CHAPTER IV
MORPHOLOGICAL STUDY OF ELECTROSPUN POLYBENZOXAZINE BLENDED WITH POLY(ETHYLENE OXIDE)

4.1 Abstract

In this work, polybenzoxazine (PBZ) based electrospun nanofibers were fabricated with the help of poly(ethylene oxide) (PEO) by electrospinning technique. The influence of PEO on the electrospinnability of the BZ solution, the effects of spinning voltage and collecting distance from the tip to the target, on the morphological appearance and average diameter of the as-spun PBZ/PEO blended fibers were investigated. The FE-SEM micrograph showed that for a 6/4 weight ratio of BZ solution to PEO solution, the PEO can enhance the electrospinnability of the BZ solution. The spinning voltage and collecting distance of 4 kV and 25 cm were used, respectively. The diameter of electrospun PBZ/PEO blended fibers was in a range of 600 nm to 1 μm, with a generally uniform thickness along the fiber and high aspect ratio.

Keywords: Electrospinning; Polybenzoxazine; Poly(ethylene oxide); Nanofibers

4.2 Introduction

Electrospinning technology is the best candidate method to product continuous fibers with sub-micrometer diameters to nanometers from polymer solutions or melts in high electric fields because this technique has shown to be a simple but powerful technique and low cost for the fiber preparation. Due to the high surface area to volume of the fibers and the high density of pores on the sub-micrometer length scale of the obtained electrospun fibers, are of great interest for a wide range of applications such as high-performance adsorption, filtration, protective clothing and biomedical usage, tissue engineering and sensor application [1].

Heavy metals can cause serious environmental damage because they are very toxic and non-biodegradable and they release to water can affect human health. Thus, the removal of heavy metals from wastewater has become concern.

Previous study, polybenzoxazine, a new high performance thermosetting resin and a porous material, was investigated as a chelating polymer for wastewater treatment. During polymerization, benzoxazine undergoes thermally activated ring-opening polymerization to form a Mannich base bridge [2], which is known to form complexes with transition metal ions [3].

Increasing an aspect ratio by electrospinning can enhance the efficiency of polybenzoxazine as an adsorbent to remove heavy metals from waste organic solvent or water. However, electrospinning of polybenzoxazine is limited by its rigidity and brittleness. To overcome this limitation, poly(ethylene oxide) was added to adjust the solution viscosity [4]. Since poly(ethylene oxide) is soluble in dimethylformamide (DMF), it can be well mixed into as-synthesized benzoxazine precursor.

The purpose of this work is to prepare the polybenzoxazine/poly(ethylene oxide) blended fibers by using electrospinning technique to increase the surface area which will enhance the ability of polybenzoxazine to form complex with transition metal ions by optimizing the composition of poly(ethylene oxide) solution in polybenzoxazine solution and electrospinning process parameters such as the applied voltage, the distance between the tip of the needle and the target and the needle diameter.

4.3 Experimental

4.3.1 Materials

All chemicals were used without further purification. Bisphenol-A ($C_{15}H_{16}O_2$) was purchased from Aldrich, Germany. Formaldehyde solution (CH_2O) (37% by weight) was purchased from Merck, Germany. Triethylenetetramine (TETA, $C_6H_{18}N_4$) was purchased from Fluka, Switzerland. Dimethylformamide (DMF, C_3H_7NO) was purchased from Labscan, asia Co., Ltd., Thailand. Poly(ethylene oxide) (PEO, $C_{2n+2}H_{4n+6}O_{n+2}$) was purchased from Aldrich, Germany. Poly(ethylene oxide) was used without further.

4.3.2 Measurements

A Fourier Transform Infrared Spectroscope (FT-IR), Nicolet Nexus 670, was used to identify structural characteristics of benzoxazine precursor, poly(ethylene oxide) and polybenzoxazine/poly(ethylene oxide) blended fibers in absorption mode with 64 scans and a resolution of $\pm$ 4 cm^{-1} and wave numbers range of 4000-400 cm^{-1}. Optical grade KBr (Carlo Erba Reagent) was used as the background material. The morphology of polybenzoxazine/poly(ethylene oxide) blended fibers was investigated by using Field Emission Scanning Electron Microscope (FE-SEM), Hitachi S-4800, with an accelerating voltage of 2 kV. Samples were coated with platinum under vacuum before observation. The thermogravimetric analyzer (TGA), TGA Q50 was used to determine the thermal behavior of polymers. The experiments were carried out by weighting a powdered sample of 5-10 mg in a platinum pans, and then heated them under nitrogen flow with a heating rate 10°C/min from 30-800°C.

4.3.3 Methodology

4.3.3.1 Preparation of Benzoxazine Precursor

Benzoxazine precursor was prepared by using bisphenol-A, formaldehyde and triethylenetetramine with mole ratio of 1:4:1, respectively. The synthesis procedure included dissolving bisphenol-A (2.283 g) in dimethylformamide (20.964 g) in a glass bottle and stirred until the clear solution was obtained. Formaldehyde solution (3.243 g) was then added into the bisphenol-A

solution and stirred continuously for approximately 20 min while the temperature was kept under 10°C using an ice bath. After that triethylenetetramine (1.723 g) was added dropwise into the mixture and stirred continuously for approximately 15 min while the reaction was cooled with the ice bath until transparent yellow viscous liquid was obtained.

4.3.3.2 Preparation of Poly(ethylene oxide) Solution

Poly(ethylene oxide) solution was prepared by dissolving poly(ethylene oxide) (M.W. = 900,000) in DMF at a concentration of 5 %w/v and stirred continuously for approximately 3 hours while the temperature was kept under 50°C.

4.3.3.3 Preparation of Polybenzoxazine/Poly(ethylene oxide) Blended Fibers

The polybenzoxazine/poly(ethylene oxide) blended fibers were prepared by mixing benzoxazine precursor and poly(ethylene oxide) solution with various weight compositions; 100:0, 90:10, 80:20, 70:30 and 60:40 and stirred continuously for 15 min. Electrospinning was done at a voltage ranging from 4 to 8 kV, with distance between the tip of the needle and the grounded aluminium from 10 to 25 cm, and using needles with diameter varied from 0.8 and 0.5 mm.

4.3.3.4 Characterizations of Benzoxazine Precursor, Poly(ethylene oxide) Solution and Polybenzoxazine/Polyethylene Blended Fibers

Proton Nuclear magnetic Resonance (^{1}H NMR) was used to identify the chemical composition of benzoxazine precursor. The structural characteristics, the fiber morphology and the thermal stability of polybenzoxazine, poly(ethylene oxide) and polybenzoxazine/poly(ethylene oxide) blended fibers were investigated by using Fourier Transform Infrared Spectroscope (FT-IR), Field Emission Scanning Electron Microscopy (FE-SEM) and Thermogravimetric Analyzer (TGA).

4.4 Results and Discussion

4.4.1 Preparation of Benzoxazine Precursor

Benzoxazine precursor was prepared by using bisphenol-A, formaldehyde and triethylenetetramine with mole ratio of 1:4:1, respectively. The synthesis reaction of polybenzoxazine is shown in Figure 4.1.

Figure 4.1 Synthesis of benzoxzine precursor.

4.4.2 Preparation of Poly(ethylene oxide)

Poly(ethylene oxide) solution was prepared by using dimethylformamide as a solvent at a concentration of 5 %w/v. Figure 4.2 depicts the chemical structure of poly(ethylene oxide).

Figure 4.2 The chemical structure of poly(ethylene oxide).

4.4.3 Preparation and Characterizations of Polybenzoxazine/Poly(ethylene oxide) Blended Fibers

4.4.3.1 Effect of Weight Compositions of Benzoxazine Solution and Poly(ethylene oxide) Solution on the Morphology of Polybenzoxazine/Poly(ethylene oxide) Blended Fibers

In order to find the appropriate weight composition, the applied voltage was varied. It was found that 5 kV was the suitable voltage in which smooth electrospun fibers were obtained. FE-SEM was used to investigate the morphology of electrospun polybenzoxazine/poly(ethylene oxide) blended fibers, which prepared by applying a voltage of 5 kV, at the distance between the tip of the needle and the target of 20 cm, using a needle diameter of 0.8 mm. The composition of benzoxazine precursor to poly(ethylene oxide) solution was varied as follows; 100:0, 90:10, 80:20, 70:30 and 60:40 (Figure 4.3).
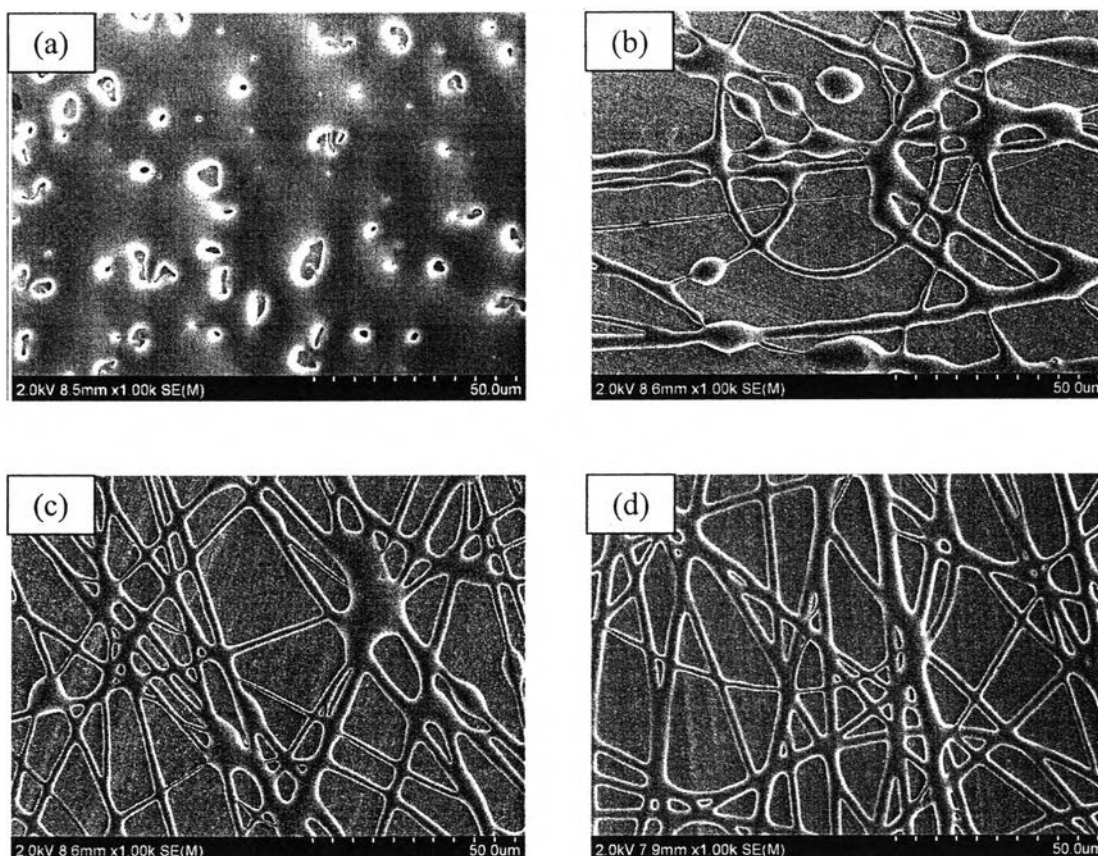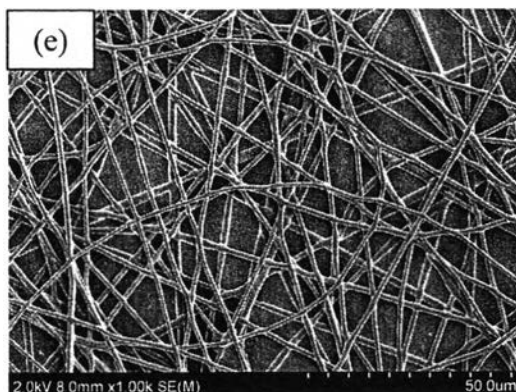
Figure 4.3 FE-SEM micrographs of polybenzoxazine/poly(ethylene oxide) blended fibers with the applied voltage 5 kV and the distance between the tip of the needle and the target of 20 cm with various weight compositions of benzoxazine precursor to poly(ethylene oxide) solution (a) 100:0, (b) 90:10, (c) 80:20, (d) 70:30 and (e) 60:40; 1000x.

Benzoxazine precursor cannot be electrospun (Figure 4.3 (a)), as the viscosity and surface tension of the solution were not high enough to maintain a stable drop at the end of the capillary tip. Moreover, benzoxaxine molecules contains aromatic structure and can form H-bonding with neighboring molecules, causing benzoxazine precursor to have significant rigidity which makes it difficult to spin. However, the electrospinnability of polybenzoxazine can be greatly improved with the addition of poly(ethylene oxide) to improve chain flexibility of polybenzoxazine. In this study, poly(ethylene oxide) (M_w = 900,000) at a concentration of 5% w/v in dimethylformamide, which was the lowest concentration that can help benzoxazine precursor to formed fibers, was used. At the weight compositions of benzoxazine precursor to poly(ethylene oxide) solution equaled to 90:10, 80:20 and 70:30, some beads were obtained. However, it can be seen that increasing poly(ethylene oxide) leads to reduction of the number of bead defects because the chain entanglement in poly(ethylene oxide) disrupted H-bonding in benzoxazine molecules. In addition, blending of benzoxazine precursor with poly(ethylene oxide) also decrease the diameter of electrospun fibers since benzoxazine molecules became less aggregate and were aligned due to electrostatic

force. We found that the weight composition of 60% benzoxazine precursor to 40% poly(ethylene oxide) solution was the best composition that gave the smooth fibers (Figure 4.3 (e)). Furthermore, blending of benzoxazine with poly(ethylene oxide) not only affected the electrospinnability of benzoxazine precursor but also the diameter of electrospun fibers.
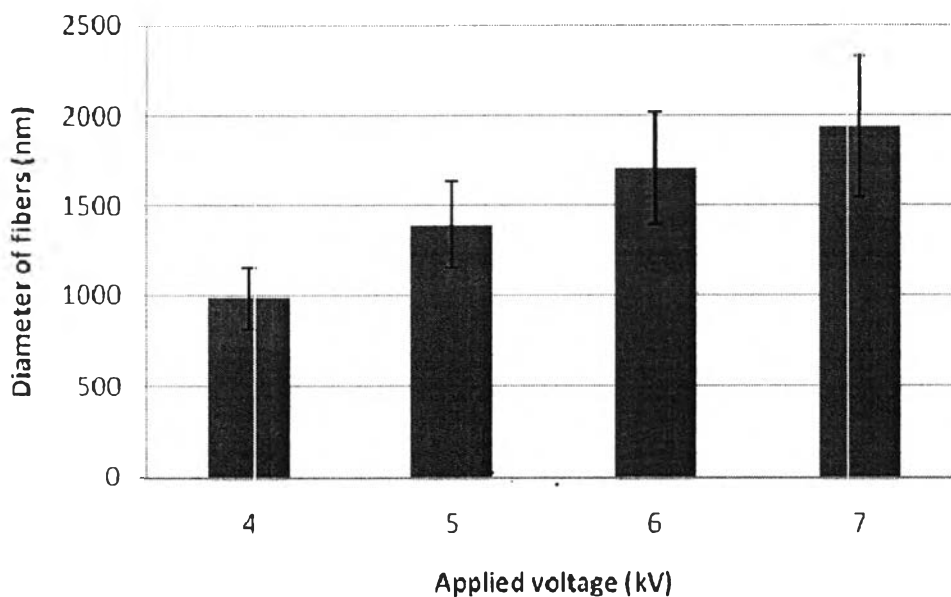
4.4.3.2 Effect of the Applied Voltage on Morphology of Polybenzoxazine/Poly(ethylene oxide) Blended Fibers

After the proper weight composition was clarified, the effect of the applied voltage was investigated by varying the applied voltages from 4 kV to 7 kV and fixed the distance between the tip of the needle and the target at 20 cm, using the needle with a diameter of 8 mm. The fiber morphology of the polybenzoxazine/poly(ethylene oxide) blended fibers was again examined using FE-SEM as shown in Figure 4.4. With increasing of the applied voltage, the average diameter of polybenzoxazine/poly(ethylene oxide) blended fibers was slightly increased (Figure 4.4 and 4.5) and the fibers were rougher and flatter, implying that lower spinning voltage was good to obtain thinner polybenzoxazine/poly(ethylene oxide) blended fibers, especially the electrospun fibers at 4 kV showed the smallest diameter. The increasing spinning voltage not only elongated the jet to create smaller diameter fibers, but also drawn more solution out of the capillary which resulted in the increase of the fiber diameter [5]. If the applied voltage is higher, the greater amount of charges cause the jet to accelerate faster and more volume of solution would be drawn from the tip of the needle, resulting in a smaller and less stable Taylor Cone [6], yielding fibers with larger diameter.
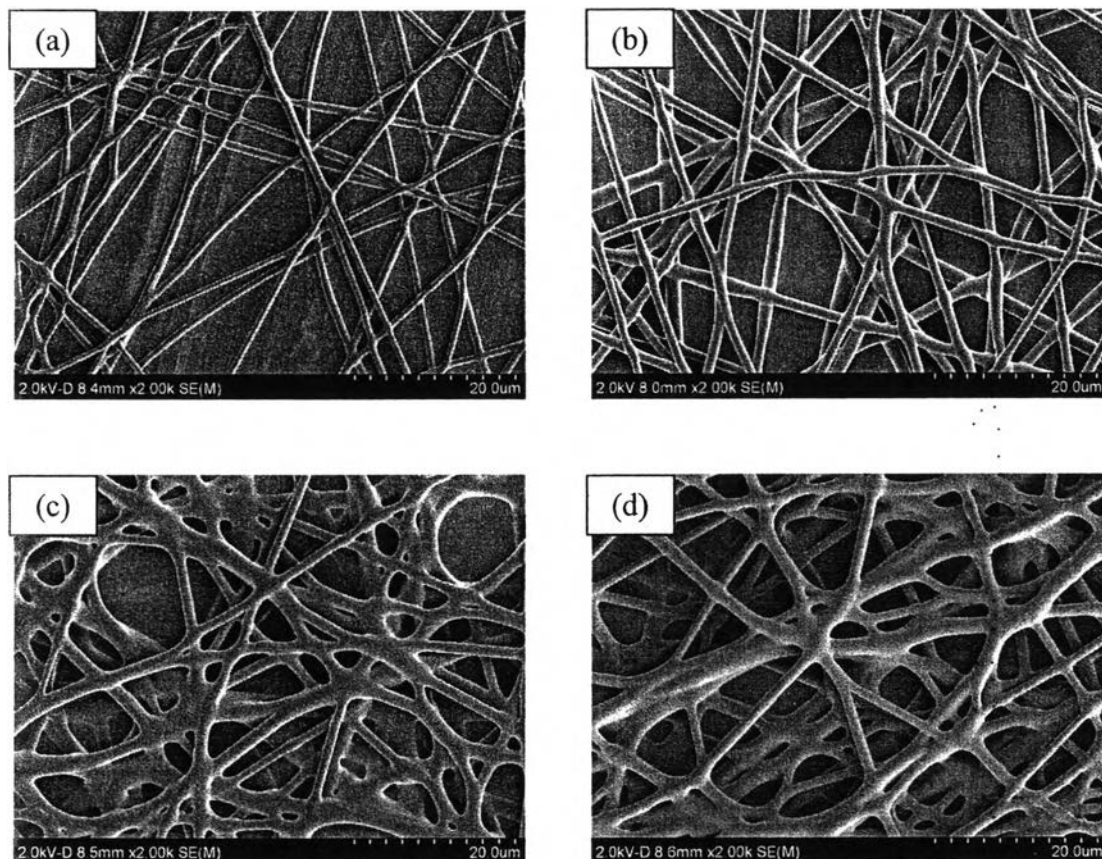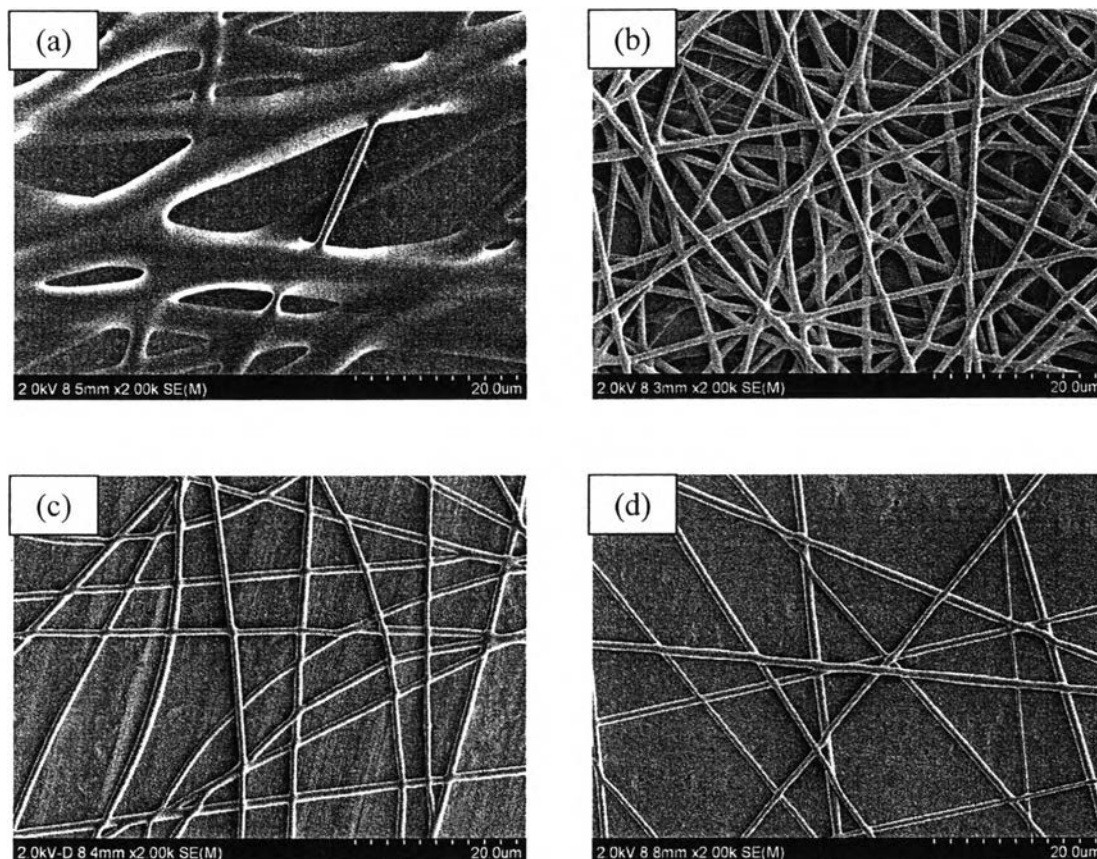
Figure 4.4 FE-SEM micrographs of polybenzoxazine/poly(ethylene oxide) (60:40) blended fibers with the distance between the tip of the needle and the target of 20 cm and the applied voltage at (a) 4 kV, (b) 5 kV, (c) 6 kV and (d) 7 kV; 1000x.

Figure 4.5 Diagram of fiber diameter of polybenzoxazine solution/poly(ethylene oxide) solution (60:40) blended fibers with the distance between the tip of the needle and the target of 20 cm and the applied voltage at 4 kV, 5 kV, 6 kV and 7 kV.

4.4.3.3 Effect of the Collecting Distance on Morphology of
Polybenzoxazine/Poly(ethylene oxide) Blended Fibers

On the other hand, electrospinning was carried out with the weight composition of polybenzoxazine solution to poly(ethylene oxide) solution as 60:40 and varying the distances from 10 to 20 cm by maintaining the applied voltage and the needle diameter of 4 kV and 0.8 mm, respectively. The SEM micrographs of the resulting fibers are shown in Figure 4.6.
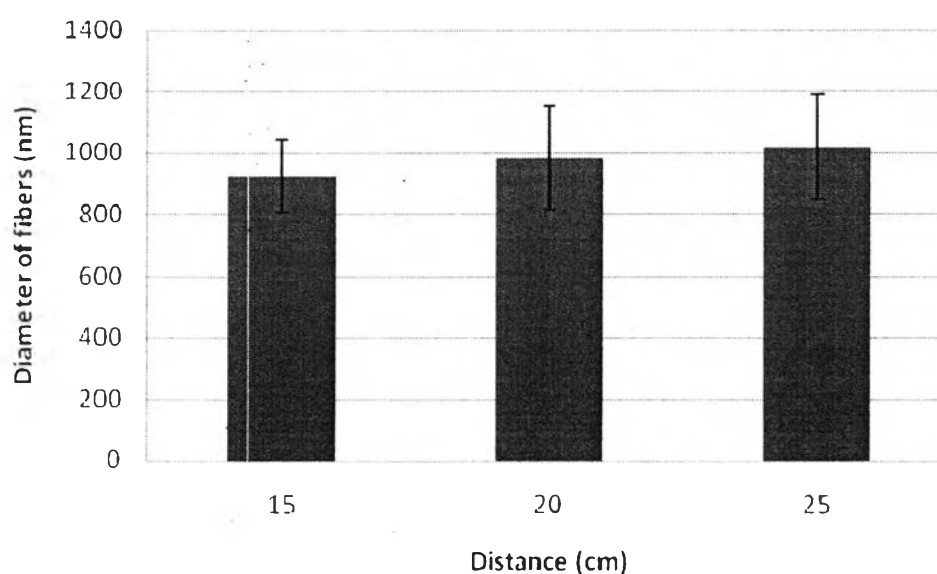
Figure 4.6 FE-SEM micrographs of polybenzoxazine solution/poly(ethylene oxide) solution (60:40) blended fibers with the applied voltage of 4 kV and the distance between the tip of the needle and the target at (a) 10 cm, (b) 15cm, (c) 20 cm and (d) 25 cm; 2000x.

Hence, the distance between the tip of the needle and the target was also a major factor in determining the time available for fiber drying and the space available for spraying and whipping of fibers to take place. The flat fused fibers were obtained at the collecting distance of 10 cm because this distance was so short, causing incomplete solvent evaporation before reaching the target. The remaining solvent would make the fibers re-dissolve and fibers tended to stick to the collecting device as well as to each other [1],[5].

The average diameter was dramatically decreased and ultrafine fibers were obtained with increasing the distance between the tip of the needle and the target from 10 cm to 15 cm. The average diameter of

polybenzoxazine/poly(ethylene oxide) blended fibers with increasing the distance between the tip of the needle and the target from 15 to 25 cm exhibited no significant effect on the fiber as shown in Figure 4.7. In 2000, Reneker *et al.* [7] pointed out that a charged jet traveled in a liner trajectory for a short distance before undergoing a bending instability, which finally caused the formation of the looping trajectory of the jet and this was assumed to be the main reason for the obtained smaller diameter fibers.
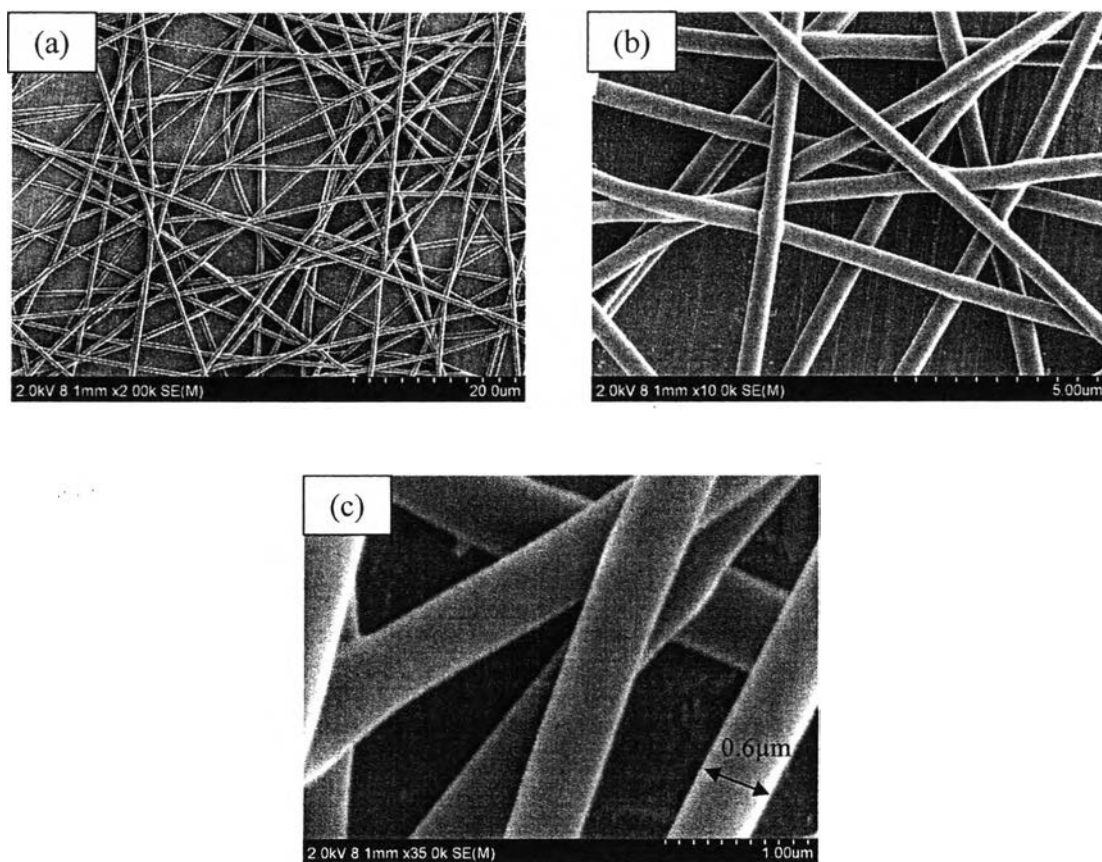

Figure 4.7 Diagram of fiber diameter of polybenzoxazine solution/poly(ethylene oxide) solution (60:40) blended fibers with the applied voltage of 4 kV and the distance between the tip of the needle and the target at 15cm, 20 cm and 25 cm.

4.4.3.4 Effect of the Needle Diameter on Morphology of
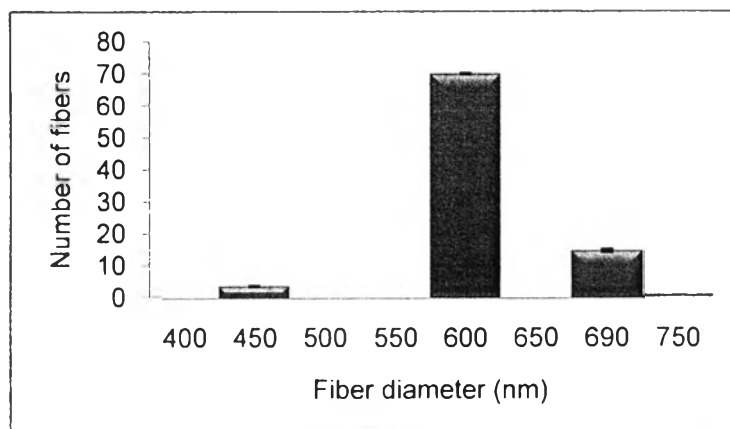
Polybenzoxazine/Poly(ethylene oxide) Blended Fibers

Due to the diameter of polybenzoxazine/poly(ethylene oxide) blended fibers with the distance between the tip of the needle and the target of 20 and 25 cm were not significantly changed, the effect of the diameter of the needle to the fiber diameter was investigated.

The FE-SEM micrographs (Figure 4.7) show that decreasing the needle diameter from 0.8 mm to 0.5 mm reduced the fiber diameter and obtaining uniform fibers. This can be explained that with a larger needle diameter, there was a larger amount of polymer present at the cross sectional tip of the needle and the diameter of the polymer jet coming out of the needle would have been larger for a larger needle size. This agreed with Mo *et al.* [8] who found that a smaller internal diameter reduced clogging as well as the number of beads on the surface of the fiber, resulting in smooth fibers with smaller diameters.

Figure 4.8 FE-SEM micrographs of polybenzoxazine solution/poly(ethylene oxide) solution (60:40) blended fibers, the applied voltage of 4 kV and the distance between the tip of the needle and the target at 20 cm and the needle diameter of 0.5 mm with a magnification of (a) 2000, (b) 10,000 and (c) 35,000.

Figure 4.9 Diameter distributions of polybenzoxazine/poly(ethylene oxide) blended fibers.

From the statistical analysis of 100 fibers, the fiber diameter was found to be in the range of 450-750 nm and the average fiber diameter was 600 nm, corresponding with FE-SEM micrographs shown in figure 4.8.

4.4.4   Characterization of Benzoxazine Precursor, Poly(ethylene oxide), and Polybenzoxazine/Polyethylene Blended Fibers

*4.4.4.1 Proton Nuclear Magnetic Resonance (^1H NMR)*

The ^{1}H NMR measurement was conducted to confirm the synthesis of benzoxazine precursor (Figure 4.10). The characteristic peaks assigned to the methylene protons of (O–CH$_2$–N) and (Ar–CH$_2$–N) of oxazine ring were observed at around 4.82 and 3.94 ppm, respectively. The methyl protons of bisphenol-A were observed at 1.55 ppm. The protons of aliphatic diamine (TETA) showed the peaks around 2.86 ppm [9].
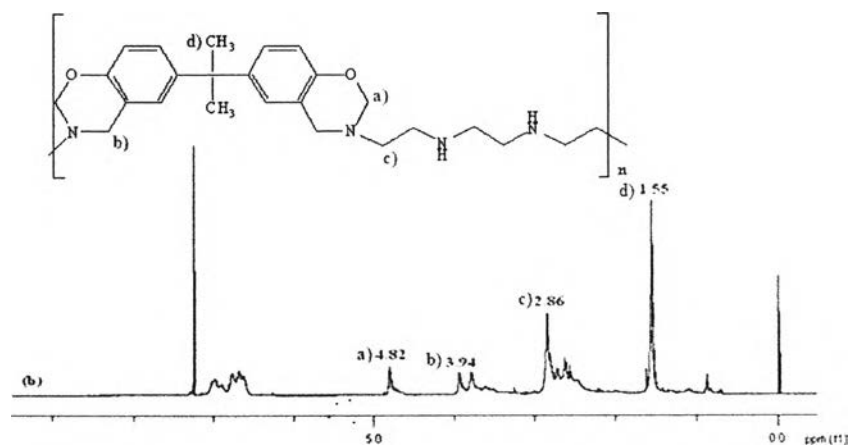
Figure 4.10 ^{1}H NMR spectrum of benzoxazine precursor.

4.4.4.2 Fourier Transform Infrared Spectroscope (FT-IR)

Benzoxazine · precursor, poly(ethylene oxide), and polybenzoxazine solution/poly(ethylene oxide) (60:40) blended fibers were characterized by using FT-IR to examine the functional groups. The spectra are shown in Figure 4.11(a) –(c).
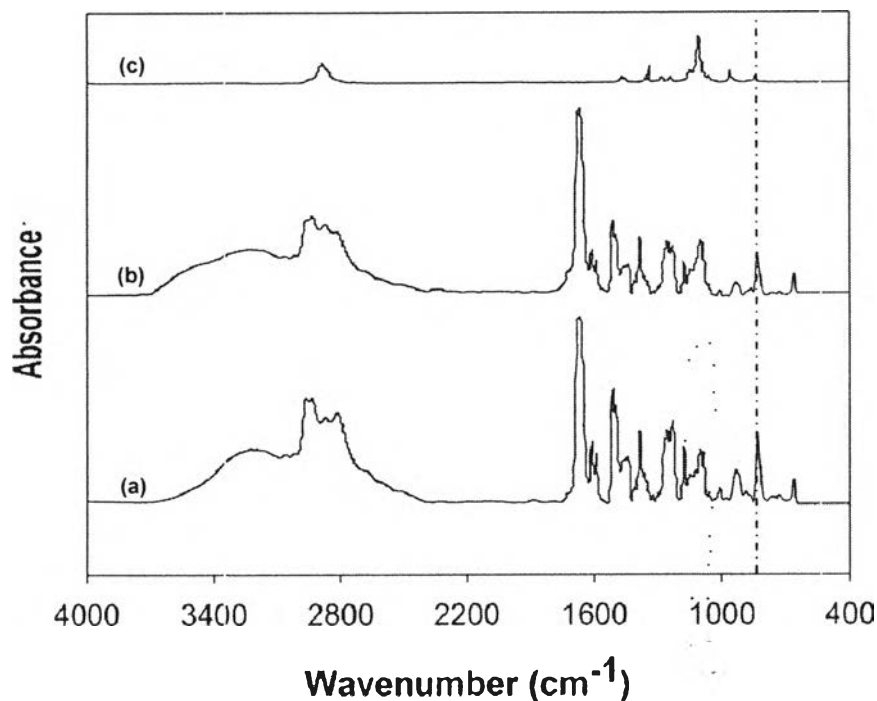
Figure 4.11 FT-IR spectrum of (a) benzoxazine precursor, (b) poly benzoxazine/poly(ethylene oxide) (60:40) blended fibers and (c) poly(ethylene oxide).

The FT-IR spectrum of benzoxazine precursor (Figure 4.11 (a)) show the asymmetric stretching band of C–N–C at 1177 cm^{-1}. The absorption band at 1231 cm^{-1} and 1386 cm^{-1} indicated asymmetric stretching of C–O–C of oxazine and CH_2 wagging of oxazine, respectively. The peaks at 1513 cm^{-1} assigned to stretching tri-substituted benzene ring and the out of plane bending vibrations of C–H was observed at 934 cm^{-1}. According to Takeichi *et al.* [10], it was confirmed that precursor containing benzoxazine structure in the backbone was obtained.

Furthermore, the characteristic peaks for pure poly(ethylene oxide) precursor was identified at 2889, 1106 and 936 cm^{-1}. The absorption peak at 2889 cm^{-1} can be attributed to the molecular stretching of methylene group (CH_2) while peaks at 1106 and 936 cm^{-1} were due to the stretching of C–O–C group in poly(ethylene oxide) [11].

The Infrared absorption spectrum of poly benzoxazine/poly(ethylene oxide) blended fibers indicated that electrospun fibers were composed of both polybenzoxazine and poly(ethylene oxide). Moreover, the intensity of the out-of-plane bending vibrations of C–H at 934 cm^{-1} was decreased significantly, implying that the cured polybenzoxazine/poly(ethylene oxide) blended fibers were obtained. This FT-IR result agrees with the study of Dunkers *et al.* [12], suggesting a change of the characteristic absorption due to the ring-opening polymerization of the benzoxazine.

4.4.4.3 Thermogravimetric Analyzer (TGA)

The thermal stability of polybenzoxazine/poly(ethylene oxide) blended fibers was investigated by TGA, and the result is shown in Figure 4.12.
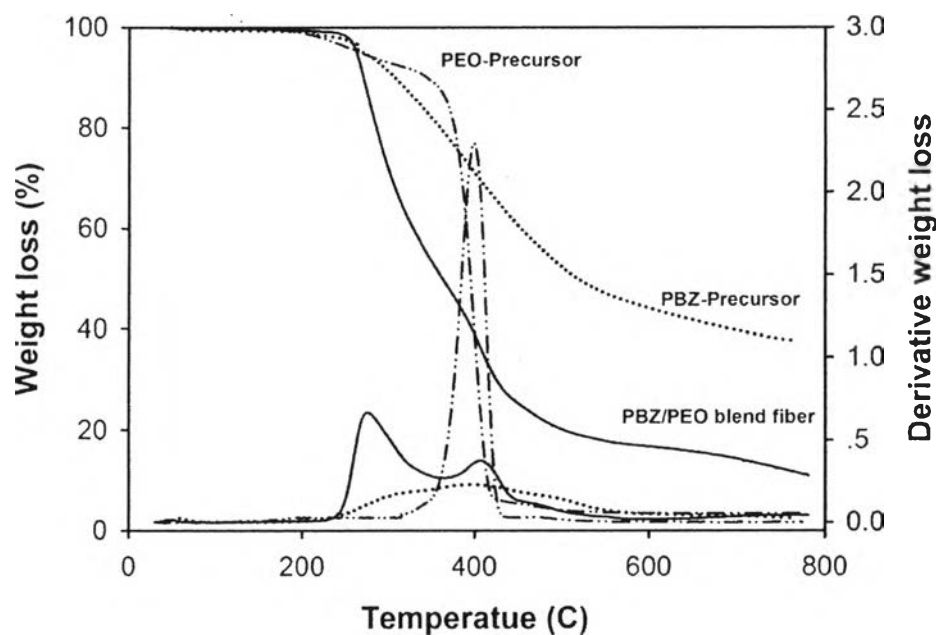
Figure 4.12 TGA of polybenzoxazine/poly(ethylene oxide) blended fibers.

The TGA thermogram of polybenzoxazine, poly(ethylene oxide) and polybenzoxazine/poly(ethylene oxide) blended fibers are presented in Figure 4.12. Polybenzoxazine started to degrade after 270°C. The significant weight loss was observed between 270°C and 600°C. The char residue of 37% was found at 800°C. This result agrees with that of Chaisuwan *et al.* [3], in which the thermal stability of the partially-cured polybenzoxazine precursor started to lose weight at 250°C and the maximum weight loss was observed at between 250°C and 600°C. Hemvichian *et al.* [13] identified the decomposition of polybenzoxazines through TGA and GC–MS techniques and found that the decomposition products were a combination of benzene derivatives, amines, phenolic compounds, and Mannich base compounds.

The T_d at 5 % weight loss and the char yield are summarized in Table 4.1.The T_d at 5 % weight loss of polybenzoxazine is higher than that of aliphatic poly(ethylene oxide) due to the aromatic structure of polybenzoxazine.

Table 4.1 Thermal properties of polybenzoxazine, poly(ethylene oxide) and Polynenzoxazine/Poly(ethylene oxide) blended fibers

Material	$T_{d5\%}$(°C)	Char yield(%)[a]
Poly(ethylene oxide)	266	3
Polybenzoxazine	270	37
Polynenzoxazine/Poly(ethylene oxide) blend fibers	262	11

[a] At 800°C.

4.5 Conclusions

Polybenzoxazine blended with poly(ethylene oxide) was successfully fabricated in nanoscale by using electrospinning technique. The weight composition of 60% benzoxazine precursor to 40% poly(ethylene oxide) solution was the best composition for the fabrication of polybenzoxazine/poly(ethylene oxide) blended fibers, using the applied voltage of 4 kV, the distance between the tip and the target at 20 cm, and the needle diameter of 0.5 mm. The diameter of polybenzoxazine/poly(ethylene oxide) blended fibers was in the range of 600-1000 nm.

4.6 Acknowledgements

4.7 References

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