Synthesis and application of dual functionalized task specific ionic liquid for bamboo dissolution

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Abstract. A new class of dual functionalized imidazolium based ionic liquid (IL) namely 3-(2-cyano-ethyl)-1-(2-ethoxy-ethyl)-3-imidazolium bromide [CNEIM][Br], was synthesized and characterized to study their potential in bamboo dissolution. The chemical structure for the IL was characterized using NMR (^{1}H and ^{13}C). Thermal properties, surface morphology and functional group of the native bamboo and IL treated bamboo were analyzed by Thermal Gravimetric Anaylysis (TGA), Scanning Electron Microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR) respectively. The new IL was able to dissolve up to 5wt% of bamboo biomass within 48 hours and 100°C.

1 Introduction

Presently, the world facing of deficiency of non-renewable resources such as coal, petroleum and natural gas. Hence, it is necessary to utilize renewable resources to fulfill the energy needs of our society [1]. Cellulosic biomass is one of the possible alternatives to petroleum-based feedstocks for fuels and chemicals because it is renewable, abundant, and inexpensive [2]. Cellulose comprise of recalcitrant polymer of 1–4 linked β-d-glucose repetitive units with inter- and intramolecular hydrogen bonding [3]. It is very hard to convert cellulose into biofuels and biochemical because its recalcitrant nature due to the presence of inter and intramoleculer H-bonding network. In recent years, significant efforts have been made to develop new techniques for the conversion of cellulose into biofuels and platform chemicals [4, 5]. Numerous pre-treatment procedures such as alkaline and acid pretreatment, ammonia fiber explosion and steam treatment have been established for the utilization of biomass [6]. However, an effective, inexpensive and sustainable process still needs to be developed. Recently, pretreatment of biomass using ionic liquids (ILs) has appeared as an alternative to the conventional methods due to its high capacity and capability.

Ionic liquids (ILs) are molten salts that are entirely ionic in nature, containing both cationic and anionic species and mostly having a melting point below 100 °C [7, 8]. The choice of cations and anions has a large influence on their properties. Hence, by changing the cation or anion of the ILs, their physical properties can be tailored per the requirements of a process. These properties include melting point, density, viscosity, solubility and hydrophobicity. ILs is unique due to their certain remarkable properties which differentiate them from conventional organic solvents. They have a very low vapor pressure, wide liquids range, flammability and recyclability property [9, 10]. ILs has been recently investigated for a wide range of potential applications such as catalytic synthesis [11], nanotechnology [12] and electrolytes for dye-sensitized solar cell [13]. Functionalized ILs may be defined as ionic liquids in which a functional group is covalently attached either to the cation or to the anion or even to both. The advantage of introducing a functional group into ILs is the fine-tuning of their properties for a particular application.

The types of anions and cations and functional groups attached to the cations/anions can affects the biomass dissolution potential of ILs. Imidazolium-based ILs has been used widely for dissolution of hardwoods and softwoods [14]. Some of the ILs cation increase the

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cellulose dissolution by forming hydrogen bonds with the hydroxyl and ether oxygen of cellulose [3]. Besides, cyano (nitrile) group shows better dissolution ability compared to allyl group because of its smaller size and electron withdrawing nature [10].

The attachment of ether / PEG functional group to the side chain of imidazole cation would results in lowering the viscosity of IL compared to simple alkyl side chain [15]. Researcher has shown that hydrogen bond accepting ability of the IL anions related to its ability to dissolve cellulose. ILs containing anions with H-bond acepting ability such as chloride, formate, acetate or alkylphosphonate showed high biomass dissolution potential [16].

The present work focus on designing a new functionalized ILs containing nitrile and ether group for the dissolution of bamboo biomass. Bamboo was selected for this research due to the widely available in Malaysia. Besides, bamboo is very cheap, renewable and sustainability properties [17]. In this work, 3-(2-cyano-ethyl)-1-(2-ethoxy-ethyl)-3-imidazolium bromide was successfully synthesized and characterized. The synthesized ionic liquid was finally tested for the biomass dissolution process.

2 Experimental

2.1 Materials and Chemicals

Acetone, 99%, 2-bromoethyl ether, 90%, and imidazole, 99%, were acquired from Sigma Aldrich. Chloroform, 99.8% acyrolinitrile, 99%, and ethyl acetate, 99.8% was purchased from Fisher Scientific. Bamboo (Gigantochloa scortechini) was gained from local market in Perak, Malaysia. The bamboo size was standardise using Restesh Test sieve less than 500µm. All chemicals (analytical reagent grade) were commercially obtained and used without further purification unless otherwise stated.

2.1 Synthesis of Propionitrile imidazole

Imidazole (0.74mol, 50gm) was dissolved in chloroform (50 mL) in a round bottom flask and acrylonitrile (0.74mol, 38 gm) was added dropwise and stirred for 48 hours at 65^{o}C. The viscous liquid was cooled and dried using rotary evaporator. Yield about (68g) 77%.

2.2 Synthesis of 3-(2-cyano-ethyl)-1-(2-ethoxy-ethyl)-3-imidazolium bromide [CNEIM][Br]

The propionitrile imidazole (0.41mol, 50gm) was added to 2-bromoethyl ether (0.41mol, 63gm) and stirred at 85^{o}C for 72 hours. The viscous ionic liquid was washed with ethyl acetate (4×20mL). The residue is dried using rotary evaporator. Yield about (90g) 79%.

2.3 Characterization for IL

^{1}H and ^{13}C NMR spectrum of the IL are recorded on a Bruker Avance 500 spectrometer. ^{1}H-NMR (500Mhz, DMSO-d6): δ= 9.297(s,1H), 7.887(d,2H), 4.566(t,2H), 4.415(t,2H), 3.740(m,2H), 3.473(t,2H), 3.268(t,2H), 1.093(t,3H). ^{13}C-NMR (125.77Mhz, DMSO-d6) : δ=137.28, 123.65, 122.76, 118.16, 67.86, 66.05, 49.61, 44.93, 19.13, 15.30.

Thermogravimetric analysis is using Perkin Elmer STA600 analyser is carried out on an average of 5-10 mg of samples. The experiment is carry out at a constant heating rate of 10 ^{0}C/min from 50 to 800 ^{0}C in inert atmosphere (pure nitrogen).

2.4 Bamboo dissolution

The bamboo (2wt %, 3wt %, 4wt %, 5wt %) was mixed with 3 gram of IL in 12mL vial. The mixture was then stirred at 100ºC for 48 hours using hotplate. The temperature of bamboo dissolution experiment was controlled by using oil bath. The solubility of bamboo in IL was checked visually after 48 hours by using a handheld microscope, Dino-lite Pro AM413T. After complete dissolution of bamboo, acetone (5×10 mL) was added to regenerated cellulose. The regenerated cellulose was filtered and washed with water to remove any trace of ILs. The cellulose was dried in an oven at 60ºC for 48 hours.

2.5 Characterization for regenerated bamboo

The spectra of the samples was recorded on a FTIR spectrometer model Nicolet iS5 which is equipped with an attenuated total reflectance (ATR) unit (Thermo Scientific). The spectra was conducted over the range of 4000 to 500 cm^{-1}.

The morphology of untreated and treated bamboo was obtained using a Hitachi TM 3030 model scanning electron microscope (SEM) operated at 15 kV accelerating voltage. The free and fracture surfaces of the film are sputtered with gold, and then observed and photographed. The samples are sputter coated with gold before analysis to avoid electrical charging of the samples during micrographs by using Quorum SC 7620 sputter coater. The TGA of untreated and treated bamboo was carry out at a constant heating rate of 10 ^{0}C/min from 50 to 800 ^{0}C in inert atmosphere (pure nitrogen).

3 Result and discussion

3.1 Thermal properties of [CNEIM][Br]

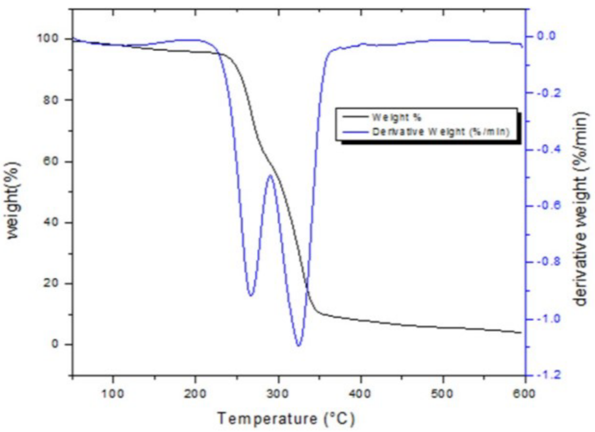

Fig. 1. TGA for [CNEIM][Br]

The TGA profile displaying the thermal decomposition of [CNEIM][Br] is shown in Fig. 1. As shown in Fig. 1, there are two thermal decomposition temperature noticed. The decomposition temperature of [CNEIM][Br] IL are at 248.89 ^{O}C and 306.50 ^{O}C. According to, Liang et al [18] the two-thermal decomposition is due to the anion. This indicates that the IL is highly stable and suitable for reaction that require high or extreme temperature.

3.1 Bamboo Dissolution

The dissolution of bamboo in [CNEIM][Br] IL was studied at different condition. Each mixture of bamboo and IL was heated at 100^{o}C for 48 hour with different loading of bamboo from 1 wt% to 5wt%. After heating for 48 hour at 100^{o}C and under vigorous stirring. The microscopic visual changes of bamboo before and after the dissolution process was observed and showed in **Fig 2.** From the microscopic visual of bamboo dissolution, it can see that there was brownish fiber. Meanwhile after the dissolution it can see that a clear liquid. Thus, it shows that [CNEIM][Br] IL could dissolve bamboo at 100 ^{O}C within 48 hr. Swatloski et al. [20] conduct a study on cellulose dissolution using 1-butyl-3-methylimidazolium ([Bmim]+) cation with different combination of anion which are Cl^-, $PF_6{}^-$, Br^-, SCN^-, and $BF_4{}^-$. It shows that only Cl^-, SCN^- and Br^- anion containing ionic liquids could dissolve cellulose at 100 to 110 ^{O}C. The dissolved biomass was precipitated by adding acetone and the biomass was filtered using filter paper. The biomass was washed with water till the complete removal of ILs. The ILs was regenerated by evaporating the solvent under vacuum. The regenerated ionic liquid was successfully characterized using ^{1}HNMR and no changes in the structure is observed **Fig. 3**.

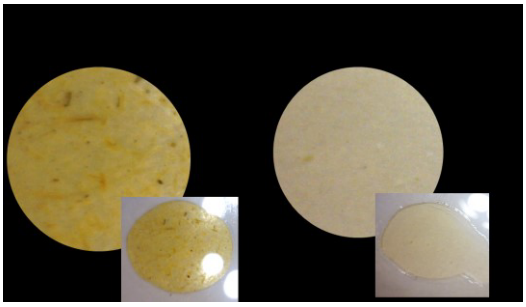

Fig. 2. Microscopic visual changes of bamboo before and after dissolution process.

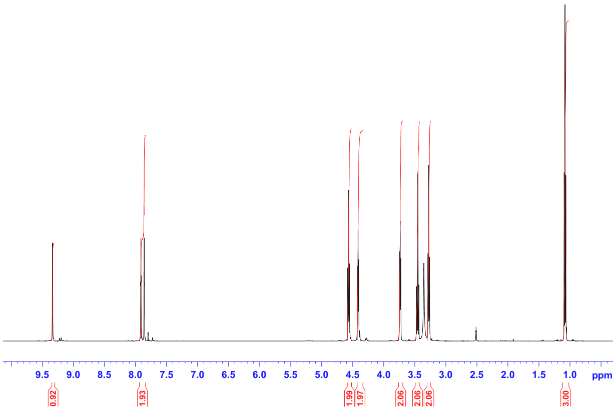

Fig. 3. ^{1}H-NMR for regenerated [CNEIM][Br]

The capability of the IL to dissolve bamboo is confirmed by studying the morphology of bamboo after the dissolution (**Fig. 4)**. The IL treated bamboo showed a significant amendment in morphology compared to the untreated bamboo. The untreated bamboo seemed to have a circular [21], rough surface and compact. Similar observation was reported by using oil palm biomass treated with 1-ethyl-3-methylimidazolium-diethyl phosphate IL. According to Financie et al. [22] it might be due to the lignin covered on cellulose and hemicellulose. The treated bamboo showed modification in the fiber where there is a crack and curly structure [23, 24]. This shows that the [CNEIM][Br] IL was completely disrupting the cell wall of bamboo.

 DOI: 10.1051/matecconf/201711103002

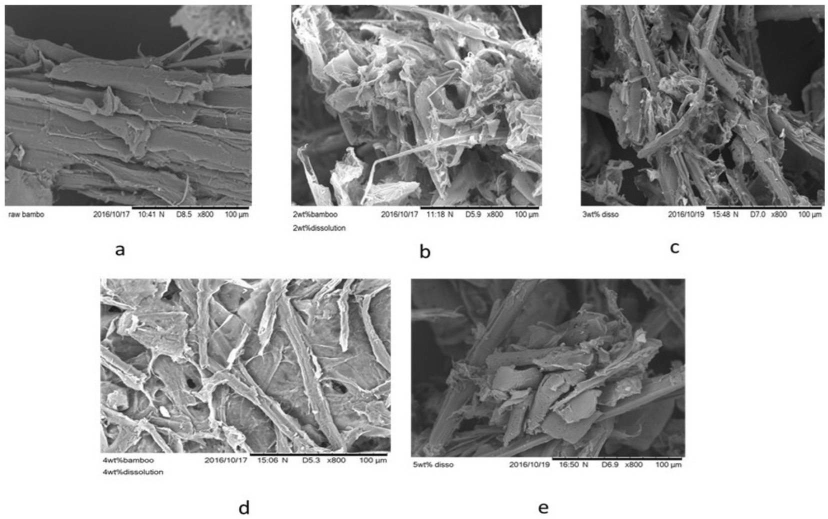

Fig. 4. Morphology of (a) untreated bamboo (b) treated bamboo at 2wt% (c) treated bamboo at 3wt% (d) treated bamboo at 4wt% (e) treated bamboo at 5wt%.

FTIR analysis was conducted to analyze any structural changes on bamboo during IL treatment. The FTIR spectra of the untreated and treated bamboo are shown in **Fig. 5**. The FTIR spectrum of treated and untreated bamboo is found to be similar. The presence of hydroxyl, carbonyl, methoxyl and carboxyl functional groups have been reported for identification of lignin [24]. A broad band of hydroxyl and methoxyl groups are observed around 3336 cm^{-1} and 2895 cm^{-1} respectively. The strong intensity bands at 1602 to 1504 cm^{-1} was attribute to the aromatic skeleton from lignin component [17, 25, 26, 27]. The peak value at 1240 cm^{-1} is due to phenol ether bonds of lignin while 1158 cm^{-1} and 1031cm^{-1} are due to structural contribution of cellulose and hemicellulose [26]. A band of range (896 - 561) cm^{-1} represent the alkane group (CH-CH) and the deformation of cellulose [26].

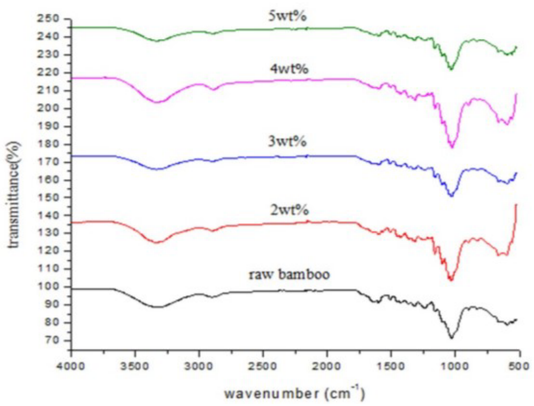

Fig. 5. FTIR spectra for untreated and treated bamboo

The thermal stability of treated and untreated bamboo was determined using TGA analysis. The thermogram of treated and untreated bamboo was shown in **Fig. 6**. The results showed the thermal stability of the bamboo reduce after the IL pretreatment. The decomposition of the treated and untreated bamboo could be divided into three stage. The first stage involved moisture evaporation at around 150ºC, measured at 4wt% loading. This is followed by the decomposition of the hemicellulose at around 300ºC [28, 29]. Hemicellulose can be categorized as the most reactive and easily degrade constituent compared to cellulose and lignin. In the third stage, which covers the temperature range from 350 to 400°C, represents the thermal degradation of the cellulose. This is due to higher amount of hydrogen bonds existed between cellulose chains which leads to more ordered and packed cellulose regions [30]. The temperature range between 300 and 600ºC is due to the weight loss stage of lignin composition in bamboo [31].

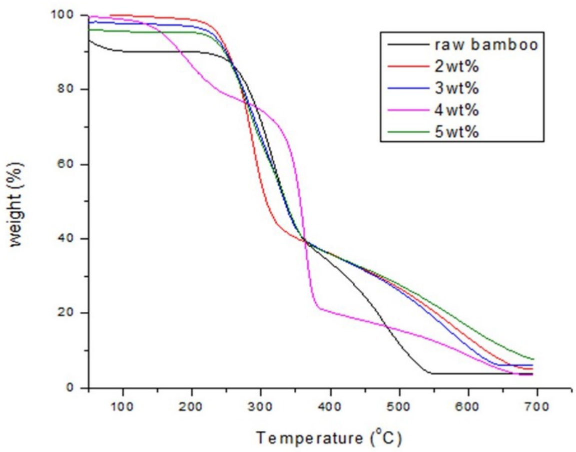

Fig. 6. TGA curve untreated and treated bamboo.

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Table 1. Thermal decomposition of untreated and treated bamboo

Biomass loading	Thermal decomposition (°C)	
Raw bamboo	269.25	469.73
2wt%	244.18	470.50
3wt%	238.93	491.63
4wt%	319.72	493.94
5wt%	220.25	469.73

Fig. 7 showed the differential thermal gravimetric (DTG) curve for untreated and treated bamboo. DTG shows that at 4wt% of bamboo dissolution shows a high thermal stability compared to untreated bamboo, 2wt%, 3wt% and 5wt%. The present of two distinct peaks in DTG is due to the degradation of hemicellulose followed by cellulose [31]. The thermal degradation between 400 and 600°C may be due to degradation of lignin [32].

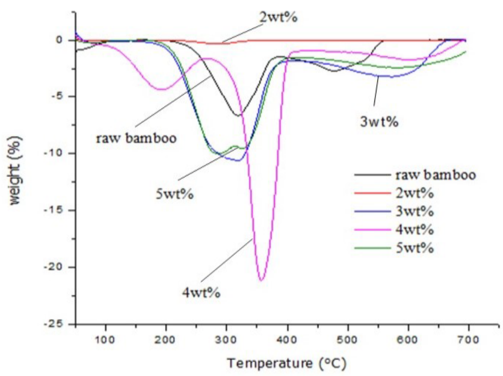

Fig. 7. DTG curve for untreated and treated bamboo.

4 Conclusion

Synthesizing and characterizing of [CNEIM][Br] has been successfully achieved. Based on the analyzed data, this type of IL with nitrile and ether functionalized group, is proven to have the potential and capability of dissolving the bamboo and the dissolution capacity can reach up to 5wt%. There is no degradation of ILs was observed after the dissolution process. Moreover, significant changes was occurred after pretreatment with IL.

The authors would like to thank to center of research in ionic liquid and also FRGS grant for financial support.

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