Factors Affecting Spinnability of Oil Palm Mesocarp Fiber Cellulose Solution for the Production of Microfiber

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Cellulose microfiber (MF) formation by electrospinning is affected by several factors. In this paper, fabrication of MF from oil palm mesocarp fiber (OPMF), a biomass residue abundantly available at the palm oil mill, was conducted by electrospinning. The effect of OPMF-cellulose solution properties on the spinnability of the solution was determined. Extracted cellulose from OPMF was dissolved in four different formulations of ionic liquids: (i) ([EMIM]Cl), (ii) ([EMIM][Cl]:DMF, (iii) ([EMIM]Cl):([C_{10}MIM][Cl]), and (iv) ([EMIM]Cl):([C_{10}MIM][Cl]):DMF at cellulose concentrations of 1% to 9% (w/v). Scanning electron microscopy (SEM) analysis showed that MF formed had diameter sizes ranging from 200 to 500 nm. MF was formed only at 6% (w/v) cellulose concentration, when DMF was mixed in the solution. The results showed that cellulose concentration and viscosity played major roles in the spinnability of cellulose solution, in which too high viscosity of the cellulose solution caused failure of the electrospinning process and eventually affected the formation of MF. The characteristics of MF obtained herein suggest the potential of OPMF cellulose as a starting material for the production of MF.

Keywords: Oil palm mesocarp fibers; Microfibrillated cellulose; Spinnability; Electrospinning; Ionic liquids

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INTRODUCTION

Electrospinning has gained much interest from researchers due to the growing demand for micro- and nano-sized fibers in various industries, such as in the production of composites (Zhu *et al.* 2011), energy devices (Shi *et al.* 2015), and tissue scaffolds for biomedical purposes (Yoshimoto *et al.* 2003). This method produces high surface area (Zhu *et al.* 2011), permeability (Cengiz *et al.* 2009), thermal resistance (Bordes *et al.* 2009), and crystallinity, as well as finer and continuous fiber materials with sizes ranging from microns to several nanometers (Khajavi and Abbasipour 2012). Due to its capability, electrospinning has been widely used for the production of cellulose microfiber (MF); however, most of the previous studies focused on using commercialized cellulose as a starting material (Quan *et al.* 2010; Freire *et al.* 2011; Chen *et al.* 2015). Because of the difficulty in finding the most appropriate conditions suitable for natural cellulose to be electrospun, it is a less attractive option, so researchers tend to use commercialized cellulose for electrospinning. Appropriate conditions are required to ensure the formation of stable and continuous fiber spinning (Freire *et al.* 2011), and generally there are three main factors that affect fiber formation by electrospinning: solution parameters, process parameters, and ambient conditions (Shi *et al.* 2015). Of these factors, solution parameters are the most crucial to control, as electrospinning cannot be conducted without a solution. Solution parameters such as concentration, surface tension, and conductivity greatly affect electrospinning, and all of these factors depend on the starting material used.

In terms of raw material, instead of continuously depending on commercialized cellulose, the potential of lignocellulose as a starting material for MF production should be investigated. In Malaysia, oil palm biomass has great potential due to its abundant availability and high cellulose content. Oil palm mesocarp fiber (OPMF) is a residue obtained from oil palm fruits after oil extraction. In 2013 it was reported that the global production of palm oil was 56 million metric tons. For every metric ton of palm oil produced, 4 tons of dry biomass is generated, of which 12% are OPMF (Geng 2014). Therefore, it is estimated that the global OPMF production in 2013 was 26 million tons. In Malaysia alone, the generation of OPMF is about 11.5 million tons (Hoe 2014). Unlike oil palm empty fruit bunch (OPEFB), which has been extensively studied as a raw material for the production of various bioproducts such as biocomposite, biochar, biofuel, and biocompost, OPMF is usually used in palm oil mills as boiler fuel or burnt as waste, which is wasteful and indirectly contributes to environmental pollution (Then *et al.* 2013). As a lignocellulosic material, OPMF has potential as an alternative raw material for various bio-based products manufacturing, as it contains approximately 60% cellulose, 11% lignin, and 3% ash content (Sreekala *et al.* 1997). OPMF also offers high mechanical strength; for example, it has a tensile strength, Young's modulus, and elongation at break of 80 MPa, 500 MPa, and 17%, respectively (Sreekala *et al.* 1997). These unique characteristics indicate OPMF for MF production, as it offers good chemical and mechanical properties.

The use of OPMF as a resource for MF production is considered here for the first time. The goal is to identify the potential of this material for nanofiber application. In this study, cellulose was extracted from OPMF, and the OPMF-cellulose was later dissolved in different ionic liquid formulations to determine the effect of the solvents on the properties of the liquid, which eventually affected the spinnability and hence the production of MF by electrospinning.

EXPERIMENTAL

Materials

Oil palm mesocarp fiber (OPMF) was obtained from Seri Ulu Langat Palm Oil Mill, Dengkil, Selangor, Malaysia. The samples were cleaned, dried, and stored in a sealed plastic bag at room temperature prior to further study (Nordin *et al.* 2013). Potassium hydroxide (KOH), sodium chlorite ($NaClO_2$), and ionic liquids (namely 1-ethyl-3- methylimidazolium chloride ([EMIM]Cl), 1-decyl-3-methylimidazolium chloride ([C_{10}MIM][Cl]), and N,N-Dimethylformamide (DMF)) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Methods

Chemical pretreatment of oil palm mesocarp fiber (OPMF) for cellulose extraction

The OPMF was pretreated using 5% (w/v) sodium chlorite ($NaClO_2$) at pH 4 to 5, 70 °C, for 90 min, followed by 6% (w/v) potassium hydroxide (KOH) at room temperature for 24 h to remove both hemicellulose and lignin (Iwamoto *et al.* 2008). The materials were ground with a hammer mill (Miki Pulley Co., Ltd., Japan), and the OPMF-cellulose obtained had an approximate size of 0.5 to 1 mm. The OPMF-cellulose powder was stored in a sealed plastic bag prior to use. All reagents were used as received.

Ionic liquid formulations for determination of liquid properties prior to electrospinning

Prior to electrospinning, the OPMF-cellulose powder was dissolved in ionic liquid. Imidazolium-based ionic liquids, namely 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) and 1-decyl-3-methylimidazolium chloride ([C_{10}MIM][Cl]), were used. In addition to ([EMIM]Cl), which acted as the main solvent to dissolve OPMF-cellulose, and ([C_{10}MIM][Cl]), which acted as the second ionic liquid to reduce the solution surface tension, N,N-Dimethylformamide (DMF) was also used as a co-solvent to improve spinnability and enhance the uniform MF formation (Karimi *et al.* 2014). The four ionic liquid formulations are modified from Härdelin *et al.* (2012) and are presented in Table 1.

Table 1. Different Formulations of Ionic Liquid for Dissolution of OPMF-Cellulose

Amount of OPMF-Cellulose in Solvents (wt.%)	**Types of Solvent**			
	([EMIM]Cl) (wt.%)	([EMIM]Cl): ([C_{10}MIM][Cl]) (wt.%)	([EMIM]Cl): DMF (wt.%)	([EMIM]Cl): ([C_{10}MIM][Cl]): DMF (wt.%)
1%	100	90:10	90:10	80:10:10
3%				
6%				
9%				

To prepare the solution, an appropriate amount of DMF was added to the OPMF-cellulose, followed by ([C_{10}MIM][Cl]) and ([EMIM]Cl). The diffusion rate of ionic liquid into cellulose is enhanced by adding the co-solvent first (Härdelin *et al.* 2012). Each mixture was heated at 80 °C and stirred at 200 rpm for 12 h to produce a homogenous cellulose solution, which was subjected to electrospinning and analyses.

Electrospinning

MF prepared by electrospinning were spun using a voltage of 25 kV, working distance of 12 cm, and a rate 10 mL/min onto a water bath type collector (modified from Härdelin *et al.* 2012). After completing the electrospinning process, the ionic liquids remaining in the electrospun MF were removed using ethanol and they were washed in a flow deionized water. The MF then were oven-dried prior to analyses.

Characterization

Chemical composition analysis

Chemical composition analysis was conducted as reported by Nordin *et al.* (2013). The dry basis content of cellulose, hemicellulose, and lignin in the starting material was calculated gravimetrically. The OPMF was soaked in a 5% (w/v) sodium chlorite ($NaClO_2$) solution of pH 4 to 5 at 70 °C for 90 min. The samples were oven-dried for 24 h and cooled in a desiccator until a constant weight was recorded. Weight loss after this treatment was considered lignin composition, and the remaining weight was considered holocellulose, which consists of hemicellulose and cellulose composition. The holocellulose was rinsed with deionized water prior to further chemical treatment using 6% (w/v) potassium hydroxide (KOH) at 25 °C for 24 h to remove hemicellulose and retain cellulose. The treated samples were oven-dried for 24 h and cooled in a desiccator prior to analysis. The final weight of the samples was considered cellulose content.

Surface tension analysis

Surface tension analysis was conducted as reported by Seo *et al.* (2009). The surface tension of each mixture was measured using an EZ-Pi Surface Tensiometer (Kibron Inc, Helsinki, Finland). Deionized water was used to calibrate the samples. For analysis, the tip of the probe was immersed in 3 to 3.5 mL of sample.

Viscosity analysis

Viscosity was measured to determine the flow resistance of solution as described in Wahab *et al.* (2013). The viscosity of OPMF-cellulose solutions was measured using a Brookfield viscometer model 02072 (Stoughton, MA, USA) at room temperature using a SC43 (31) spindle, and the spindle speed was selected according to the viscosity of the ionic liquids solution.

Degree of polymerization measurement

The degree of polymerization of OPMF-cellulose was measured using a viscometer according to TAPPI T230 om-94 (1994) and ISO 5351-1 as reported by Chauve *et al.* (2013). The OPMF-cellulose was diluted in solutions containing distilled water and copper (II) ethylenediamine (CED) solution with a ratio 0.01:1:1 (OPMF-cellulose: distilled water: CED). The fiber solution was shaken until all fibers were completely dissolved. The OPMF-cellulose solution was then poured into the Ubbelohde viscometer tube (Type 231, PTA Laboratory Equipment, Vorchdorf, Austria), and the process was carried out at 25 °C for 10 to 15 min. The molecular weight of OPMF-cellulose was determined using the Mark-Houwink approach, which was using Eq. 1,

$$[\eta] = KM^{\alpha} \tag{1}$$

where [η] is the intrinsic viscosity and M is the molecular weight. $K = 0.42$ and $\alpha = 1$ are constant values of CED solvent (Chung and Um 2014).

Morphological analysis

To observe cellulose dissolution in different ionic liquid solutions, the morphology of the OPMF-cellulose solutions was analyzed using a light microscope (Motic, Model BA310, Richmond, BC, CA) at 40x magnification. The morphology of the electrospun MF was analyzed using field-emission scanning electron microscopy (FE-SEM) (Sirion 200, FEI, Eindhoven, Netherlands) with accelerating voltage of 5 kV. The MF were coated with platinum using a vacuum sputter coater prior to observation by FE-SEM.

X-ray diffraction (XRD) analysis

XRD was performed on a Philips PW3040/00 X'Pert MPD system (Eindhoven, Netherlands) to determine the crystallinity index of MF. The X-ray pattern was recorded in the 2θ range of 5 to 50°, and the crystallinity was calculated using Eq. 2,

$$\mathrm{CrI} = \frac{I_{002} - I_{am}}{I_{002}} \times 100\% \qquad (2)$$

where I_{002} was evaluated at an angle of $2\theta = 23$, and it refers to the peak of the crystalline portion of biomass (*i.e.*, cellulose). I_{am} refers to the peak at about $2\theta = 18$, which corresponds to the amorphous region (Nordin *et al*. 2013)

Thermogravimetric analysis

The thermogravimetric (TG) analysis was performed using a TG analyzer (TG 400, Perkin Elmer, Waltham, MA, USA) to identify the thermal stability and decomposition temperature of the raw OPMF, OPMF-cellulose, and OPMF-MF. Samples (about 10 mg) were placed in aluminum cups, and the analysis was carried out from 50 to 550 °C at a heating rate 10 °C/min under nitrogen flow of 20 mL/min.

RESULTS AND DISCUSSION

Characteristics of OPMF Cellulose

Chemical composition analysis showed that the raw OPMF contained 43% cellulose, 33% hemicellulose, and 22% lignin. The hemicellulose and lignin components of OPMF were reduced after chemical pretreatment, leaving approximately 99% cellulose (Table 2). This result is attributed to the use of $NaClO_2$ and KOH during pretreatment.

Table 2. Chemical Composition of the Oil Palm Mesocarp Fibers

Oil Palm Biomass	Cellulose (%)	Hemicellulose (%)	Lignin (%)
Raw oil palm mesocarp fiber (OPMF)	43 ± 0.7	33 ± 1.2	22 ± 2.0
Chemically treated oil palm mesocarp fiber (OPMF)	99 ± 0.8	1 ± 1.3	0

Note: Results are means of 3 replicates ± S.D.

The viscosity-average molecular weight and degree of polymerization of the OPMF-cellulose were determined using an intrinsic viscosity measurement. From Table 3, it is shown that molecular weight of the OPMF-cellulose was 157,000 g/mol, while the degree of polymerization was 967. It has been reported that molecular weight and degree of polymerization may affect cellulose properties such as cellulose solubility, mechanical properties of cellulose-based materials, and spinnability (Audrey *et al*. 2006). From the same table, it is seen that the molecular weight and degree of polymerization of OPMF-cellulose was comparable to cellulose from other lignocellulosic materials. Degree of polymerization of other cellulose samples ranged from approximately 400 to 3000; while the molecular weight ranged from approximately 90,000 to 300,000 g/mol.

X-ray diffraction patterns of the raw and OPMF-cellulose are shown in Fig. 1. Both raw and OPMF-cellulose had diffraction patterns at around 2θ = 23 and 2θ = 18, which represented the crystalline and amorphous regions, respectively (Nordin *et al.* 2013). The range of crystallinity index increased after chemical pretreatment from 15-18% to 51-55%. The increment of fiber crystallinity index is related to the removal of hemicellulose and lignin from OPMF (Jonoobi *et al.* 2009), which led to cellulose realignment (Chen *et al.* 2011). The crystallinity index of OPMF cellulose is comparable to that of other celluloses, as indicated in Table 3. Spectra c and d which represent MF will be discussed later in this paper.

Table 3. Properties of Cellulose from Various Sources

Source of Cellulose	Degree of Polymerization (DP)	Molecular Weight (g/mol)	Thermal Degradation T_{max}, (ºC)	Crystallinity Index (%)	Reference
Jute	< 400	-	-	85	Gassan and Bledzki 1998
Commercialized bleached *Picea abies*	1280	285,700	-	-	Henriksson *et al.* 2007
Commercialized cotton linters pulp	-	90, 000 - 127,000	-	53 - 55	Qi *et al.* 2009
Wheat straw	-	-	232	78	Alemdar and Sain 2008
Kenaf (*Hibiscus cannabinus)*	-	-	321 to 342	68 - 77	Jonoobi *et al.* 2009
Bamboo fiber	891	-	-	53	Wang *et al.* 2010
Flax	2801	-	-	67	Wang *et al.* 2010
Oil palm empty fruit bunches	1776	-	250	55	Wang *et al.* 2010
Wood powder from poplar trees	-	-	300	69	Chen *et al.* 2011
Oil palm mesocarp fiber	967	157,000	300	51 - 55	This study

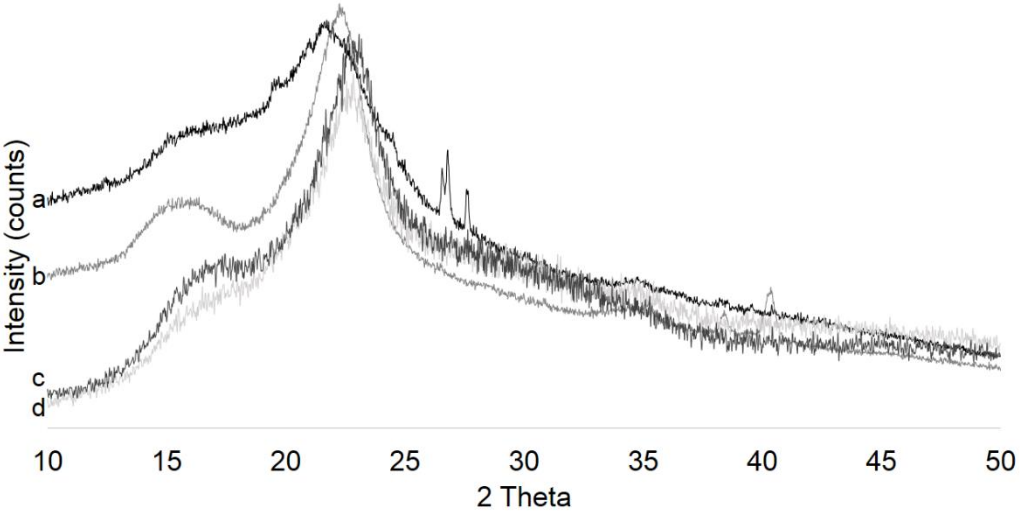

Fig. 1. X-ray diffraction patterns of (a) raw OPMF, (b) OPMF-cellulose, and MF from (c) 6% (w/v) ([EMIM]Cl):([C_{10}MIM][Cl]):DMF and (d) 6% (w/v) ([EMIM]Cl):DMF solutions

The thermal stability of OPMF is presented in Fig. 2. The decomposition temperature for 10% degradation ($T_{d10\%}$) of the raw OPMF and OPMF-cellulose was 230 °C and 300 °C, respectively. The increment of fiber thermal stability was mainly related to the removal of thermally unstable hemicellulose. Hemicellulose has a thermal degradation temperature in the range of 190 to 230 °C, but cellulose starts to degrade at 210 °C and higher (Nordin *et al.* 2013). Because OPMF-cellulose contained almost exclusively cellulose, it had better thermal stability than the raw OPMF. Additionally, the higher thermal stability for OPMF-cellulose could be explained by the higher crystallinity of the sample, which was due to the removal of amorphous regions from the raw OPMF as a result of hemicellulose removal. This is in agreement with the report by Si *et al.* (2014). Residue remaining after heating to 550 °C indicates the presence of carbonaceous materials in both raw OPMF and OPMF-cellulose (Nordin *et al.* 2013).

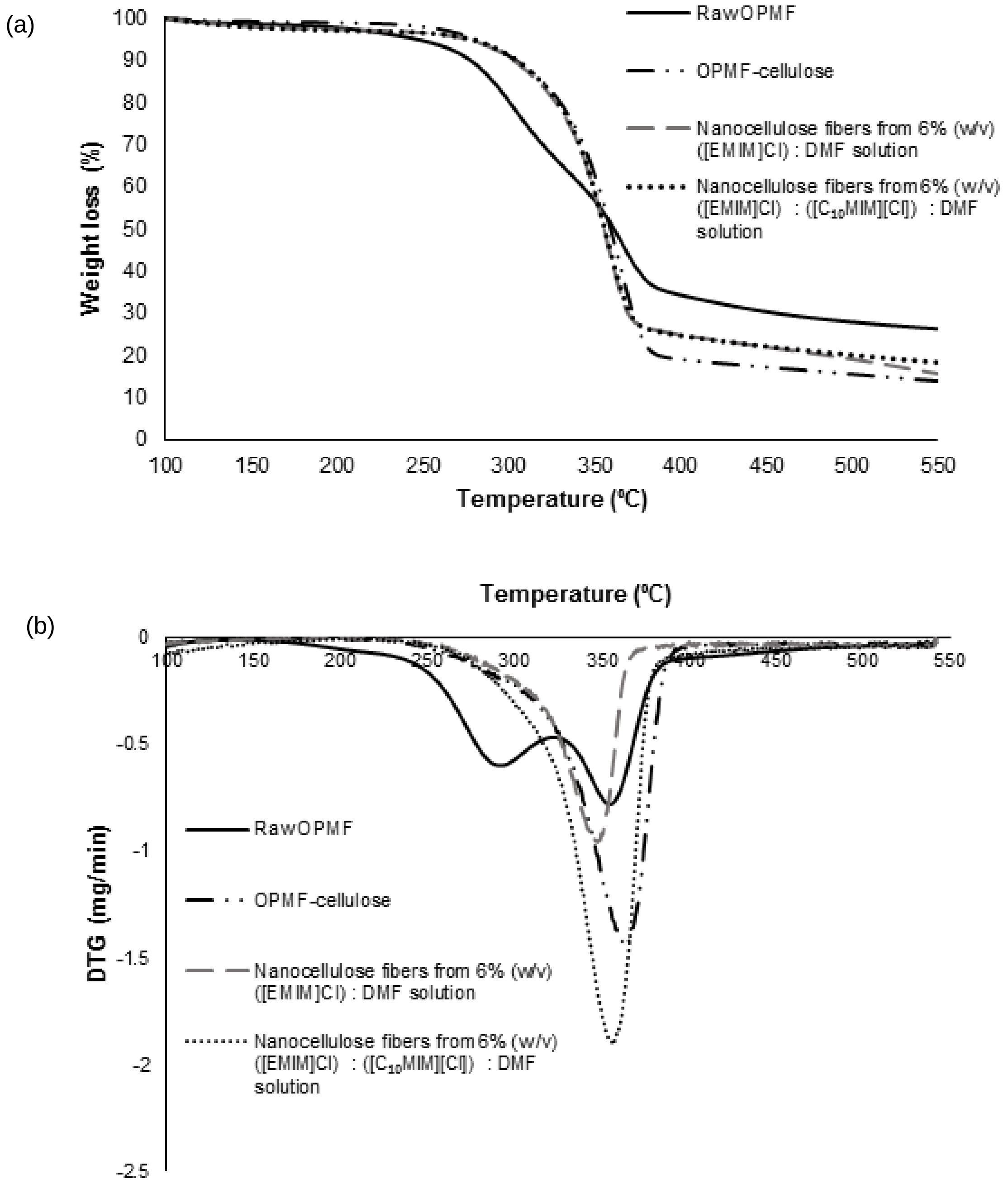

Fig. 2. (a) TGA and (b) DTG thermograms of raw OPMF, OPMF-cellulose, MF from 6% (w/v) of ([EMIM]Cl):DMF solution and ([EMIM]Cl):([C_{10}MIM][Cl]):DMF solution

Spinnability of OPMF-Cellulose

The spinnability of the OPMF-cellulose in four different ionic liquid formulations was evaluated. ([EMIM]Cl) was selected as the main solvent because it has low viscosity, low toxicity (ED50 = 2860 mg dm^{-3}), low corrosiveness, low melting temperature (< 253 K), and high ability to dissolve cellulose (Sun *et al.* 2009; Quan *et al.* 2010). An additional ionic liquid ([C_{10}MIM][Cl]) was chosen, as it can act as a surface active ionic liquid that reduces the surface tension (Freire *et al.* 2011) of the OPMF-cellulose solutions. DMF acted as a co-solvent to enhance the spinnability (Ferrer *et al.* 2012).

The spinnability properties of the OPMF-cellulose solutions are summarized in Table 4. The presence of co-solvent, *i.e.*, DMF, assisted in the spinnability of OPMF-cellulose solutions. All samples dissolved in ionic liquids without DMF were unable to be electrospun, and hence, there was no formation of MF. DMF has relatively high dielectric constant properties; it enhances the conductivity of OPMF-cellulose solutions, which indirectly enhances fiber formation (Bhardwaj and Kundu 2010). The presence of DMF in cellulose solutions aids in the formation of bead-free and smaller diameter MF (Bhardwaj and Kundu 2010; Gholipour and Bahrami 2011).

Table 4. Spinnability of OPMF-Cellulose in Different Ionic Liquid Solutions for Microfibrillated Cellulose Formation

OPMF-cellulose concentration in solvents (wt.%)	**([EMIM]Cl)**	**([EMIM]Cl) : DMF**	**([EMIM]Cl) : ([C_{10}MIM][Cl])**	**([EMIM]Cl) : ([C_{10}MIM][Cl]) : DMF**
1	-	+	-	+
3	-	++	-	++
6	-	+++	-	+++
9	-	+	-	+

Notes: -, cannot be electrospun; +, can be electrospun, beads formation with size approximately >1 µm; ++, can be electrospun with discontinuous MF formation; +++, can be electrospun with continuous MF formation

It is interesting to note that MF formation from the OPMF-cellulose solutions in the presence of DMF varied with the variation in cellulose concentration in the solvents. In both ionic liquids with DMF, only solutions with 6% (w/v) OPMF-cellulose were able to form MF continuously. At 3% (w/v) cellulose concentration, MF was formed discontinuously. There was no MF formation for 1 and 9% (w/v) OPMF-cellulose solutions. This is an interesting finding because MF formation did not have a linear relationship with the OPMF-cellulose concentrations. To explain this finding, cellulose dissolution, the viscosity of cellulose solution, and its surface tension were examined.

OPMF Cellulose Dissolution

Figure 3 shows microscopic images of the OPMF-cellulose solutions. Complete dissolution was achieved for all four ionic liquid formulations at concentrations of 1, 3, and 6% (w/v). ([EMIM]Cl), ([C_{10}MIM][Cl]), and DMF dissolved cellulose, which is the crucial step in electrospinning. Thus, the selection of solvent is important, as it may influence the dissolution of cellulose and subsequently, spinnability.

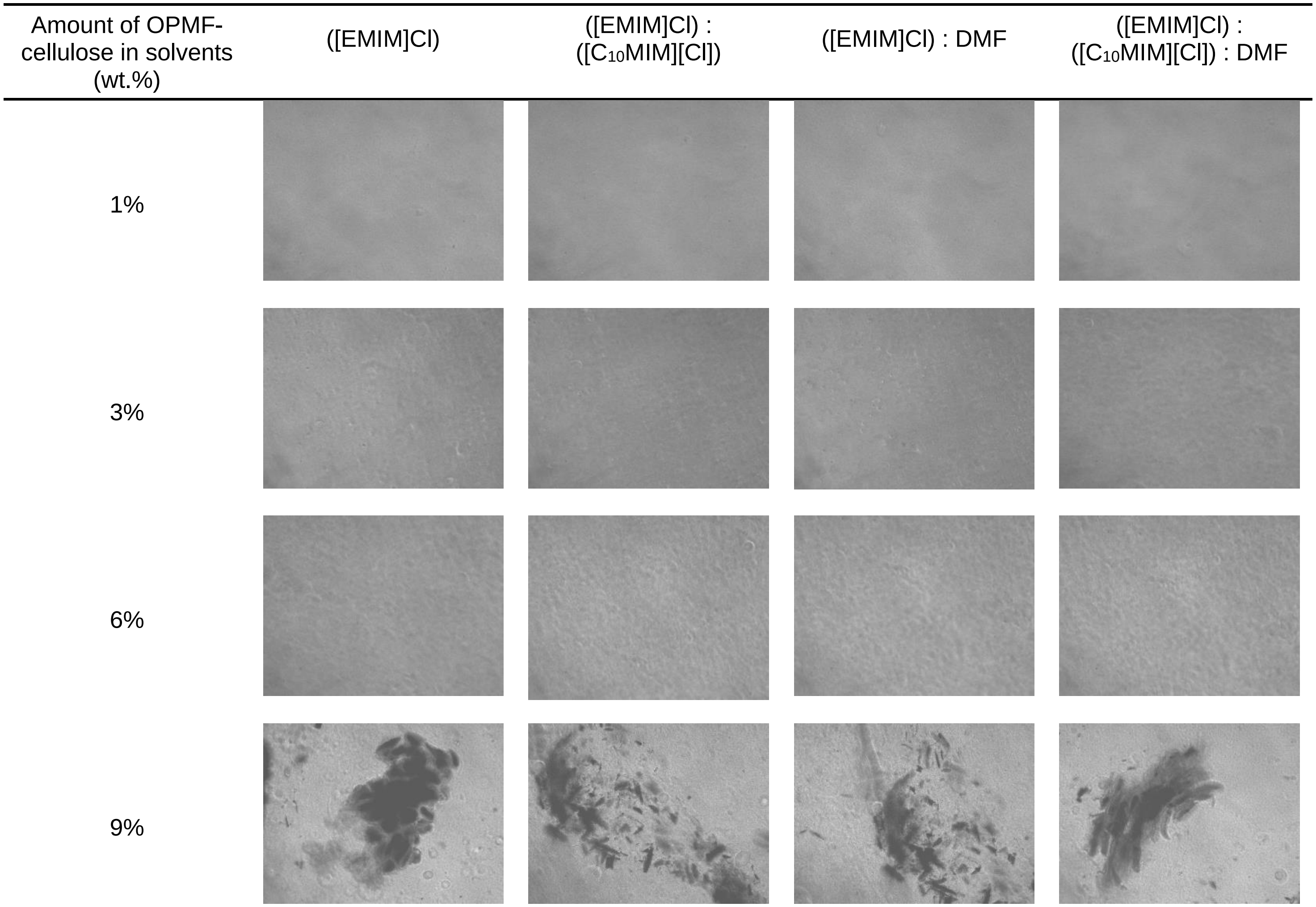

Fig. 3. Dissolution of OPMF-cellulose in different ionic liquid solutions as observed under light microscope (40x magnification).

A small amount of non-dissolved OPMF-cellulose was seen when 9% (w/v) OPMF-cellulose was used, in all ionic liquid solutions. This result indicates that incomplete dissolution occurred at high concentration solutions. Cellulose tends to agglomerate with ionic liquids in 9% (w/v) OPMF-cellulose solutions and solidified as they were unable to mix well with the ionic liquids. This condition might affect the degree of chain entanglement afterwards, which is a key factor in the formation of continuous fibers.

OPMF-Cellulose Solution Viscosity

Different formulations influenced the solution viscosity values (Fig. 4). OPMF-cellulose in ionic liquid formulations without DMF exhibited higher viscosity than formulations with DMF. The increment in cellulose concentration in the solution caused the solution to have higher viscosity, as expected. The highest viscosity was recorded by 9 wt.% OPMF-cellulose in ([EMIM]Cl) : ([C$_{10}$MIM][Cl]), at 29,897 mPa.s, followed by 9 wt.% OPMF-cellulose in ([EMIM]Cl), ([EMIM]Cl) : ([C$_{10}$MIM][Cl]) : DMF, and ([EMIM]Cl) : DMF at 28,720, 22,671, and 9,879 mPa.s, respectively.

This result showed that ([C$_{10}$MIM][Cl]) enhances solution viscosity. Furthermore, intermolecular forces between both ([EMIM]Cl) and ([C$_{10}$MIM][Cl] were strong, as it recorded higher viscosity than the OPMF-cellulose solutions without ([C$_{10}$MIM][Cl]). This condition might be due to the entanglement between long alkyl side chain of ([C$_{10}$MIM][Cl] to ([EMIM]Cl). The viscosity of solutions containing solely ionic liquid was relatively high. The use of high viscosity ionic liquids in electrospinning is challenging because it may affect the polymer concentration, which affects the degree of chain entanglement and the formation of continuous sprayed fibers (Gholipour and Bahrami 2011). Therefore, instead of solely depending on ionic liquids, the addition of co-solvent reduces solution viscosity, and this effect was successfully achieved in this study.

Rapid viscosity reduction was observed after DMF was added in OPMF-cellulose solutions. DMF affected the solutions properties, as it reduces friction between solution molecules, which indirectly reduces the solutions resistance (Yakymovych *et al.* 2016). This explains the function of DMF in reducing viscosity.

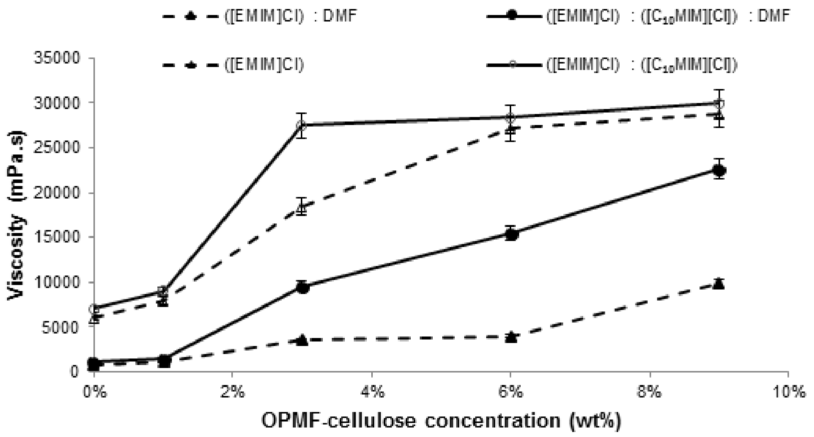

Fig. 4. The effect of DMF addition on the viscosity of the OPMF-cellulose solutions at different cellulose concentrations

Viscosity increased regularly with increased OPMF-cellulose concentration regardless of the ionic liquid formulations, and this result is comparable to that reported by Si *et al.* (2014). In electrospinning, an optimum solution concentration is required because it influences fiber formation. If the solution concentration is too low, high surface tension of the polymer solution may cause interruption during spraying which consequently causes the fibers to turn into beads (Haider *et al.* 2015). A highly concentrated solution is preferred for electrospinning, as it increases viscosity, which indirectly increases the chain entanglement and overcomes the surface tension to form beadless MF. However, if the polymer concentration and viscosity are too high, fibers with larger diameters are formed because the solution cannot be sprayed continuously (Si *et al.* 2014).

In this study, the viscosity of the solution was affected by cellulose concentration and the use of co-solvent. It is important to have these two parameters balanced in order to achieve the appropriate viscosity for electrospinning of the cellulose solution.

Surface Tension of OPMF-Cellulose Solutions

Ionic liquid formulations also influenced the surface tension of OPMF-cellulose solutions (Fig. 5). The use of ([EMIM]Cl) alone contributed to higher surface tension than combined ionic liquids. DMF addition resulted in higher surface tension. Statistical analysis showed that there was significant difference between different OPMF-cellulose concentrations as well as between different ionic liquid formulations.

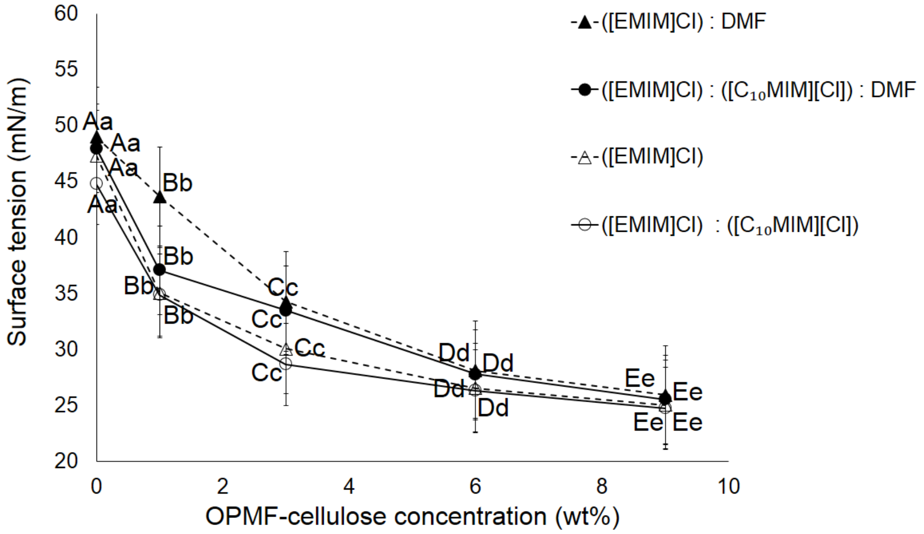

Fig. 5. The effect of DMF addition on the surface tension of the OPMF-cellulose solutions at different cellulose concentrations. Capital letters indicate differences ($P < 0.05$) for OPMF-cellulose concentration, while small letters indicate differences ($P < 0.05$) for ionic liquid formulations. All data are means of 3 replicates ± S.D. (Different alphabets indicate significant difference, and *vice-versa*).

Although there was no significant difference in surface tension for all the solutions tested at similar concentration, the addition of ([C$_{10}$MIM][Cl]) as a second ionic liquid reduced the overall surface tension of the cellulose solution. This result reflects that ([C$_{10}$MIM][Cl]) has a tendency to migrate to the vapour-liquid interface in polar medium and causes reduction in the surface tension of the solution (Freire *et al.* 2011). In contrast, the addition of DMF in OPMF-cellulose solutions containing ionic liquid contributed to higher surface tension, which is attributed high surface tension of the DMF (36.73 mN/m) (Härdelin *et al*. 2012).

Surface tension of the OPMF-cellulose solution was also dependent on solution concentration. The surface tension was reduced with increased OPMF-cellulose concentration regardless of solution formulations. Surface tension of all the solutions without the addition of OPMF-cellulose (0%) ranged between 45 and 49 mN/m. This value declined after OPMF-cellulose was added; for example, the surface tension of 1% (w/v) OPMF-cellulose solution was 35 to 44 mN/m. The lowest surface tension range was recorded at 9% (w/v) OPMF-cellulose solution, at 25 to 26 mN/m. This data shows that surface tension can be lowered in viscous and concentrated solutions.

Factors Affecting Spinnability and MF Formation

Table 5 summarizes the liquid characteristics and their effect on spinnability and MF formation. OPMF-cellulose solution properties such as concentration, viscosity, solubility, and surface tension remarkably affected the spinnability and MF formation. The desired morphology and structure of MF can be obtained by manipulating these parameters during electrospinning.

It is interesting to note that MF was formed only when 6% (w/v) of OPMF-cellulose was used and when the solutions contained DMF. To clarify this result, it is important to relate the solution concentration with viscosity. Figure 4 shows that the OPMF-cellulose solution viscosity increased simultaneously with OPMF-cellulose solution concentration. Nevertheless, the viscosity range was lower when DMF was used. For instance, 6 wt.% OPMF-cellulose in ([EMIM]Cl) had viscosity value of 27,123 mPa.s, while the viscosity decreased drastically to 3,986 mPa.s in the presence of DMF. A marked difference in OPMF-cellulose solution viscosity affected the spinnability, despite the same concentration of OPMF-cellulose being used, *i.e*., 6 wt.%. The same result was observed for OPMF-cellulose in ([EMIM]Cl) : ([C_{10}MIM][Cl]) solution, where the presence of DMF reduced the viscosity. Similarly, only cellulose concentration at 6 wt% was electrospun for the production of MF.

As discussed earlier, surface tension was not significantly affected by cellulose concentration and type of ionic liquid formulation. Table 5 shows that surface tension for all ionic liquid solutions containing 6 wt.% OPMF-cellulose was in the narrow range of 26 to 28 mN/m. It is therefore difficult to justify the effect of surface tension on spinnability of OPMF-cellulose solution.

Based on these results, both solution concentration and viscosity determined the spinnability of cellulose solution in the formation of MF. Too high or too low concentration and viscosity caused failure during electrospinning. Reduced cellulose solution viscosity due to the addition of DMF seemed to assist the solution to be electrospun into MF for 6 wt.% OPMF-cellulose solution, which may indicate that the solution having lower viscosity may have better spinnability. However, for low concentration of cellulose, for example at 1 wt.%, no fiber formation was observed despite the low solution viscosity. It is believed that fiber deformation has occurred due to charges instability and insufficient amount of cellulose. As the result, beads were mainly formed. There have been research on the formation of beads from low concentration solutions; these results are probably due to the insufficient viscosity to continuously generate fibers (Chung and Um 2014; Okutan *et al.* 2014; Nitanana *et al.* 2015).

The results showed that viscosity alone was not the reason for the formation of MF. Cellulose concentration in the solution and the addition of DMF, which eventually stabilized the solution charges, also played important roles. Sufficient charges are needed to stretch the solution from the tip to collector; otherwise continuous MF cannot be obtained (Dufresne 2012). The formation of MF in OPMF-cellulose solutions containing DMF could also be attributed to its properties, *i.e.*, high dielectric constant, high electric conductivity, and low vapor pressure (Dufresne 2012).

Table 5. Summary of OPMF-Cellulose Solutions Concentration, Viscosity, and Surface Tension and their Relationship with OPMF-Cellulose Spinnability

Ionic Liquid Solution	Concentration (wt.%)	Viscosity (mPa.s)	Surface Tension (mN/m)	Spinnability
([EMIM]Cl) : DMF	0%	786	49	NA
	1%	1068	44	+
	3%	3516	34	++
	6%	3986	28	+++
	9%	9879	26	+
([EMIM]Cl) : ([C$_{10}$MIM][Cl]) : DMF	0%	1098	48	NA
	1%	1557	37	+
	3%	9595	34	++
	6%	15530	28	+++
	9%	22671	26	+
([EMIM]Cl)	0%	5981	47	NA
	1%	7917	35	-
	3%	18425	30	-
	6%	27123	27	-
	9%	28720	25	-
([EMIM]Cl) : ([C$_{10}$MIM][Cl])	0%	6998	45	NA
	1%	8997	35	-
	3%	27487	29	-
	6%	28366	26	-
	9%	29897	25	-

Notes: -, cannot be electrospun; +, can be electrospun, beads formation with size approximately >1 μm; ++, can be electrospun with discontinuous MF formation; +++, can be electrospun with continuous MF formation

Härdelin *et al.* (2012) reported that cellulose solutions with surface tension greater than 42 mN/m could be electrospun. The results reported here do not support that conclusion, as it was shown that MF formation was best at a surface tension around 28 mN/m. However, there was no marked difference in the effect of surface tension on spinnability, as the spinnability depends on cellulose concentration and viscosity, not only surface tension. Si *et al*. (2014) mentioned that solutions with very high surface tension may inhibit electrospinning due to instability of the charged jet towards the cellulose solution. The electrical charges need to be high enough to overcome the high surface tension of the solutions. Contrary to solutions that recorded high surface tension, MF with high uniformity can be generated from solutions with low surface tension. The contradiction between the two authors might be due to the properties of the cellulose used, selection of solvents and co-solvent, and other factors such as applied voltage and distance between tips to collector.

Characteristics of MF from OPMF-Cellulose

FE-SEM micrographs of electrospun MF from OPMF-cellulose solutions are shown in Fig. 6. There were no beads and droplets found on the electrospun MF. The average diameter of fibers produced from 6% (w/v) ([EMIM]Cl): DMF solution was 300 to 600 nm, while the diameter of fibers produced from 6% (w/v) ([EMIM]Cl): ([C_{10}MIM][Cl]):DMF solution was 200 to 500 nm. This result indicated that electrospun MF produced from ([EMIM]Cl):DMF had a wider diameter range than that from ([EMIM]Cl):([C_{10}MIM][Cl]):DMF.

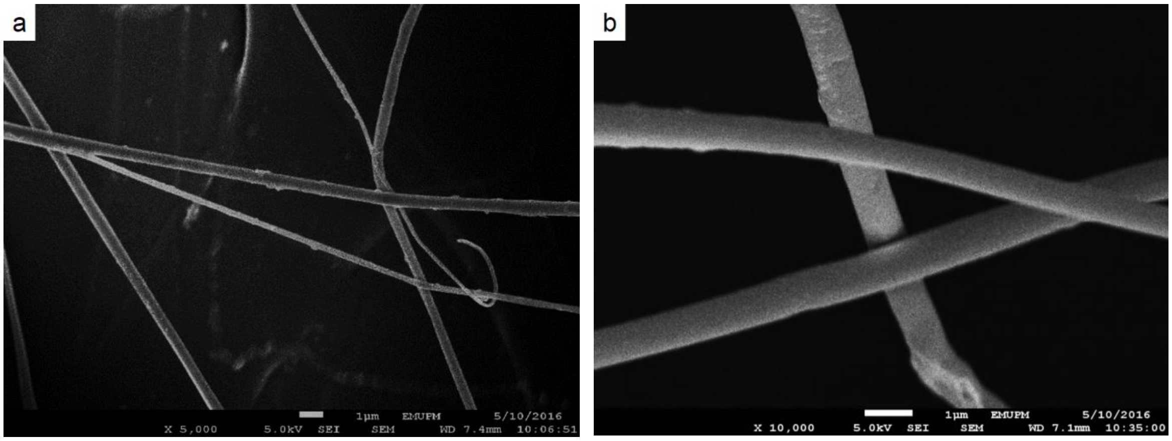

Fig. 6. Microfibrillated cellulose produced from 6% (w/v) OPMF-cellulose dissolved in ([EMIM]Cl) and DMF under (a) 5,000x and (b) 10,000x magnifications

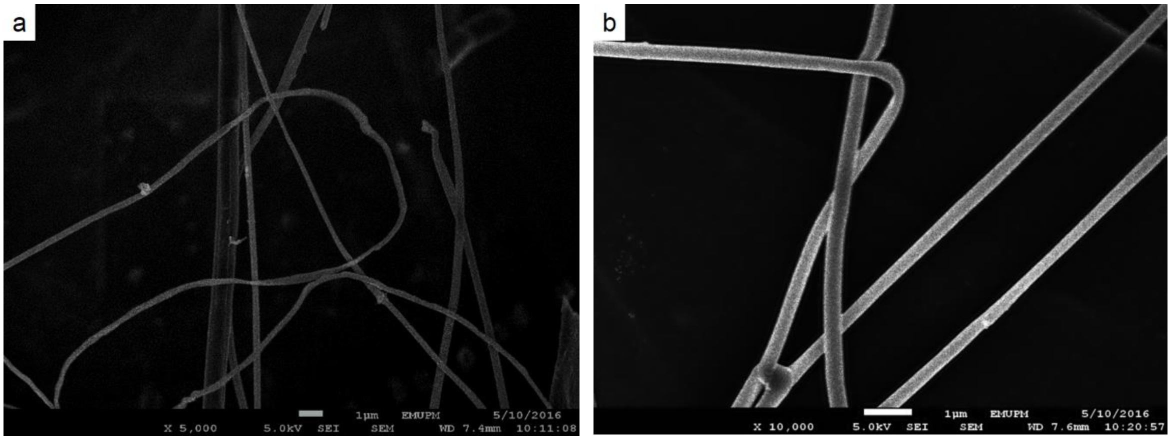

Fig. 7. Microfibrillated cellulose produced from 6% (w/v) OPMF-cellulose dissolved in (([EMIM]Cl), ([C_{10}MIM][Cl]) and DMF under (a) 5,000x and (b) 10,000x magnifications

The range of crystallinity index of the raw OPMF, OPMF-cellulose, and OPMF-MF was obtained from XRD analysis. Table 6 shows that there was increased crystallinity range after electrospinning, which was 55 to 57% for MF produced from 6% (w/v) ([EMIM]Cl):DMF solution and 57 to 60% for MF produced from 6% (w/v) ([EMIM]Cl:([C_{10}MIM][Cl]):DMF solution, compared with OPMF-cellulose at 51 to 55% (Table 3). The pattern of XRD diagram is shown in Fig. 1. The increased crystallinity index confirmed that electrospinning improved the crystallinity value of OPMF fiber. Increased crystallinity may increase the tensile strength (Alemdar and Sain 2008). Hence, the MF from the OPMF-cellulose may be suitable as filler for the manufacturing of nanocomposites, as they enhance the thermal, tensile, and mechanical properties of the nanocomposite (Alemdar and Sain 2008)

Table 6. Comparison of Electrospun Microfibrillated Cellulose from Commercialized Cellulose

Sources	Conditions	Average Diameter (nm)	Crystallinity Value (%)	Degradation Temperature (°C)	References
Commercialized corn cellulose (Jinan Shengquan Group Co., Ltd)	- Voltage: 15-21kV - Concentration: 9% (w/v) - Solvent: DMAc/LiCl	500 – 2,000	57 – 60	-	Chen *et al.* 2015
Commercialized cellulose (Sigma)	- Voltage: 20kV - Concentration: 8% (w/v) - Solvent: [C_2MIM][CH_3CO_2] and ([C_{10}MIM][Cl])	120 – 470	59	230	Freire *et al.* 2011
Commercialized cellulose (Hyosung)	- Voltage: 15kV - Concentration: 4% (w/v) - Solvent: BMIMCl and DMSO	500 – 800	-	260	Quan *et al.* 2010
OPMF cellulose	- Voltage: 15kV - Concentration: 6% (w/v) - Solvent: ([EMIM]Cl), ([C_{10}MIM][Cl]) and DMF	200 – 500	56	254	This study

Thermal stability of MF from both ionic liquid formulations was analyzed, and the TG and DTG curves are shown in Fig. 2. The MF produced from 6% (w/v) ([EMIM]Cl) and DMF solution started to decompose above 302 °C, while MF from 6% (w/v) ([EMIM]Cl, ([C_{10}MIM][Cl]) and DMF solution started to decompose above 304 °C. Residues were formed after heating to 550 °C, which indicates the presence of carbonaceous materials in the fibers (Nordin *et al.* 2013). This result clearly illustrates that the thermal stability of OPMF-MF increased after electrospinning, and this could be attributed to the reduction of amorphous region, which happened due to high degree of crystallinity of the MF after electrospinning (Jonoobi *et al*. 2009; Nordin *et al*. 2013).

Given the morphology, average diameter, crystallinity, and thermal stability of MF produced from the OPMF-cellulose, OPMF-cellulose can be used as a feedstock for MF production. The analyses showed that the properties of MF produced from the OPMF-cellulose were comparable to those from commercialized cellulose, as shown in Table 6. The average diameter of MF produced from commercialized cellulose was approximately 120 to 2,000 nm, while this study shows that MF of less than 500 nm were produced from OPMF-cellulose. The crystallinity and thermal decomposition of these MF was also not significantly different than MF from other sources. This result suggests that the OPMF-cellulose can be used as an alternative feedstock for large-scale MF production especially in Malaysia, as it can be obtained easily from palm oil mills throughout the year.

CONCLUSIONS

1. The spinnability of OPMF-cellulose solution for the production of MF was greatly affected by the cellulose concentration and viscosity of the solution. The use of DMF in ionic liquid affected the viscosity of cellulose solution very much, despite the same concentration of cellulose used in the ionic liquid without DMF. This condition assisted in spinnability of the cellulose solution. This study shows that MF can only be formed from 6% (w/v) OPMF-cellulose solutions in the presence of DMF.
2. Surface tension was mainly affected by the cellulose concentration. The use of DMF and co-solvent did not vary the surface tension value significantly. MF formation did not rely solely on the surface tension value.
3. MF from OPMF-cellulose dissolved in ([EMIM]Cl:([C_{10}MIM][Cl]):DMF had a diameter of 200 to 500 nm, which is comparable to that produced from commercialized cellulose. The characteristics of MF produced in this study indicate that OPMF is a promising candidate for MF production.

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