



Journal of Applied Sciences

ISSN 1812-5654

science
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Dissolution of Bamboo (*Gigantochloa scortechinii*) Using Ionic Liquids

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Abstract: In today's world the energy crisis is the main concern. It has been tried to develop substitute materials of petroleum and other decreasing natural fuel resources. Biomass is an abundant and renewable resource and it impelled researcher to develop suitable and proficient ways for converting it to valuable chemicals, biofuels and biomaterials. Due to their several advantageous properties ionic liquid was used for the dissolution of biomass. Biomass after dissolution in ionic liquids was regenerated with reconstitutes solvents (acetone/water). The regenerated material was characterized by FT-IR, XRD and SEM and compared with untreated biomass. The regenerated material was found to exhibit more homogeneity in the microstructure and the fibrous nature of material disappeared after dissolution. The crystallinity of cellulose was changed from cellulose I to amorphous during dissolution and regeneration from ionic liquids.

Key words: Biomass, ionic liquids, dissolution, regeneration, characterization, crystallinity

INTRODUCTION

Biomass is the total quantity or weight of plants and animals in a particular area or volume (Hornby, 2000) and is one of renewable resources. Plant biomass includes dead trees and branches, yard clippings and wood chips and also includes plant used for production of fibers, chemicals or fuel. Biomass is mainly consisted of cellulose, lignin and hemicellulose. Cellulose, the main part of wood, constitutes 45-50%, Hemicellulose constitutes 15-25% (Browning, 1975) and lignin constitutes 23-33% in softwood and 16-25% in hardwoods (Rowell, 1984). Dissolution of biomass in common solvents is practically difficult due to the three dimensional network structures of lignin which binds the plant cells together providing mechanical strength to structure. Recently various types of solvents have been used for processing of cellulose. For example in paper making, wood is treated with alkaline solution (Elton, 2006) and in the preparation of cellulose xanthate carbon disulphide is used as the solvent (Blanco, 1926). But the conventional solvents used for cellulose, suffer from some drawbacks related to volatility, generation of toxic gas and difficulty in recovery for recycle use (Ohno and Fukaya, 2009). Ionic liquids are organic salts with melting point less than 100°C (Plentnev *et al.*, 2004). They are considered as green solvent because of their several benign properties like negligible vapor pressure, non-flammability, non-explosiveness, electrochemical stability, thermal stability, high conductivity and ease of recycling (Li, 2005). Because of their

advantageous properties, ionic liquids attract great attention in many fields (Liu *et al.*, 2008; Fukumoto *et al.*, 2005; Muldoon *et al.*, 2007; Xiaohui *et al.*, 2004). Graenacher (1934) worked on the dissolution of cellulose in n-ethylpyridinium chloride, in the presence of nitrogen containing bases. This was the initial use of ionic liquids for cellulose dissolution. Later on Rogers and his group carried out comprehensive studies on cellulose dissolution and its regeneration (Swatloski *et al.*, 2002). Kilpelainen *et al.* (2007) observed the dissolution of hard and soft woods in ionic liquids of imidazolium base cations. To improve the dissolution properties of ionic liquids, a large no of anions were combined with imidazolium-based cations. Swatloski *et al.* (2002) studied the effect of anion on the dissolution of wood. When 1-butyl-3-methylimidazolium cation was combined with Cl^- , PF_6^- , Br^- , SCN^- and BF_4^- anions, it was observed that only Cl^- SCN^- and Br^- anion containing ionic liquids were able to dissolve wood at 100-110°C. Erdmenger *et al.* (2007) studied on the effect of alkyl chain length on 1-alkyl-3-methylimidazolium cations combined with chloride anion on cellulose dissolution. Both even and odd numbers of alkyl chain, length i.e., C_2 - C_{10} was investigated by the authors. It was observed that even the number of alkyl chain length had a great effect on the dissolution of cellulose. Luo *et al.* (2005) introduced -OH groups on the imidazole cation and synthesized 1-(2-hydroxyethyl)-3-methyl imidazolium chloride (HEMimCl) ionic liquid. The synthesized ionic liquid was found to have better dissolution capacity and cellulose dissolution reached to 6.8% at 70°C in it. For biomass dissolution it

is necessary, to break this network among its constituents. Ionic liquids which have greater ability to make hydrogen bond (hydrogen bond basicity β) are good solvents for biomass dissolution. Fukaya *et al.* (2006) prepared a series of 1, 3-dialkylimidazolium formate ionic liquids, which had low viscosity, polarity and were free of halogen. These ionic liquids have efficient potential for the dissolution of polysaccharides. It has been attributed to its low viscosity 66 cP at 25°C and high hydrogen bond basicity β (0.99) as compared to 1-allyl-3-methylimidazolium chloride (AmimCl) and 1-butyl-3-methylimidazolium chloride (BmimCl), which had 0.83 and 0.84, respectively. In another work, both BmimCl and EmimOAc ionic liquids were used for the dissolution of hard and soft wood. It was observed that EmimOAc was more effective in dissolution as BmimCl ionic liquid and it was also attributed to high hydrogen bond basicity of EmimOAc ionic liquid (Sun *et al.*, 2009). Swatloski *et al.* (2002) observed that the solubility of cellulose in ionic liquids could be improved by microwave heating. Under similar conditions the microwave heating was found to be more effective compared to general heating, as it is related to internal heating of the material while general heating, relates to conduction of heat. Vesa and Reijo (2005) worked on the dissolution of wood, straw, plywood, softwood in BmimCl ionic liquid under microwave irradiation and pressure. Swatloski *et al.* (2002) observed that the solubility of cellulose decreased in the presence of water in ionic liquids. It was related to the competition of water hydrogen bonds and cellulose hydrogen bonds for anion part of ionic liquid. Rayne and Mazza (2007) pointed out that dissolution in BmimCl on large scale has practical limitation due to the hygroscopic nature of BmimCl.

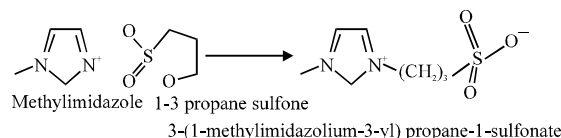
In this study some ionic liquids have been synthesized and were used for the dissolution of biomass. To confirm the dissolution effect of ionic liquids on biomass, the regenerated material from ionic liquids has been characterized by TGA, FTIR, XRD and SEM

MATERIALS AND METHODS

Materials: 1, 3-propane sulfone (purchased from Merck), 1-methylimidazole (purchased from Sigma), H_2SO_4 (purchased from Fisher), toluene (Merck), Sodium hydroxide (Merck), ethanol amine (Merck), acetic acid (Merck) were used as received. Tri-octyl-tetra decyl phosphonium chloride (TTPCl) ionic liquid was synthesized in our laboratory. Bamboo plant was received from local market and it was grind and pass through sieve for different particle size (250 μm to 1 mm).

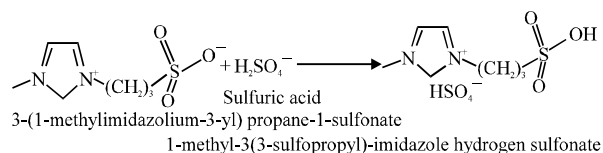
Synthesis of ionic liquids

Synthesis of 3-(1-methylimidazolium-3-yl) propane-1-sulfonate ionic liquid:



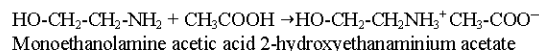
Synthesis of 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ((PSmim) HSO_4^-), ionic liquid:

1, 3-propane sulfone was charged in three-necked flask and was dissolved in toluene. 1-methylimidazole was added drop wise to the cold mixture and stirred it for 2 h. The resultant mixture was filtered to get a white precipitate. The precipitate was washed three times with diethyl ether and dried using rotary under vacuum at 80°C for 6 h. The white powder MIM-PS zwitterions ionic liquid was obtained (Liu *et al.*, 2008).



3-(1-methylimidazolium-3-yl) propane-1-sulfonate ionic liquid (MIM-PS) was dissolved in deionized water and equal-mole of sulfuric acid was added drops wise slowly at room temperature. The mixture was stirred at 25°C for 30 min and then heated in an oil-bath at about 90 °C for 2 h. The water of the mixture was evaporated under vacuum by using rotary for 6 h at 90 °C and vacuum oven for 2 days at 80°C; the colorless viscous liquid of ($\text{HSO}_3^-\text{pmim}$) HSO_4^- was obtained (Liu *et al.*, 2008).

Synthesis of 2-hydroxyethanaminium acetate ionic liquid:



0.125 moles of MEA was dissolved in 25 mL ethanol and was loaded in 250 mL round bottom flask equipped with reflux condenser, a magnetic stirrer and inlet and out let for N_2 gas. The flask was mounted in ice. A mixture of 0.125 moles of acetic acid dissolved in 25 mL ethanol was added drop wise to cold MEA containing flask in about 70 min. The reaction mixture was heated with stirring for 24 h at 37°C. The resultant brown and viscous product was distilled in rotary vacuum pump to remove solvent. Then it was washed three times with acetonitrile. Keep in vacuum oven for 24 h to remove any remaining solvent. The ionic liquid 2-hydroxyethanaminium acetate will be kept under nitrogen gas until use (Yuan *et al.*, 2007).

Dissolution and regeneration of biomass: 5 wt. % solutions of dried biomass (moisture content 3% by mettler Toledo HR 73 Halogen Moisture Analyzer) were made in above-mentioned ionic liquids. In case of 3-(1-methylimidazolium-3-yl) propane-1-sulfonate ionic liquid the solution was heated at 165°C for 12 h while for 1-methyl-3- (3-sulfopropyl)-imidazolium hydrogen sulfate, Tri-octyl-tetra decyl phosphonium chloride (TTPCl) and 2-hydroxyethanaminium acetate it was heated for 24 h in oil bath at 105°C with magnetic stirring of 500 rpm.

After dissolution, the dissolved material was regenerated by pouring the bamboo/ILs solution in a beaker containing mixture of acetone/water (3:2 v/v). The beaker was sealed with parafilm and the mixture was stirred at room temperature for 30 min. The precipitated cellulosic-rich materials were separated by vacuum filtration through nylon filter paper, while the lignin was precipitated by evaporation of acetone and separated by vacuum filtration. Ionic liquids were recycled by evaporation of water (Sun *et al.*, 2009).

Characterization: FTIR Spectra for the samples were taken by using SHIMDZU 8400S in wave number range of 400-4000 cm^{-1} .

The crystallinity of bamboo powder and regenerated cellulose-rich materials were monitored by powder X-ray diffraction (PXRD), using a Bruker D8 Advance horizontal X-ray diffractometer equipped with Cu anode, at room temperature. The samples were scanned within 5.00-40.00° 2 θ in step mode with a step of 0.01° and a rate of 1° min^{-1} .

SEM images of the sample were taken at 3000x magnification using a LEO VP1 430 SEM instrument which was operated at 15 kV accelerating voltage. Prior to imaging, the samples were sputter-coated with gold to make the fibers conductive, avoiding degradation and build up of charge on the specimen.

RESULTS

The sample bamboo wood (125 μm particle size) was loaded in two fractions of 5-wt % ionic liquids of 3-(1-methylimidazolium-3-yl) propane-1-sulfonate (MIM-PS), 1-methyl-3- (3-sulfopropyl)-imidazolium hydrogen sulfate ((PSmim) HSO_4), 2-hydroxyethanaminium acetate and Tri-octyl-tetra decyl phosphonium chloride (TTPCl). During dissolution process it was observed that only 3-(1-methylimidazolium-3-yl) propane-1-sulfonate (MIM-PS) ionic liquid has the ability to dissolve biomass completely while in case of 1-methyl-3- (3-sulfopropyl)-imidazolium hydrogen sulfate ((PSmim) HSO_4) ionic liquid partial dissolution was observed. The others two ionic liquids i.e., 2-hydroxyethanaminium acetate and Tri-octyl-tetra decyl phosphonium chloride (TTPCl) was found ineffective in the dissolution process of bamboo biomass.

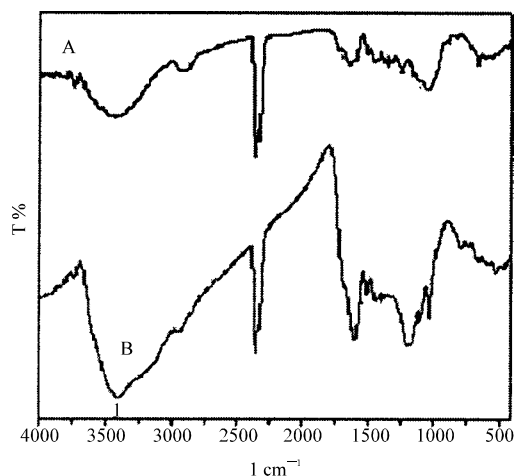


Fig. 1: FT-IR spectra for bamboo powder (A) and regenerated cellulosic-rich material from MIM-PS ionic liquid

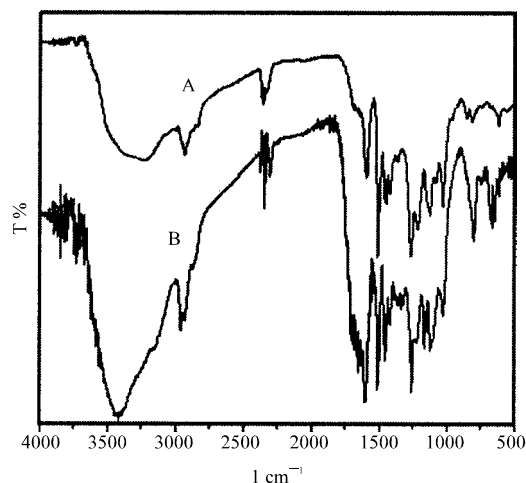


Fig. 2: FT-IR spectra of lignin alkali (A) and regenerated lignin from MIM-PS ionic liquid

FTIR spectra of untreated bamboo and regenerated material from MIM-PS ionic liquid showed the same basic structure as shown in Fig. 1. There was a strong broad O-H stretching absorption around 3425 cm^{-1} and a prominent C-H stretching absorption around 2939 cm^{-1} . The non-conjugated C-O stretch was observed at 1730 cm^{-1} , in spectra (A) that was absent in the spectra (B). In spectra (B), peak around 1693 cm^{-1} was observed which was absent in spectra (A) while other peaks at 1604, 1512 cm^{-1} , 1330, 1161, 1037 and 894 cm^{-1} was observed in both spectra.

The spectra of lignin, recovered from 3-(1-methylimidazolium-3-yl) propane-1-sulfonate (MIM-PS) ionic liquid treatment and lignin alkali standard (purchased from sigma) has been shown in Fig. 2. It was

observed that both the spectra showed similar pattern of peaks.

XRD spectra were collected for untreated bamboo powder as shown in Fig. 3a and for regenerated cellulose rich materials from Tri-octyl-tetra decyl phosphonium chloride (TTPCl) and 2-hydroxyethanaminium acetate ionic liquid as shown in 3b and 3-(1-methylimidazolium-3-yl) propane-1-sulfonate and 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate ionic liquids as shown in Fig. 3b. In figures and two typical diffraction peaks (at $2\theta = 16.3^\circ$ and 22.2°) were observed for all spectra. In Fig. 3c., the upper spectra showed one broad peak at $2\theta = 22.2^\circ$ while no such peak was observed in lower peak of Fig. 3c.

SEM images of the morphology of the Bamboo and regenerated materials from 3-(1-methylimidazolium-3-yl)

propane-1-sulfonate, 1-methyl-3-(3-sulfopropyl)-imidazolium hydrogen sulfate, Tri-octyl-tetra decyl phosphonium chloride (TTPCl) and 2-hydroxyethanaminium acetate ionic liquids have been shown in Fig. 4a-e, respectively. From SEM images it has been observed that regenerated materials from ionic liquids have different morphology as compared to untreated material of bamboo. Again from the microstructure it was further apparent that different ionic liquids have different dissolving tendency for bamboo biomass.

DISCUSSION

Dissolution of biomass in ionic liquid depends on initial sample load, particle size, temperature water

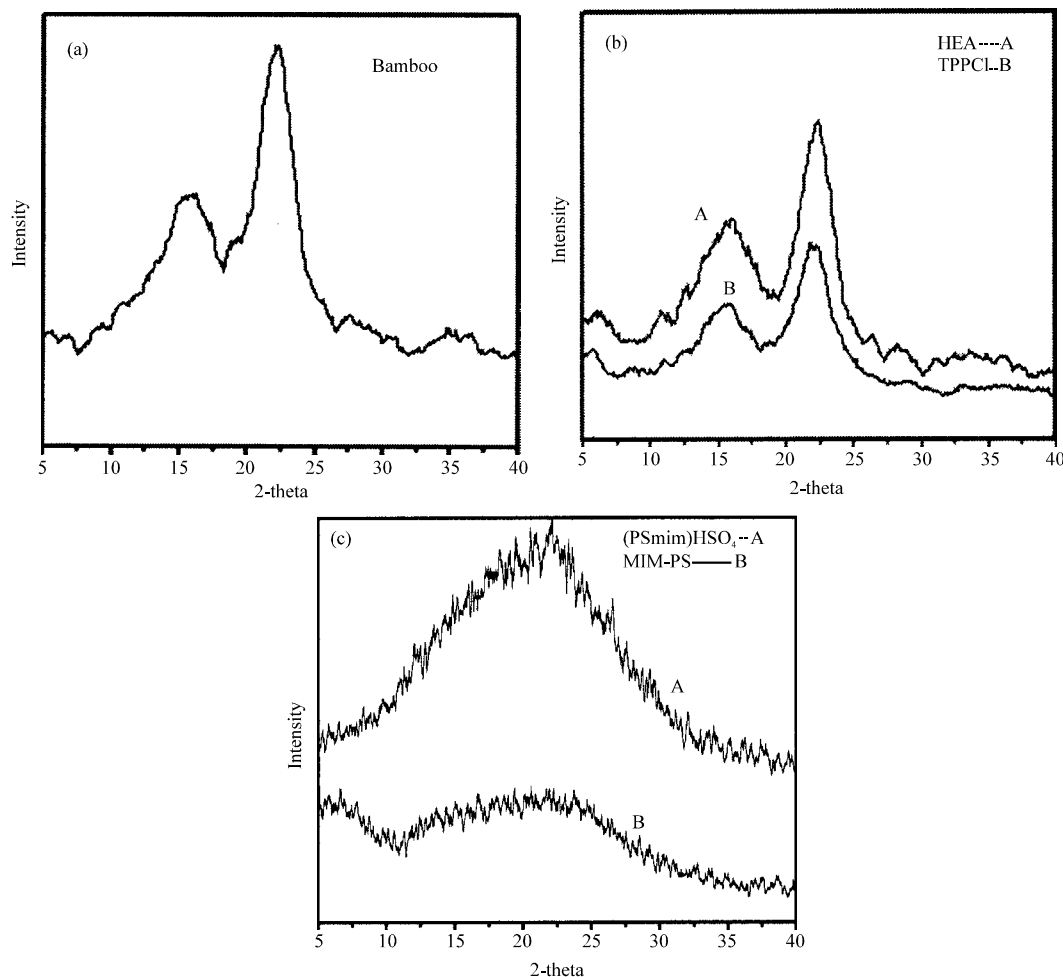


Fig. 3: (a) Diffractograms of (a) Bamboo powder. (b) (a) regenerated material from 2-hydroxyethanaminium acetate Ionic Liquid (b) regenerated material from Tri-octyl-tetra decyl phosphonium chloride (TTPCl) ionic liquid and (c) Diffractograms of regenerated material from (a) ((PSmim) HSO₄) ionic liquid and (b) MIM-PS ionic liquid

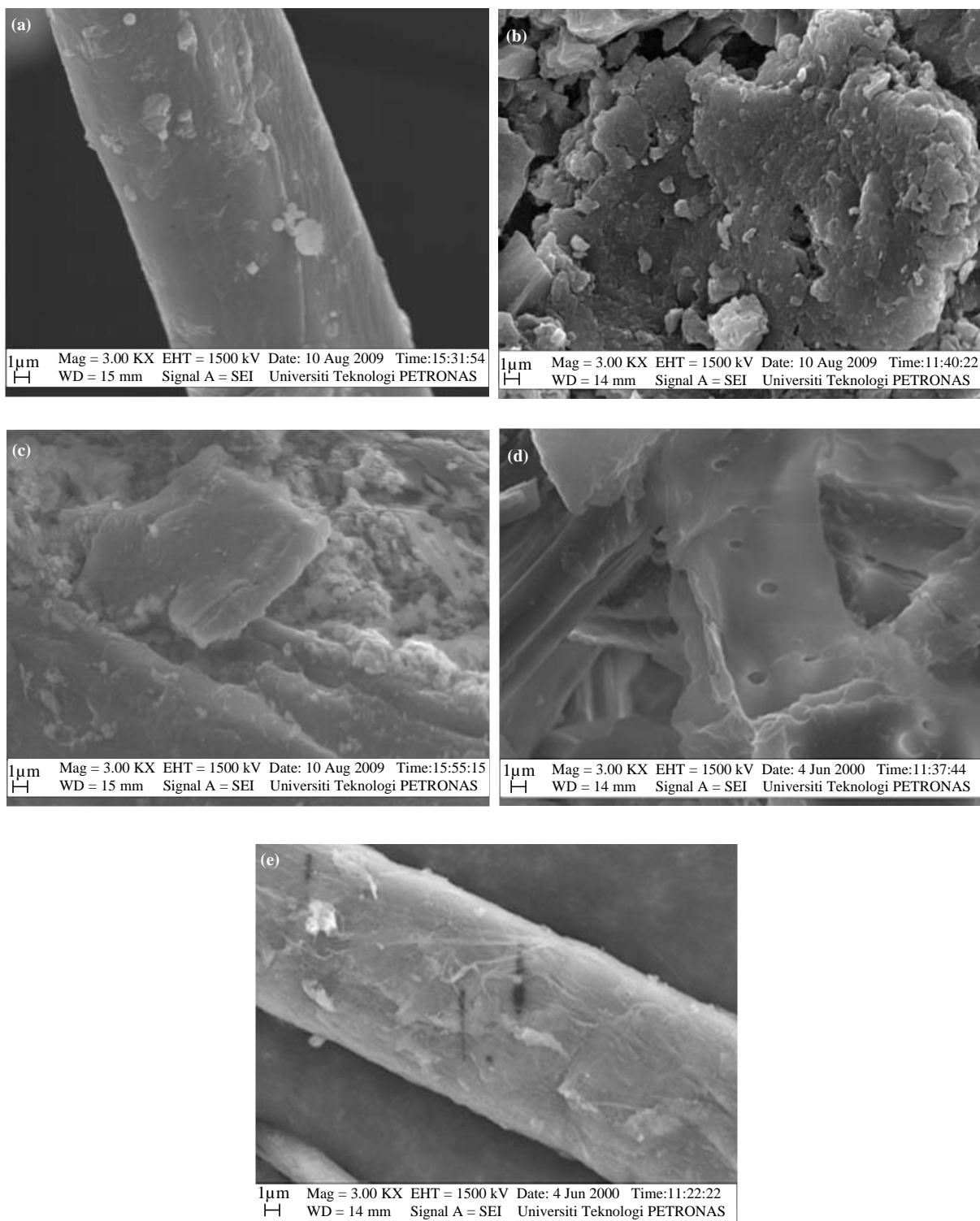


Fig. 4: SEM images of bamboo fiber, (a) regenerated materials, (b) from MIM-PS, (c) ((PSmim) HSO₄), (d) TTPCl and (e) HEA ionic liquids

content and high hydrogen bond basicity of ionic liquid (Sun *et al.*, 2009). The sample of bamboo wood (125 μm particle size) was loaded in two fractions of the 5 wt. % solution to the ionic liquid. The increased dissolution of smaller wood particles is likely due to increased surface area and more mechanical grinding is required to obtain smaller particles. In this study 5 wt. % of the sample was loaded for rapid dissolution at 105°C. This high temperature along with ease of dissolution reduced the effect of water content on dissolution. If the water content exceeds more than 1-wt %, it would impair the dissolution process as hydrogen bonding in water would compete for hydrogen bonding in cellulose for the anionic part of ionic liquids (Swatloski *et al.*, 2002). During dissolution of biomass in MIM-PS and ((PSmim) HSO₄) it was observed that MIM-PS ionic liquid due to its zwitterions effect has the ability to dissolve biomass. However it required more energy due to its high melting point. While ((PSmim) HSO₄) ionic liquid has high acidity it was not so much effective in dissolution of biomass because of the presence of extra hydrogen, which interrupted in the dissolution process. Tri-octyl-tetra decyl phosphonium chloride (TTPCl) was found not effective in dissolution of biomass due to the bulky substituents on phosphonium, which reduce chloride content and also non-aromatic nature of phosphonium, which does not interact with lignin aromaticity during dissolution of biomass. In 2-hydroxyethanaminium acetate ionic liquid, although acetate ion has high hydrogen bond basicity (the ability to make hydrogen) for the dissolution of biomass but due to the presence of OH group and non-aromatic nature of cation, it was found ineffective in the dissolution of biomass.

From FTIR spectra as shown in Fig. 1, in the fingerprint region between 800 and 1800 cm^{-1} , many well-defined peaks were observed which provided abundant information on various functional groups present in bamboo and regenerated material from MIM-PS ionic liquid. For example, the non-conjugated C-O stretch (in hemicellulose) was observed at 1730 cm^{-1} , in spectra (A) that was absent in the spectra (B). It was due to loss of hemicellulose during dissolution and regeneration from ionic liquid (Sun *et al.*, 2009). However in spectra B, peak around 1693 cm^{-1} appeared which was related to carbohydrates. It showed the increase in carbohydrates content of regenerated material. The aromatic skeletal vibration in lignin appeared at 1604 and 1512 cm^{-1} , while the peaks around 1330, 1161, 1037 and 894 cm^{-1} mainly related to the carbohydrates were observed in both spectra as shown in Fig. 1 (Xiaoqing and Haiqing, 2008). However, from spectra of regenerated material it has been

observed that ionic liquid treatment partially removed lignin. The peaks of lignin still persist in the regenerated material.

The close similarity of spectra (B) to the spectra (A) as shown in Fig. 2, showed that the recovered material from MIM-PS ionic liquid after evaporation of acetone was lignin. The typical peaks of lignin were observed in both spectra.

XRD spectra (Fig. 3a, b) showed two typical diffraction peaks (at $2\theta = 16.3^\circ$ and 22.2°) for cellulose I. While in Fig. 3c., the upper spectra showed one broad peak at $2\theta = 22.2^\circ$ which revealed the partial dissolution in this case. However the lower spectra in Fig. 3c. showed amorphous nature of material, which confirmed the dissolution of material. It was reported that during the dissolution of biomass using ionic liquid, crystallinity of cellulose change from cellulose I to cellulose II (Takahashi and Matsunaga, 1991; Raymond *et al.*, 1995; Kolpak and Blackwell, 1976; Zhang *et al.*, 2009). However reappearance of cellulose II crystallinity during regeneration depends upon way of stirring of dissolved material with non-solvent (water). It has been reported that rapid stirring of dissolved biomass with non-solvent cause the formation of amorphous nature of material, which has been observed in this work too as shown in Fig. 3c (Kilpelainen *et al.*, 2007).

From SEM images it has been observed that before dissolution of biomass in ionic liquid, the fibers were present as shown in Fig. 4a. However in Fig. 4b the fibers were completely dissolved and changed into particle nature of material, which confirmed the dissolution of biomass. Figure 4c showed a partial dissolution of bamboo biomass due to presence of some fibers. Figure 4d and e showed the presence of fibers, which revealed no dissolution.

CONCLUSION

Ionic liquids have been used for dissolution of bamboo biomass. It has been observed that only 3-(1-methylimidazolium-3-yl) propane-1-sulfonate (MIM-PS) ionic liquid due to its zwitterions effect has the potential to dissolve biomass. From FTIR spectra of regenerated material it has been concluded that lignin could be partially removed by ionic liquid treatment. From XRD analysis it has been observed that during dissolution of biomass in ionic liquid the crystallinity of cellulose changed from cellulose I to its amorphous state. From SEM analysis it has been observed that fibrous nature of material disappeared and it was converted into particle nature of material.

ACKNOWLEDGMENT

This research was supported by Ionic Liquid Laboratory, Department of Chemical Engineering, Universiti Teknologi PETRONAS, Malaysia.

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