEM images of the electrospun nanofibrous mats of PTT solutions of different viscosities are shown in Fig. 3 (under a voltage of 13 kV). It is impossible to collect a fiber at concentration below 5 wt%. A mixture of large beads and fibers was generated by electrospinning at

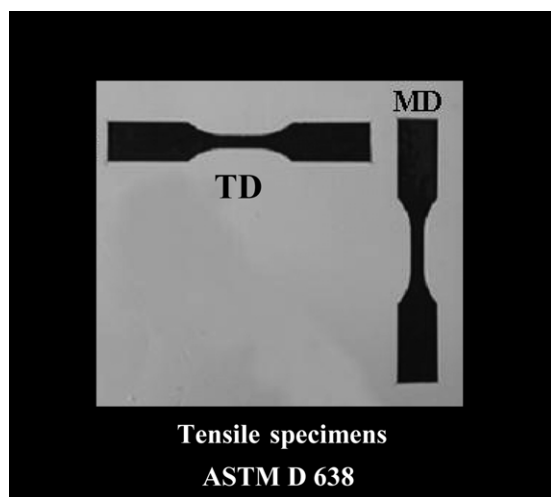


Fig. 1. Photograph of dumbbell-shaped test specimen.

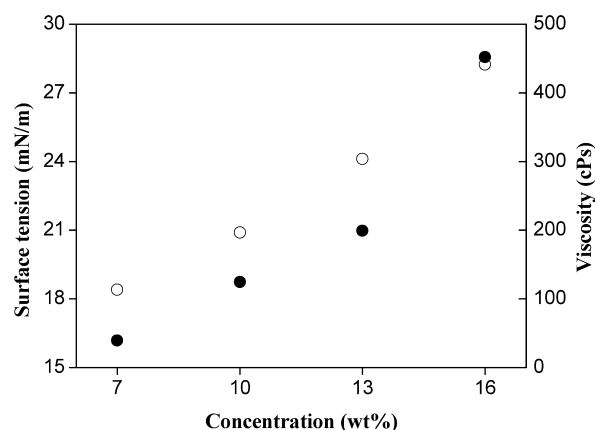


Fig. 2. Solution surface tension (○) and solution viscosity (●) as a function of solution concentration for PTT dissolved in TFA/MC (50/50, v/v).

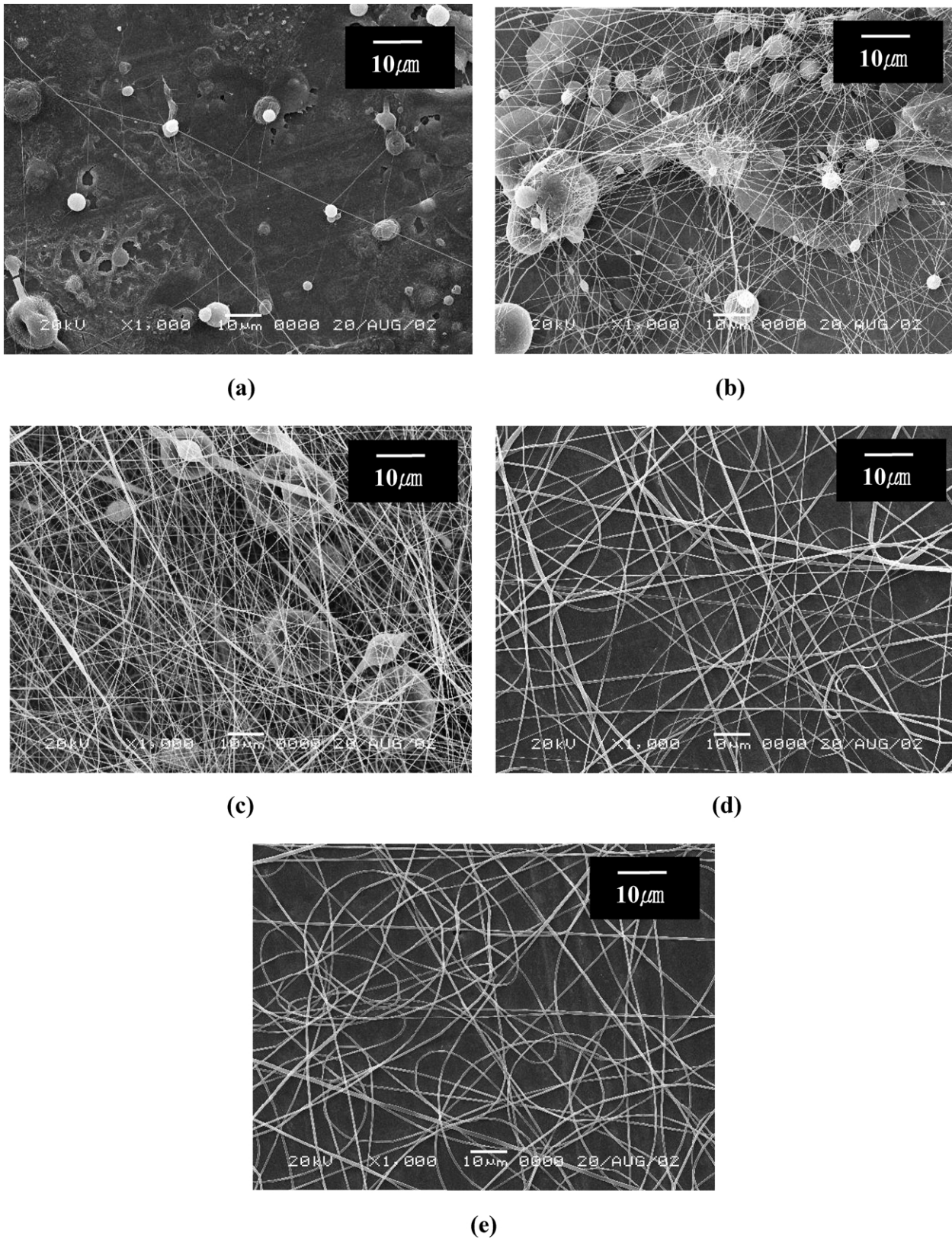


Fig. 3. SEM images of electrospun PTT nanofibers as a function of the solution concentration (TFA/MC = 50/50, v/v). (a) 5 wt%, (b) 7 wt%, (c) 10 wt%, (d) 13 wt%, and (e) 16 wt%. The applied electric field was 13 kV and the tip-to-collector distance was 13 cm.

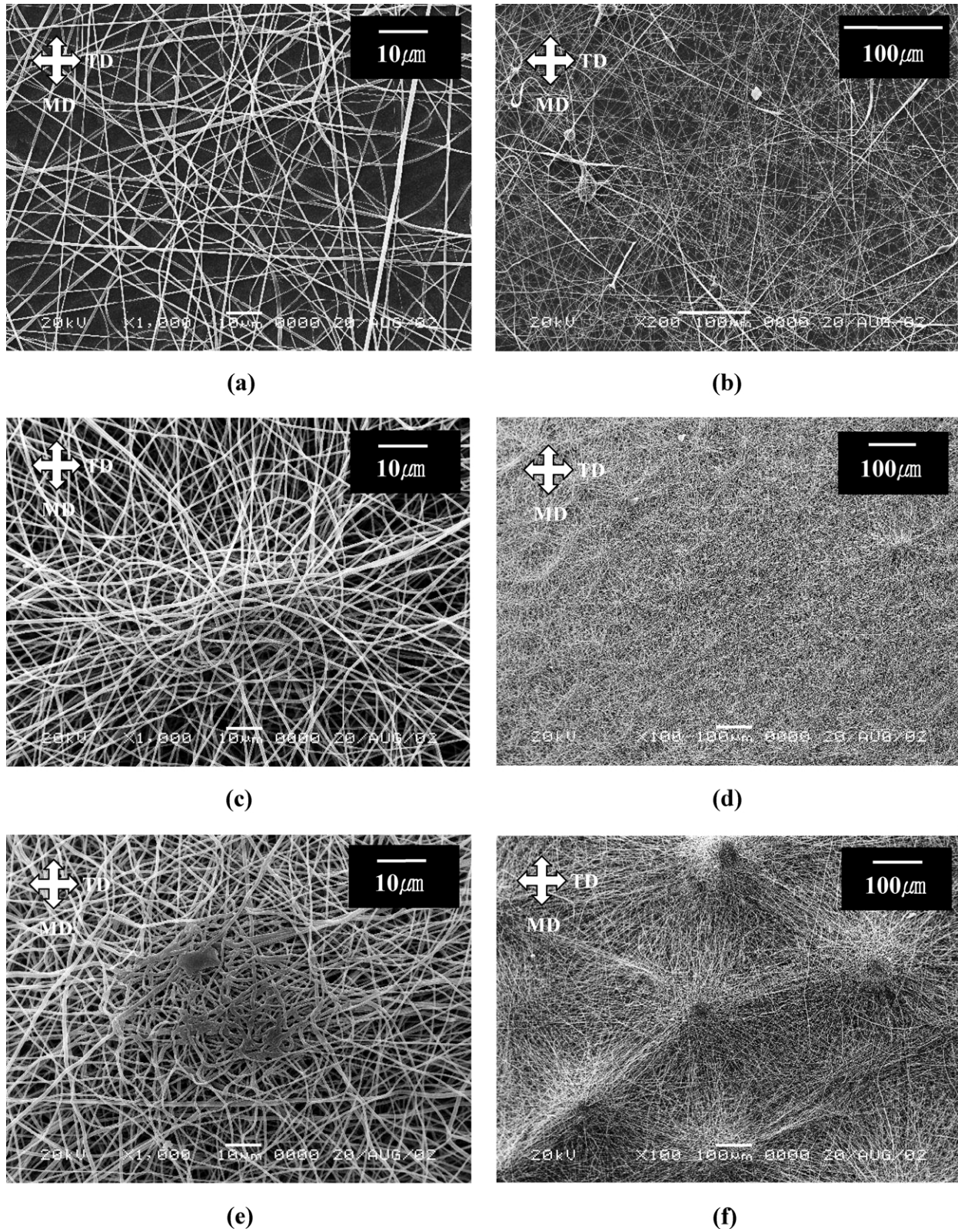


Fig. 4. SEM images of electrospun nanofibrous mats with different deposition time. (a), (b) 20 min; (c), (d) 60 min; (e), (f) 120 min (MD, machine direction; TD, traverse direction).



7 wt%. The diameter of beads becomes bigger as the viscosity increases. Meanwhile, the shape of the beads changes from spherical to spindle-like. At concentration 16 wt%, it can be seen that the fibers are uniform as the solution viscosity increased. Beads and beaded fibers are less likely to be formed for the more viscous solution. The average diameter of fiber electrospun is 400 nm. Fong et al. [13] has reported that increasing the viscosity and the associated electrical forces favor the formation of circular fibers. Major competition has been found between the surface tension and viscoelastic force. But, in this work, it is evident for the formation of circular fibers as a result of increased solution concentration, which gives less solvent composition. The circular fibers apparently have less MC in them as the viscosity increases. When they hit the surface, fibers are continuously elongated because they are not completely solidified. Fig. 4 shows a series of nanofibrous mats produced at 13 kV and the distance between tip and collecting drum, 13 cm, as a function of deposition time. Linear velocity of drum surface was fixed at 1.3 m/min, while the velocity of traverse was 3 m/min. SEM images of Fig. 4(a), (c) and (e) are corresponding to the electrospun nanofibrous mats with deposition time of 20, 60, and 120 min, respectively. SEM images of Fig. 4(b), (d) and (f) are of the same electrospun nanofibrous mats with the low magnification to show periodic surface roughness. Above the deposition time of 60 min, surface morphology of the nanofibrous mats was greatly changed. Some parts of nanofibrous mats exhibited the different morphology with relatively more fiber bundles and junctions indicating high fiber density. Diamond-shaped structure, with the major axis and the minor one, was shown at the deposition time of 60 min. The anisotropy structure that is not equal at a distance of axis is induced by difference of velocity between TD and MD. Based on the current results, through limitation will be remain from electrospinnability, other solvent can be introduced for the further study.

Fig. 5 shows schematic diagram for elucidating the formation of diamond-shaped structure. For the more detailed explanation, three methods can be introduced to understand this phenomenon. One is the chain mobility of PTT dissolved in MC/TFA and the second is bond-to-bond distances between fibers. Also, the third is related to the boiling point of both solvents. Formation of the part with higher fiber density depends on the amount of bonding element added and arrangement of fibers. As expected, increased deposition time results in increased bonding element. Bonding of the electrospun fibers within nanofibrous mat readily increase at the fiber intersections as the increasing bonding element. Therefore, bond-to-bond distance between fibers is closer as amount of bonding point increased. PTT electrospun fibers undergo larger deformation to accommodate the fiber rearrangement in the direction of the applied stress. From this result, axis distance of the diamond-shape structure can be controlled by varying the ratio of drum rotation velocity and traverse velocity. It is

well known that PTT has higher chain mobility than that of the other polyester family like polyethylene terephthalate (PET) and polybutylene terephthalate (PBT) [19]. Fig. 6 shows the SEM images of other polyester family for identifying peculiar structure originated from PTT nanofibrous mats. For the comparison, electrospinning conditions such as viscosity (450 cPs), solvent mixing ratio (TFA/MC = 50/50, v/v), tip-to-collector distance (13 cm), applied voltage (13 kV), and deposition time (60 min), were fixed. From the SEM result, surface morphology of PTT nanofibrous mats is different from the others at the same condition. This characteristic phenomenon might be inferred from higher chain mobility of PTT. Moreover, previous study has reported that polymer chain mobility is increased sufficiently as the solvent penetrates the amorphous phase of PTT [20]. When the voltage reaches up to critical value, the jet is initiated from the apex of the Taylor cone [21]. As the charged jet travels in air, most of solvent is evaporated. The fibers hit the surface on the rotating drum and solidify rapidly because of the low boiling point of MC and TFA. As the deposition time reach up to 60 min, the surface morphology of electrospun PTT nanofibrous mats is greatly changed. Fig. 5(a) shows simple point bonding structure at its initial stage. As the increase of the deposition time, higher fiber bundles and point bonding between the

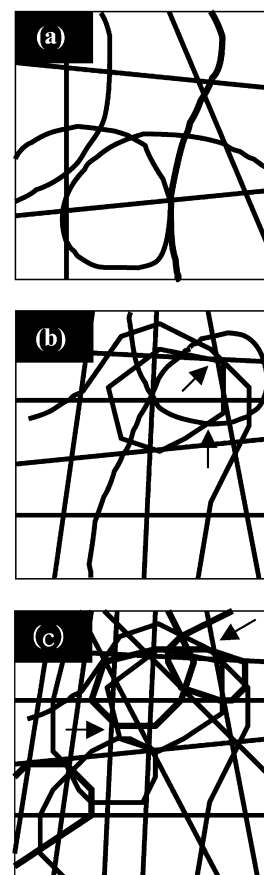
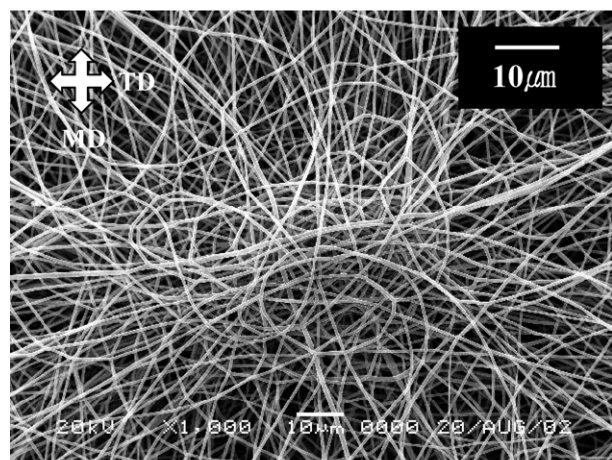
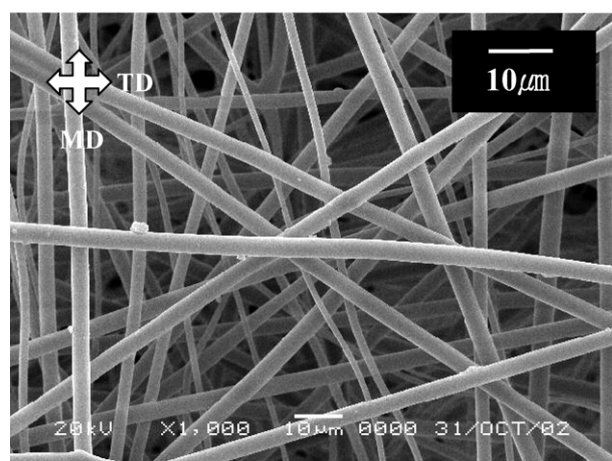


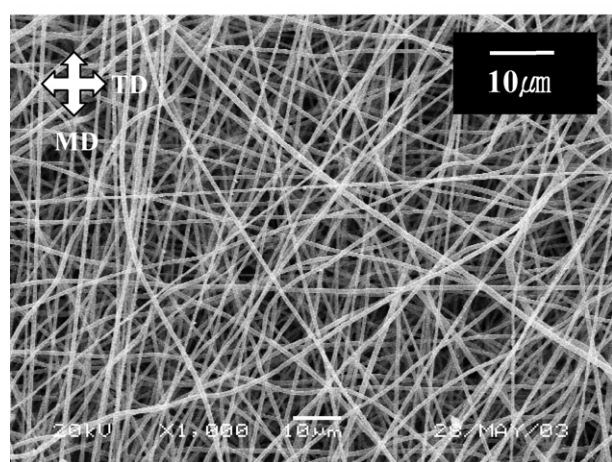
Fig. 5. Schematic diagrams for elucidating the formation of diamond-shaped structure as a function of deposition time.



(a)



(b)



(c)

Fig. 6. SEM images of other polyester family. (a) PTT (poly(trimethylene terephthalate)), (b) PET (poly(ethylene terephthalate)), and (c) PBT (poly(butylenes terephthalate)). For the purpose of comparison, electrospinning conditions such as viscosity (16 wt%), solvent mixing ratio (TFA/MC = 50/50, v/v), tip-to-collector distance (13 cm), applied voltage (13 kV), and deposition time (60 min), were fixed (MD, machine direction; TD, traverse direction).

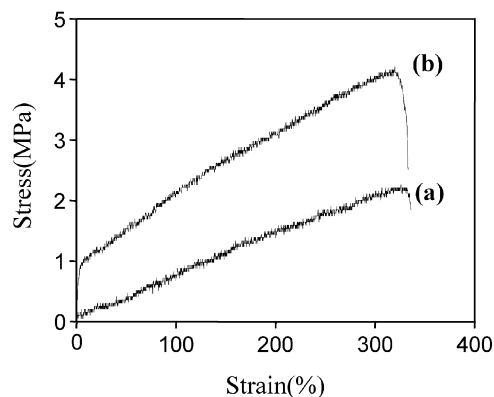


Fig. 7. Stress–strain curves of PTT nanofibrous mats obtained from the sample to (a) MD and (b) TD. This sample was prepared at 13 kV, the distance between tip and collecting drum of 13 cm, solution concentration of 16 wt% and deposition time of 120 min.

fibers are appeared as depicted in Fig. 5(b) (arrow means a bonding point). As the solvents are rapidly evaporated on the surface, point bonding is tightly formed between neighboring fibers. Lower bond-to-bond distances restrict freedom of fiber movement, which can only occur between the bond points. In some parts with higher fiber density on the nanofibrous mats plane, fiber does not extend outward from the center of fiber bundle and make open loop at the vicinity of fiber bundle (Fig. 5(c)). Contacts between loops increase with increasing the deposition time. Consequently, some parts with the higher fiber bundles and junction on electrospun PTT nanofibrous mats are exhibited the diamond-shaped structure as shown in Fig. 4.

Fig. 7 shows the stress–strain curves along the TD and MD for electrospun PTT nanofibrous mats. Previous work in our laboratory dealt with the difference of mechanical properties as the direction of TD and MD [22]. In general, electrospun fibers are distributed so randomly in all direction that electrospun nanofibrous mats have uniform structure. When the velocity of the traverse (TD) is different from that of the rotating collector (MD), differing stress–strain curves are observed. The exceptional morphology of electrospun PTT nanofibrous mats result in differentiating the tensile strength of two samples with different direction. Tensile strength in the TD was higher than that in the MD. Higher strength towards the TD compared to the MD shows the higher order of point bonding in the nanofibrous mat and fiber orientation toward the TD because these properties depend on the linear velocity of the collector drum.

#### 4. Conclusions

Electrospun nanofibrous mats of PTT were obtained and the morphology was effectively characterized. The circular fibers were formed as the solution viscosity increased. One of the most interesting resulted from the dependence of deposition time was that high fiber density arose from circular fiber junctions and bundles during electrospinning.

Surface morphology of the nanofibrous mats with deposition time of 60 min was greatly changed. Some parts of surface exhibit different morphology with relatively more fiber bundles and junctions indicating high fiber density. This phenomenon could be interpreted by chain mobility of PTT, bond-to-bond distance between fibers, and low boiling point of MC and TFA. The most interesting of this study was patterned electrospinning without the grounded template.

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