

A novel method of selecting solvents for polymer electrospinning

C.J. Luo, M. Nangrejo, M. Edirisinghe*

Department of Mechanical Engineering, University College London, Torrington Place, London WC1E 7JE, UK

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ABSTRACT

The selection of a desirable solvent or solvent system as the carrier of a particular polymer is fundamental for the optimisation of electrospinning. Solvent selection is pivotal in determining the critical minimum solution concentration to allow the transition from electro spraying to electrospinning, thereby significantly affecting solution spinnability and the morphology of the electrospun fibres. 28 solvents diversely positioned on the Teas graph were studied for their solubility and electrospinnability for making polymethylsilsequioxane (PMSQ) solutions. The results are combined and mapped on the Teas graph using different colour codes. Based on this new spinnability–solubility map, various solvent systems for PMSQ are methodically developed. Solvents are selected to produce binary solvent systems that have solvent parameters close to a good single solvent for electrospinning of the polymer solution. This work shows that solvents of high solubility do not necessarily produce solutions good for electrospinning. Polymethylsilsequioxane solutions of the same concentration in solvents of partial solubility showed better spinnability than solutions in solvents of high solubility. A methanol–propanol binary solvent system produced electrospun fibres with high surface porosity, showing that high volatility and high vapour pressure difference among solvents mixed can induce phase separation in electrospinning. It is noteworthy that the binary solvent system mixing 2-nitropropane (high solubility) and dimethylsulphoxide (non-solvent), neither of which exhibited high volatility, also produced highly porous electrospun fibres. This demonstrates that phase separation can be induced by solubility difference in the electrospun polymer solution.

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1. Introduction

Electrospinning has become one of the most prominent modern methods of fibre and scaffold production for electrical, chemical and biomedical applications [1]. In electrospinning, usually a polymer solution is subjected to a very high electrostatic force which causes the polymer solution or melt to eject and spray or spiral rapidly from a nozzle or a spinneret and deposit randomly on an electrically grounded collector as fibres or fibrous mats. The outcome of an electrospinning process is under the influence of a large number of interrelated variables, including operating parameters (such as applied voltage, flow rate, collection distance and nozzle tip polarity), polymer molecular chain length, attributes of the solution (such as concentration, presence of additives, and solvent and solution properties), size of the nozzle orifice, and physical nature and geometry of the collecting substrate. A delicate balance among all the above-mentioned variables governs the success of an electrospinning process. To date, due to the lack of a complete understanding of the complex interplay of the interrelated variables

influencing the process, the optimisation of electrospinning parameters is still largely carried out on a trial-and-error basis subjective to the individual design of the experiment [2,3].

Previous results have suggested that attributes of the polymer solution and applied voltage dominate the onset of the transition from electro spraying to electrospinning to form fibres, and the morphology of the as-spun fibres [4]. To produce nanofibres, one of the most influential variables to consider is polymer solution concentration. A critical minimum concentration c_c is needed to allow molecular chain entanglements and for electrospinning to proceed. This critical minimum concentration is defined as the minimum concentration required for forming beaded nanofibres [5,6]. Concentrations below c_c will produce droplets when electrified (electro spraying). At concentrations above c_c , electrospun fibre diameter increases and frequency of bead-on-string formation decreases with increasing concentration. However, the value of c_c is dependent on the molecular chain length, the chemical nature of the polymer and the solvents selected for the polymer solution. When a particular polymer of specific average molecular weight and molecular chain length is used in electrospinning, the selection of solvents for the polymer solutions plays a pivotal role in determining the value of c_c . Consequently, the selection of a “good” solvent and the development of a suitable solvent system for

* Corresponding author. Tel.: +44 20 7679 3942; fax: +44 20 7388 0180.
E-mail address: m.edirisinghe@ucl.ac.uk (M. Edirisinghe).

a given polymer are fundamental to the success of an electrospinning process for nanofibre production [1–9].

Solubility parameters are used to aid the search for suitable solvents and solvent systems for polymers used in electrospinning. Among the large variety of solubility scales in the literature, a ternary solubility diagram, also named as the Teas graph, has been repeatedly mentioned in literature for its usefulness to select solvents for making polymer solutions. Compared to other 2D and 3D diagrams such as Crowley's solubility maps and Hansen graphs, the Teas graph benefits from having all three solubility parameters presented onto a 2D graph, allowing a more straightforward analysis of the solubility behaviour of the polymer of interest [3,10–12].

Teas introduced fractional cohesion parameters f_d , f_p , and f_h , mathematically derived from the dispersion forces component δ_d , the polar force component δ_p and the hydrogen bonding component δ_h of the Hansen parameters, respectively. Teas graph expresses the fractional parameters on a ternary plot drawn as a triangle. Each side of the triangle represents a distinct variable and has a scale of 0–100. Any solvent with defined Hansen parameters [13] can be exclusively located by plotting the three corresponding fractional parameters on the Teas graph. Positions of solvents of the same class have a tendency to cluster in a linear pattern inclined to the bottom right of the Teas graph, which emphasizes dispersion forces. This is because dispersion forces are ubiquitous in all solvents, unlike polar forces and hydrogen bonding [11]. Although all the data of the Teas graph is empirically derived, the Teas graph has been adopted and tested in many previous studies and has shown a reasonable degree of accuracy and practicality for providing insights on the solubility of many polymers [2,11,14,15]. Because solvent positions on the Teas graph are unique and invariable, if a given polymer is tested for solubility in a selection of solvents, keeping other variables such as solution concentration, operating temperature and pressure constant, the solubility region of the polymer can be defined on the Teas graph. This empirically determined solubility region on the Teas graph provides a valuable means for solvent system selection.

In recent years, some electrospinning studies have used the Teas graph as a means to select solvents for electrospinning, based on a theory that a suitable solvent for electrospinning should have solubility parameters fallen within the parameter zone where the polymer appear most soluble on the Teas graph [2,10,12,15]. However, previous literature has abundantly suggested that a solvent may dissolve a polymer of interest well, but whether the resulted solution could be fabricated into fibres by electrospinning cannot be guaranteed [16–19]. This work uses the Teas graph to select solvent and solvent systems, and we attempt to elucidate the correlation between solubility behaviour of the polymer and the electrospinnability of the polymer solutions made with solvents mapped from the Teas graph from both different parameter zones, as well as different chemical groups. Furthermore, we venture to verify that when a polymer dissolves in a solvent better than another solvent, if that would mean the resulting solution in the former is better suited for electrospinning.

Polymethylsilsesquioxane (PMSQ) is used in this work as a model polymer to illustrate the method. PMSQ is an interesting material for both polymer and ceramic materials engineering because the PMSQ polymeric architectures can be directly converted to ceramic silicon oxycarbide via pyrolysis [20]. PMSQ is a non-polar, biocompatible polymer comprising methylsilsesquioxane units which are trifunctional organosilicon units. PMSQ can take a fine white powder form composed of minute spherical particles usually having a particle diameter of 0.05–100 μm . It has good slip properties and disperses excellently into organic liquids [21]. Silicon oxycarbide is robust, stable and has demonstrated potential applications in blood contact devices [22].

2. Experimental

2.1. Materials

PMSQ polymer, average molecular weight 7465 g/mol, polydispersity 3.4, was obtained from Wacker Chemie AG. Acetone, acetonitrile, aniline, *n*-butyl acetate (BuAc), chloroform, cyclohexanone, diethylene glycol (DEG), diethylene glycol monoethyl ether, *N,N*-dimethylformamide (DMF), diacetone alcohol, dimethylsulphoxide (DMSO), ethanol (EtOH), 2-ethoxyethanol, 2-ethoxyethyl acetate, ethyl acetate, ethylene dichloride (EDC), ethylene glycol (ethanediol), glycerol, methanol (MeOH), methyl acetate (MeAc), methylene chloride (DCM), morpholine, 2-nitropropane (2NP), 1-pentanol, *n*-propanol (PrOH), propylene carbonate, and tetrahydrofuran (THF) were obtained from Sigma-Aldrich. All reagents were of analytical grade and were used as received.

2.2. Mapping solubility region of PMSQ on the Teas graph

Solubility of a selection of 28 diversely positioned common solvents on the Teas graph was tested with PMSQ at 60%w/w PMSQ concentration, atmospheric pressure and ambient temperature of 22 °C. Solvent positions on the Teas graph are identified by their respective fractional cohesion parameters based on Barton [13]. The degree of swelling or dissolution was visually assessed after stirring for 10 min, 30 min and 24 h respectively. Assessed solubility was categorised and recorded as insoluble, poor, partial, partial to high and high, based on the time taken for PMSQ to dissolve in a solvent to form a homogeneous solution. The categorised results were mapped on the Teas graph by highlighting the solvent location on the Teas graph with designated colours, i.e. black denotes insoluble; grey denotes poor solubility; blue denotes partial solubility; green denotes partial to high solubility; and red denotes high solubility. The solubility map of PMSQ is identified by drawing a contour around the solubility test results of the selected solvents on the Teas graph.

2.3. Selection and testing of binary solvent systems

Our hypothesis for the selection of a solvent system for electrospinning using a Teas graph is that the solvent system should dissolve the polymer and allow electrospinning if the position of the solvent system on the Teas graph lies in close proximity to the position of a good solvent for electrospinning for a particular polymer. This method becomes valuable when mixing two originally unsuitable solvents to create a solvent system desirable for electrospinning, because the proportion of the solvents mixed can be geometrically determined based on the Teas graph using the lever rule as illustrated in literature: first, a line joins the positions of the two solvents selected on the Teas graph, solvent A and B. If this line significantly crosses the solubility region of the given polymer, the solvent system mixed using the following method is hypothesised to dissolve the polymer well. A point on this line (P) that lies in the closest proximity to the position of an empirically tested good solvent for electrospinning of the polymer is then selected and the fraction of each solvent component in the solvent system is calculated using the relationships: volume fraction of solvent A = length of BP/length of AB, and volume fraction of solvent B = length of AP/length of AB [11]. The solubility of the solvent systems mixed was tested at 60%w/w PMSQ concentration, atmospheric pressure and ambient temperature of 22 °C. The solubility results were compared to predictions drawn from the Teas graph.

2.4. Solution electrospinnability and electrospun fibre morphology

If a solvent or solvent system dissolves PMSQ, the resulting solution was tested for electrospinning with a 330 μm orifice diameter stainless steel nozzle connected to a high voltage power supply (Glassman Europe Limited, Bramley, UK) which generates positive DC applied voltages up to 30 kV. Spinning parameters were set at flow rate of 20 $\mu\text{L}/\text{min}$ controlled by a Harvard syringe pump (Harvard Apparatus Ltd., Edenbridge, UK), deposition distance of 80 mm and applied voltage was maintained at 20 kV. All electrospinning were conducted at an ambient temperature of 22 $^{\circ}\text{C}$, and 59% humidity. Fig. 1 shows a schematic diagram of the electrospinning setup for this investigation. Fibres were deposited on glass slides covering a grounded stainless steel collection platform. The morphology of the electrospun PMSQ fibres was analysed visually with an optical microscope, Nikon Eclipse model ME600; and from scanning electron micrographs taken with a field emission scanning electron microscope (SEM), model JSM-6301F. For SEM, each sample was coated with gold for 60 s prior to observation under the SEM. The average diameter was determined by analysing the SEM images using Fovea Pro 4.0 (Reindeer Graphics Inc., Asheville, NC, USA), a 16 Bit Image Processing and Analysis Tool for Adobe Photoshop[®] 7, CS(8) and CS2(9). The results of solution electrospinnability were combined with the solubility map on the Teas graph to produce a spinnability–solubility map for PMSQ.

3. Results and discussion

3.1. Solubility and solution electrospinnability

The issue of solvent suitability for electrospinning is complex. Considerable efforts have been spent on the development of suitable solvents and solvent systems for electrospinnable polymer solutions. The spinnability of a polymer solution has been explained based on solution concentration and solvent and solution properties. It is often only mentioned that “good solvents” for a particular polymer were employed. However, no clear standard has been established for judging whether a solvent of high solubility for a polymer will produce a solution good for electrospinning [2,15,17,23].

Considering the above-mentioned lacunae, we explore the effect of solvent solubility for the electrospinning of the polymer solution. In this work, a polymer solution is considered to exhibit good electrospinnability when continuous and stable fibre production with uniform fibre morphology and minimal ‘bead-on-string’ formations

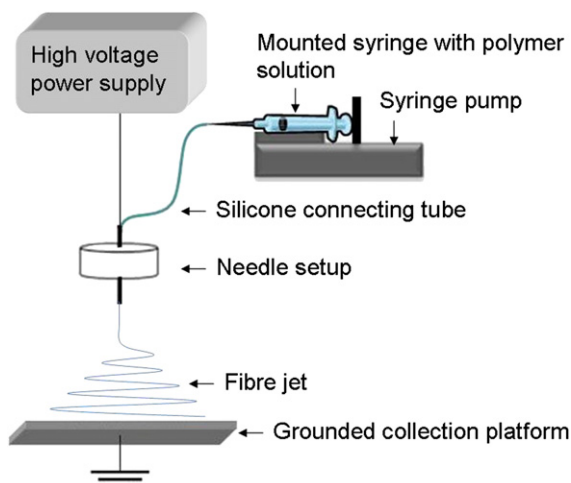


Fig. 1. Schematic diagram of an electrospinning setup.

Table 1

PMSQ solubility, solution electrospinnability and fractional solubility parameters of solvents used in this work. List is in alphabetical order. Fractional solubility parameters are based on Barton [13].

Solvent	PMSQ solubility	Electrospinnability	100f _a	100f _p	100f _h
Acetone	Partial	Spin	47	32	21
Acetonitrile	Insoluble	–	39	45	16
Aniline	Poor	–	50	19	31
<i>n</i> -Butyl acetate	High	Spray	60	13	27
Chloroform	Partial	Spin	67	12	21
Cyclohexanone	High	Spray	55	28	17
Diacetone alcohol	Poor	–	45	24	31
Di(ethylene glycol)	Insoluble	–	31	29	40
Diethylene glycol monoethyl ether	Poor	–	48	23	29
<i>N,N</i> -Dimethylformamide	Insoluble	–	41	32	27
Dimethylsulfoxide	Insoluble	–	41	36	23
Ethanedione	Insoluble	–	30	18	52
Ethanol	Partial	Spin	36	18	46
2-Ethoxyethanol	Partial to high	Transition	42	20	38
2-Ethoxyethyl acetate	High	Spray	51	15	34
Ethyl acetate	High	Spray	51	18	31
Ethylene dichloride	Partial to high	Transition	67	19	14
Glycerol	Insoluble	–	25	23	52
Methanol	Partial	Spin	30	22	48
Methyl acetate	Partial	Spin	45	36	19
Methylene chloride	Partial to high	Spin (beaded fibres)	59	21	20
Morpholine	Poor	–	57	15	28
2-Nitropropane	Partial to high	Transition	50	37	13
1-Pentanol	High	Spray	46	13	41
<i>n</i> -Propanol	Partial	Spray	40	16	44
Propylene carbonate	Insoluble	–	48	38	14
Tetrahydrofuran	Partial	Spin	55	19	26
Water	Insoluble	–	18	28	54

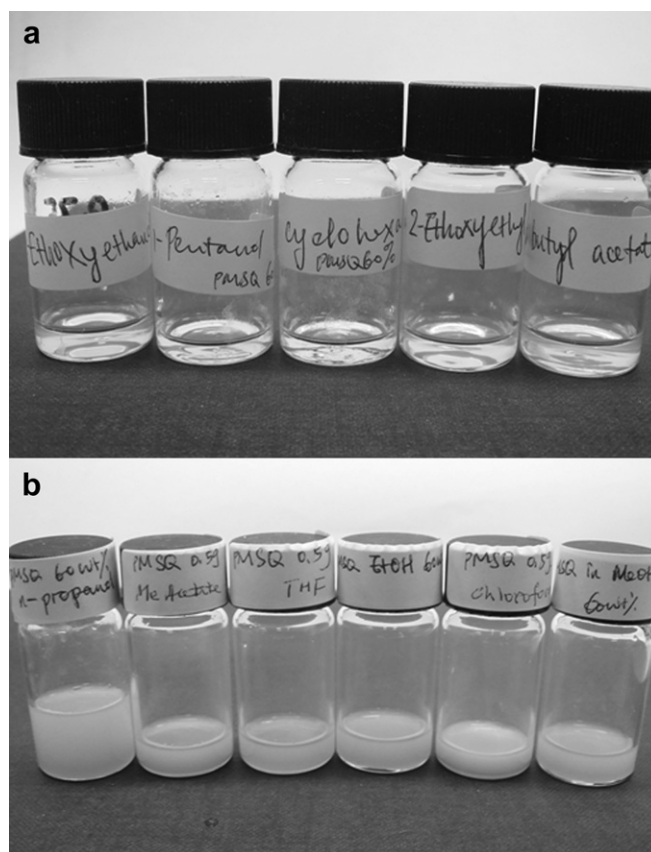


Fig. 2. (a) Samples with high solubility for PMSQ formed colourless solutions. (b) Samples with partial solubility formed white solutions.

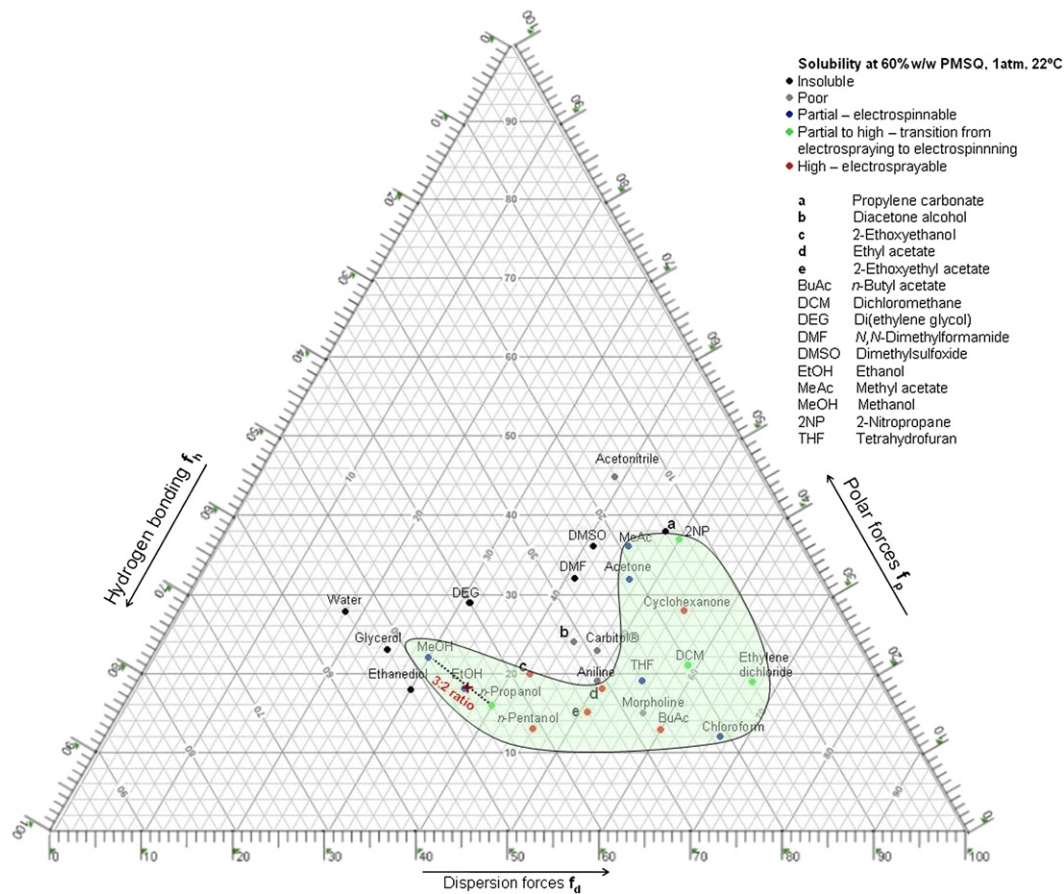


Fig. 3. Spinnability–solubility map for PMSQ based on the ternary fractional parameter solubility diagram, tested on solubility of PMSQ at 60%w/w PMSQ concentration, 1 atm, 22 °C. Successful solutions were tested for electrospinnability. Positions of solvents are based on fractional solubility parameters from Barton [13]. The figure also shows an illustration for locating geometrically on the Teas graph identities and proportions of solvents mixed, using the lever rule, to create desirable binary solvent systems for electrospinning. For example, MeOH and PrOH are mixed. A line joins the position of the two solvents. EtOH is then identified as a good electrospinnable solvent which lies in the closest proximity to this line. A point on the line that's closest to the position of EtOH is then marked as a cross. The ratio of the lengths from this point to MeOH and PrOH respectively is calculated. This ratio (3:2 with respect to PrOH:MeOH) is the volume ratio of the solvents in the binary solvent system.

are observed during electrospinning. Interestingly, by combining solubility and spinnability results in Table 1, it is evident that polymer solutions in solvents of high solubility produce electrospun beads and droplets and are unsuitable for electrospinning a 60%w/w PMSQ system. On the other hand, except for *n*-propanol, all the solutions in solvents of partial solubility for PMSQ demonstrated good electrospinnability at 60%w/w concentration. This result shows that solvents of partial solubility produced electrospinnable solutions at 60%w/w PMSQ concentration, while solvents of high solubility need a concentration higher than 60%w/w to be electrospinnable, or they may be unsuitable for electrospinning all-together. Incidentally, Shenoy et al. [17] reported that polyvinylidene fluoride (PVDF) solution in acetone, a poor solvent for the polymer, can produce electrospun fibres at concentrations as low as 7.5%w/w; whereas, a concentration of 30%w/w PVDF ($M_w = 180$ k) in DMF—a good solvent, was believed to be necessary to obtain electrospun fibres. Their findings concurred with our results. In addition, except for *n*-propanol, solutions in solvents of high solubility for PMSQ appeared colourless or very faintly white [Fig. 2a], while solutions in solvents of partial solubility for PMSQ appeared white [Fig. 2b].

The assessed results of PMSQ solubility and electrospinnability in Table 1 are mapped and colour-coded on the Teas graph and the combined spinnability–solubility map of PMSQ is then drawn as a contour around the solubility results and demonstrated in Fig. 3 as a green shaded region. Solvents positioned within the region are expected to dissolve the polymer. It must be noted that the

solubility region of a polymer is dependent on the chemical and physical nature of the polymer, and the concentration, temperature and pressure at which the solubility tests are conducted.

3.2. Binary co-solvent system selection for electrospinning

To maximise the degree of polymer molecular chain entanglement for electrospinning of ultra-fine fibres, choice of solvent and solvent system is crucial for a polymer solution of fixed polymer average molecular weight and concentration. Polymer solution viscosity varies with the position of the solvent in the given polymer solubility region as the quality of solvent–polymer interactions affects the chain geometry of the polymer [24]. This work used solubility and spinnability maps drawn on the Teas graph to identify and combine solvents of different chemical nature, solubility and spinnability to create suitable binary solvent systems for

Table 2

An illustration showing how fractional parameters of a solvent mixture can be calculated using fractional parameters of the solvent components, following the lever rule.

Solvent	f_d	f_p	f_h
MeOH	$30(\times 2/5) = 12$	$22(\times 2/5) = 8.8$	$48(\times 2/5) = 19.2$
PrOH	$40(\times 3/5) = 24$	$16(\times 3/5) = 9.6$	$44(\times 3/5) = 26.4$
MeOH:PrOH 2:3 ratio	$f_d = 12 + 24 = 36$	$f_h = 8.8 + 9.6 = 18.4$	$f_p = 19.2 + 26.4 = 45.6$

Table 3
Solubility and electrospinnability results of 60%w/w PMSQ in binary solvent systems developed using the Teas graph.

Solvent mixture	Ratio	Prediction	PMSQ solubility	Electrospinnability	Average fibre diameter (μm)
DMF (non-solvent): Cyclohexanone (high solubility)	1:1	Partial to poor	Poor After standing for 2 hrs, mixture appeared as a tough colourless gel.	–	–
MeOH (partial solubility): <i>n</i> -Propanol (partial-high solubility)	2:3	Partial	Partial	Spin, porous	0.8
DMSO (non-solvent): 2NP (partial-high solubility)	3:2	Poor to partial	Partial	Spin, porous	1.0
<i>n</i> -Pentanol (high solubility): water (non-solvent)	3:2	Partial	Poor	–	–
MeOH (partial solubility): <i>n</i> -Pentanol (high solubility)	2:1	Partial to high	Partial to high	Transition	–
EDC (partial-high solubility): BuAc (high solubility)	1:1	Partial to high	Partial to high	Transition	–
DCM (partial-high solubility): Acetone (partial solubility)	1:1	Partial to high	Partial to high	Transition	–
MeAc (partial solubility): 2NP (partial-high solubility)	1:1	Partial to high	Partial to high	Transition	–
Ethanol (partial solubility): Acetone (partial solubility)	1:1	Insoluble	Partial	Spin	3.0
Ethanol (partial solubility): Acetone (partial solubility)	2:1	Insoluble	Partial	Spin	3.0
Ethanol (partial solubility): Acetone (partial solubility)	3:1	Insoluble	Partial	Spin	2.2

electrospinning of PMSQ solutions. The new combined spinnability–solubility map allows for a systematic selection of solvents for creating electrospinnable binary solvent systems for PMSQ, based on the theory that the mixed solvent system should dissolve the polymer and allow electrospinning if the solubility parameter of the solvent system is close to that of a good solvent for electrospinning for a particular polymer. When mixing two solvents, the proportion of each solvent component in the solvent system can be derived geometrically on the Teas graph using the method described in the [Experimental section](#) (Fig. 3). Hence, the new map on the Teas graph has significant practicality in solvent selection and solvent system development for a particular polymer in electrospinning, especially when the solvents mixed have different solubility or electrospinnability for the polymer. For example, to make an electrospinnable solvent system from a non-solvent and a solvent of high solubility, or to mix two solvents originally non-electrospinnable to create a solvent system which allows electrospinning to proceed. Our spinnability–solubility map greatly simplifies the binary solvent mixing process, and is a first, to the best of our knowledge.

A very comprehensive illustration of selecting solvent mixtures using the Teas graph can be found in Burke [11]. To illustrate this, a binary solvent system mixing methanol (MeOH, partial solubility) and propanol (PrOH, partial solubility) in a 2:3 volume ratio will have their fractional parameter values f_d , f_p and f_h of 36, 18.4 and 45.6, respectively (Table 2, Fig. 3). On the Teas graph, this mixture is positioned in close vicinity to ethanol, which is a commonly used and desired solvent for PMSQ electrospinning. Therefore, the mixture is expected to be a suitable solvent system for electrospinning.

The method allows the possibility of mixing together specific solvents originally unsuitable for electrospinning to create a solvent system that allows electrospinning to proceed. Hence, becoming useful when a solvent does not make an electrospinnable solution on its own for the polymer of interest, but is particularly preferred to, for reasons such as higher bio-safety or selective dissolution. Shenoy et al. [17] discussed the effect of solvent quality in their studies and their findings supported our supposition that mixing solvents of lower solubility with higher solubility can produce electrospinnable solutions at a lower critical concentration. They mentioned addition of poor solvent acetone to a PVDF solution ($M_w = 180$ k) in good solvent DMF significantly lowers the critical concentration necessary for fibre formation. Our empirical solubility results for the binary solvent systems created in this work showed an acceptable degree of consistency with the theoretical predictions drawn from the Teas graph (Table 3). The Teas graph provides a reasonable guidance for the solubility of binary solvent systems for a particular polymer, especially for the prediction of non-solvent and good solvent mixtures. However, when mixing

acetone and ethanol, both partial solvents good for electrospinning for PMSQ, the mixture showed partial solubility and was electrospinnable in 1:1, 2:1 and 3:1 mass ratios of ethanol:acetone, though this theoretically falls outside the solubility map on the Teas graph. The mixture of acetone and ethanol is positioned within the large insoluble zone on the Teas graph, bounded clockwise by DMF, Carbitol[®], Aniline and DEG. It is possible that there may exist a small soluble region within this insoluble zone, beyond the 28 solvent samples we have tested.

Furthermore, the Teas graph has been mentioned for its potential to help create solvent systems for selective polymer solubility, where one polymer is dissolved leaving the rest in situ [2]. This is desirable when a multi-component fibrous structure requires targeted dissolution of one component to achieve porosity or a tubular shape [25,26]. The solubility regions of both polymers can be overlapped on one Teas graph and a solubility area mutually exclusive to both polymers can be located. A selective solvent system that dissolves one but not the other can be developed using the previously illustrated geometrical method, as long as the line linking two solvent components crosses the mutually exclusive area on the overlapped solubility regions [11].

Our work focused on the empirical development of a solvent selection method for making solvent systems for electrospinning. A

Table 4
Electrospinnability results of 60%w/w PMSQ solutions in various single solvent systems electrospun at applied voltage 20 kV, flow rate 20 $\mu\text{l}/\text{min}$, and collection distance from nozzle tip to substrate 80 mm.

Sample	Solvent	Average fibre diameter (μm)	Fibre morphology
A	Ethanol	0.83	Beads and short fibres, ribbon cross-section
B	Methanol	0.40	Beads and droplets, short nanofibres, uneven surface
C	Acetone	2.0	Smooth continuous fibres, circular cross-section
D	THF	3.5	Smooth continuous long fibres
E	Methyl acetate	3.3	Smooth continuous long fibres
F	Chloroform	–	Needle blockage, viscosity too high, not electrospinnable
G	<i>n</i> -Propanol	–	Beads (electrospray)
H	<i>n</i> -Pentanol	–	Beads (electrospray)
I	Cyclohexanone	–	Beads with 'tapered tails' (transition)
J	<i>n</i> -Butyl acetate	–	Beads (electrospray)
K	2-Ethoxyethanol	–	Beads with 'tapered tails' (transition)
L	2-Ethoxyethyl acetate	–	Beads (electrospray)
M	DCM	2.6	Continuous long fibres with beads

detailed comparison between our empirical results and the existing extensional rheology and flow kinematics of the solution jet [4,27,28] should be further explored in future works, but is out of the scope of this work.

3.3. Electrospun fibre morphology

3.3.1. Single solvent systems

The characterisation of the electrospun fibre morphology for single solvent systems is summarised in Table 4. 2-Ethoxyethanol and cyclohexanone are good solvents for PMSQ. When their solutions at 60%w/w PMSQ concentration were electrospun, beads with 'tapered tails' were produced, which demonstrate a transition state

from electrospaying to electrospinning (Fig. 4). THF, acetone, methyl acetate, DCM, methanol and ethanol showed partial solubility and produced white solutions of PMSQ. 60%w/w PMSQ solutions of methyl acetate, acetone and THF produced bead-free smooth electrospun fibres of length 50–1000 mm, average diameters 3.3 μm , 2.0 μm , and 3.5 μm , respectively. Solutions in DCM showed high electrospinning productivity but beading was present in the as-spun fibres. Average fibre diameter was 2.6 μm . Solutions in methanol and ethanol produced shorter fibres of length 1–500 mm, and smaller average diameters of 0.40 μm and 0.83 μm , respectively (Fig. 4). Previous literature has shown that solvent properties, such as density, boiling point, dielectric constant, conductivity, surface tension, and viscosity, influence the electrospun fibre morphology

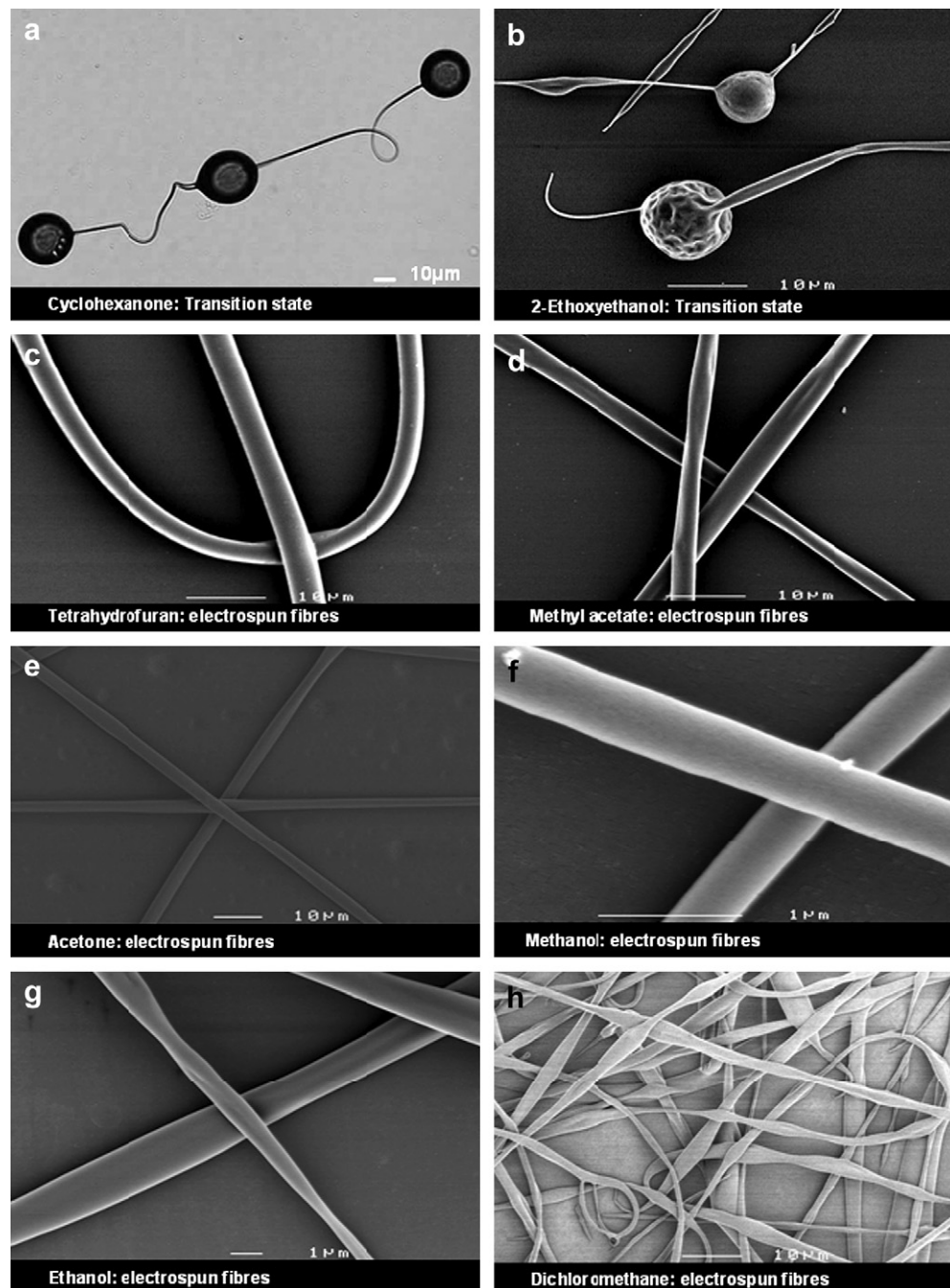


Fig. 4. (a) An optical micrograph of fibres electrospun from 60%w/w PMSQ solution in cyclohexanone. (b–h) Scanning electron micrographs of fibres electrospun from 60%w/w PMSQ solutions in (b) 2-ethoxyethanol; (c) THF; (d) methyl acetate; (e) acetone; (f) methanol; (g) ethanol; and (h) DCM.

Table 5
Comparison of solvent properties among solvents mixed, based on Smallwood 1996 [37].

Solvent	T_b (°C)	ϵ (20 °C)	Dipole	Conductivity (Scm ⁻¹)	Absolute viscosity @ 25 °C cP	Vapour pressure @21 °C mmHg
Methanol	64	32.6	1.7	1.5 E-9	0.6	103
<i>n</i> -Propanol	97	20.1	1.7	9.0 E-9	1.72	13.4
Ethanol	78	22.4	1.7	1.4 E-9	1.08	45.7
Acetone	56	20.6	2.9	5 E-9	0.33	17.8
Methyl acetate	57	6.7	1.7	3.4 E-6	0.37	171
DCM	40	9.1	1.8	4.3 E-11	0.44	376
2-Nitropropane	120	25.5	1.9	5 E-7	0.74	16
Dimethylsulphoxide	189	46.6	3.96	2 E-9	2.0	0.7

[4]. Solvent evaporation has been reported to decrease the elongation factor during electrospinning [29]. However, thinner fibre production in methanol and ethanol compared to that in THF, methyl acetate and acetone is not a direct result of the volatility difference among these solvents. For instance, boiling point (T_b) of methanol (65 °C) and THF (66 °C) are comparable but the average diameters of their electrospun fibres are 0.4 μm and 3.5 μm , respectively. Furthermore, the dielectric constant of the solvents showed a direct correlation with the average electrospun fibre diameter (Table 5, Fig. 5). This result demonstrates the dominant effect of dielectric constant of solvents over the rate of evaporation on fibre diameter.

3.3.2. Binary solvent systems

Previous literature has reported on the porous fibre formation when a binary solvent system was employed, and phase separation was the main reason believed to have caused the porosity [30–32]. In this work, electrospun fibres from binary solvent system mixing MeOH (high vapour pressure) and PrOH (moderate vapour pressure) showed high porosity. On close inspection, porous fibres spun from the MeOH:PrOH solution appeared to be solid and porosity occurred only on the fibre surface (Fig. 6). It has been reported that solvents of high volatility and vapour pressure cause phase separation and surface porosity in electrospun fibres, and the above result agrees with the literature [33]. During electrospinning, the electrified solution jet accelerates towards the grounded substrate and elongates rapidly. The surface area of the jet is dramatically increased during this process and this leads to an increased rate of solvent evaporation. The evaporative cooling during the loss of solvent leads to thermodynamic instability, which results in phase separation within the electrospun solution and the as-spun fibres phase into polymer-rich and solvent-rich phases. As the fibres dry on the collector, the polymer-rich phase remains and the solvent-rich phase forms pores on the fibres. The evaporative cooling during electrospinning also leads to the occurrence of breath figures as a consequence of water vapour in the air condensing onto the

fibre surface as droplets. As the fibre dries, the water droplet evaporates and leaves a pore on the fibre surface. Moreover, water vapour in the air is a non-solvent for PMSQ and the possible penetration of water vapour into the electrospun fibre may also lead to vapour-induced phase separation [31–36]. In this work, humidity causing the occurrence of breath figures and vapour-induced phase separation can play an important role in the formation of surface porosity. Irregular circular pores can be found on the rough ridged surface of the as-spun fibres from the MeOH:PrOH solution (Fig. 6). Moreover, our laboratory humidity reads 59%, which falls within the higher humidity range that has resulted in a broad pore size distribution in the studies by Casper et al. [31].

In addition, based on information drawn from the Teas graph, it is calculated that if 2NP and DMSO are mixed in 2:3 volume ratio with respect to 2NP:DMSO, the mixture should be a good electrospinnable solvent system for PMSQ. Electrospinning of the solution showed good spinnability and the electrospun fibres showed high porosity with a ridged or a rough fibre surface (Fig. 7). This is noteworthy because neither 2NP nor DMSO exhibited high volatility (2NP T_b at 120 °C; DMSO T_b at 180 °C), contrary to the highly volatile solvents often included in mixed solvent systems that have produced porous fibres. Furthermore, unlike the solid porous fibres with only surface porosity spun from the MeOH:PrOH solution, the fibres spun from the 2NP:DMSO solution showed large cavities inside the beads on the fibres (Fig. 7b). Megelski et al. [33] believed that solvent vapour pressure was critical for pore formation. They reported decreased surface porosity and smoother fibre surface morphology as they decreased the solvent volatility by reducing

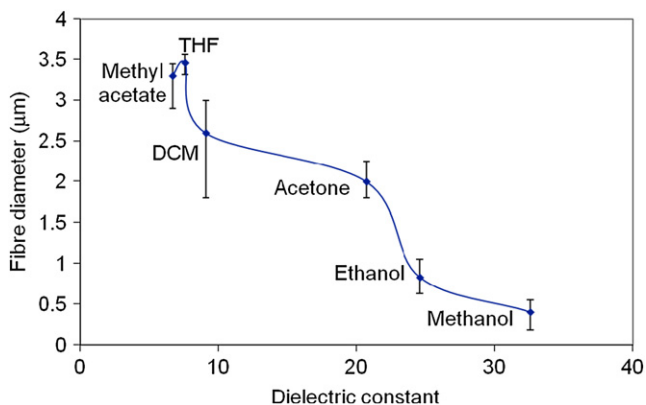


Fig. 5. Correlation between electrospun fibre diameter (μm) and dielectric constant of solvents.

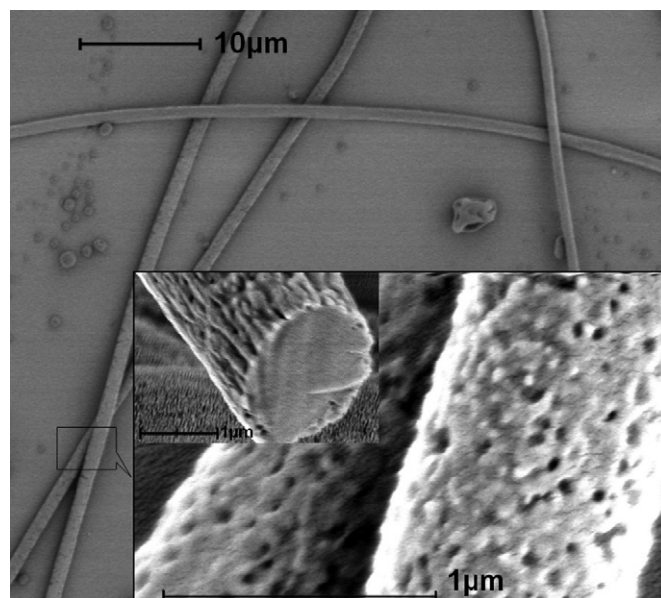


Fig. 6. Scanning electron micrographs of fibres electrospun from 60%w/w PMSQ solution in binary solvent system MeOH:PrOH of volume ratio 2:3.

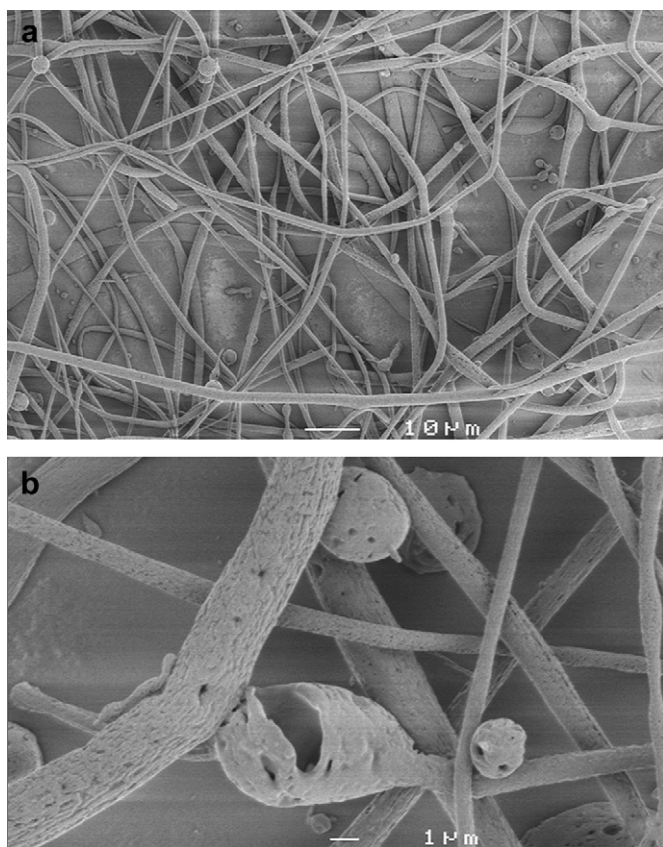


Fig. 7. Scanning electron micrographs of fibres electrospun from 60%w/w PMSQ solution in binary solvent system DMSO:2NP of volume ratio 3:2. (a) An overview; (b) fibre porosity observed at a higher magnification.

THF content from polystyrene (PS) solution in THF/DMF binary solvent system and PS fibre spun from 100% DMF showed no surface porosity on SEM. Whether interior porosity existed in the PS fibres spun from 100% DMF was not mentioned. The relative humidity of their spinning environment was not specified [33]. On the other hand, Pai et al. [36] reported PS fibres from 100% DMF with smooth surface but highly porous interiors when electrospun in a high humidity (30–50%) environment. They attributed this finding to the presence of high humidity in their experiment. Water vapour, a non-solvent for PS, miscible with DMF, may diffuse into the liquid jet, leading to liquid–liquid phase separation and interior pore formation prior to fibre solidification. In our result, 2NP:DMSO binary solvent system with none of the solvent component exhibiting high volatility, produced porous fibres in 59% relative humidity, appear to agree with Pai et al. [36] and demonstrated that fibre porosity could occur without the presence of high vapour pressure in electrospinning. We believe in this 2NP:DMSO solvent system, liquid–liquid phase separation in the electrospun fibres can be induced by the significant PMSQ solubility difference between 2NP (partial to high solubility) and DMSO (non-solvent), resulting in fibre porosity. In addition, water, a non-solvent for PMSQ, is miscible with 2NP and DMSO. The high percentage of water vapour present in the air can also diffuse into the spinning jet and induce liquid–liquid phase separation, resulting in pore formation.

4. Conclusions

Solubility map for PMSQ was developed on the Teas graph and successful PMSQ solutions were tested for electrospinning. The electrospinnability results were combined with the solubility

results and mapped onto the Teas graph. This new spinnability–solubility map allowed for a systematic selection of solvents for creating electrospinnable binary solvent systems for PMSQ. Rather than a hit-and-miss solvent selection process, the spinnability–solubility map simplified the solvent selection process by allowing mixed solvent systems to be developed using a geometrical method based on the solubility region of the polymer. Electrospun fibres with no bead-on-string defects or very few beads were produced using solutions in partial solvents; whereas solvents with high solubility for PMSQ demonstrated electrospinning or transition state from electrospinning to electrospinning. It is suggested that lower solubility can be better suited for making good electrospinnable solutions than solvents of high solubility. High solvent dielectric constant showed a significant effect in reducing electrospun fibre diameter. Solution in binary solvent system mixing MeOH and PrOH produced electrospun fibres with surface porosity, supporting the theory that phase separation can be induced by high vapour pressure of at least one solvent component. Porous fibres were spun from solution in binary solvent system mixing 2NP, a solvent of high solubility, and non-solvent DMSO, in which both solvent components have low volatility. This demonstrates that phase separation in electrospinning can occur even if none of the solvent components in the solvent system exhibits high vapour pressure. Solubility difference and high relative humidity can contribute to pore formation in electrospun fibres. A comparison between our empirical results and the existing extensional rheology and flow kinematics of the solution jet should be further explored in future works.

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