



## Scission of electrospun polymer fibres by ultrasonication



Marini Sawawi<sup>a,b</sup>, Ting Yi Wang<sup>a</sup>, David R. Nisbet<sup>a,c</sup>, George P. Simon<sup>a,\*</sup>

<sup>a</sup> Department of Materials Engineering, Monash University, Clayton 3800, Victoria, Australia

<sup>b</sup> Faculty of Engineering, Universiti Malaysia Sarawak, Kota Samarahan 94300, Malaysia

<sup>c</sup> Research School of Engineering, The Australian National University, Acton 0200, ACT, Australia

### ARTICLE INFO

#### Article history:

Received 1 March 2013

Received in revised form

22 May 2013

Accepted 26 May 2013

Available online 4 June 2013

#### Keywords:

Electrospinning

Nanofibers

Ultrasonication

### ABSTRACT

In this work we show that sonication alone can be used to scission bulk electrospun membranes into short fibres. The mechanism of such scission events is bubble cavitation stimulated by the ultrasonic probe, followed by bubble implosion. The tendency of polymer nanofibres to undergo failure by such a scission process appears to primarily depend on the ductility of the polymer, with brittle, electrospun polymer membranes such as poly(styrene) and poly(methyl methacrylate) readily producing short fibres of approximately 10  $\mu\text{m}$  length. More ductile polymers such as poly(L-lactide) or poly(acrylonitrile) require additional processing after electrospinning and before sonication, to make them conducive to such sonication-based scission. Both the initial diameter of the fibres and the degree of nanofibre alignment of the electrospun membrane influence the final length of the resultant short fibres. It was found that the chemical and physical properties of the short nanofibres were unaltered by the sonication process. We are thus able to demonstrate that sonication is a promising method to produce significant quantities of short fibres of nanometre diameter and microns in length.

© 2013 Elsevier Ltd. All rights reserved.

### 1. Introduction

Electrospinning has become an often-reported technique for the fabrication of polymeric fibrous membranes that have been used for a variety of applications including membrane technologies, sensors and in particular for tissue engineering as scaffolds that mimic features of the extracellular matrix [1–6]. Electrospinning results in the production of continuous fibres that deposit onto a collector as a nonwoven membrane. It is inherently difficult to spin and retrieve individual electrospun fibres in large quantities that can be readily handled. Parallel, knife-edge electrodes is a possible method that has been used to obtain individually-aligned fibres for the purpose of single fibre testing, however very limited amounts of fibre can be produced in this way [7,8].

To date, there has been little work reported on producing individual, short micrometre-length fibres directly from convention, electrospun membranes. The ability to convert an electrospun membrane into discrete, short fibres of nanometre dimension would be advantageous as it would lead to a methodology to produce significant quantities of such short fibres. Such short fibres may be desirable for a number of applications, such as additives for incorporation into polymers and films to enhance properties such

as modulus and toughness, whilst maintaining the transparency of the nanocomposite due to the similarity of the refractive index of the nanofibres and the matrix. Short fibres would also be very useful for biomedical applications as vessels for the containment of drugs or in tissue engineering as injectable fibrous scaffolds such as in anisotropic cavities such as neural pathways. It is also beneficial to have short fibres in hydrogel systems, where they can act as tissue scaffolds or as slow drug release vehicles. The anisotropic, high aspect ratio of the fibres means that they could also have the effect of structurally reinforcing the hydrogel, in addition to their functional properties. In this case, the mechanical properties of the fibres are important (due to high levels of orientation of the molecules within the short fibres), as well as the ability to diffuse drug or other molecules out of the fibre. Such fibres are also amenable to further chemical functionalisation, which may be useful for dispersion and to provide more “cell-friendly” surfaces. In this work, we report the use of ultrasonication as a method to produce short fibres from a nonwoven, electrospun membrane, whilst also investigating the effects of material properties and processing parameters on the process and its outcome.

There have been a few reports of non-ultrasonic methods to breakdown the non-woven electrospun membrane for composite reinforcement that have shown varying degrees of success. A simple method which is difficult to control is mortar grinding [9,10] which was found most effective for brittle electrospun membranes such as carbonised poly(acrylonitrile) [10]. Rubber milling [11] and

\* Corresponding author. Tel.: +61 3 990 54936; fax: +61 3 990 54940.

E-mail address: [george.simon@monash.edu](mailto:george.simon@monash.edu) (G.P. Simon).

cryogenic milling [12] have been shown to be better options for the scission of electrospun membranes, where the cycle and rate of the impactor can be accurately controlled. However, it is difficult to make comparisons between each of the techniques, as the characteristics of the resultant short fibres were not always well reported. Other mechanical methods such as razor blade cutting under nitrogen [13] have been used to produce short magnetic composite fibres from a mixture of a methyl methacrylate–vinyl acetate copolymer combined with superparamagnetic cobalt nanoparticles, yielding fibres of approximately 50–100  $\mu\text{m}$  length. Another method to produce discrete fibres from the electrospun membrane has involved 1  $\mu\text{m}$  step-sliced cryomicrotoming to produce short nylon electrospun fibres, however this involves tedious, repeated steps [14]. Polymer degradation using UV light was used to produce reduced poly(butadiene) electrospun fibre mats where the UV light was shined through masks with well defined slit sizes and inter-slit distances, laid on top of the mesh [15], but although this cut the fibres, the aim was to produce smaller, controlled fibre bundles, as opposed to the individual fibres we seek here.

In this work we demonstrate that we can use ultrasonication directly, under appropriate conditions, to produce short nanofibres from electrospun membranes. For this we use an ultrasonic probe apparatus that is already widely used in most laboratories for applications such as cleaning and mixing, and has a working frequency of 20 kHz [16]. During sonication, such a probe causes bubbles in the fluid medium grow and collapse, and in so doing, release energy. Bubble growth is initiated from cavities with a diameter of 1  $\mu\text{m}$  and grow to ca. 50  $\mu\text{m}$  under negative pressure [17]. Under such sonication conditions, the bubble can grow in 20  $\mu\text{s}$ , and collapse over a time of the order of ns [18].

This method has previously been utilised to facilitate the dispersion of carbon nanotubes in a solvent or mixture [19] and has also been shown that it can lead to carbon nanotube scission [20]. Most researchers currently use sonication for the mixing of CNTs in solution, and size reduction is often of secondary interest. The basic mechanism for the scission of carbon nanotubes has not been fully elucidated, although a number of papers have made a series of instructive observations. Recently Hennrich et al. [19] investigated the decrease in length of CNTs and the underlying mechanism during ultrasonic processing, making clear that the break-up was due to an associated cavitation phenomenon (bubble growth and collapse) within the solvent, which leads to local regions of high strain and shear stress. These include the separation, thinning and shortening of the CNTs due to the mechanical effect of sonication which occurs upon bubble implosion, yielding a maximum tensional force at the nanotube centre which is similar to the observation of single molecule polymer degradation due to scission [19,21,22]. The mechanism of scission largely depends on the position of the nanotubes relative to the bubble during implosion and how it approaches (or is drawn towards) the imploding bubble. If the longitudinal axis of the nanotube aligns normal to the bubble surface, this would lead to a high frictional force between the fibre and solvent, which causes a high tensile force at the nanotube centre [19,22]. However, nanotubes that become aligned tangential to the bubble surface would result in axial compression that results in buckling and fracture of the nanotube due to atom ejection [23,24].

Recent modelling work by Pagani et al. [24] suggests that the mode which dominates (tangential or radial) depends on the size of the nanotube. Whilst the growth of the bubble causes tangential alignment of the nanotubes, shorter nanotubes radially rotate and are drawn towards the nanotube, with subsequent tensile stretching and failure, whilst longer nanotubes do not rotate in such a fashion, but rather the opposing torques at either end cause bending and buckling (which may also lead to failure). The mode of

deformation notwithstanding, the ultimate molecular failure mechanisms invoked were also often related to the precise chemical structure of the materials, such as defects in carbon nanotubes or the carbon-framework (in the case of carbon nanotubes), and may not be as relevant for polymer nanofibre scissioning. Other researchers propose alternate mechanisms to explain nanotube scission, such as bubble implosion leading to high temperatures that can cause failure on the nanotube surface [25], although others refute such claims and state that such extreme thermal events are unlikely to occur [21,23]. It has also been proposed that bubble collapse would lead to microjets that impinge on the surface leading to their ultimate failure [26–28], the mechanism by which ultrasonics is used to clean surfaces contaminated by organics. It is likely that scissioning of polymer nanofibres could be due to a combination of factors such as material properties and the processing conditions. The possible mechanisms for failure in these systems will be discussed below, based on the observations made and results obtained.

To date, there has been little study on the use of sonication as a method to produce small fibres from electrospun membranes. Transverse fragmentation of fibres by first chemically-modifying poly(lactide) nanofibres by aminolysis [29,30], in combination with some sonication has been reported, however in this case, the scission of fibres was largely due to the chemical treatment, and the sonication was used more to disperse the resultant, chemically-cut fibres, rather than being the primary mechanism for fibre scission. One recent study has reported in passing, the direct use of ultrasonication as a means of producing short fibres from electrospun membranes. The short fibres produced were subsequently incorporated into a hydrogel for a tissue engineering applications [31] to improve interactions between the hydrogel and the cells. However, in this work sonication was used as a means to an end to produce short nanofibres, with investigation of the control of scission events and a mechanistic understanding being outside the scope of that research.

In this work we have investigated the effect of the ultrasonication on electrospun membranes, varying material properties and processing variables, in order to gain a more detailed understanding of how to optimise the resultant short nanofibres and obtain a mechanistic understanding of the process itself. As a point of comparison with previous methods of producing short nanofibres from electrospun membranes, we have also conducted cryogenic milling of electrospun membranes.

## 2. Experimental method

### 2.1. Materials

Poly(L-lactide) acid (PLLA, Inherent viscosity = 0.9–1.2 dL/g) was purchased from Lactel, USA. Poly(acrylonitrile) (PAN,  $M_w = 120,000$ ), poly(methyl methacrylate) (PMMA,  $M_w = 486,000$ ) and poly(styrene) (PS,  $M_w = 230,000$ ), dodecyl trimethyl ammonium bromide (DTAB), potassium bromide (KBr) and Rhodamine B were purchased from Sigma Aldrich, Australia. Chloroform, dimethylformamide (DMF) and acetone from Merck Pty Ltd, Australia. Deionised water was obtained from Direct-Q3 water purification system, Millipore.

### 2.2. Electrospinning

The polymers were dissolved at room temperature overnight in the solution using a magnetic stirrer (except for PLLA, which was heated at 70 °C for 2 h) prior to electrospinning. Then, the polymer solution was placed in a 10 mL syringe prior to electrospinning using the parameters listed in Table 1 for each material. These

Download English Version:

<https://daneshyari.com/en/article/5182072>

Download Persian Version:

<https://daneshyari.com/article/5182072>

[Daneshyari.com](https://daneshyari.com)