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Electrospun Conditions of Poly(vinyl chloride) Nanofibrous Membrane Plasticized with Polyurethane

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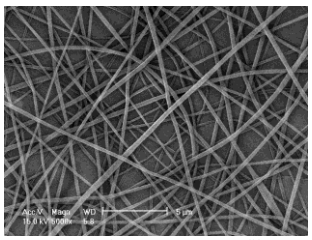
Graphical abstract



PVC-PU electrospun nanofiber

Abstract

Electrospun poly(vinyl chloride) (PVC) nanofibrous were prepared by electrospinning. Various concentration of polyurethane (PU) were added to PVC solution for plasticization of the electrospun nanofibrous. The pristine and plasticized nanofibrous were characterized by field emission scanning electron microscopy (FE-SEM), differencial thermal analysis (DTA), and thermogravimetry analysis (TGA), respectively. Thermal properties form DTA and TGA results indicated that the addition of PU decreased glass transition temperature (Tg) of PVC and increased heat resistance of PVC nanofiber. The dielectric constant of plasticized nanofibrous measured using precision LCR meter indicated that the membrane were dense.

Keywords: Electrospinning; poly(vinyl chloride); polyurethane; membrane

1.0 INTRODUCTION

Thermoplastic elastomers are of the most widely used materials in the plastic industry. This class of polymer is explained to a variety of materials that have elastomeric properties at ambient temperatures and prevent the need for the vulcanization step to develop typical rubberlike elasticity. Thermoplastic elastomers are primary stage to replace specialty rubbers in a wide variety of applications [1].

Polyurethane (PU) is formed by reacting an isocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain on average two or more functional groups per molecule. While most polyurethanes are thermosetting polymers that do not melt when heated. Polyurethane has the flexibility and strength of rubber and the the hardness of plastic, Many commercially available PU can be used to make good electrospinning solutions [2]. Poly(vinyl chloride) (PVC) is an important commercial polymer. PVC is hard, stiff material, although, mechanical properties, notably the flexibility, can be extensively modified with plasticization [1]. Important disadvantage in the manufacture and use of PVC is its low thermal stability. At high temperatures well below its decomposition temperature, PVC loses hydrogen chloride and becomes mottled. Because these changes are accompanied by deterioration on some of the useful properties of the polymer.

Unlike conventional fiber spinning techniques (wet spinning, dry spinning, melt spinning, gel spinning), which are capable of producing polymer fibers with diameters down to the micrometer range, electrostatic spinning, or electrospinning is a process capable of producing polymer fibers in the nanometer diameter range [3]. Electrospinning is the process in which a polymer solution is ejection from a syringe that has a directly attached to a high power supply. This power source generates a high voltage difference, usually selected between 5–30 kV, which support the ejection of a liquid or split, resulting in smaller diameter fibers. Therefore, by controlling the electrospinning parameters, optimal nanofibers can be prepared.

In this research, the effects of electrospinning condition including electric voltage, tip-to-collector distance and polymer solution concentration were studied on the morphological and physical properties of PU/PVC nanofibrous.

2.0 EXPERIMENTAL

2.1 Polymer Preparations

Polyvinyl chloride (PVC) with *K*-value of 580 was kindly supplied by Thai Plastic and Chemicals Co., Ltd. The solvent *N, N*-dimethylformamide (DMF) and tetrahydrofuran (THF) were used as received. PVC was dissolved in a mixed solvent of DMF/THF (at weight ratio 5:5) by varying the PVC concentration for 10% and 15% by weight at 50°C. Polyurethane (PU) (Dow Chemical Co., Ltd.) was dissolved in the same solvent mixtures as PVC solution. The PU solution concentration at 10% by weight. The PU solution was directly mixed with PVC solution at room temperature.

2.2 The Electrospinning Process

Electrospinning is easily realised by applying a high voltage to a capillary filled with the polymer fluid to be spun with help of an electrode. The resulting fibers are collected on a grounded plate, which can be covered with a fabric for example. A diagram of the electrospinning process is shown in Figure 1.

The nanofibrous membranes were prepared by eS-robot electrospinning capable of generating voltages up to 30 kV at room temperature. Electrospinning was performed at a flow rate of 0.5 mL/h with applied voltage between 12 and 15 kV. The distance between the syringe tip and collector plate was varied from 12 to 18 cm. The nanofibrous was then deposited on the collector plate and formed thin film with thickness around 0.1 mm.

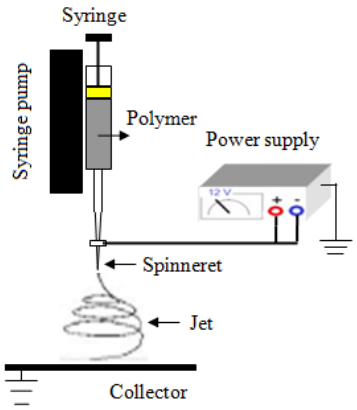


Figure 1 Experimental setup for the electrospinning process

2.3 Characterization

2.3.1 Scanning Electron Microscopy

The membrane was carbon sputtered using a Joel JFC-1100 fine coater before studied the surface morphology using a Philips XL30 field emission scanning electron microscope (FESEM, Japan).

2.3.2 Thermal Properties

The thermal properties of membranes were performed using differential thermal analysis (DTA) (TA Instruments Q200, USA) under nitrogen gas with a flow rate of 50 ml/min. The samples were put in alumina pans and were heated from -90°C to 350°C with heating rate of 20°C/min. and thermal stability was studied by using a thermogravimetric analyzer (TGA) (TA Instruments Q600, USA) under nitrogen atmosphere at a heating rate of 20°C/min.

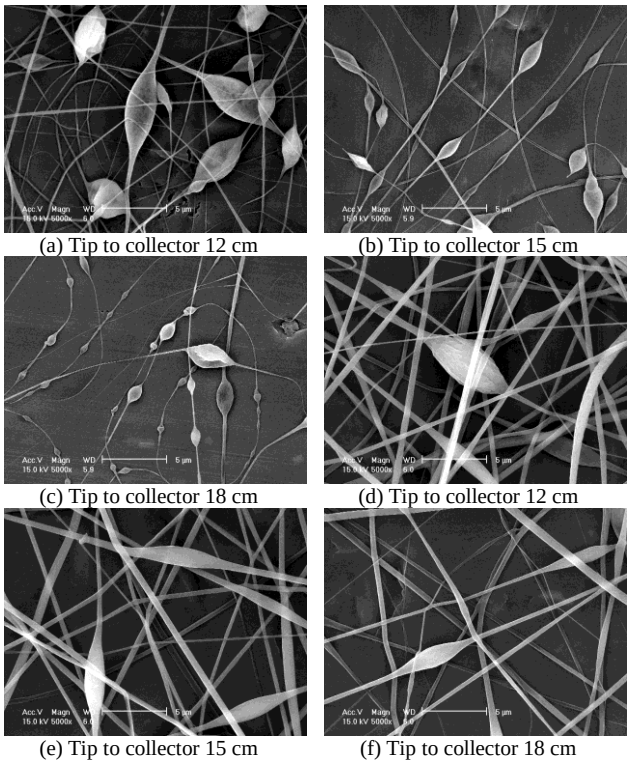
2.3.3 Dielectric Properties

Dielectric measurements were carried out in the frequency range 75 kHz up to 30 MHz by using Precision LCR meter (Agilent 4285A).

3.0 RESULTS AND DISCUSSION

3.1 Scanning Electron Microscopy

The picture of PVC nanofibrous obtained from SEM shows the morphological variation depends on PVC concentration and electrospinning conditions as illustrated in Figure 2. The surface instabilities induced by electrospun jet motion and charge interaction. At PVC low concentration led to the formation of beads on the fiber to disruption the jet into beads. In this studied, PVC nanofibrous were prepared from PVC solution at 15% by weight with applied voltage 12 kV and distance between the syringe tip and collector plate is 15 cm. At lower concentrations, a bead was obtained, but the average diameter gradually increased with higher concentrations, which can be attributed to higher viscosity. As shown in Figure 3. The morphological structure can be changed by adding the PU solution at 10% by weight of PU concentration. PU blending with PVC, it clearly shows the beads on the fiber be disappear, which PU composition can be attributed to higher viscosity and surface tension with increasing PU composition [5]. Viscosity and surface tension play an important role in determining the fiber formability and diameter.

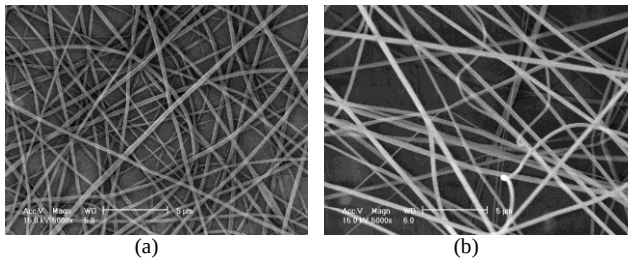


(a) Tip to collector 12 cm (b) Tip to collector 15 cm

(c) Tip to collector 18 cm (d) Tip to collector 12 cm

(e) Tip to collector 15 cm (f) Tip to collector 18 cm

Figure 2 SEM images of electrospun nanofiber 10% by weight PVC (a, b, c) and 15% by weight PVC (d, e, f) at voltage 12 kV



(a) (b)

Figure 3 SEM images of electrospun nanofiber from PU/PVC blends: (a) PVC 10% solution mixed with PU 10% solution and (b) PVC 15% solution mixed with PU 10% solution

3.2 Thermal Properties

The PVC nanofiber prepared from 10% by weight is rigid than that from 15% by weight which correspond with DTA thermogram. The 10% PVC has high exothermal peak at 30°C and 275°C while the 15% PVC shows endothermal peak. The thermal properties of nanofibers were improved after mixing PVC with PU. The mixture of PVC with high PU content gave more flexible nanofiber with lower glass transition temperture (Tg) and heat resistance as illustrated in Figure 4. For higher concentration of PVC (15% PVC) is high viscous and was not easily to mixed with PU solution results in difference DTA thermogram. The nanofiber spun from high concentration of PVC mixed with PU which was heterogeneous solution need to optimized the electrospinning condition. As shown in Figure 5. shows the thermal stability of the nanofibrous membranes. The TG curve of the PVC membrane has two obvious decompositions, which is basically according with the reported TG curve. The TG curve of the PU membrane shows that the decomposition temperature (T_1) is about 250°C, weight-loss rate is the biggest at approximately 300°C. There are two decompositions at the TG curve of PU/PVC nanofibrous membrane. The first decomposition occurs at 275°C (T_3) with a weight loss of about 10%, which may be due to the decomposition of PVC in the membrane. The second weight loss of about 62% occurs at around 433°C (T_3), which may be due to the first decomposition of the composite membrane. These results indicate that the PU/PVC membrane has a good thermal stability.

Dielectric properties. Figure 6 shows the permittivity of PVC and PVC blending with PU nanofibrous which were measured over the frequency range from 75 kHz up to 30 MHz at room temperature. Dielectric constant of the membrane prepared from 10% PVC mixed with high PU content reduced the dielectric constant due to dense of PU phase. The dielectric properties of 15% PVC mixed with PU were not changed with PU contents due to the prepared nanofibrous membrane were dense.

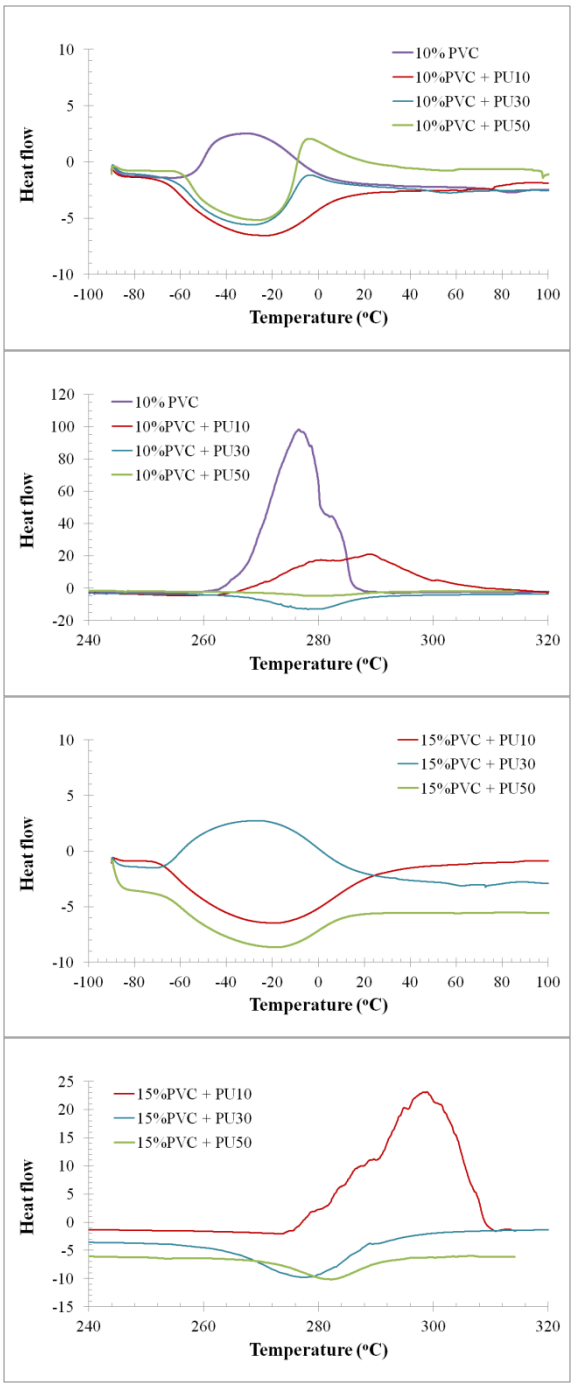
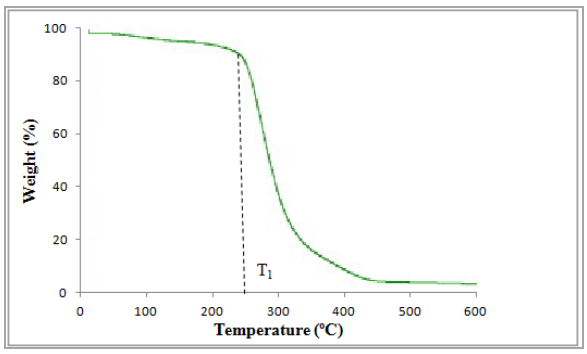


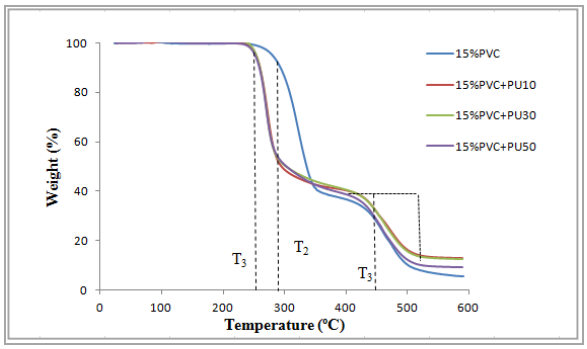
Figure 4 DTA thermogram of nanofibrous from PVC and PVC blending with PU by varying PVC concentration and blending ratio

■4.0 CONCLUSION

The plasticized PVC nanofibrous membrane with PU can be prepared from electrospinning method by choosing high concentration of PVC in mixed solvent between DMF and THF. The eletrospinning condition with applied voltage 12 kV and distance between the syringe tip and collector plate is 15 cm gave smooth surface PVC nanofibrous and desired properties. Addition of PU decreased heat resistance of PVC nanofibrous while the dielectric constant was slightly decreased.



(a)



(b)

Figure 5 TGA of nanofibrous from (a) PVC and (b) PVC blending with PU at difference ratio

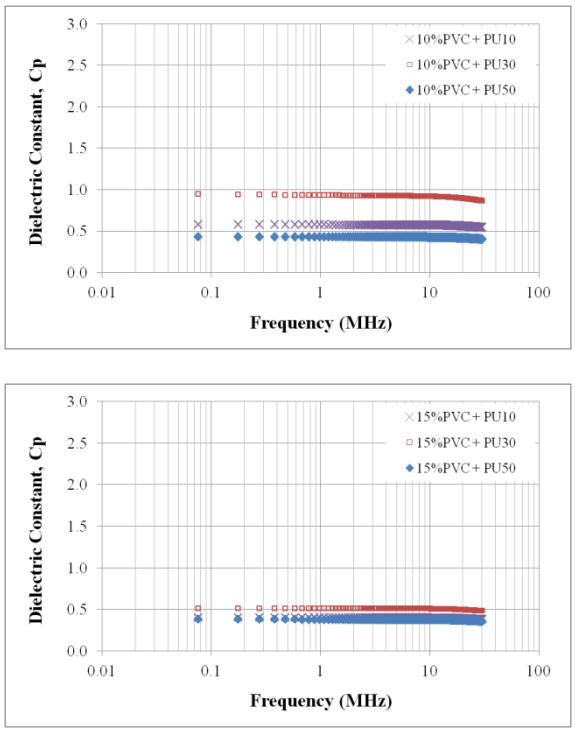


Figure 6 Dielectric properties of PVC nanofibrous in difference solvent

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