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LETTER

A non-destructive method for thickness measurement of thin electrospun membranes using white light profilometry

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Introduction

In recent years, the electrospun nanofibre membranes have gained a great deal of attention due to their unique contribution of properties such as small pore size, fine fibre diameter, light weight and larger surface-to-volume ratio compared to bulk fibres and film [1–3]. Such membranes fabricated by spinning fibres in the presence of an electric field, known as electrospinning. A charged jet of polymer solution is accelerated across a distance and is deposited onto the grounded collector as nanofibres.

Membrane thickness is one of the crucial properties for electrospun membrane. In air filtration, the membrane thickness has significantly influenced the membrane permeability [4, 5]. A number of studies have been carried out on filtration properties of electrospun membrane [4–10]. Barhate and Ramakrishna [7] reported that one of the characteristics of nanofibrous filter media is the membrane thickness. Two common methods for thickness measurement of electrospun membranes are, (1) scanning electron microscopy (SEM) [5] and (2) digital micrometer [8, 11, 12]. SEM has been used widely to measure thicknesses of materials because of its measurement accuracy and the ability to gain detailed information of sample surfaces. For an electrospun membrane, the membrane thickness is usually determined by measuring the membrane cross section. As reported by Barhate et al. [5], the thicknesses of their electrospun polyacrylonitrile are relatively easy to measure using SEM in a range of 100–240 μm. However, several problems were encountered mainly in SEM sample preparation. SEM requires cutting the membranes, which could distort the membrane structures. In addition, the SEM method is time consuming and relatively complex as instrumentation. A micrometer is fast and easy technique to measure thicknesses of any materials. It requires direct contact with the sample which involves applied force to determine the thickness. This is particularly a problem for electrospun membranes which may result in sample compression. The compression of electrospun membrane has been reported by Nisbet et al. [13]. Given its highly porous structures, the electrospun membranes are likely to be compressed and distorted during testing [13]. Another drawback of micrometer is the limitation of the micrometer measurement at such thicknesses.

A white light profilometry would be an ideal instrument to determine material thicknesses particularly for porous and fibrous material. It is equipped with a non-contact sensor device, which is more suitable for compressible membranes with open pore structures. Figure 1 illustrates the basic principle of white light profilometry which uses the reflection of white light to determine the sample height above a reference surface. The scanned surfaces form an image of 3-dimensional surface topography from which the sample thicknesses can be determined. This method has been reported by Menzies et al. [14] to determine thin film thickness of approximately 9 ± 1 μm. Apart from image analysis (3-dimensional surface topography), step height measurement is another potential method to determine sample thickness using white light profilometry.

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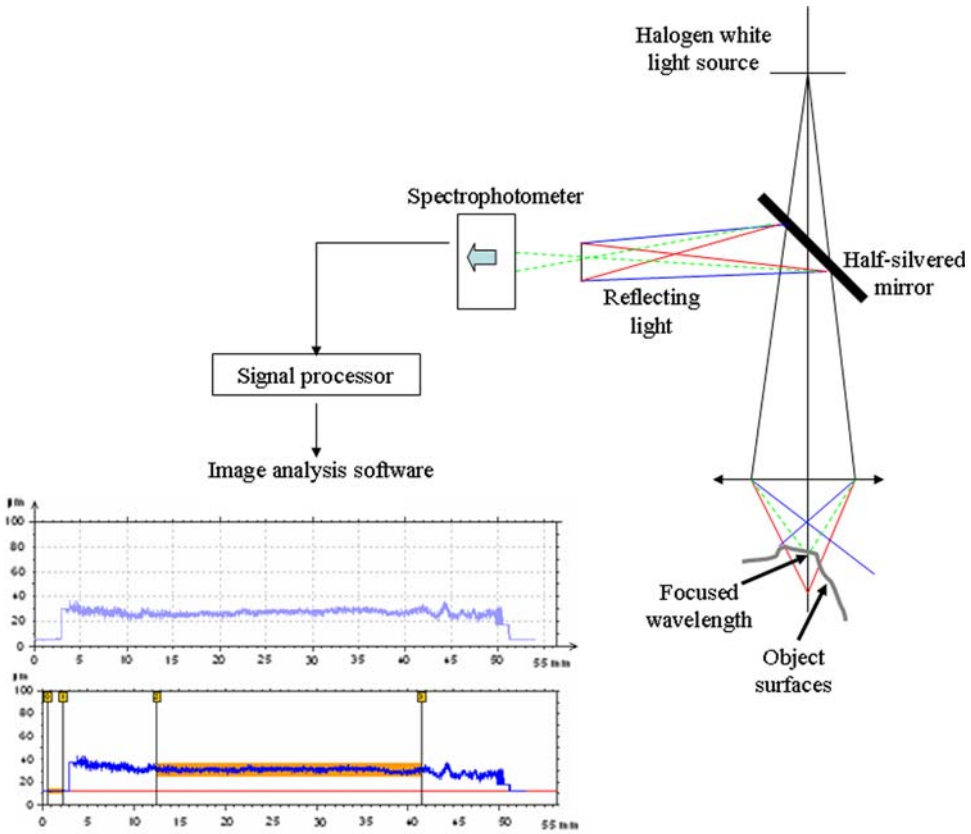

Fig. 1 Schematic diagram of white light system

The step height measurement has been recognized as a method to measure the thickness of thin film [15, 16]. With the aid of surface analysis devices such as white light interferometry [15–18] and atomic force microscopy (AFM) [19], the thickness of film can be determined by scanning across two different film surfaces, reference surfaces (reference plane) and film surfaces. A large step from the reference surfaces (reference plane) to film surfaces gives sufficient information on the film thickness [18].

To date, there have been no reports of using white light profilometry to measure the thickness of electrospun membrane. The paper reports on the suitability of white light profilometry for thickness measurements of electrospun PAN and Nylon 6 membranes. The polymers PAN and Nylon 6 were selected because of the resultant fibre diameters and pore sizes for both polymeric membranes were significantly different. In addition, a comparative study was made using a micrometer.

Principle of white light profilometry

The basic principles of the white light profilometry are illustrated in Fig. 1. It consists of a white light source (quartz–halogen), lens, spectrophotometer, a signal processing system and image analysis software. The white light focuses through a lens that imparts a high level of axial chromatic aberration onto the sample surfaces. As the white light is scanned across the sample, the light is reflected from the sample surface to a spectrophotometer. The software selects the wavelength that is focused on the surface point. The relative height of the surface points forms the step height graphs. Details about the white light profilometry can be found elsewhere [20].

Experimental method

Solution preparation

Two polymers were selected for the study, polyacrylonitrile (PAN) and Nylon 6. The PAN solution was prepared at 10% concentration w/w by dissolving the PAN (Sigma–Aldrich, Mw 150,000) in dimethyl formamide (DMF) at 50 °C for 4–5 h with stirring. The Nylon 6 (Ultramide BS700, BASF) was dissolved in formic acid at 16% concentration w/w and shaken at room temperature for 2–3 days. The solvents DMF and formic acid were analytical grade and obtained from Merck and BDH laboratory supply, respectively.

Electrospinning

Figure 2 illustrates the schematic diagram of the electrospinning system used in this study. The electrospinning conditions were a single nozzle spinneret consisting of 23G (Ø0.65 mm) needle, 0.2 mL/h flow rate, 20 cm distance-to-collector and 40–60% relative humidity at room temperature. The electrospinning voltages were at 9.2 and 32 kV for PAN and Nylon 6, respectively. The sample was prepared with two different surfaces, smooth glass surfaces (A and C) and electrospun membrane surfaces (B) (shown in Fig. 3a). The glass surfaces (A and C) were prepared by covering the glass edges with aluminium foils in order to prevent membrane formation (Fig. 2 inset). The uncovered glass slide forms the membrane surfaces (B). Both polymeric electrospun membranes (PAN and Nylon 6) were collected at five different collection times of 5, 10, 15, 30 and 60 min. The thicknesses of the membranes were measured using a non-contact white light profilometry and micrometer.

Step height measurement by white light profilometry

A white light profilometry (Cotec Altisurf 500 white light) was scanned across the electrospun glass slide from A to B to C (shown in Fig. 3a) with approximately 1000 data points/mm. The accuracy of the white light profilometry is approximately 0.05 μm. A lower probe sensor (which is in a range of 9.2–300 μm) was selected in the study in order to prevent the white light from passing through the glass. Ten separate line measurements were performed across the sample.

Digital micrometer measurement

The same sample used in step height measurement was also measured using a simple electronic digital micrometer (Kincrome with the lower limit of approximately 4 μm). Ten sets of measurements were taken at different places at random along the sample and the thicknesses were determined by Eq. 1.

$$h = h_1 - h_2 \tag{1}$$

where h, the thickness of electrospun membrane (μm), h_1 is the total thickness consisting of electrospun membrane and glass slide (μm) and h_2 is the thickness of glass slide (μm)

Characterization

Electrospun membranes were characterized using a Philips XL30 Field Emission Scanning Electron Microscope (FESEM). The membranes were coated with iridium for approximately 5 min. Digital images of sample were taken using a digital camera (Canon Power Shot G6). The pore size of electrospun PAN and Nylon 6 membranes were measured using the capillary flow porometer (Porous Media Inc.).

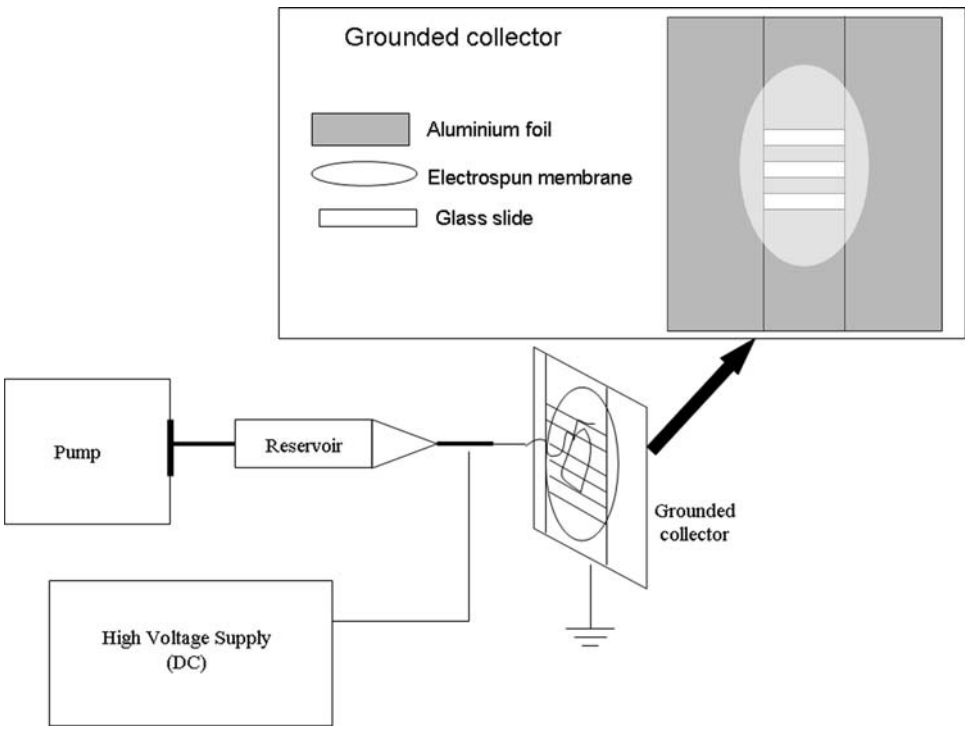

Fig. 2 Schematic diagram of electrospinning system used in this study. The inset provides details on how the electrospun membrane was collected on the collector electrode

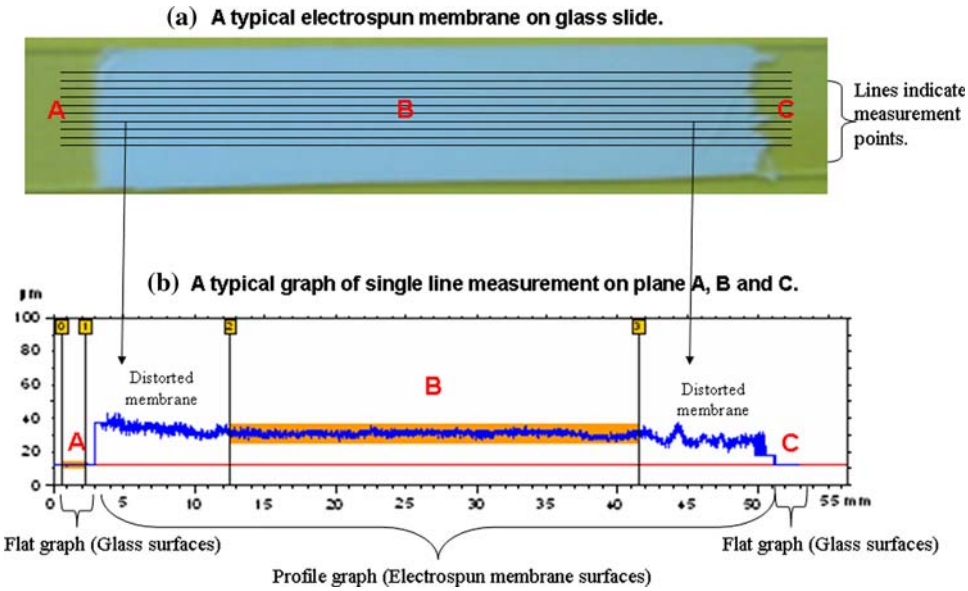

Fig. 3 **a** Photograph of a typical electrospun membrane deposited on a glass slide. The *green* regions (labelled A and C) and *white* region (labelled B) correspond to the glass and electrospun membrane, respectively. **b** A typical graph of single line measurement taken from A to C

Result and discussion

A typical step height result of a single line measurement is presented in Fig. 3b. The flat regions at either end represent the glass surface (A and C), while the profile graph in the middle represents the electrospun membrane surface (B). The average height of the electrospun surface above the glass determines the membrane thickness. The edges of the electrospun membrane were not used because the membrane structure was stretched and distorted while the sample was transferred from the aluminium foil.

Comparison of electrospun membrane thicknesses as measured by white light profilometry and a digital micrometer

The thickness of electrospun PAN and Nylon 6 as measured by white light profilometry and digital micrometer is shown in Table 1. The micrometer gave lower values for PAN and Nylon 6 membranes as compared to the step height measurement (white light profilometry). The results indicate that the membranes are compressed by the micrometer. This is confirmed by the white light profilometry profiles shown in Figs. 4, 5, 6 and 7, which were taken after measurement with a micrometer. An indentation is clearly observed where the micrometer measurement was taken. Furthermore, the indentation depth corresponds closely to the difference between the micrometer measurement and white light profilometry. In Table 1, the difference in measurement between white light profilometry and micrometer for electrospun PAN-(30 min) is 11 μm, which is closely corresponded to the same indentation in Fig. 4b. For electrospun PAN-(60 min), Nylon6-(30 min) and Nylon 6-(60 min), the indentation depths are approximately 15, 4 and 10 μm, respectively (Figs. 5, 6, 7). Compression of the samples is understandable given the highly pore structures of these membranes. In Fig. 8, a membrane made of small fibre diameters and smaller pore sizes such as Nylon 6 produces more compact structures that does not compress as much as structures made of larger fibre diameter such as PAN. More work is required to confirm this general phenomenon.

Table 1 The thickness of electrospun PAN and Nylon 6 as measured by white light profilometry and a digital micrometer

Electrospun membrane	Collection time (min)	Thickness (μm)	
		White light profilometry (step height)	Digital micrometer
PAN-(30 min)	30	21 ± 1.1	10 ± 0.7
PAN-(60 min)	60	46 ± 0.8	30 ± 0.1
Nylon 6-(30 min)	30	10 ± 0.3	7 ± 0.6
Nylon 6-(60 min)	60	16 ± 0.1	6 ± 0.1
Glass slide[a]	–	1100 ± 0.1	1100 ± 0.1

[a] Control

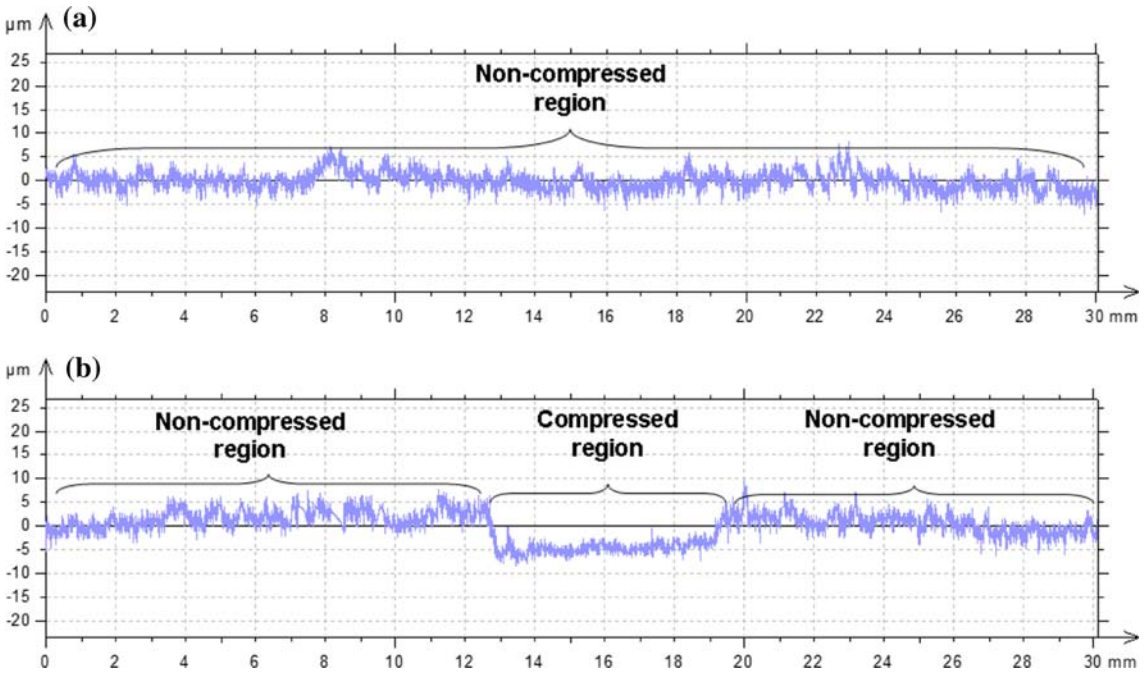

Fig. 4 Profile obtained from white light profilometry for electrospun PAN-(30 min) of the B region. **a** Before measurement with a micrometer and **b** After measurement with a micrometer. The deformation caused by the micrometer can be clearly seen corresponding to a compression of 10 µm

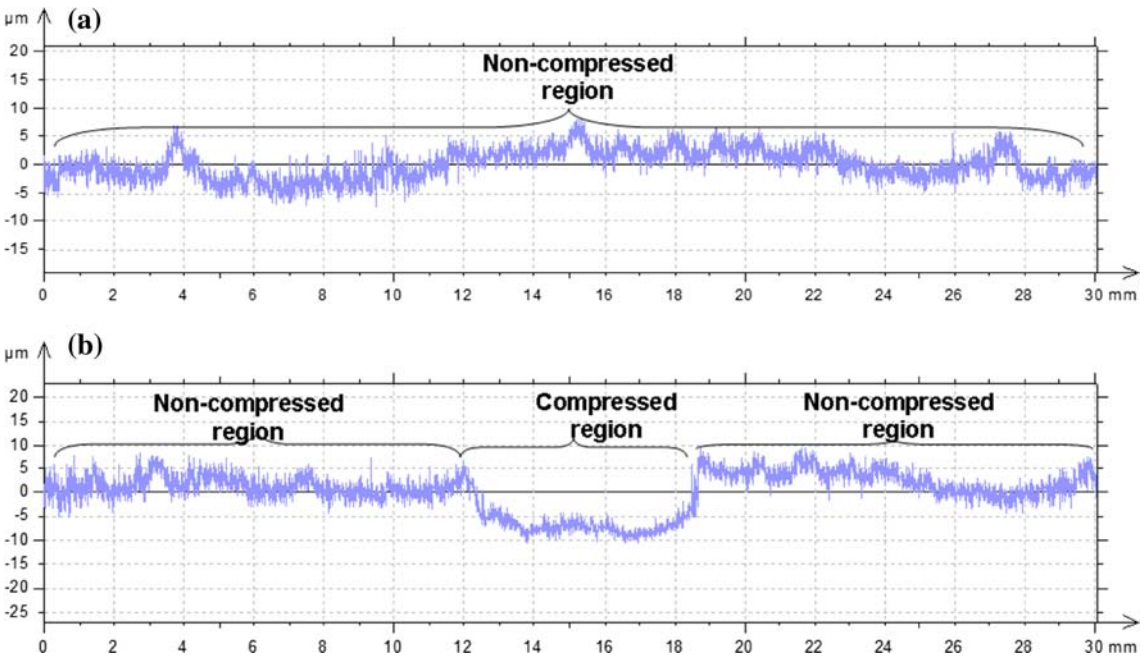

Fig. 5 Profile obtained from white light profilometry for electrospun PAN-(60 min) of the B region. **a** Before measurement with a micrometer and **b** After measurement with a micrometer. The deformation caused by the micrometer can be clearly seen corresponding to a compression of 15 µm

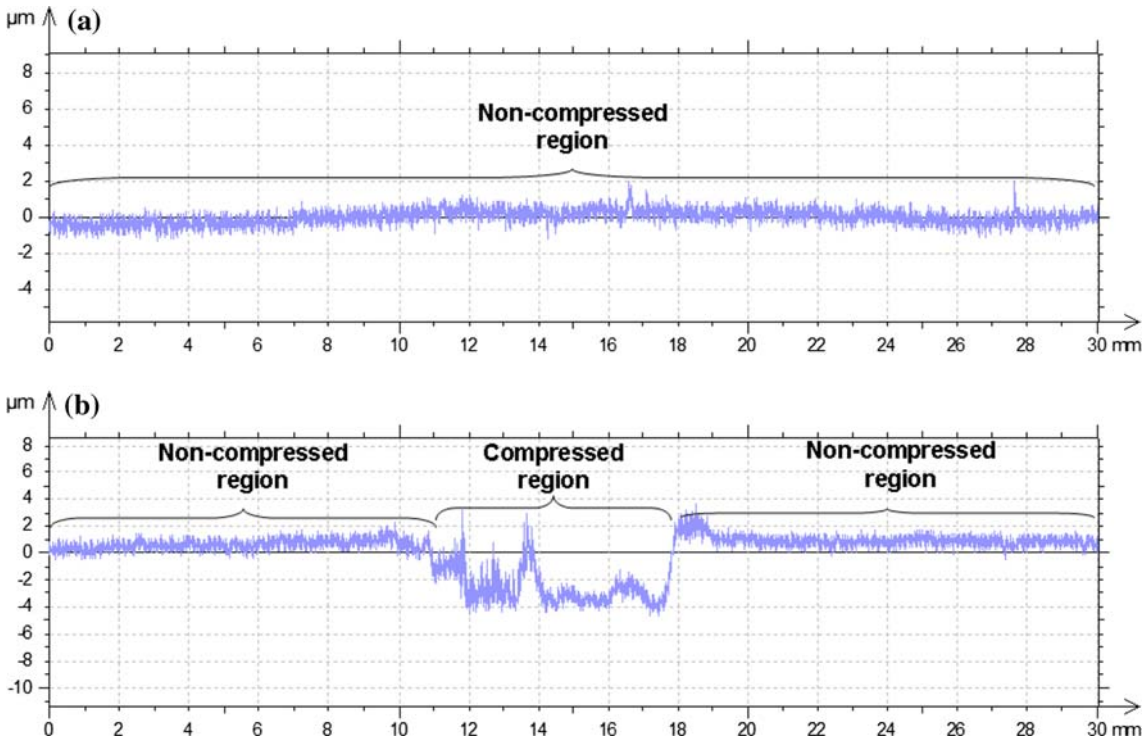

Fig. 6 Profile obtained from white light profilometry for electrospun Nylon 6-(30 min) of the B region. **a** Before measurement with a micrometer and **b** After measurement with a micrometer. The deformation caused by the micrometer can be clearly seen corresponding to a compression of 4 µm

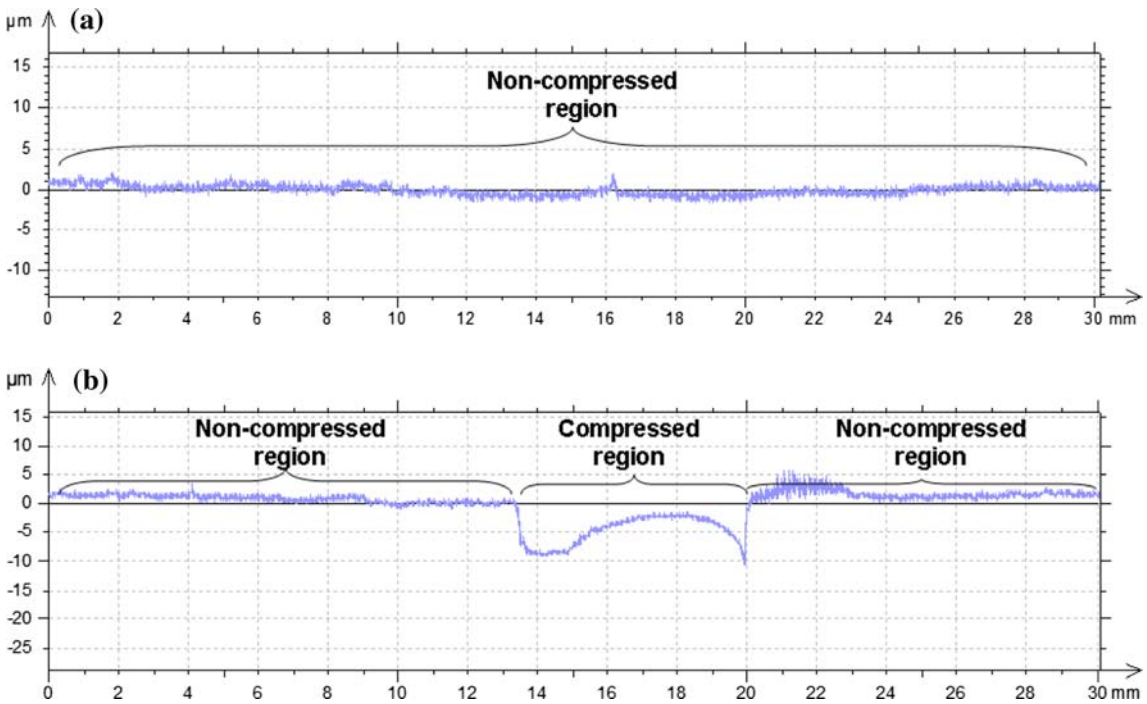

Fig. 7 Profile obtained from white light profilometry for electrospun Nylon 6-(60 min) of the B region. **a** Before measurement with a micrometer and **b** After measurement with a micrometer. The deformation caused by the micrometer can be clearly seen corresponding to a compression of 10 µm

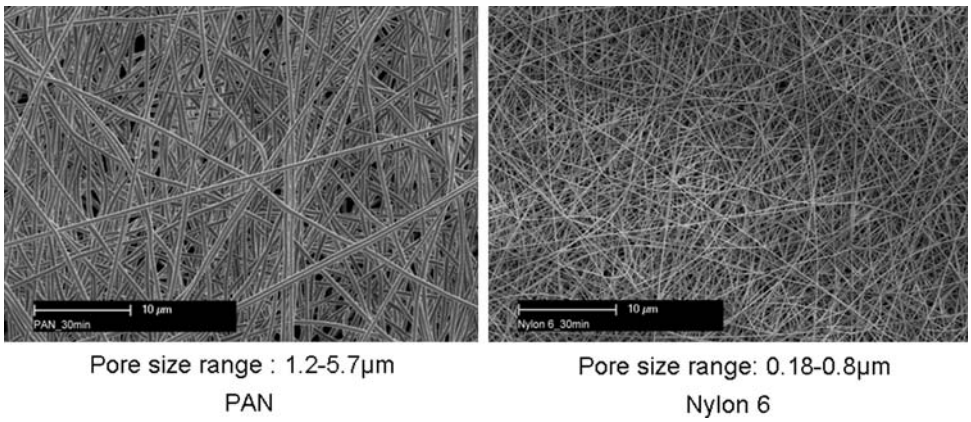

Fig. 8 SEM images of electrospun PAN and Nylon 6 membrane collected for 30 min

Membrane thicknesses at different collection time

Figure 9 represents the thickness of PAN and Nylon 6 collected for 5, 10, 15, 30 and 60 min as measured by white light profilometry. It was found that the thicknesses of PAN and Nylon 6 were linearly proportional to the electrospinning collection time. The membrane thickness increases with deposition time. At 5 min collection time, the thickness of PAN and Nylon 6 were 2 ± 0.1 and 0.8 ± 0.1 μm, respectively. The results indicate only a few fibres were deposited in the first 5 min. As the collection time was increased, an opaque membrane was formed for both polymeric electrospun membranes.

The electrospun PAN has greater thickness than that of the electrospun Nylon 6 because the PAN fibres having large fibre diameter as compared to the Nylon 6 membrane (shown in Fig. 8). The stacking of larger fibre diameters on top of each other produces thicker membrane.

In addition, the large pore sizes of PAN (shown in Fig. 8) form spongy and open pore structures of PAN membrane. For Nylon 6, the fine pore sizes form a compact and therefore thinner structure membrane.

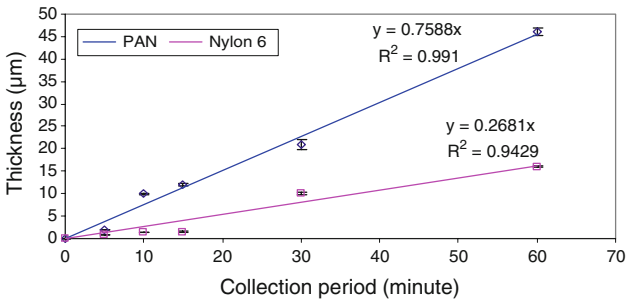

Fig. 9 A plot of membrane thickness versus collection period for the electrospun PAN and Nylon 6 membranes as measured by white light profilometry. Values represent the average of 10 measurements at different places

Conclusion

The experimental results have shown a correlation between the membrane thickness and the collection period. Results from this method were compared to those using a micrometer. The thicknesses found using the micrometer gave lower thickness values for the same sample due to sample compressions. The advantages of using step height measurements are:

1. The use of white light to scan the sample will not damage the sample. The scanned sample is reusable for other testing.
2. The step height technique using white light profilometry does not compress a sample and therefore it is more suitable for spongy membranes with open pore structures.
3. The step height method can measure the electrospun thickness in the nanometer range, which is beyond the limit of a micrometer. The minimum measurement of micrometer is approximately 4 μm.
4. The technique is able to measure the thickness across a large region. In the SEM, only the cross section can determine the electrospun thickness.
5. It is a faster method to measure the thickness of electrospun membrane compared to SEM. Ten measurements can be done over a 30 min period (depending on the sample length).
6. Minimal sample preparation (no freeze-sectioning and coating) is required for this method.

This study has shown that white light profilometry can successfully employed to measure the thickness of thin electrospun membranes onto glass slide.

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