Preparation of Novel partially Bio-Based Thermoplastic Polyurethane /Polyacrylonitrile Electrospun Fiber Mats

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Abstract. The partially bio-based thermoplastic polyurethane/polyacrylonitrile electrospun fiber mats at various weight ratio was fabricated via electrospinning technique. A partially bio-based thermoplastic polyurethane was prepared from caprolactone diol and partially bio-based diisocyanate at a mole ratio of 2.1:1. Ethylene glycol was used as a chain extender. Three major effects i.e. solution concentration, distance from tip to collector and applied voltage on morphology of the obtained electrospun fiber mats were systematically investigated using a scanning electron microscope. The design of experiment, namely, Taguchi method was also applied. The morphology of the prepared electrospun fiber mats revealed continuous and smooth fibers without the formation of beads. The fiber diameters of the thermoplastic bio-based polyurethane/polyacrylonitrile were in micron size ranging from 0.2 to 1.4 µm. Moreover, the results showed that with the decrease of concentration, the fiber diameter decreased where the changes of applied voltage and distance from tip to collector resulted in negligible changes in fiber diameter. The findings can be further applied as processing conditions to meet properties requirements for the high-performance separator application.

1. Introduction

Electrospinning is a technique of producing polymer fibers using electrostatic forces. The fibers obtained from this process have higher surface area, lightweight and higher porosity than fibers obtained from other processes [1]. Electrospinning equipment consists of a high voltage direct current power supply, a collector, and a syringe pump. The production of fibers through electrospinning process begins with the electric potential of the solution at the tip of the syringe, which accumulates enough charge to cause the polymer solution to spill out into the collector. The variables that affect the diameter of fiber are electric potential, distance between the tip of the syringe and collector, flow rate, and solution concentration. Polyacrylonitrile (PAN) is widely used due to its excellent spin-ability, and good thermal stability. However, it possesses poor mechanical properties [2]. Therefore, the blending of PAN/high flexible thermoplastic polyurethane (TPU) can help improve their mechanical properties. Moreover, TPU also provides superior physical performance, and chemical resistance. Due to the environmental concern of using petroleum-based polymer, partially bio-based thermoplastic polyurethane (PBPU) is synthesized in this research. The electrospun fiber mats of PAN/PBPU was prepared by electrospinning...
2. Experiment

2.1. Materials

Partially bio based diisocyanate (PBDI) (Tolonate TM X FLO 100) was provided by Vencorex Chemical, France. Polyacrylonitrile (PAN), Polycaprolactone 2000 diol (PCL), Ethylene glycol (EG), Dimethylformamide (DMF) and Dibutyltin dilaurate (DBTDL) were all from Sigma Aldrich.

2.2 Synthesis Method of PBPU

The synthesis of PBPU was carried out using partially bio-based diisocyanate (PBDI), caprolactone diol having MW of 2000 and ethylene glycol (EG) at a mole ratio of 2.1:1:1, respectively. The prepolymerization of PBDI and caprolactone diol was prepared at a temperature of 70°C for 4 h under dry nitrogen atmosphere. EG was then added and continually reacted for 4 days. The obtained product was purified and dried at a temperature of 70 °C for 24 h under vacuum and stored in a desiccator.

2.3 Preparation of PAN/PBPU Fibers

The PAN and PBPU were mixed at 75:25 by weight, and dissolved in dimethylformamide (DMF) for 2 h to obtain final concentrations of 8, 10, 12 and 14 wt%. The mixture was transferred to a syringe and conducted to a syringe pump at a controlled flow rate of 0.5 ml/h and applied high voltage of 19, 21, 23 and 25 kV. The tip to collector distance was in the range of 16, 18, 20 and 22 cm. The electrospinning condition was controlled at a temperature of 25 ºC and 38 % humidity. The electrospinning set up is shown in Fig 1.

2.4 Characterizations

The microscopic morphology and fiber diameter of the PAN/PBPU were investigated by a scanning electron microscope (SEM, SU3500, Hitachi Ltd.). The average fiber diameter of 100 counts was determined using ImageJ Software.

2.5 Taguchi Experimental Design & Grey Relational Analysis

In this study, the three factors i.e., concentration, tip to collector distance, and voltage with four levels are used to study the fiber diameter of PAN/PBPU fiber mats. The parameters and their variation levels are shown in Table 1. To investigate the optimum design of factors and levels, the signal to noise (S/N) ratio is used. The signal is the desirable of output characteristics where the noise represents the undesirable output characteristics. The noise represents the undesirable output characteristics. There are three categories of S/N ratio i.e. (1) nominal is better, (2) smaller is better and (3) larger is better [3]. The smaller better type quality characteristic provides the better performance in the diameter of fiber mats. Therefore, the “smaller is better” was selected for the optimization of parameters in this study.

Figure 1 Set up equipment of electrospinning [1].
Table 1. Parameters levels of three factors.

| Sample no. | Concentration (wt%) | Applied voltage (kV) | Tip to collector distance (cm) |
|------------|---------------------|----------------------|-------------------------------|
| 1          | 8                   | 19                   | 16                            |
| 2          | 8                   | 21                   | 18                            |
| 3          | 8                   | 23                   | 20                            |
| 4          | 8                   | 25                   | 22                            |
| 5          | 10                  | 19                   | 18                            |
| 6          | 10                  | 21                   | 16                            |
| 7          | 10                  | 23                   | 22                            |
| 8          | 10                  | 25                   | 20                            |
| 9          | 12                  | 19                   | 20                            |
| 10         | 12                  | 21                   | 22                            |
| 11         | 12                  | 23                   | 16                            |
| 12         | 12                  | 25                   | 18                            |
| 13         | 14                  | 19                   | 22                            |
| 14         | 14                  | 21                   | 20                            |
| 15         | 14                  | 23                   | 18                            |
| 16         | 14                  | 25                   | 16                            |

3. Results and Discussion

The three parameters and four levels were chosen on behalf of visual identification of jet stability, no droplet formation and no mats surface breakage. The diameter and S/N ratio of PAN/PBPU fiber were plotted for each factor and their levels as shown in Figures 2. The diameter values of PAN/PBPU fiber were in the range of 0.26 to 1.4 µm. The diameter of fibers increased with increasing polymer concentration. It is due to lower extension of the jet at higher concentration and viscosity. The result is corresponded to that reported by Sadrjahani et al [4]. The fiber diameters decreased with the increase in the tip to collector distance and applied voltage. It is due to the stretching of the polymer solution in correlation with the charge repulsion within the polymer jet. The behavior was also observed by Karakas et al [5]. Optimal factors and levels providing smallest diameter of 0.26 µm was at the concentration of 8 wt%, the applied voltage of 25 kV and the tip to collector distance of 22 cm. The higher S/N ratio response value at each level implied that the effect of contributing factor was more significate to decrease the diameter of PAN/PBPU fiber. It was clearly seen that solution concentration was a major contributing factor which affected a reduction of the diameter. The applied voltage and tip to collector distance affected the diameter slightly probably because the conditions are too close, making it impossible to distinguish the impact.

Figure 2 Effect of factors on diameter: (circle) diameter value and (square) S/N ratio.
The representative SEM micrographs with insets of fiber diameter distribution of PAN/PBPU electrospun fiber mats show randomly continuous oriented fibers with bead free smooth surface fibers. The diameter of the fibers produced at concentrations of concentrations 8, 10, 12 and 14 wt% were 0.27±0.043, 0.42±0.048, 0.58±0.044 and 1.4±0.046 μm respectively, showing a significant increase in diameter as the concentration increased. (in Figure 3)

![Figure 3](image)

**Figure 3** Representative SEM images of the fibers at a) 8wt% b) 10wt% c)12wt%, and d)14wt% concentration with a 21kV applied voltage.

4. Conclusions
In this study, PAN/PBPU electrospun fiber mats at 75:25 by weight were prepared. Effects of solution concentration, applied voltage and distance from tip to collector on morphology the electrospun fiber mats were investigated. The experiment was designed and optimized based on Taguchi method coupled with Grey relational analysis. It was found that all obtained fiber mats illustrated smooth and continuous fiber without any bead formation. Moreover, the results showed that with decrease of concentration, the fiber diameter decreased where the increase of applied voltage and distance from tip to collector resulted in no significant change in fiber diameter. The processing condition which provides the smallest fiber diameter of 0.26 μm was at the concentration of 8 wt%, the applied voltage of 25 kV and the distance from tip to collector of 22 cm.

Acknowledgements
This work is financially supported by Chulalongkorn University:CU_GR_63_51_62_01. The Energy Policy and Planning Office, Ministry of Energy is also acknowledged. Bio-based isocyanate is supported by Vencorex (Thailand) Company Ltd.

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