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RESEARCH ARTICLE

Effect of solvent combination on the formation of ethylcelluloseelectrospunfibre and bead morphology

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Abstract

Ethylcellulose (EC) is biocompatible, biodegradable, synthetic polymer. It is widely used in pharmaceuticals, drug delivery systems, topical formulations and many more. The EC nanofibres could be useful for above applications due to unique properties of nanofibres. In the present work, EC nanofibres were produced by electrospinning using alternative binary solvent system of toluene (To):ethanol(Et) in different proportions. The EC solution parameters such as conductivity, surface tension and viscosity were measured. The different solvent ratio combinations affected fibre morphology from round shaped collapsed beaded fibre with 100% Et to spindle shaped collapsed beaded fibres , spindle shaped solid beaded fibres to beadless fibres as To proportion increased and finally to very thick beadless fibre at 100%To proportion. The effects of applied voltage and needle to collector distance (NTCD) on EC fibre morphologies were also studied. The average EC fibre diameter reduced with increase in applied voltage and NTCD. Differential Scanning Calorimetry (DSC) and Fourier Transform Infrared (FTIR) spectroscopy was also performed for characterization of EC nanofibres.

Introduction

The nanofibres are of interest in many fields such as biomedical R & D, defense, textiles, filtrations, engineering, sensors, cosmetics etc. due to special properties gifted by their ultrafine dimension [1], [2]. The ultrafine dimension of the fibre leads to unique properties such as high surface area to volume/mass ratio, high aspect ratio (length to diameter ratio), high porosity, heavily interconnected porous structure, cellular (sub-micron) dimension, flexibility to produce different morphologies etc.[2]–[4]. The material behaves different at nano dimensions and sometimes shows superior properties with more reactive and enhanced surface properties, compared to their properties when they are at micro or macro dimension from the same material [5], [6].

Electrospinning is more versatile, economic and industry viable process to produce nanofibres among different methods such as phase separation, template synthesis, self-assembly, drawing etc.[1], [2]. The process of electrospinning is described by many researchers[2], [7]. Electrically charged solution, melt is fed towards collector via needle / spinneret by pump, gravity or air force. Round shaped solution droplet on the tip of the spinneret is pulled to conical shape (called 'Taylor cone') due to electrical force between droplet and collector and coloumbic forces among the solution /melt molecules. "physically the phenomenon of electrospinning is a consequence of a tug of war between electrostatic and capillary forces"[8]. When electrical forces overcome the capillary forces at Taylor cone, the jet of liquid emerges. The jet follows longer path, circular (envelop zone) and zigzag path under the

influence of electrical force, coloumbic forces to minimize the surface energy. The ultrafine fibres are produced due to stretching, splitting and evaporation of solvent. Wet / dried fibres are collected on the collector. Electrospinning is a versatile method. Ultrafine fibres can be produced from the solution / melt (with optimum viscoelasticity and conductivity) of different polymers, ceramics, composites, materials.
Cellulose is the most abundant naturally available polymer. Cellulose and its derivatives are used in paper textile, pharmaceutical and coating (specialty additive, packaging, film/membrane) industries. EC is synthetic, odourless, nontoxic ,nonirritant, nonallergic, inert, thermoplastic, film forming, hydrophobic, colourless, noncaloric, tasteless cellulosic derivative with excellent plasticity, biocompatibility. EC is widely used as drug releasing agent, topical formulator, binder, tough/flexible film former, flavor fixative, water barrier, emulsion stabilizer, rheology modifier, organogelator; whose main attractive features are its biocompatibility and degradation to nontoxic products [9]–[14].
The size and morphology of the polymer matrix plays very important role in various fields such as tissue engineering, drug delivery etc. [15]. In electrospinnig different variables such as polymer properties, solvent properties, process atmospheric etc. can be altered to get desired polymer matrix morphology [7], [16], [17][18]. Different researchers produced nanofibres from cellulose and its derivatives [19], Cellulose acetate[20]–[22], EC[13], [23]–[25] etc. Alternative solvent systems are always of interest for the processing of cellulosic derivatives for number of industrial applications considering toxicity, environment, health considerations, solubility of additives etc. [26], [27]. In the present work, effects of ethanol (Et): toluene (To) blends on electrospun fibre morphology were investigated. It will widen the selection of solvent system for EC nanofibre production. EC is water insoluble but it is soluble in many organic solvents such as benzene, carbon tetrachloride, ethylene dichloride, methylene chloride, toluene, xylene etc.[28][27]. In turn , this will widen the solvent selection options compatible with the active ingredients [29].

Materials and methods

Materials

Ethanol was purchased from Fisher scientific, Toluene from Rathburn and EC (Ethoxyl content 48%, 45cP of 5% EC in 60:40 toluene: ethanol at 25^{o} C) was purchased from Aldrich. All the chemicals were used without further purification.

Solution Preparation

EC powder was thoroughly dissolved in Et and TO mixture (in proportion of 0:100, 40:60, 50:50, 60:40, 100:0) to prepare 15% (w/w) solution. The EC solutions are referred by short name further in the article as below. EC (w/w) solution in 100% toluene is referred as 15EC100To, EC solution in 60:40(To:Et) is referred as 15EC60To or 15EC40Et, likewise 15EC60Et or 15EC40To for 60:40 Et:To, 15EC100Et for 100% Et as solvent.

Electrospinning Setup

The 15EC solutions were injected by microprocessor syringe pump (M22 PHD 2000, Harvard Apparatus, Eden bridge Kent, United Kingdom) via blunt needle “spinneret” towards collector using above syringe pump. The high voltage supply (MK35P2.0-22, Glassman, New Jersey, USA) was connected to needle and collector. The effect of varying different parameters such as solvent ratio (Et:To), applied voltage and NTCD on the fibre and nano fibrous mat morphology were studied using scanning electron microscopy.

Solvent and Solution Properties (Viscosity, Surface Tension and Conductivity)

EC solution viscosity, surface tension, conductivity were measured using Brookfield DV-II Pro viscometer with a S63 spindle, Kruss surface tension meter model K6, Oakton con 110 handheld conductivity meter respectively.

Visual Observation

Fuji film finepix A805 camera was used by to see changes in turbidity of EC solutions in different solvent mixtures.

Scanning Electron Microscopic (SEM)

The electrospun webs were observed under cold field emission HITACHI (model: S-4300, Japan) scanning electron microscope (CFE-SEM). The electrospun mats were sputter coated with gold palladium for 60 seconds in a sputter coater unit (Polaron SC7620). The coated samples were observed at accelerating voltage 1 kV in CFE-SEM.

FTIR (Fourier Transform Infrared Spectroscopy)

A Perkin Elmer Spectrum 100 ATR-FTIR Spectrophotometer was used to get the FTIR spectra. The IR spectra were taken using a ZnSe diamond ATR device. The ATR device was set to base value with air.

Differential Scanning Calorimetry (DSC)

All the samples were sealed in pierced aluminum pan for thermal analysis. The samples were weighed up to 5 mg and heated at rate of 10^{o}c/min in atmosphere air.

Results and discussion

Surface tension and Conductivity

The Et:To solvent mixtures as well as 15EC solution surface tensions were also affected by solvent type (Fig.1). The surface tension of 15EC solutions and To:Et solvent increased as To proportion increased from 0% to 100% and Et proportion reduced from 100% to 0%.

The Et:To solvent conductivity reduced as the proportion of To increased from 0% to 100% (Fig.3, Table 1). In other words the conductivity of Et:To solvent increased from 0µs to 3.30µs as Et proportion increased from 0% to 100%. Similar trend also observed in 15EC solution. 15EC 100Et has highest conductivity 119.2µs, while 15EC100To has zero conductivity. The 15EC solution conductivity is reduced as the proportion of To is increased in the solvent. The overall conductivity of all 15EC solution were found higher compared to Et:To solvent mixtures. This can be due to presence of EC ions contributing to increased solution conductivity.

Effect of solvent system on viscosity, solubility and turbidity

Number of parameters such as polymer properties, solvent properties , final solution properties, process parameters, atmospheric conditions etc. influence fibre and mat morphology in electrospinning [1], [7], [29]. Solution properties such as conductivity, surface tension, solution viscosity, molecular chain length, polymer–polymer interactions / polymer-solvent interaction etc. play very crucial role in deciding final nanofibre properties [2], [16], [30], [31]. In good solvent, Polymer-solvent interactions are high compared to polymer -polymer interactions. Polymer either swells or completely dissolves in good solvent. A good solvent either breaks the polymer-polymer bonds to make polymer solution or diffuse solvent into polymer-polymer network to form the gel. The polymer solution viscosity increases due to increased polymer-solvent interaction and easy expansion of polymer chains in the good solvent system [2]. In case of poor solvent, the polymer-polymer molecule interactions are very high compared to polymer-solvent. Hence, all solvent molecules are going to be squeezed out and the solvent is not allowed to enter into polymer-polymer bond. The polymer chains gets collapsed and curled in poor solvent. Hence, usually solution viscosity reduces in case of poor solvent [2], [16], [30]–[34].

Solution viscosity and turbidity usually can be very important indicators to determine polymer solubility in solvent. Poor solvent, where very small quantity of the polymer is dissolved has poor solution viscosity and higher turbidity[31], [35]. In the present work, the I5EC100Et solution (Fig.2, Table 2) showed the lowest viscosity among all 15EC solutions. The 15EC solution viscosity increased with the gradual increase in To proportion. The 15EC100 To showed highest viscosity, while 15EC100Et solution showed lowest viscosity among all the 15EC solutions. The 15EC100Et solution showed highest turbidity and 15EC100To has no turbidity (i.e. clear solution) compared to other 15EC solutions. The solution appearance has changed from heavily turbid to clear solution from 15EC100Et to 15EC100To as the proportion of Et is reduced and proportion of To is increased. This proves that EC is poorly/partially soluble in Et compared to To. In other word, To is a good solvent for EC compared to Et[35], [36].

Effect of solvent on fibre morphology

Electrospinning is the practical and successful method for the production of nanofibres. Fibre morphologies can be changed/controlled by changing different parameters (process, solution, polymer, atmospheric etc.)[2], [29]. In the present work, the EC nanofibres with bead morphologies were studied using new solvent combinations of To:Et. Solution conductivity and rheological properties such as viscosity and surface tension are the main parameters in deciding new fibre as well as bead structure formation. Usually, higher surface tension favours round shaped bead formation [2], [37], [38]. The surface tension mainly depends on solvent composition.

Viscosity depends mainly on polymer chain entanglement, polymer molecular weight, solution concentration, polymer structure, polymer-solvent interaction etc. Usually, higher solution concentration and polymer molecular weight increases solution viscosity[2]. Generally, High solution viscosity favours beadless, more uniform and thicker fibres [2]. If there is no chain entanglement in solution means only round shaped beads will be formed due to surface tension. Lower solution viscosity favors more splitting and stretching compared to high solution viscosity. Hence, the electrospun fibres from lower viscosity solution generate thinner, beaded and smaller fibres. As viscosity increases jet resists further splitting and stretching, due to which fibre become thicker, beadless and of more continuous nature. As the viscosity increases, the bead shape changes from spherical to spindle like and finally smooth beadless fibres. In order to form fibre at least one entanglement per polymer chain is needed[39]. "Complete and stable fibre formation occurs at >= 2.5 entanglements per chain" [32].

In present work, the fibres produced from 15EC100ET were found with irregular, nearly round shaped beads. The surface tension and viscosity of 15EC100Et is lowest among all EC solutions. The lower viscosity means fewer chain entanglements per polymer chain, which means it will not resist bead formation compared to other 15EC solutions. It can be inferred that, the chain entanglements in 15EC100Et are not high enough to overcome the tendency of the surface tension to produce round shaped beads. At the same time, the chain entanglements are high enough to produce thin connecting string between beads. Hence, the 15EC100Et jet emerging from needle produces bead on string structure. The 15EC100Et beads on string (Table 3, Fig.5) are almost round shaped, irregular and collapsed. The surface tension produce round shaped beads and faster evaporation of ethanol produced collapsed, irregular shaped beads. Celebioglu et al [40] observed similar trend and reported formation of flat, collapsed cellulose acetate fibre, when volatile solvent system was used.

The 15EC60Et fibres have spindle shaped irregular, collapsed beads on fibre structure (Fig.5). The changed solvent ratios from 100% ethanol to 60% ethanol: 40% toluene increased solution viscosity and surface tension. The forces of viscosity were high enough to resist the effect of surface tension. Increased chain entanglements due to higher viscosity resisted round shaped bead formation on the jet due to surface tension. Hence, the beads with elongated shape were generated rather than round shape. Similar to 15EC100Et, the ethanol evaporated faster in 15EC60Et as the proportion of ethanol is higher than toluene the fibres became collapsed. As the toluene proportion increased from 40% to 50% in solvent mixture, the 15EC50Et fibres were produced with regular solid (i.e. not collapsed) but elongated shaped beads.

As discussed earlier, the viscosity forces opposed the surface tension forces to prevent formation of full round shaped beads in 15EC50Et. Hence, elongated spindle shaped beads are produced. In 15EC50Et, the evaporation of solvent is lower as toluene evaporates slowly. Drying of the fibres take place slowly. Hence, membrane of the beads becomes more solid due to slow evaporation, prevention of membrane collapse. So, 15EC50Et fibres are more regular and solid in appearance (Fig.5).

As the toluene percentage increased from 50% to 60% the fibres become almost beadless (Fig.5). The surface tension and viscosity of 15EC60To was increased compared to 15EC50To. The 15EC100To fibres were thicker, and beadless. In case of 60% and 100% To, the increased viscosity forces opposed surface tension, which led to beadless fibres. Similar results were found in nylon 4,6. The surface tension and viscosity of nylon 4,6 increased with increasing concentration. Although higher surface tension produces beaded fibres, the increase in viscosity was rapid, hence beadless smooth Nylon4, 6 fibre were obtained [41].

In case of 15EC100To, the zero conductivity was measured. But solution conductivity is essential characteristic for electrospinnability. During electrospinning, elongation of 15EC100ToTaylor cone as well as whipping of jet was found. This indicates presence of small amount of conductivity in 15EC100To solution, which was not measured by conductivity meter.

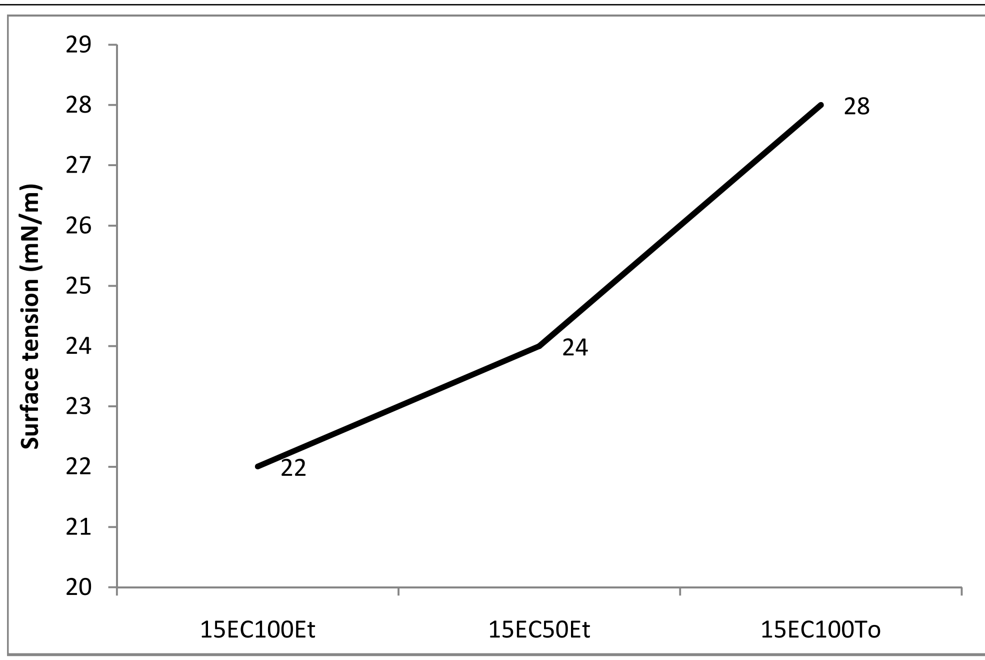


Fig.1 Influence of solvent type on the surface tension (mN/m) of EC solution

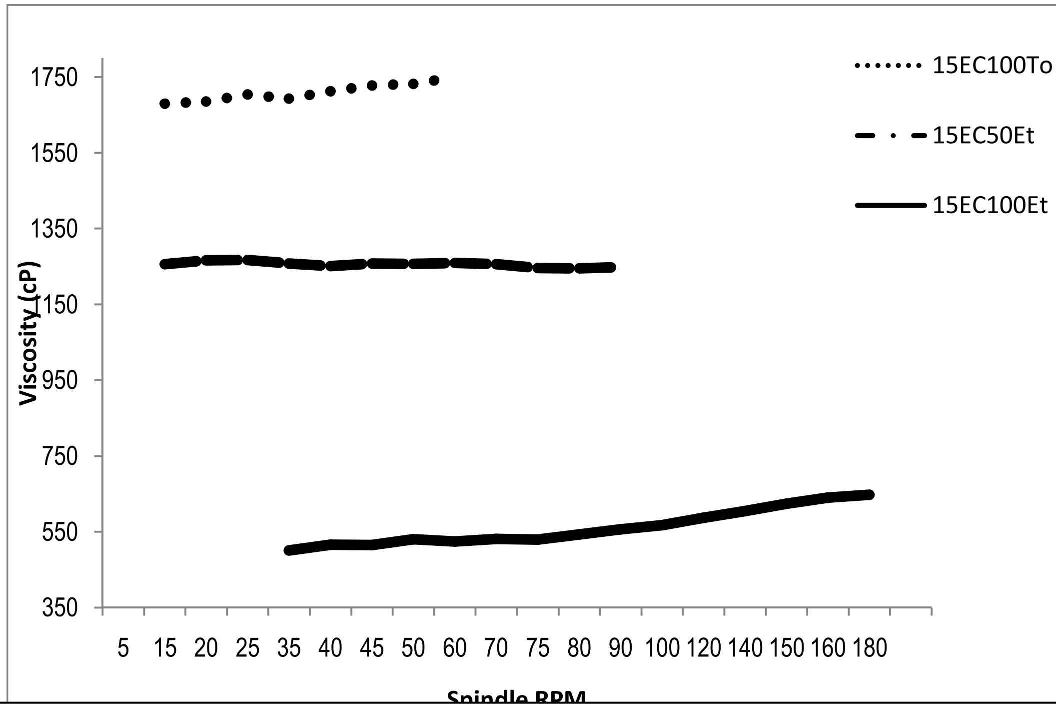


Fig.2 Viscosity of 15EC solutions in different solvent systems at different spindle rpm

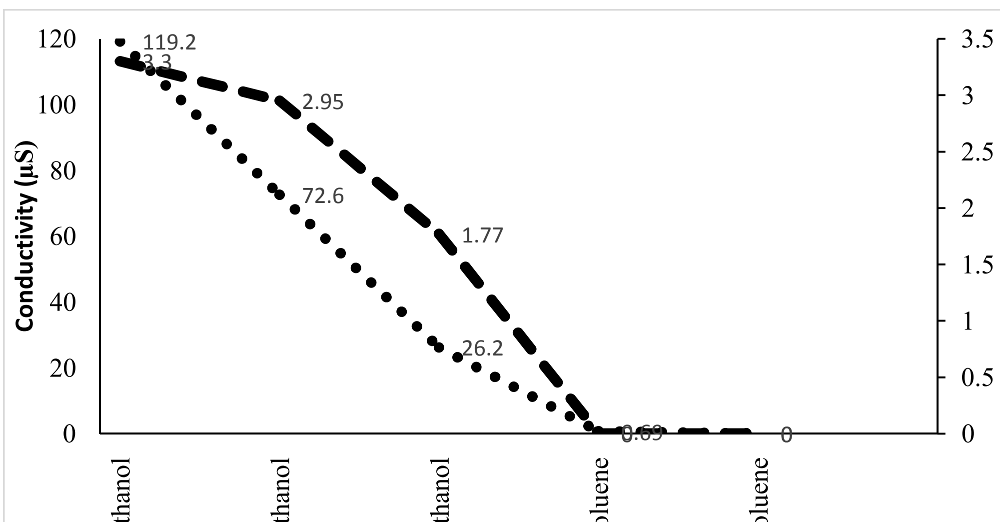
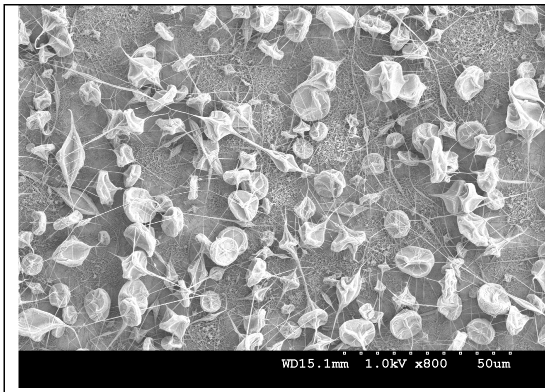


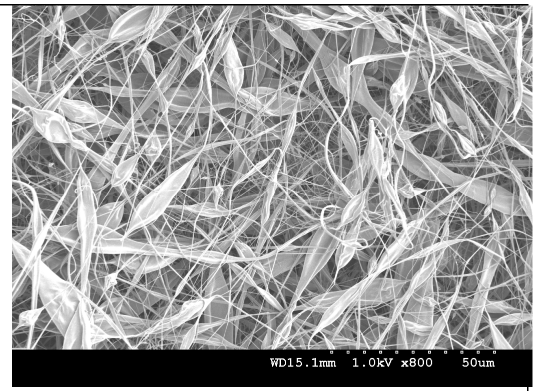
Fig.3 Solvent conductivity and Influence of solvent type on the conductivity (µS) of EC solution.

Solutions in different solvents
Bottle 1- 15% EC in 100% Ethanol
Bottle 2- 15% EC in Ethanol/toluene (50/50)
Bottle 3-15%EC in toluene

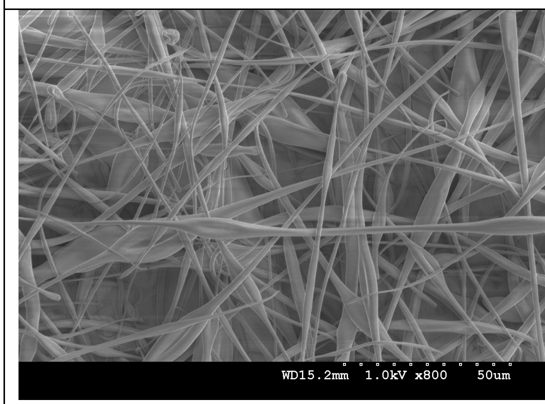
Fig.4 Comparison of turbidity of Ethyl cellulose solutions



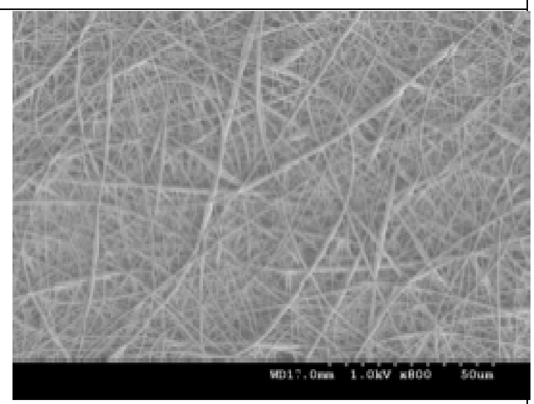
(100:0)Ethanol: Toluene



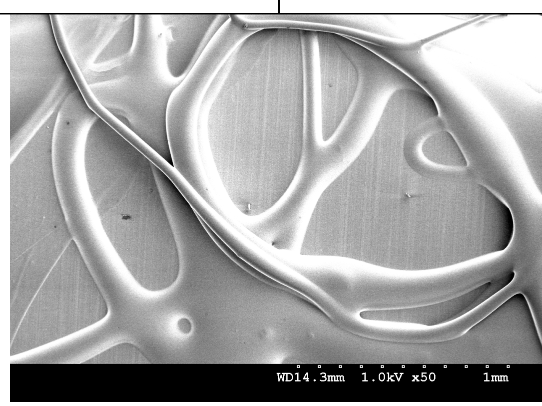
(60:40)Ethanol: Toluene



(50:50)Ethanol: Toluene

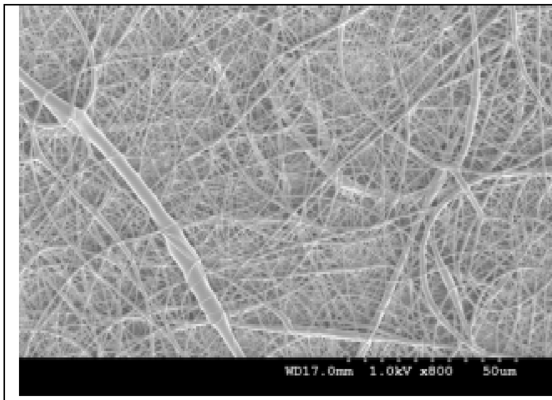


(40:60)Ethanol: Toluene

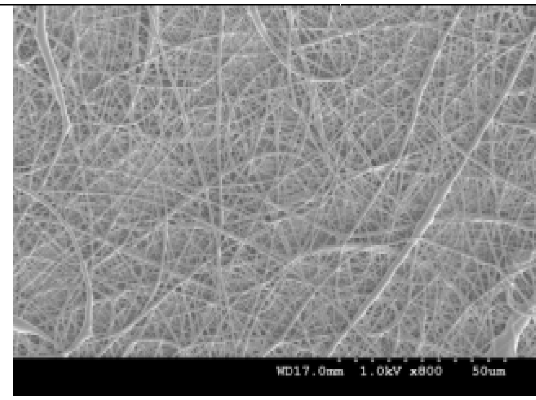


(0:100)Ethanol: Toluene

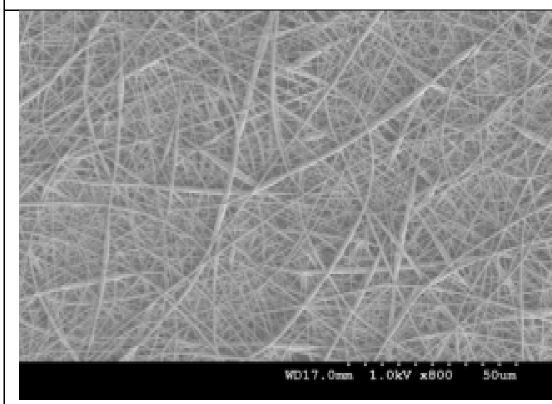
Fig.5 Effect of solvent proportion on fibre morphology



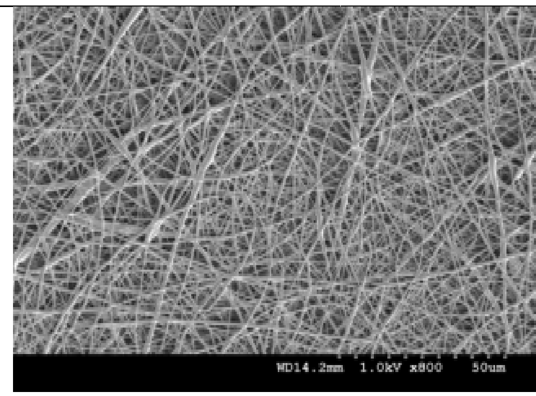
12kV



16kV



21kV



26kV

Fig.6 Effect of applied voltage on 15EC60To fibre morphology

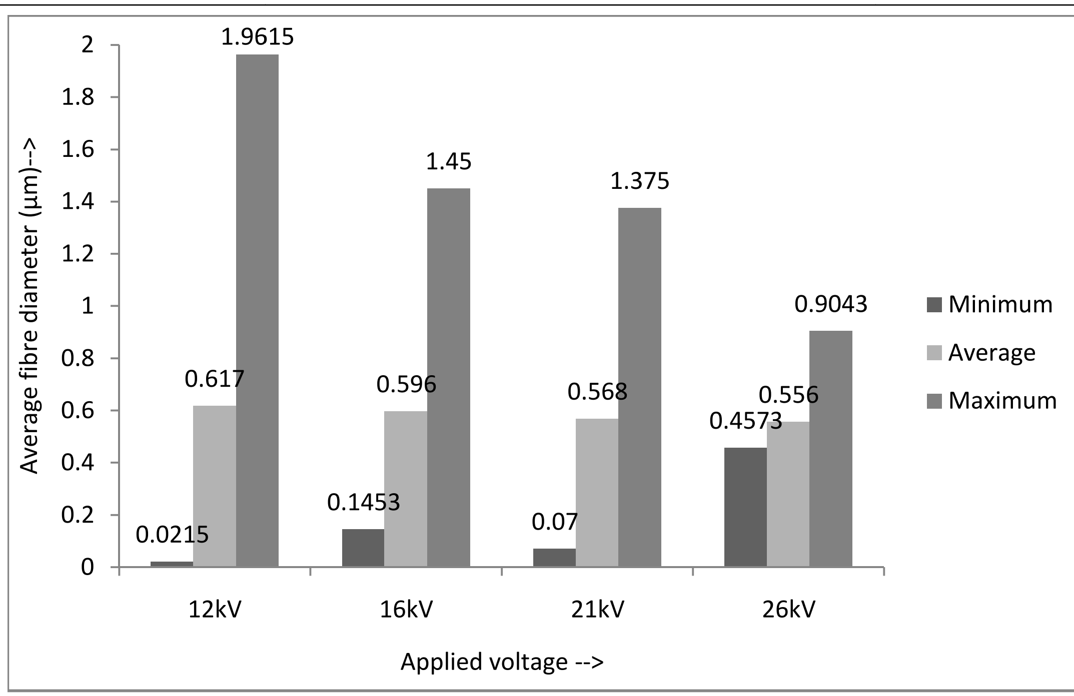
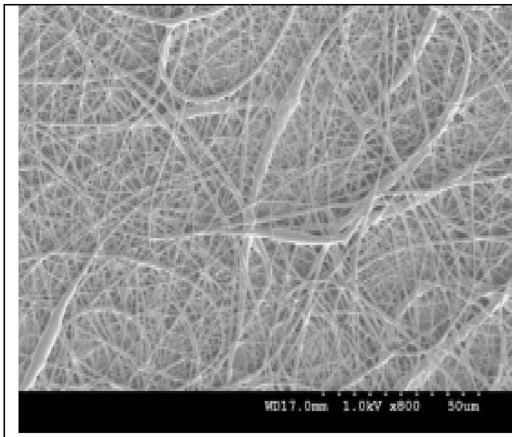
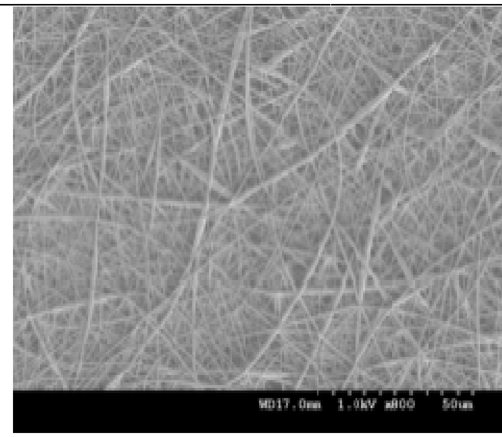


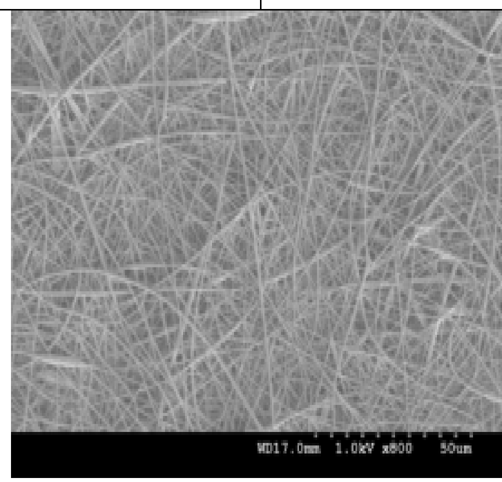
Fig.7 Effect of applied voltage on 15EC60To fibre diameter



10cm



20cm



30cm

Fig.8 Effect of NTCD on 15EC60To fibre morphology

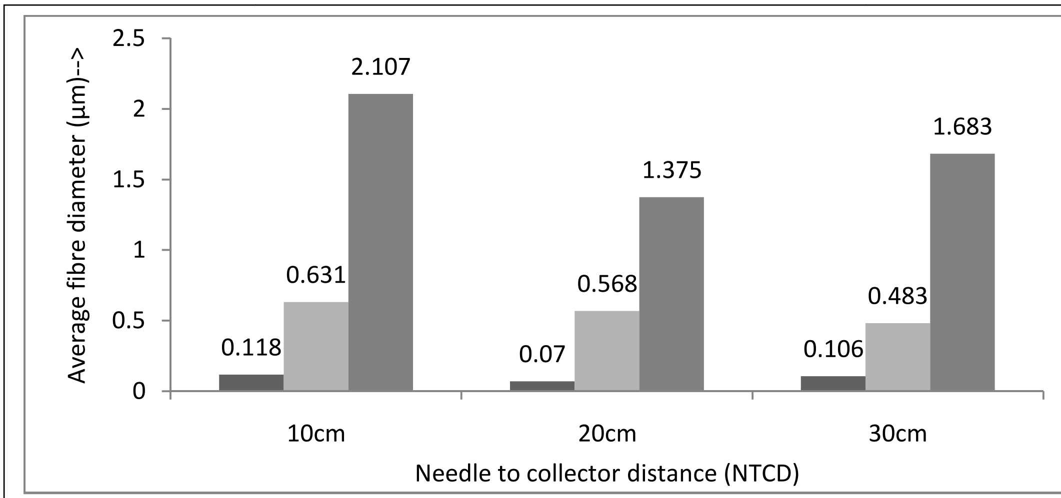


Fig.9 Effect of NTCD on 15EC60To fibre diameter

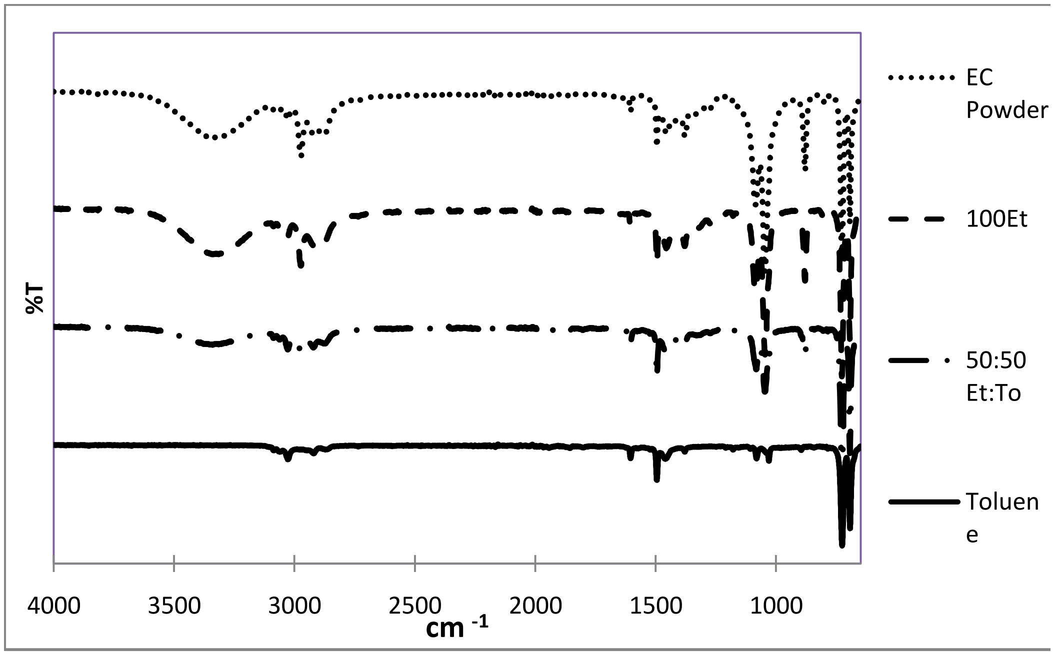


Fig.10 FTIR of solvents

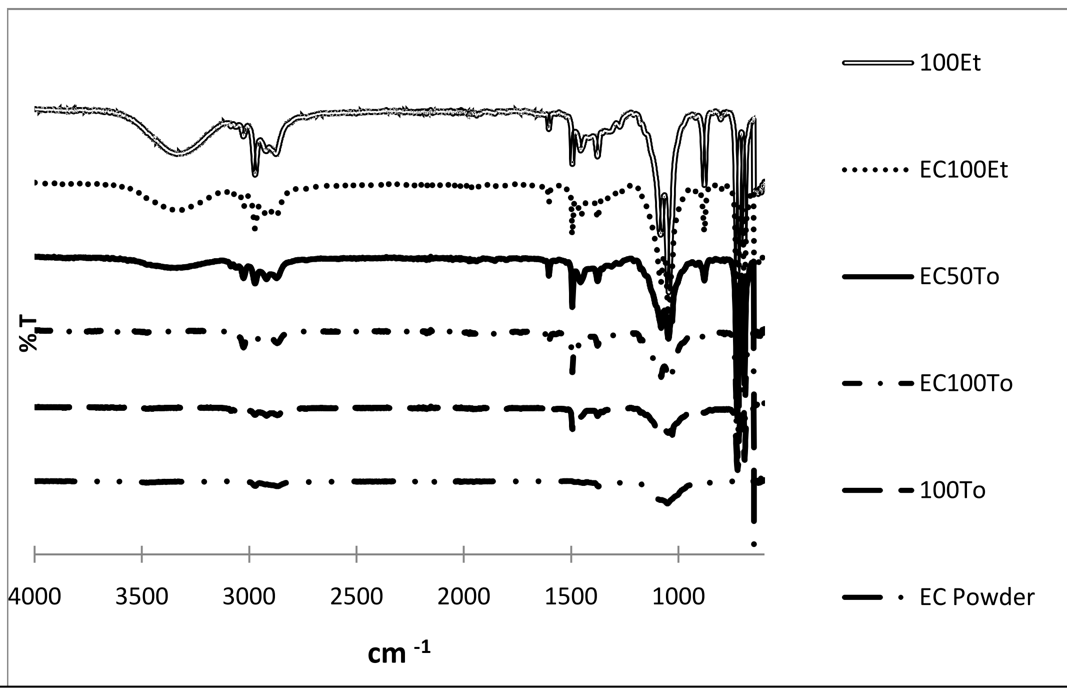


Fig.11 FTIR of solvents and EC solutions

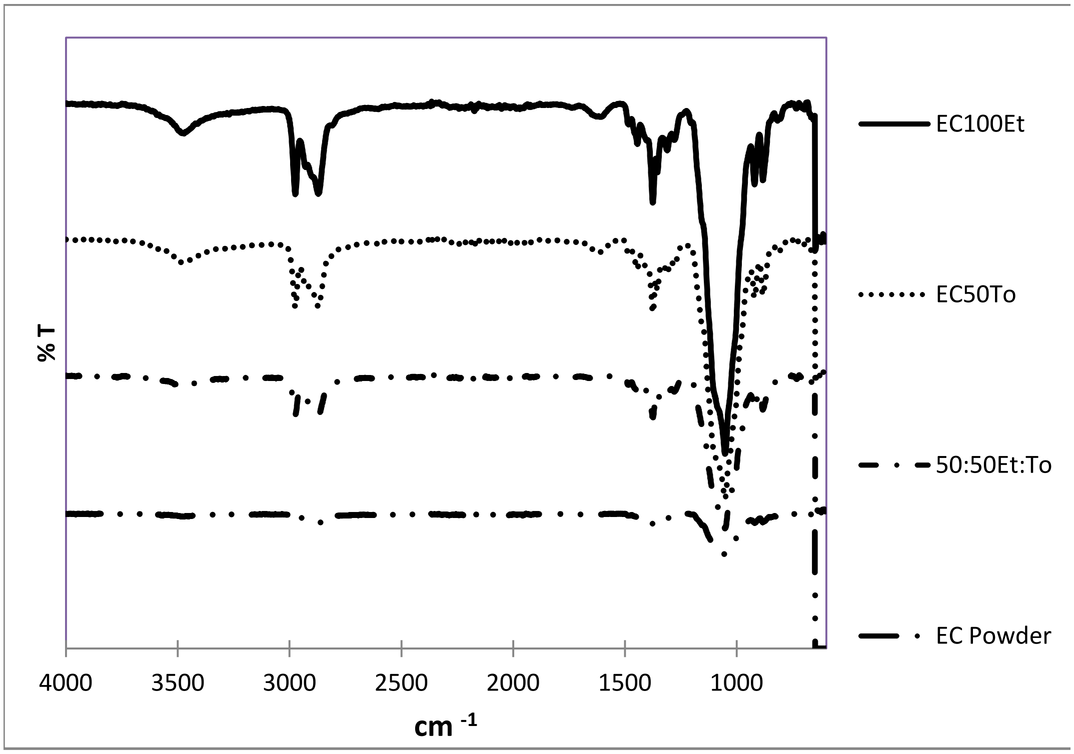


Fig.12 FTIR of EC mats

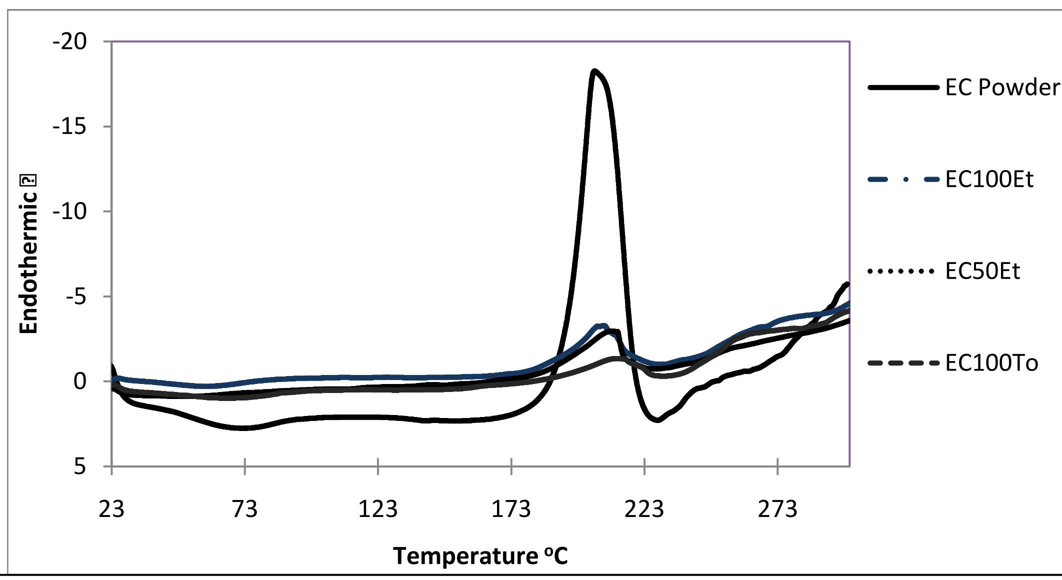


Fig.13 Differential scanning calorimetry

Tables

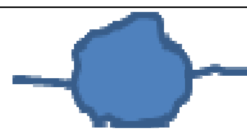
Table 1 Conductivity of EC solvents

No	Solvent		Solution	
	Ethanol: Toluene	Conductivity (μS)		Conductivity (μS)
1	100:0	0	15EC100Et	0
2	60:40	0	15EC60Et	0.69
3	50:50	1.77	15EC50Et	29.2
4	40:60	2.95	15EC60To	72.6
5	0:100	3.30	15EC100To	119.2

Table 2 Visual appearance of Ethyl cellulose solution

No.	Solution detail	Solution appearance
1	15EC100Et	More cloudy (Not transparent)
2	15EC50Et	Less cloudy (Semi-transparent)
3	15EC100To	Clear (transparent)

Table 3 Effect of solvent on ethyl cellulose electrospinning

Solvents (Ethanol: Toluene) ratio	Shape	Remark
100:0		Irregular / collapsed round bead on string
60:40		Irregular / collapsed elongated bead on string
50:50		Regular / solid elongated bead on string
40:60		Thin fibres
0:100		Thick fibres

Effect of applied voltage of fibre morphologies

Higher applied voltage has two effects in electrospinning. Higher applied voltage between needle and collector creates high attractive field for droplet to form droplets/fibres. At the same time higher applied voltage increases repulsive forces among bead solution molecules due to same polarity applied voltage. So, molecules from bead will have tendency to repel each other and come out of bead to produce fibres. Electrospinning process depends on applied voltage. The fibre formation takes place only at critical voltage when forces due to applied voltage overcome surface tension at Taylor cone.

Usually, higher applied voltage means higher coloumbic forces. Higher applied voltage stretches the jet as well as stimulates jet splitting, and hence finer fibres are obtained. In some cases, higher voltage attracts more solution rapidly, which will not allow fibres to stretch, and hence thicker fibres can be obtained [2], [3].

In present work, 15EC60To fibres were spun at different voltages from 12kV, 16kV, 21kV and 25kV keeping all other parameters constant (feed rate-1.5ml/hr, NTCD-20cm). As the applied voltage increased from 12kV, 16kV, 21kV to 25kV the average fibre diameter reduced from 0.617μm, 0.596μm, 0.568μm to 0.556μm respectively (Fig.6, Fig.7).

Effect of NTCD on EC fibre morphology

The NTCD affects jet flight time, evaporation time, voltage field, flight distance etc.. Usually higher NTCD means more distance to travel, so more whipping instabilities to undergo and hence drier and finer fibres are produced. In some cases higher NTCD means reduced applied voltage per unit distance, so less applied voltage and columbic forces per unit square area. Hence, stretching and splitting of jet may become very less which will produce thick fibers[2].

15EC60To fibres were spun at different NTCD keeping feed rate-1.5ml/hr and applied voltage at 21kV. As the NTCD is increased from 10cm, 20cm to 30cm, the average fibre diameter reduced from0.631µm, 0.568µm to 0483µm. Other parameters were kept same (feed rate-1.5ml/hr, applied voltage - 21kV) (Fig.8, Fig.9).

FTIR (Fourier Transform Infrared Spectroscopy)

In present study, FTIR of solvents, EC solutions and EC mats were taken (Fig.10 , Fig.11, Fig.12). The –OH stretching vibration in EC showed peak at 3476cm^{-1}. The –C-O-C stretching vibration showed peak at 1052cm^{-1} . 2973cm^{-1}and 2871cm^{-1}peak can be attributed to C-H stretching bands in EC powder. Toluene showed peak at 3037cm^{-1}, 3062 cm^{-1}, 3027cm^{-1} for the =C-H stretches of aromatic ring. Another peak at 2920cm^{-1} can be attributed to the alkyl (methyl) group. The carbon-carbon stretch can be observed in aromatic ring at 1604cm^{-1}, 1495cm^{-1}, 1459cm^{-1}. The peak at 3325cm^{-1} shows O-H band of ethanol, C=H band at (2973cm^{-1}, 2924cm^{-1}, 2879cm^{-1}), C=C band at 1648cm^{-1} , CH_2 band at (1453 cm^{-1}, 1471 cm^{-1}, 1379 cm^{-1}, 1328 cm^{-1}, 1274cm^{-1}) and C-O band at 1087cm^{-1}, 1045cm^{-1} can be attributed. In case of ethanol.EC solutions show effect of solvent in FTIR for e.g. gradual disappearance of –OH stretch at around 3325cm^{-1} from 100% ethanol to 100% toluene.

DSC (Differential scanning calorimetry)

A thermal analysis of EC powder and 15EC fibres prepared from the different solvent ratios (15EC100Et, 15EC50Et and 15EC100To). The melting temperature and crystallinity depends on the solvent and polymer type. The EC powder showed exothermic peak at 69.7^{o}C and sharp endothermic melting peak at 203.6^{o}C (Fig.13). The DSC curve of 15EC100Et showed broad exothermic peak at 56.1^{o}C and sharp endothermic peak at 206^{o}C. the DSC curves of 15EC100To showed exothermic peak at 63.3^{o}C and endothermic peak at 211.5^{o}C. while 15EC50Et DSC curve showed exothermic peak at 53.1^{o}C and endothermic peak at 208.9^{o}C.

Conclusions

The higher viscosity and clear EC solution formation in To compared to lower viscosity and turbid EC solution in Et, proves To as good solvent and Et is poor solvent for EC. 15 EC solution using To:Et mixture in different proportions can electrspin EC nano fibres into different morphologies from collapsed round shaped bead on string structure, collapsed elongated beads on string to solid elongated beads on string to beadless fibres. The above morphologies were affected by solution viscosity, surface tension and conductivity. Fast evaporation of Et and effect of surface tension with low viscosity allowed to form collapsed round shaped fibres from 15EC100Et solution. As the To proportion increased the increased viscosity created spindle shaped beads at the same time higher proportion of Et evaporated faster to create collapsed spindle shaped 15EC60Et beads. Increased viscosity with increase in To proportion opposed bead formation due to surface tension. At the same time, slower evaporation of To created solid elongated beads in case of 15EC50To. There were no beads in 15EC60To and 15EC100To, but fibre diameter increased due to increased viscosity. The beadless 15EC60To average fibre diameter reduced from 0.617µm, 0.596µm, 0.568µm to 0.556µm as applied voltage increased from 12kV, 16kV, 21kV to 25kV respectively. Average 15EC60To fibre diameter reduced from0.631µm, 0.568µm to 0.483µm as NTCD increased from 10cm, 20cm and 30cm respectively.

Declaration

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