FABRICATION AND MECHANICAL PROPERTIES OF POLYMER COMPOSITE NANOFIBER MATS

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Abstract. In recent years, as microelectronics technology advances, the number of miniature devices has increased as well as the demand for power supply. Polymer-based electrospun nanofiber membranes have been used as lithium-ion (LI) battery separators and filtration medium. This study investigates the mechanical properties of orientated polyamide 6 (PA6) and polyacrylonitrile (PAN) nanofiber mats prepared by electrospinning a solution containing PAN and PA6, separately. The PA6 granules and the PAN powder were dissolved in formic acid solvent and N, N-dimethylformamide solvent, respectively. To generate the composite mat, the PA6 nanofiber mat was first electrospun, followed by the PAN nanofiber mat directly electrospun on the PA6 nanofiber mat. In our experiment, we employed the following electrospinning parameters: a voltage of 25 kV, a flow rate of 0.65 ml/h, 25 cm between the tip of the syringe and the drum collector centre, and a constant rotating speed of 1800 rpm. The mechanical properties of nanofiber composite mats, such as the tensile strength and Young's modulus, were examined. The results demonstrate a reduction in the tensile strength and an increase in the elastic modulus of the composite nanofiber mats by 12% and 126% compared to PA6 nanofiber mats, respectively. The structure of spun nanofibers enables their use as separators for lithium-ion batteries and as a filtering medium. This article suggests the improved mechanical characteristics of nanofiber membranes for use as a barrier in lithium-ion batteries and for filtration.

Keywords: electrospinning, nanofiber, membrane, tensile strength, nano composites.

Introduction

Electrospinning is well known to be a low-cost method for producing polymeric fibres with diameters in the range of ten to a few hundred nanometres. Electrospun nanofibers are used as optical materials, sensor materials, laminated nanocomposites [1], reinforced with nano particles [2], short fibre composites for structures [3; 4], tissue scaffolds [5], 3D printed scaffolds [6], wound treatment, drug delivery technologies[7; 8], water filtration [9], efficient air filteration [10; 11], protective gear [12], and smart textiles [13; 14].

Polymer composite nanofiber mats have received a lot of attention in the recent decades due to their excellent mechanical quality, high ratio of surface to volume [15], and a distinctive surface shape [16]. Electrospinning can produce fibres with diameters ranging from a few tens of nanometres (5-10 nm) to a few micrometres (5-10 µm), which is commonly used to create these mats [17]. Nanofiber mats consist of a network of interwoven fibres that form an extremely porous and lightweight structure [18]. This makes them useful for several applications in biomedical engineering [19; 20], energy [21], and environmental sciences [22].

As microelectronics technology advances, more miniature devices demand power supply in the twenty-first century. Lithium batteries are now widely used in portable electronics [23]. Lithium batteries convert chemical energy into electrical energy and circulate electricity in the electrolyte using electrons from the electric pole [24]. Separator thickness, pore dispersion, and mechanical quality impact the battery life cycle, electrical capability, and protection [25]. Hence, the separator is most crucial to battery safety [26].

In recent years, mobile phone batteries have exploded and expanded, making lithium battery safety one of the most important initiatives [27]. Lithium batteries need a cathode, anode, separator, and electrolytes. The separator prevents short-circuit by splitting the positive and negative rods. It also has strong electrolyte conductivity, and the separator completely influences battery efficiency and safety. Hence, enhancing the separator performance is a top research priority [28]. The advantage of employing the PAN nanofiber mat in the composite is that it has a higher strength compared to the PA6 nanofiber mat [18], but the disadvantage is that it has a bigger porosity than the PA6 nanofiber mat; whereas the PA6 nanofiber mat has extremely low porosity, making it a suitable separator in batteries [29]. This study focuses on the fabrication of polymeric composite mats and the mechanical characteristics of these nanofiber mats.

Materials and methods

PA6 (CAS: 25038-54-4; density: 1,06-1,16 g·cm^{-3}), formic acid (CAS: 64-18-6), polyacrylonitrile (PAN) powder (CAS: 25014-41-9), and N, N–dimethylformamide were acquired from Sigma-Aldrich chemicals, Germany).

PAN solution was set up by adding the PAN powder to the solvent (DMF) by 12% wt./wt. and blending it for 9 hr. on the magnetic stirrer (Thermo Scientific™ Cimarec + ™ Stirring Hotplates Series, USA) at a + 78 ℃ stirring speed of 1000 rpm. Similarly, a PA6 solution was prepared by adding 10% wt./wt. and mixing it for four hours at + 40 ℃. The solutions were kept at room temperature + 25 ± 1 ℃ for one hour.

The composite mats were prepared by electrospinning both solutions one by one at + 22 ± 1 ℃ using the following devices: Fisherbrand™ Single Syringe Pump, a needle-based electrospinning machine, Danbury, CT 06811, United States; with drum collector RC-5000, D140, L50, Shenzhen Tongli Tech Co Ltd, D-601, Shenzhen, China. A five-mL syringe and a 20G needle were used. During the experiment, the electrospinning parameters were 25 kV voltage, 0.65 mL/h flow rate, and 25 cm between the syringe tip and the centre of the collecting drum. To collect the nanofibers, the rotational speed of the rotating drum collector was maintained at 2000 rotation/min, and aluminium foil was applied to the drum.

The tensile properties were measured with Mecmesin's Multi-Test 2.5-i tensile testing machine (PPT Group UK Ltd., t/a, Mecmesin, United Kingdom). The specimens were 40 mm × 10 mm. Five measurements were taken to determine what the tensile properties were. The thickness of the test pieces was measured with a IP65 0-25 mm, digital micrometre (Mitutoyo, Poland). The specimen's thickness is equal to the average of the three thickness measurements. The piece was cut in the same direction as the nanofibers. To attach both edges of the specimen to the paper template, a 20 mm × 20 mm cut-out was made on the inside of a 40 mm × 40 mm paper frame [30].

For comparison, the elastic modulus of the nanocomposites was also measured with the help of the fundamental rule of mixing (ROM) [31].

$$E_C = E_{PAN}V_{PAN} + E_{PA6}(1 - V_{PAN}), \tag{1}$$

where E_C – nanocomposite Young's modulus;
  E_{PAN} and E_{PA6} – experimental Young's modulus of nanofiber mats, respectively.

E_C value forecasts the linear relation between both nanofiber mats.

Similarly, Young's modulus was computed using the Tsai-Pagano model in equation (2) assuming random in-plane fibre orientation [31].

$$E_c = \frac{3}{8}E_L + \frac{5}{8}E_T, \tag{2}$$

$$E_L = E_{PA6}V_{PA6} + E_{PAN}(1 - V_{PA6}), \tag{3}$$

$$E_T = \frac{E_{PA6}N_{PAN}}{E_{PA6}(1 - V_{PA6}) + E_{PA6}V_{PAN}}, \tag{4}$$

where E_L and E_T – longitudinal and transverse moduli of the nanocomposite, calculated longitudinally and transversely to the direction of the nanofibers, assuming a unidirectional composite with cylindrical fibres.

Results and discussion

The stress (σ) – strain (ε) graphs of the PAN nanofiber mats, PA6 nanofiber mats, and composite nanofiber mats are shown in Fig. 1 and Table 1, respectively. During tensile testing, there were no failures of the clamps because of the clamping pressure. The graph clearly demonstrates that the elastic modulus is greater than that of PA6 and less than of the PAN nanofiber mat.
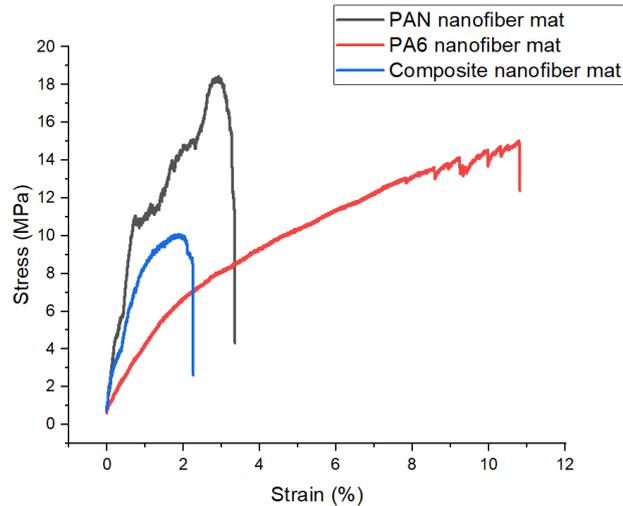
Fig. 1. **Representative stress-strain graph of PAN, PA6 and composite nanofiber mat**

The PAN and PA6 nanofiber mats exhibit average tensile strengths of 19.1 ± 1 MPa and 14.9 ± 2 MPa, respectively, whereas the composite nanofiber mat has an average maximum tensile strength of 13.1 ± 1 MPa. The elastic modulus of PAN and PA6 nanofiber mats was 1510 ± 11 MPa and 405 ± 6 MPa, whereas the composites' elastic modulus was 917 ± 8 MPa.

Table 1

Average mechanical properties of PAN, PA6 and composite nanofiber mat

Materials	Tensile strength at break (MPa)	Young's modulus, E (MPa)	Strain (%)
PAN nanofiber mat	19.1 ± 1	1510 ± 11	3.5 ± 0.2
PA6 nanofiber mat	14.9 ± 2	405 ± 6	11.2 ± 0.5
Composite nanofiber mat	13.1 ± 1	917 ± 8	2.8 ± 0.3

Electrospinning directly on the nanofiber mat is advantageous compared to combining the nanofiber mat with additional materials after manufacturing to produce a nano-composite [13]. By electrospinning directly on an existing nanofiber mat, the nanofibers orientation in a nanocomposite might be improved; the resultant nanofibers in the nanofiber mat could be more aligned and more ordered, resulting in higher mechanical strength and other desired physical and mechanical qualities [32]. Moreover, electrospinning directly on a nanofiber mat can facilitate the adhesion of new nanofibers to the current mat. This result increases qualities such as higher adhesion and tensile strength. Electrospun nanofibers on an existing mat also create interlocking joints as well as a bridging effect that improves adhesion between the mats [33; 34].

Electrospinning directly on a nanofiber mat eliminates the need to manufacture a separate mat for the electrospun nanofibers, thus reducing the processing time and expenses. This can be especially beneficial for large-scale production. Electrospinning directly on a nanofiber mat can also be used to create multi-layered structures in which the electrospun nanofibers are placed on distinct layers of the existing mat. This can lead to materials with novel characteristics and functions. The electrospinning directly on a nanofiber mat can be a practical and efficient method for producing nanofiber-based products with improved mechanical characteristics and functions.

Fig. 2 compares the analytical models and experimental results for the elastic areas of composites. According to ROM (based on Equation 1), the composite Young's modulus was 957.5 MPa, somewhat higher than the experimental result of 917 ± 8 MPa, but the Tsai-Pagano model (based on Equation 2) predicted 758.24 MPa, which is much less than the experimental results.
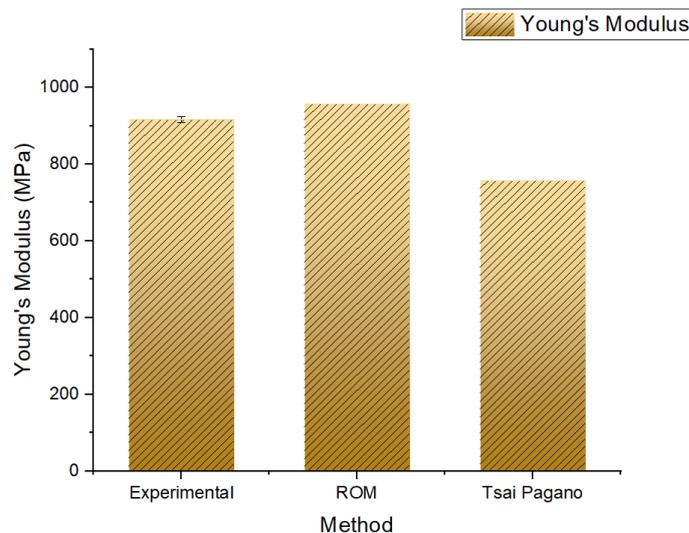
Fig. 2. **Comparison of Young's modulus with different methods**

Conclusions

On the basis of the given results, it can be concluded that electrospinning directly on a nanofiber mat has several advantages over combining the nanofiber mat with additional materials after manufacturing to produce a nanocomposite. The resulting nanofibers may have improved alignment and adhesion, resulting in a higher elastic modulus compared to the PA6 nanofiber mat. Additionally, this method reduces the processing time and expenses, making it practical for large-scale production. Owing to the direct electrospun bond between the PAN nanofiber mat and the PA6 nanofiber mat, the nanocomposite's nanofiber reinforcing action enabled efficient stress transfer, resulting in excellent elasticity. The results of the tensile test demonstrated an exceptional strengthening impact, as the tensile modulus of the nanocomposites increased by 126% to 917 ± 8 MPa compared to PA6 nanofiber mats. This study developed a technique for the direct electrospinning of high-functioning nanocomposites for use as filter media and lithium-ion battery separators.

Overall, electrospinning directly on a nanofiber mat can be an effective and productive way of producing nanofiber-based products with enhanced elastic modulus and functionality. Yet, further study may be required to enhance this technique and fully comprehend the mechanical behaviour of nanocomposite materials.

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Author contributions

Conceptualization, J.V.S; methodology, J.V.S; validation, J.V.S.; investigation, J.V.S, K.B.S., and S.P.K.; data curation, J.V.S.; writing – original draft preparation, J.V.S.; writing – review and editing, J.V.S. and S.P.K.; visualization, J.V.S.; project administration, J.V.S.; funding acquisition, J.V.S and S.P.K. All authors have read and agreed to the published version of the manuscript.

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