

SWELLING AND DISSOLUTION OF OIL PALM BIOMASS IN IONIC LIQUIDS

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ABSTRACT

Malaysia is amongst the world's top producers of palm oil and the current planted area is around 4.5 million hectares. The palm oil industry generates vast amounts of palm biomass, especially empty fruit bunches (EFB) (from the mills), oil palm fronds (OPF) and oil palm trunks (OPT) (during routine pruning and from the field during replanting). Oil palm biomass can be used efficiently after further treatment, either by physical or chemical means. In this study, the swelling and dissolution mechanisms of the lignocellulosic biomass by ionic liquids were compared. There are five modes in describing the swelling and dissolution for cotton and wood cellulose fibre, and these were compared to the results obtained. Depending on the quality of the solvent, disintegration into rod-like fragments and ballooning, followed subsequently by dissolution were all observed among the oil palm fibre. In a typical dissolution trial, 5 wt % of oil palm biomass and cellulose fibre from EFB, OPF and OPT were treated with two different ionic liquids: 1-butyl-3-methylimidazolium chloride/dimethyl sulphoxide ([bmim]Cl)/DMSO and 1-ethyl-3-methylimidazolium chloride/dimethyl sulphoxide ([emim]Cl)/DMSO at a ratio of 80:20 wt %. They were heated at different fixed times, namely 4, 6, 8, 16 and 24 hr for untreated oil palm biomass, and 1, 2 and 3 hr for cellulose fibre. The mechanisms of swelling and dissolution were monitored by optical microscopy.

Keywords: empty fruit bunches, oil palm fronds, oil palm trunks, ionic liquids, cellulose.

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INTRODUCTION

Oil palm is one of the most important economic perennial oil crops in the tropical region, especially in west Africa (Shaari and Khoo, 1991) and in the ASEAN countries such as Malaysia and Indonesia, because of its valuable oil-producing fruits. Its species name is *Elaeis guineensis*, belonging to the

family *Palmaceae*. Malaysia is one of the world's leaders in the production and export of palm oil products. The oil palm industry has contributed immensely towards the country's economic well-being. Besides palm oil, the industry also generates massive amounts of lignocellulosic residues such as empty fruit bunches (EFB), oil palm trunks (OPT) and oil palm fronds (OPF), with an estimated total amount of 65.46 million tonnes (dry weight) (MPOB, 2001). In 2007, it was estimated that around 19.3 million tonnes (wet weight basis) of EFB were available in Malaysia (Astimar *et al.*, 2002).

Oil palm biomass is considered 'green' material due to some factors. First, the materials are obtained as by-products from the oil palm industry (milling and plantation sectors). The by-products can be converted into value-added products, such as composites, pulp and paper, chemical products and other valuable products (Mott *et al.*, 1999; Dahlan,

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2000; Okudaira *et al.*, 2000). Therefore, optimising the use of all products and by-products derived from the oil palm industry is relevant. Second, oil palm biomass is renewable, thus its use will protect the forests from being felled and in turn the environment, and the materials are biodegradable (Mohamad *et al.*, 2005).

Generally, lignocellulosic biomass is composed mainly of three constituents which are cellulose, lignin and hemicelluloses. The proportions of these components in a fibre depend on the nature of the plant, its age, the source of the fibre and the extraction conditions used to obtain the fibre (Batra, 1985). The chemical, physical and mechanical properties of the oil palm biomass indicate that these materials are almost similar to wood, and are potentially suitable as raw material for wood-based panel and pulp and paper industries. These biomass constituents can be separated and then converted into useful chemicals. Sun and Sun (2003) has found that cellulose is useful as the source of various derivatives, glucose and pulp; lignin can be used to make carbon fibre (Uraki *et al.*, 1997), adhesives (Pan and Sano, 1998), and other chemicals (Kubo *et al.*, 1997), while hemicelluloses are a source of sugars or ethanol.

Cellulose is the most abundant biorenewable material and its derivitized products have many important applications in the fibre, paper, membrane, polymer and paints industries. Although cellulose has many useful applications, it also presents a tremendous challenge with regard to making sure its chemical processing is economical and environmental-friendly. To date, many derivative and non-derivative solvents for cellulose have been found, such as LiCl/*N,N*-dimethylacetamide (DMAc) (Terbojevich *et al.*, 1985; McCormick and Dawsey, 1990; Williamson *et al.*, 1998; Nishino *et al.*, 2004), LiCl/*N*-methyl-2-pyrrolidone (NMP) (Edgar *et al.*, 1995), LiCl/1,3-dimethyl-2-imidazolidinone (DMI) (Tamai *et al.*, 2004), DMSO/paraformaldehyde (PF) (Masson and Manley, 1991), *N*-methylmorpholine-*N*-oxide (NMMO) (Heinze and Liebert, 2001) and molten salt hydrates such as NaSCN/KSCN/LiSCN/water (Fischer *et al.*, 1999). However, there are some limitations in using conventional solvents due to their volatility, toxicity and high cost.

Recently, many researchers have found that ionic liquids (IL) can dissolve a large number of bio-macromolecules, such as cellulose (Swatloski *et al.*, 2002; Heinze and Koschella, 2005; Zhang *et al.*, 2005), silk fibroin (Phillips *et al.*, 2004), lignin (Pu, 2007), starch and zein protein (Biswas *et al.*, 2006), chitin/chitosan (Xie *et al.*, 2006; Wu *et al.*, 2008), wool keratin (Xie *et al.*, 2005), *etc.*, with high efficiency but no work has been done on tropical biomass fibre. They are considered to be possible alternative solvents as they have good properties

– non-volatility and non-flammability – which are due to their negligible vapour pressure at ambient temperature (Heinze *et al.*, 2005; Zhu *et al.*, 2006). On the basis of ecological and economical concerns, IL seems to be an attractive alternative compared to conventional volatile organic solvents (Turner *et al.*, 2003; Varma and Namboodiri, 2001).

In this study, the swelling and dissolution of lignocellulosic biomass from oil palm fibre in IL were observed. ILs can be claimed to be a potential solvent in dissolving carbohydrate, and have high potential as one of the green routes towards volatile organic solvent replacement.

MATERIALS AND METHODS

Materials

EFB, OPF and OPT were collected from the Biomass Technology Centre (BTC) of the Malaysian Palm Oil Board (MPOB). The fibre were cleaned, washed, shredded and refined into loose fibrous material using a thermo chemical refiner at medium density fibreboard (MDF) pilot plant in Bangi. Samples were dried to constant weight in a vacuum before further use. The IL which were 1-ethyl-3-methylimidazolium chloride ([emim]Cl) and 1-butyl-3-methylimidazolium chloride ([bmim]Cl) were acquired from Merck (Germany). IL and other reagents were used as received.

Methods

Measurements of chemical composition. The fibrous materials were dried and were refined into fine fibre with a length of <150 nm. The fibre length was measured using digital imaging microscopy [Nikon, Infinity (2 mpx), i-solution software]. Moisture and organic matter contents were determined after drying at 105°C for 24 hr, and ashing at 550°C for 4 hr, respectively. Cellulose and lignin analyses of the biomass were conducted in this study. The analytical method for cellulose and lignin contents in the biomass is as follows: first, the crushed biomass sample was extracted for 5-6 hr in an ethanol-toluene mixture in the ratio 1:2 (v/v of biomass to the solvent) in a soxhlet extraction apparatus, according to methods of T 204 om-88 (Alcohol-Benzene and Dichloromethane Solubles in Wood and Pulp) and T 264 om-88 (Preparation of Wood for Chemical Analysis) method. Then, chemical analyses on the residue after the extraction were conducted including for holocellulose, cellulose and lignin, hot water solubility and alkali solubility.

Holocellulose is defined as the water-insoluble carbohydrate fraction of plant materials. The preparation of holocellulose was modified from

the method of Wise *et al.* (1946). The preparation of α -cellulose was done by further treating the obtained holocellulose with NaOH using the method of T 203 os-74 (Alpha-, Beta-, and Gamma-Cellulose in Pulp). Determination of lignin and ash contents was determined using the method of T 222 om-88 (Acid-Insoluble Lignin in Wood and Pulp) and T 211 om-93 (Ash in Wood and Pulp). The solubility properties were also determined based on cold and hot water [T 207 om-88 (Water Solubility of Wood and Pulp)] and 1% NaOH [T 212 om-83 (One Percent Sodium Hydroxide Solubility of Wood and Pulp)] methods. The NaOH treatment can lead to an irreversible mercerisation effect which increases the amount of amorphous cellulose at the expense of crystalline cellulose.

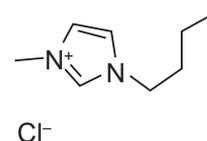
Dissolution of Oil Palm Biomass and Cellulose Fibre into Ionic Liquids

The swelling and dissolution mechanisms of fibre can be observed through an optical microscope with Metallux 3 (Leitz) [Nikon (DS-Fil-42)]. The solutions were prepared by mixing 5 wt % of the oil palm biomass or cellulose fibre of EFB, OPF and OPT in IL ([emim]Cl and [bmim]Cl) (Figure 1) separately in a vial, and the mixture was mechanically stirred at 100°C in an oil bath. They were heated at different fixed times, namely, 4, 6, 8, 16 and 24 hr for untreated oil palm biomass, and 1, 2 and 3 hr for cellulose fibre. Prior to observation, a very small amount of solution was placed on a glass plate and viewed at 20X magnification.

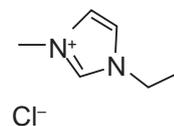
RESULTS AND DISCUSSION

Chemical Composition

Lignocellulosic biomass is composed mainly of three constituents which are cellulose, lignin and hemicelluloses. Table 1 shows the chemical



1-butyl-3-methylimidazolium chloride ([bmim]Cl)



1-ethyl-3-methylimidazolium chloride ([emim]Cl)

Figure 1. Chemical structures of ionic liquids (IL), 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and 1-ethyl-3-methylimidazolium chloride ([emim]Cl).

composition of oil palm fibre from various oil palm wastes. In the same table, the results are compared to the chemical composition of hardwood and softwood (Tsoumis, 1991). The percentage of cellulose in all three fibre was comparatively similar although fibre from EFB and OPF were slightly higher than that from OPT. The lignin content of OPT fibre was a little bit higher compared to those of EFB and OPF fibre. However, the proportion of the three components in a fibre depends on the age, nature of the plant, source of the fibre and the extraction conditions used to obtain the fibre (Batra, 1985). As reported by Basiron and Husin (1996), EFB contains about 77.7% holocellulose which consists of 44.2% and 33.5% α -cellulose and hemicellulose, respectively, and 20.4% lignin, while OPT contains 76.3% holocellulose (cellulose + hemicellulose), 30.4% hemicellulose and 18.1% lignin (Md Yusoff, 1985).

The percentage of cellulose is higher for hardwood, as well as in oil palm biomass fibre, compared to softwood, while the lignin content of hardwood and softwood is slightly higher compared to oil palm biomass fibre (Table 1).

TABLE 1. PROXIMATE CHEMICAL ANALYSES OF OIL PALM BIOMASS, HARDWOOD, SOFTWOOD AND SOME IMPORTANT NATURAL FIBRE (% , dry basis)

Fibre	Ash content (%)	Alcohol-benzene (%)	Cellulose (%)	Hemicellulose (%)	Lignin (%)	Holocellulose (%)	Hot water solubility (%)
EFB	2.5	2.9	48.0	25.1	19.9	73.1	11.6
OPF	0.5	2.5	48.4	23.1	18.1	71.5	11.5
OPT	1.5	2.6	44.4	29.3	21.2	73.7	7.2
Hardwood ^a	0.7	1.3	44.7	20.7	20.6	81.0	3.6
Softwood ^a	0.5	2.9	40.9	12.5	28.7	70.4	4.5
Coir ^b	-	-	32.0-43.0	0.15-0.25	40.0-45.0	-	-
Banana ^b	-	-	63.0-64.0	19.0	5.0	-	-
Sisal ^b	-	-	66.0-72.0	12.0	10.0-14.0	-	-
Pineapple leaf fibre ^b	-	-	81.5	-	12.7	-	-

Note: ^a Tsoumis (1991).

^b Sreekala *et al.* (2001).

Generally, wood (or trees) from the Gymnosperms, a subdivision of the division Spermatophytes (plants with seeds), are known as softwoods while wood from the Angiosperms, another subdivision of the Spermatophytes, are known as hardwoods. The chemical composition between hardwood and softwood might be different as wood is not a homogeneous material. Just as cell dimensions vary in wood taken from various parts of a tree, so too do their chemical compositions (Kollman and Cote, 1968).

The chemical compositions of oil palm biomass fibre were also compared to some other natural fibre such as coir, banana, sisal and pineapple leaf fibre (Table 1). All the properties of these natural fibres vary widely, just as the oil palm fibre from different sources. Banana fibre is weak and cylindrical in shape while coir is a hard and tough multicellular fibre with a central portion called the 'lacuna'. In some studies, it has been reported that oil palm fibre show similarity with coir fibre as they both have a hard and tough multicellular fibre (Maldas and Kokta, 1990). Previously, except for oil palm biomass fibre, no systematic work has been undertaken on natural fibre to investigate their swelling and dissolution mechanisms in IL.

Swelling and Dissolution

The morphological changes in oil palm biomass fibre which had been dissolved in IL via mechanisms of swelling and dissolution of the cellulose fibre were carefully observed with an optical microscope. Cuissinat and Navard (2006a, b) previously investigated the swelling and

dissolution of cotton and wood fibre in IL. In their study, they proposed that five modes of interactions can be considered in the dissolution of cotton and wood cellulose fibre in aqueous systems and IL, and these are:

- mode 1: fast dissolution by disintegration into fragments;
- mode 2: large swelling by ballooning and dissolution;
- mode 3: large swelling by ballooning with no dissolution;
- mode 4: homogeneous swelling with no dissolution; and
- mode 5: no swelling and no dissolution.

These modes reflect the quality of the solvents used which decrease from mode 1 to mode 5. A very good solvent disintegrates the cellulose fibre into long needles (mode 1) which are then quickly dissolved. Moderate to bad solvents normally first swell the fibre into balloons which then burst and dissolve (moderate solvent quality, mode 2), or do not dissolve (bad solvents, mode 3). However, in both modes 2 and 3, there are parts of the cellulose inside the balloons which dissolve in small quantities. Finally, non-solvents can either homogeneously swell the fibre but without dissolution (mode 4), or they do not interact at all with the cellulose (mode 5).

Oil palm fibre (from EFB, OPF and OPT) were partially dissolved in [emim]Cl and [bmim]Cl at 100°C after 16 hr. Swelling of the oil palm fibre was observed to follow mode 4 of interaction (homogeneous swelling, without dissolution) (Figures 2i-2iii). This finding is contrary to some

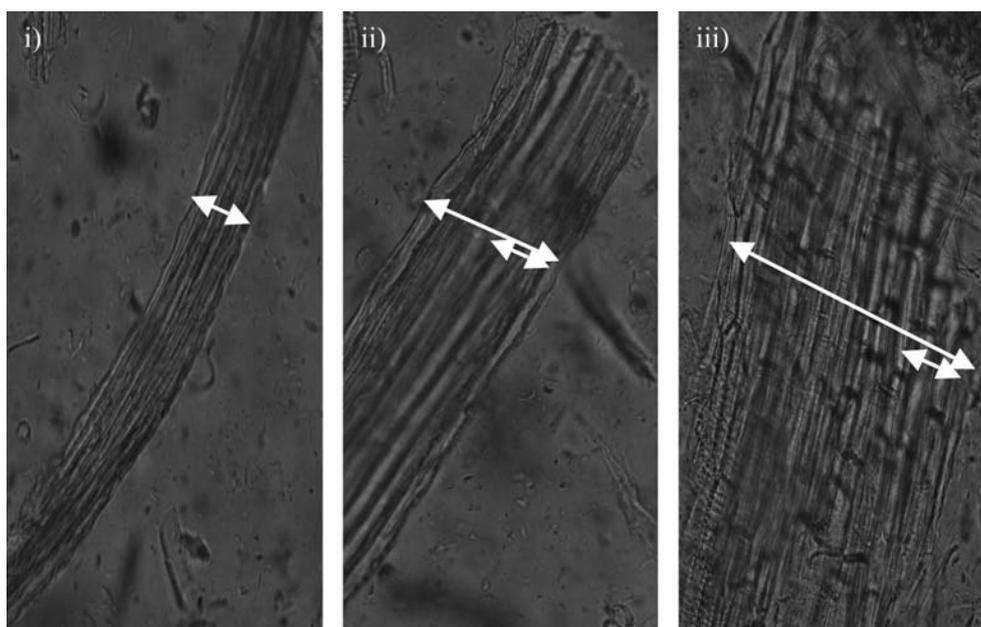


Figure 2. Swelling of oil palm empty fruit bunches (EFB) fibre (mode 4) in the ionic liquids (IL) ([emim]Cl), heated at 100°C, as a function of time: i) t^0 , ii) $t = 4$ hr, iii) $t = 24$ hr. Images were observed under an optical microscope at 20X magnification.

reports that claim that unrefined biomass sources can be readily dissolved in IL (Myllymaki and Aksela, 2005). Vanoye *et al.* (2008) found that *Miscanthus* switch grass was not completely solubilised by [emim]Cl after 24 hr at 100°C. The fibre's swell from 44.69 μm up to 101.66 μm and 301.74 μm (Figures 2i-2iii) with the swelling ratio is about 2.3 and increased up to 6.6 after 20 hr of heating. The swelling mechanism of OPF and OPT fibre was also the same as for EFB fibre in [emim]Cl and [bmim]Cl.

Theoretically, the longer the alkyl chain of the cation the less effective it is in breaking the extensive hydrogen bonding network present, thus slowing down the dissolution time. However, in the case of [emim]Cl and [bmim]Cl, the difference of the carbon atoms on the alkyl chain between the two IL did not much affect the percentage of dissolution of the fibre. Table 2 shows a slightly lower percentage of dissolution (<50%) for all the fibre in [emim]Cl compared to in [bmim]Cl.

It is generally recognised that, in order to dissolve cellulose, a disruption of its great number of inter- and intra-molecular hydrogen bonds is required. Less important are some other factors such as the presence of charges in the fibre (Carlsson *et al.*, 1983; Young, 1985; Lindström, 1992). The hydrophilic amorphous parts of the cellulose and hemicelluloses, as well as the ionic groups, are the main factors contributing to the extensive interaction between the fibre and the solvents, which are mainly water. In the case of IL which have been used successfully as solvents for cellulose, the relatively high chloride concentration (Cl⁻) and their activity were thought to play the key role in dissolving the cellulose (Anderson *et al.*, 2002; Swatloski *et al.*, 2002). The most important thing that should be of concern is that the mixture of IL with the dimethyl-sulphoxide (DMSO) solvent does not have any further effect on the dissolution of fibre (Fort *et al.*, 2007). Although DMSO is a solvent for carbohydrate-free lignin, native lignin in fibre somehow has a more complex

structure with many linkages between the lignin units and carbohydrates, which prevent it from dissolution in DMSO.

The swelling and sometimes dissolution of raw EFB, OPF and OPT fibre happened only in two of the five modes, similar to that described for cotton and wood fibre by Cuissinat and Navard (2006a). Somehow, plant fibres are easier to dissolve compared to wood and cotton. However, this is not related to the molar mass of the cellulose chain but because raw plant fibre retain most of their non-cellulosic components, for example pectin and wax, instead of being just pure cellulose. The existence of these two components at the outer layer of the fibre could have hindered the formation of balloons.

Pre-treatment of the fibre by following the TAPPI methods had been done to remove lignin and some extractives, for example wax and pectin, which are present in the fibre. The obtained cellulose fibre (from EFB, OPF and OPT) swelled by ballooning in the [bmim]Cl/DMSO and [emim]Cl/DMSO systems at 100°C, before being dissolved. The swelling and dissolution mechanism was by mode 2 for cellulose of oil palm fibre, with ballooning and complete dissolution (Cuissinat and Navard, 2006a; b), as can be seen clearly in Figure 3. Native cellulose fibre start to swell in isolated points along the fibre, forming balloons. The balloons increased in size, leading to the appearance of a beaded structure (Figure 4).

As for cotton and wood fibre in aqueous solvents (Cuissinat and Navard, 2006a, b), the structure of swelling fibre consisted of several well-defined zones: unswollen fibre along a fibre (a), helical membrane (b), balloon (c), and unswollen section between two balloons (d), as seen in Figure 3. Each of these zones had a specific way of swelling and dissolving:

- Phase 1: balloon formation;
- Phase 2: balloon dissolution;
- Phase 3: dissolution of the unswollen sections; and
- Phase 4: dissolution of the balloon membrane scraps.

These phases could be clearly observed when the cellulose of EFB, OPF and OPT fibre was dissolved in both IL. The diameter of the balloons at the ballooning step (Phase 1) was 45.66 μm (mean) while its diameter became twice as large when it reached the bursting step (Phase 2). A helical feature formed around the balloons, making one turn along one balloon length (Figure 4). The formation of balloons, their bursting, followed by the dissolution of each part of the fibre happened very quickly during the dissolution phenomenon. The unswollen sections dissolved without swelling (Phase 3) as can be seen in Figure 5.

The swelling and dissolution mechanisms of cellulose fibre are strongly influenced by solvent

TABLE 2. PERCENTAGE OF DISSOLVED OIL PALM FIBRE RELATIVE TO THE INITIAL FIBRE LOADED (5 wt %) AFTER BEING HEATED IN IONIC LIQUIDS (IL) AT 100°C FOR 16 hr

Entry	ILs	Type of fibre	Dissolution (%)
1	[emim]Cl	EFB	46.90
2		OPF	47.11
3		OPT	46.99
4	[bmim]Cl	EFB	47.60
5		OPF	47.90
6		OPT	47.35

Note: EFB - empty fruit bunches.
OPF - oil palm fronds.
OPT - oil palm trunks.

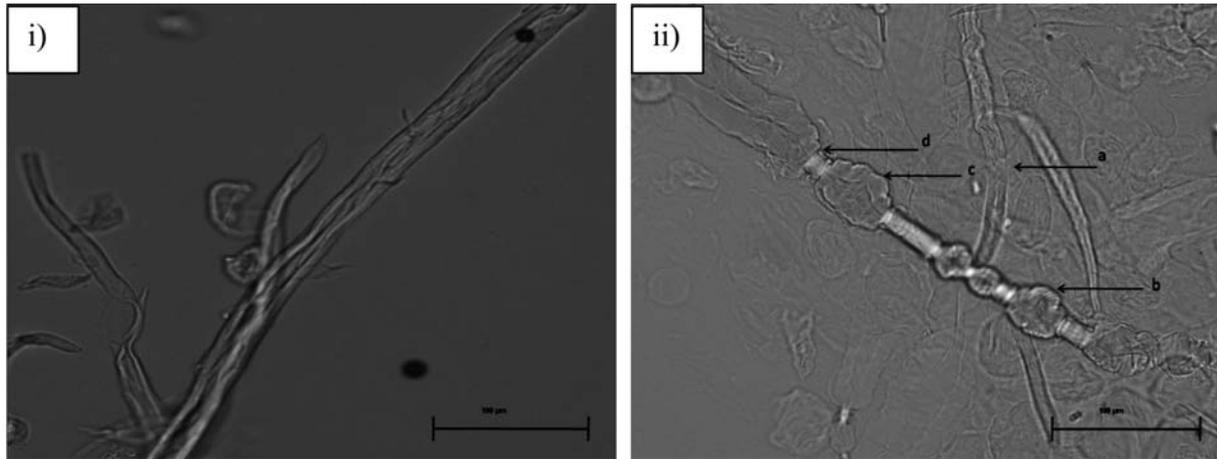


Figure 3. Swelling and dissolution (mode 2) of empty fruit bunches (EFB) cellulose fibre in ionic liquids (IL) ([bmim]Cl) heated at 100°C as a function of time: i) t^0 and ii) $t = 1$ hr. Images were observed under an optical microscope at 20X magnification. Four phases observed: (a) unswollen fibre, (b) balloon, (c) membrane, and (d) unswollen section between two balloons.

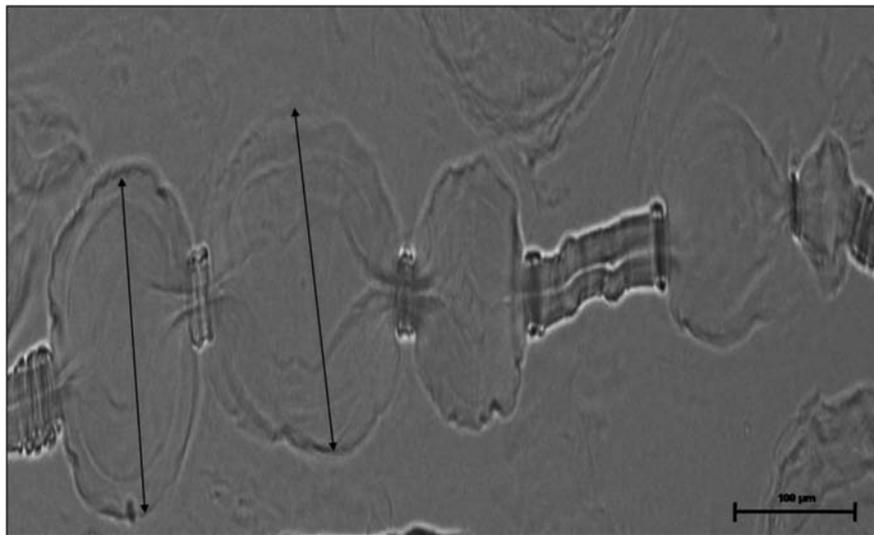


Figure 4. Swelling by ballooning (mode 2). Cellulose of empty fruit bunches (EFB) in [bmim]Cl heated at 100°C as a function of time: $t = 2$ hr. Image was observed under an optical microscope at 20X magnification.

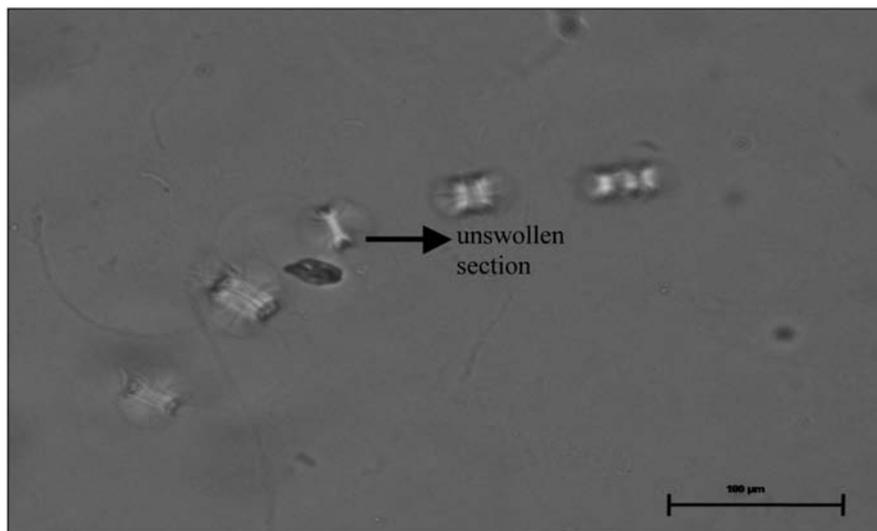


Figure 5. Third phase of mode 2. The balloons had already burst. What was left in the solution were the membrane scraps (very thin and not clear in the picture) and the unswollen sections that were between the balloons, seen as small cylinders regularly spaced. Image was observed under an optical microscope at 20X magnification.

quality, but the exact origins of such phenomena are not well understood. Theoretically, the cell wall is composed of a thin, outer primary wall and a much thicker, inner secondary wall (Klemm *et al.*, 1998; Sreekala *et al.*, 2001). This is why the solvents can penetrate easily through the primary wall of the fibre, which acts as a semi-permeable membrane. Cellulose chains which are located next to the primary wall, mainly in the secondary wall, will dissolve and swell, breaking the primary wall that cannot expand. Somehow, this mechanism does not occur along the fibre at the same time, but at more or less regular intervals, which gives a shape referred to as balloons to the swelling zones (Phase 1).

The roles of the different levels of the cellulose structure are not well established. By controlling the quality of the solvent, the dissolution conditions (as the tension) and the fibre sources, it has been shown that it is possible to reveal the characteristic mechanisms of swelling and dissolution at the different length scales of the cellulose structure, from the macromolecule to the walls of the fibre. This will be demonstrated in the next parts of this work.

CONCLUSION

The swelling and dissolution mechanisms for lignocellulosic biomass of oil palm fibre, mainly EFB, OPF and OPT, as well as cotton and wood fibre, in IL are similar, as soon as the removal of non-cellulosic components was done. Oil palm biomass EFB, OPF and OPT fibre exhibited mode 4 of interaction which is homogeneous swelling without dissolution in IL, [emim]Cl and [bmim]Cl. The existence of water in IL solutions may have also contributed to the homogeneous swelling (mode 4) which has been discussed elsewhere. However, pre-treatments on the oil palm biomass fibre by removing lignin, hemicelluloses and some other components contained in the fibre have been attributed to the subsequent swelling and dissolution mechanisms of the fibre. Cellulose fibre of oil palm biomass followed mode 2 of interaction (large swelling by ballooning, and dissolution) with phases 1-4 clearly observed during this period of interaction with the solvents. Remarkably, ballooning mechanisms are exactly similar, with the same sequence of events leading to complete dissolution, and the same helical feature around the balloon which making one turn along one balloon length. On the basis that IL are thermostable and non-volatile, and can be easily prepared and recycled, this process of dissolution and regeneration of cellulose seems to be a promising 'green' process for the preparation of regenerated cellulosic materials, and can overcome the inherent environmental problems of waste (toxic) gases in

the current industrial processes for manufacturing cellophane and viscose rayon.

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