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Effect of the Solvent System on the Morphology and Performance of Nylon 6 Nanofibre Membranes

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Abstract
Nylon 6 nanofibre membranes were prepared by electrospinning of nylon 6 solutions with various volume ratios of trifluoroethyl alcohol (TFE) and formic acid (FA). The effect of the solvent type on the morphology of nylon 6 nanofibre membranes was investigated. Results showed that all membranes studied showed uniform, defect-free structures with very thin nanofibre diameters. The addition of formic acid led to a significant decrease in average fibre diameters. The average fibre diameters were 660, 186, 87, 62 and 30 nm for nylon 6 nonofibre prepared using the binary solution system and trifluoroethyl alcohol/formic acid (100:0), (75:25), (50:50), (25:75) & (0:100) respectively. In addition, the nylon 6 nanofibre membranes prepared using formic acid showed the highest strength with the highest porosity and the lowest average fibre diameters.

Key words: *nylon 6, formic acid, trifluoroethyl alcohol, nanofibre membrane, binary solution system.*

Introduction

Electrospinning is one of the most common techniques to produce nanofibre membranes due to its simplicity and versatility. In the electrospinning technique, electrostatic forces are utilised to produce nano-sized polymeric fibres [1]. Electrospun nanofibres have been used in many applications such as separation, filtration, tissue engineering, protective textiles, biomedical, pharmaceuticals, optics, electronics, health, and environmental engineering due to their high specific surface area, good pore interconnectivity and high porosity [2-5]. It has been known that the morphology of electrospun nanofibre membranes influences their final performance, which could be altered by changing the process parameters (solution feed rate, electric potential, distance between the tip and the collector, nozzle diameter, and geometry) and solution parameters (polymer type, molecular weight, vapour pressure, diffusivity in air, additives, surfactants, salts, polymer concentration, viscosity, electric conductivity, dielectric permittivity, surface tension etc). The polymer solution has the most significant effect on the morphology, and solution properties are strongly related to the solvent type. The solution conductivity, dielectric constant, boiling point, viscosity, surface tension and interaction between the polymer and solvent influence the morphology [6].

Table 1 summarises some of the studies in literature on the effect of the solvent system on the morphology of nanofibres. Cay et al. [7] studied the effect of the solvent system on the morphology of polyurethane nanofibres. A higher conductivity, dielectric constant and dipole moment with lower viscosity of the solvent system led to lower fibre diameters. Erdem et al. [8] dissolved polyurethane in N,N-dimethylformamide (DMF) and tetrahydrofuran (THF). Larger diameters were observed with the addition of THF due to changes in the solution viscosity, surface tension and conductivity [8]. Choktaweesap et al. [9] used the acetic acid/TFE system to dissolve gelatin. Fibre diameters increased by adding TFE, which was explained by the increase in viscosity and conductivity [9]. When viscosity increases, the viscoelastic force increases and the Coulombic stretching force decreases, which leads to an increase in fibre diameters. It has also been reported that increasing the boiling point in solvent systems leads to thinner fibres. Solvents with a higher boiling point evaporate more slowly and cause the jet to stretch to a much lower diameter [6]. Tungprapa et al. [10] studied different solvent systems (N-N dimethylacetamide/acetone, chloroform/methanol, dichloromethane/methanol) for cellulose asetate. Introducing acetone resulted in an increased fibre diameter, owing to an increase in conductivity of the solutions. The increased conductivity of the solution results in an increased electrostatic force in the jet, which causes the jet to reach the collector faster and have less time to stretch under Coulombic stress [10]. Although increased conductivity results in less stretching and faster travel to the collector, in some systems an increase in conductivity leads to an increased Coulombic stretching force and a decrease in fibre diameters [10].

Nylon based materials are preferred in many applications including filtration, biomedical, and energy due to their high mechanical strength, good dimensional stability, toughness and stiffness. These properties could be explained by the high number of amide units in the main molecule chain, which gives the molecule a higher percentage of crystallinity and enhances the formation of hydrogen bonds [11]. Nylon-6 is a biodegradable, biocompatible synthetic polymeric material with strong chemical and thermal stabilities as well as good mechanical and physical properties. Therefore, it is widely used in many industrial fields including filters, reinforcements, drug carriers, and scaffolds [4, 12, 13].

Formic acid is a common solvent for nylon 6 that allows to obtain fine nanofibres with a high aspect ratio [14]. In addition, trifluoroethyl alcohol is an organic compound with the formula CF_2CH_2OH which can be used as a solvent for nylon in industrial applications, in the pharmaceutical field and especially in biomedical applications, such as producing a scaffold [15]. In this study, nylon 6 nanofibre membranes prepared by electrospinning and a binary solution system with different volume ratios (trifluoroethyl alcohol/formic acid = 100/0, 75/25, 50/50, 25/75 and 0/100) were utilised. Experimental results showed that nylon 6 membranes produced using different binary solution systems had uniform morphology without any defect for all solution systems

Table 1. *Selected solvent systems studied in literature.*

Polymer	Solvent system	Effect of the solvent system	Morphology	Ref
Polyurethane	DMF/THF and DMF/ EA(Ethylacetate)	Increase in THF and EA increased viscosity	Thicker fibre with increasing viscosity	[7]
PEO	Distilled water and methanol, ethanol, or 2-propanol in various compositional ratios (90:10, 80:20, and 70:30 v/v)	Viscosity increased, surface tension decreased with the addition of and increasing alcohol content	Introducing 2-propanol improved electrospinninability	[16]
Polyamide 6	Formic acid, Formic acid/Dichloro methane, Formic acid/Acetic acid, Formic acid/ Acetic acid, Formic acid/ Chlorophenol	The polyelectrolytic behaviour of polyamide-6 in formic acid was attributed to the partial ionisation of the amide groups along the polymer chains	The formic acid and its mixed solvent systems were good solvents for high aspect ratio nanofibres	[14]
Cellulose acetate	DMAc/Acetone	Increasing acetone content resulted in an increase in conductivity and mass throughput	Larger fibre diameters	[10]
Gelatin	Acetic acid/TFE	Increasing TFE led to an increase in conductivity and viscosity	Smooth fibres and larger fibre diameters with increasing TFE	[9]
Polylactic acid	Acetone/ dimethylformamide	Mixed effect of lower viscosity, conductivity and surface tension	Increasing amount of acetone leads to bigger nanofibres and higher standard deviation from the mean diameter.	[6]
Cellulose	Ionic liquid with (DMAc), dimethyl formamide (DMF), and dimethyl sulfoxide (DMSO)	Lower viscosity and surface tension by adding co-solvent	Electrospinninble solutions	[17]
Cellulose acetate	DMAc/Acetone	Increasing acetone led to lower viscosity	Finer diameters	[18]
Cellulose	Ionic liquid/DMSO	Adding DMSO led to a decrease in the viscosity surface tension and an increase in conductivity	Electrospinninble solutions	[19]
Cellulose acetate	Acetone/water	Water improves electrospinnability by delaying evaporation of the solvent system	Electrospinable solution by adding up to 15% water	[20]
Ethyl cellulose	THF/DMAc	Increasing DMAc increases polarity	Lower fibre diameters with increasing DMAc	[21]

Table 2. *Properties of solvents.*

Solvent	Density, g/cm^3	Boiling point, °C	Dipole moment, Debye	Dielectric constant	Ref
TFE	1.38	74	2.52	8.55	[9]
FA	1.213	100.7	1.40	58.5	[10]

studied. Moreover, nylon 6 nanofibre membranes prepared using formic acid had the highest porosity and lowest average fibre diameters. The influence of the TFE/FA solvent system on the morphology and physical properties of nylon 6 nanofibres is reported for the first time in this study.

Material and method

Nylon 6, formic acid and trifluoroethyl alcohol were purchased from Aldrich. All chemicals were used as received without further purification. Nylon 6 solutions were prepared by dissolving 13 wt % nylon 6 in trifluoroethyl alcohol/formic acid with ratios of 100/0, 75/25, 50/50, 25/75 and 0/100 (vol/vol). The solutions were stirred at room temperature for at least 8 hours to ensure dissolution of the polymer. A one-needle electrospinning set up (Nanospinner) with a rotating collector was used for all sample preparations. During the preparation of nylon 6 nanofibre membranes, a high voltage of 20 kV was applied. The feeding rate used was 1 ml/h and the tip-to-collector-distance – 11 cm. Scanning electron microscopy (FEI) were used for morphology study. The porosities of the membranes were determined by image analysis – Image J. The diameters were analysed using Revolution software. The pore size (pore diameter, D) was calculated using the equation below:

$$D = \pi d/4(1 - \varepsilon)$$

where ε is the mean porosity, and d the mean fibre diameter. The mechanical properties of the membranes were determined using a universal tensile tester (Instron) with a 100 N capacity load cell. The sample dimensions of test specimens were 10 mm width, 60 μm thickness, and 60 mm length.

Results and discussion

The morphology of nylon 6 nanofibre membranes was studied using SEM images. ***Figure 1*** shows SEM images of nylon 6 nanofibre membranes prepared using nylon 6/trifluoroethyl alcohol solution (N1) at different magnifications. The average diameter is 660 ± 162 nm. ***Figures 2-4*** show SEM images of nanofibre membranes prepared with trifluoroethyl alcohol/formic acid solvent systems. The average fibre diameters are measured as 186 ± 34, 87 ± 30, 62 ± 15 nm for nylon 6 membranes prepared using the trifluoroethyl alcohol/formic acid solvent system with ratios of 75/25, 50/50, 25/75, respectively. ***Figure 5*** shows SEM images of nylon 6 membrane prepared using formic acid. The SEM images show that all membranes have bead-free uniform morphology. In addition, introducing formic acid leads to a decrease in average fibre diameters. The average fibre diameter for nylon 6 membranes prepared with formic acid is 30 ± 6 nm. This significant decrease in average fibre diameters could be attributed to the high dielectric constant of formic acid. ***Table 2*** shows the solvents properties. The dielectric constant for TFE is 8.55, whereas that of formic acid is 58.5. The increase in the dielectric constant with an increasing formic acid ratio led to thinner fibres. Similar results were also reported by Cay et al. [7]. Due to the relatively low dielectric constant and conductivity of THF, introducing THF into DMF led to an increase in the average fibre diameter. Erdem et al. [8] studied polyurethane in the N,N-dimethylformamide/tetrahydrofuran solvent system and reported that a greater dielectric constant led to finer polyurethane fibres. The dielectric constant shows the polarity of the solvent, and charges have a more pronounced effect on polar solvents than on non-polar solvent. Polar solvents a with high dielectric constant have a higher charge density in the solution, which results in thinner fi-

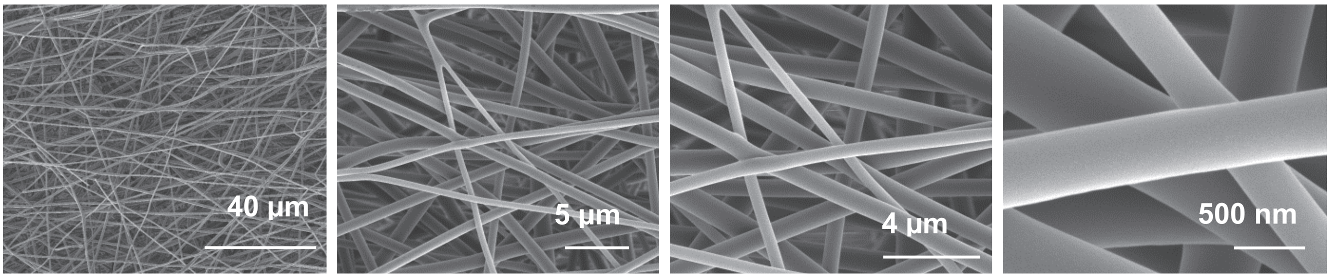

__Figure 1.__ SEM images of nylon 6 membranes prepared with trifluoroethyl alcohol.

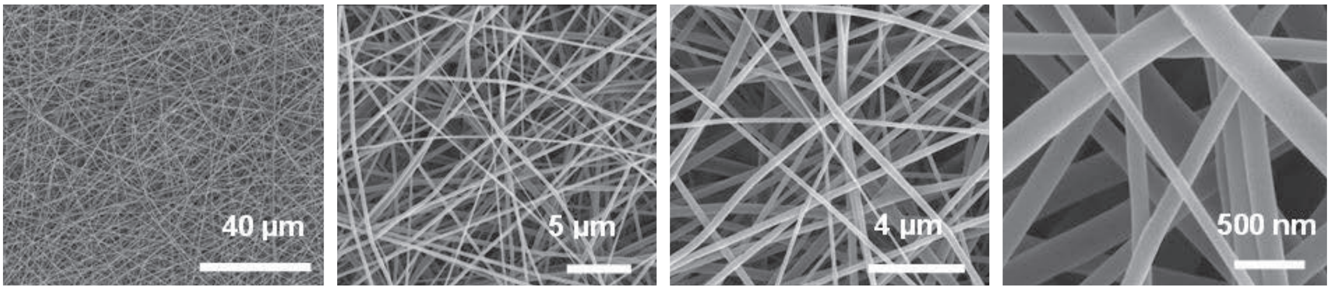

__Figure 2.__ SEM images of nylon 6 membranes prepared with trifluoroethyl alcohol/formic acid (75/25).

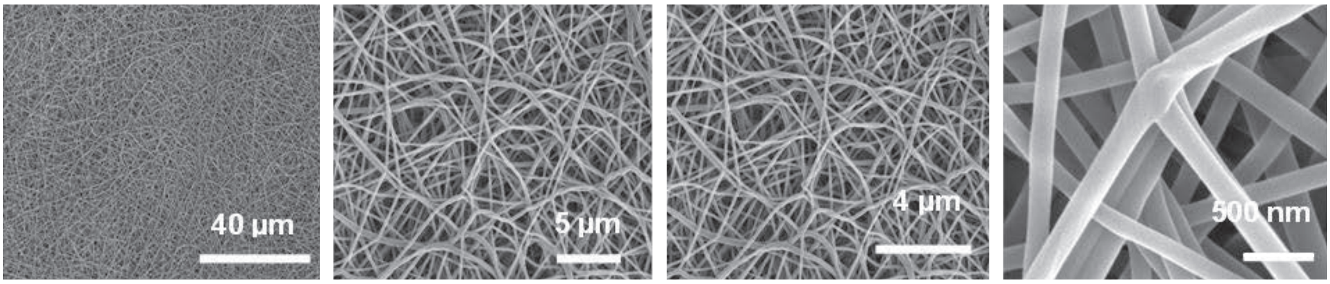

__Figure 3.__ SEM images of nylon 6 membranes prepared with trifluoroethyl alcohol/formic acid (50/50).

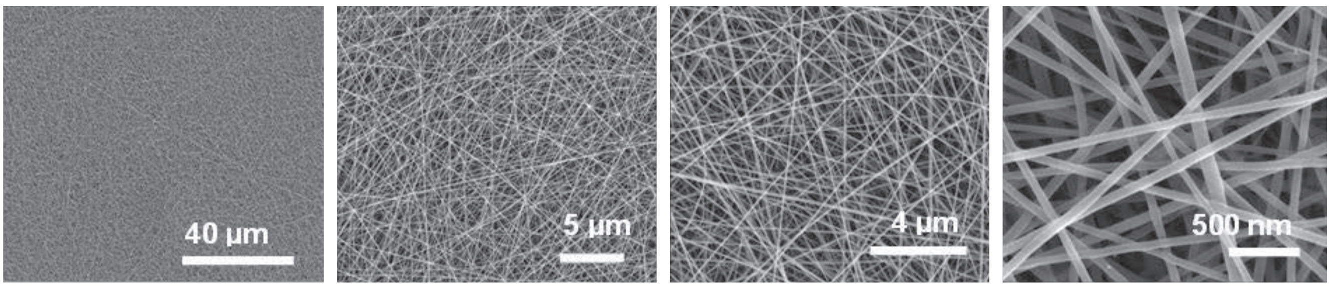

__Figure 4.__ SEM images of nylon 6 membranes prepared with trifluoroethyl alcohol/formic acid (25/75).

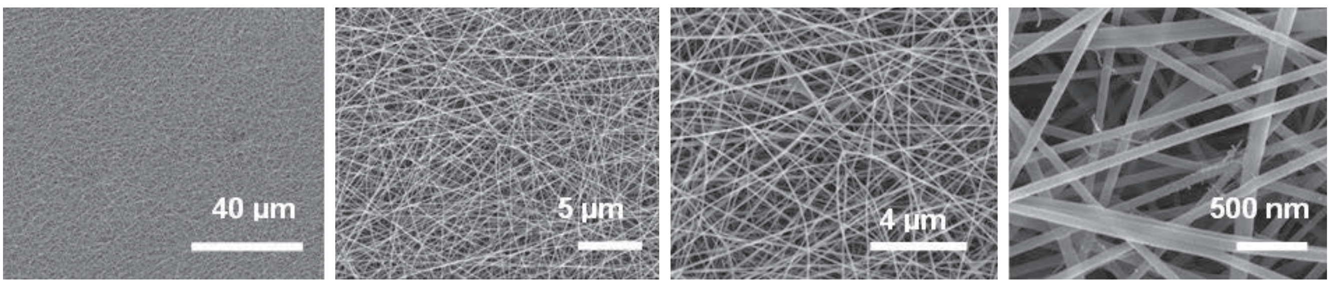

__Figure 5.__ SEM images of nylon 6 membranes prepared with formic acid.

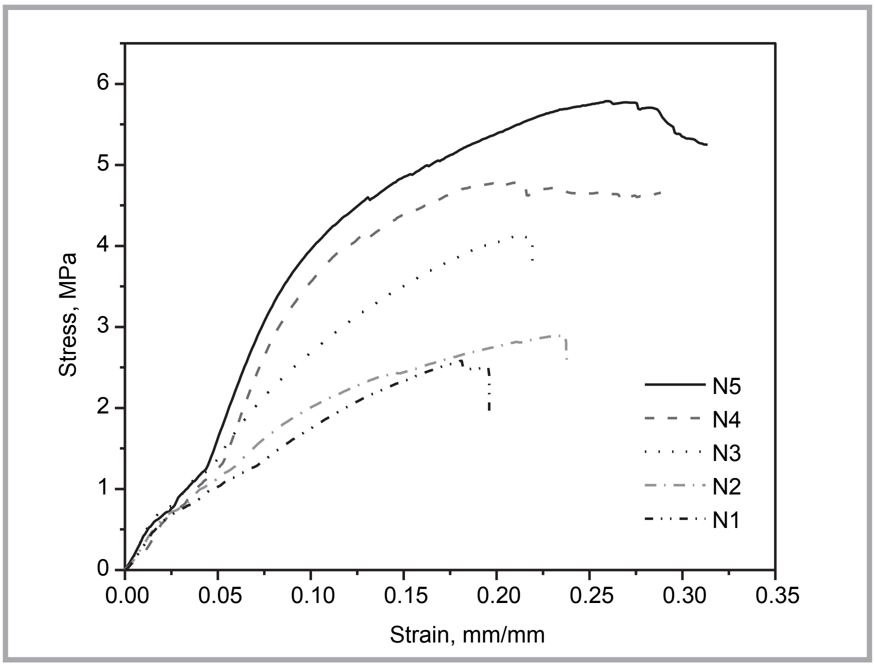

Figure 6. Stress strain curves of nylon 6 nanofibre membranes.

Table 3. Average fibre diameters and porosities of nylon 6 membranes.

Samples	Concentration	Trifluoroethyl alcohol/ Formic acid, v/v	Average fibre diameter, nm	Porosity, %	Pore size, nm
N1	13%	100/0	660 ± 162	36	810
N2	13%	75/25	186 ± 34	50	292
N3	13%	50/50	87 ± 30	66	201
N4	13%	25/75	62 ± 15	75	195
N5	13%	0/100	30 ± 6	82	130

bres, owing to larger elongation forces under the electric field [8]. Son et al. [22] studied the electrospinning of poly(ethylene oxide) in different solvents and those with a higher dielectric constant led to thinner PEO fibres [22]. Nirmala et al. [12] studied the electrospinnability of nylon 6 in different solvents including formic acid, acetic acid, hexafluoroisopropanol, trifluoroacetic acid and chlorophenol. The thinnest fibre was observed when formic acid was used, which was attributed to the high dielectric constant of formic acid [12].

The high porosity of nanofibre membrane is beneficial for many applications including electronic, filtration and biomedical [23]. ***Table 3*** presents the porosity values for nylon 6 membranes produced with different solvent systems. The introduction of formic acid changes the morphology and porosity significantly. According to ***Table 3***, porosity is increased by increasing the formic acid ratio. The porosity values are 36%, 50%, 66%, 75%, and 82%, respectively, for nylon 6 membranes prepared using the TFE/FA solvent system with volume ratios of 100/0, 75/25, 50/50, 25/75, 0/100. The increase in porosity could be explained by the significant decrease in average fibre diameter by introducing formic acid. Increasing the porosity with a decreasing average fibre diameter was also reported by Yanilmaz et al. [24].

Introducing formic acid also leads to a decrease in pore size. While the pore size is 810 nm when TFE is used, adding 25 vol% FA causes pore size reduction to 292 nm. The pore size is 130 nm when formic acid is used. Ryu et al. [25] studied nylon 6/formic acid solution and indicated that the pore size depends on average fibre diameters and increasing fibre diameters results in increased pore diameters [25].

The mechanical strength of nanofibres is important for different applications, and it has been reported that the polymer type as well as the fibre structure, fibre size distribution, porosity, orientation, defects, and geometrical arrangements of fibres and their interactions affect the mechanical properties of electrospun membranes [8]. The tensile properties of nylon 6 nanofibre membranes prepared with different solvent systems were tested, and typical stress strain curves are shown in ***Figure 6***. Nylon 6 membranes prepared with FA show a high strength of 5.5 MPa with an elongation at break of over 0.3. However, nylon 6 membranes prepared with TFE show a tensile strength of 2.5 MPa at a lower elongation at break of about 0.2. This results confirms that there is a strong interaction between the morphology and mechanical properties of electrospun membranes. The higher strength of the membranes could be attributed to higher connectivity between fibres due to the low average fibre diameters. Maleki et al. [26] also reported lower strength with an increasing fibre diameter for PLLA fibres. Erdem et al. [8] also reported that defect-free morphology resulted in higher tensile strength. Baji et al. [27] studied the mechanical properties of nylon 6.6 nanofibres with different average fibre diameters and reported that increasing average fibre diameters resulted in a decrease in strength [27].

Conclusions

Formic acid, trifluoroethyl alcohol and a mixture of these solvents were utilised to dissolve nylon 6, and these solutions were used to fabricate nylon 6 nanofibre membranes. The effect of the binary solution system on the morphology of nylon 6 nanofibre membranes was investigated. All membranes studied showed uniform defect-free structures with very thin nanofibre diameters. In addition, nylon 6 nanofibre membranes prepared using formic acid showed the highest porosity and tensile strength with the lowest average fibre diameters.

Acknowledgements

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