

## Comparison of Some Biocomposite Board Properties Fabricated from Lignocellulosic Biomass Before and After Ionic Liquid Pretreatment

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The search for sustainable raw material is of critical importance with the ever-growing environmental concerns together with the diminishing fossil fuel resources. Lignocellulosic biomass is nowadays being considered as one of the most promising alternative feedstocks for the production of engineered composite materials. In this regard, various pretreatment technologies have been employed to increase the accessibility of polysaccharide portion of lignocellulose but development of an effective and environmental benign innovative pretreatment process remains challenging. Ionic liquids (ILs) have been emerged as novel solvent for green processing of lignocellulose for its effective utilization in biocomposite materials.

In this work, effect of IL-assisted pretreatment of lignocellulosic biomass on the mechanical properties of thermo-moulded biocomposite board was evaluated. Lignocellulosic residue oil palm frond (OPF) was pretreated with ILs: 1-butyl-3-methylimidazolium chloride [Bmim][Cl] and 1-ethyl-3-methylimidazolium diethyl phosphate [Emim][DEP] and fabricated into biocomposite board by using thermoplastic starch as biopolymer binder. Fourier transform infrared spectroscopy (FTIR) and thermogravimetric analysis (TGA) was performed to understand the effect of IL treatment on the OPF fibre. Mechanical properties (flexural strength and flexural modulus) of composite board made from untreated and treated fiber were measured. It was noted that IL pretreatment significantly improved the thermal stability of OPF fiber as well as the mechanical properties of the composite board. Thus, flexural strength of the biocomposite board fabricated from [Bmim][Cl] and [Emim][DEP] treated fiber was increased by 82 % and 70 % respectively as compared to untreated fiber composite board. ILs were successfully recycled and could be re-used. The present paper demonstrates that IL-assisted pretreatment could be a highly promising and green technology for effective utilization of lignocellulose in biocomposite field.

### 1. Introduction

Global environmental awareness, concepts of sustainability and industrial ecology has remarkably influenced the materials engineering and design and renewed the interest in the utilization of lignocellulosic biomass in the field of composite materials. Agri-based lignocellulosic residue typically consists of up to 50% cellulose that is rigid semicrystalline embedded in amorphous hemicelluloses and lignin network. The availability of low-cost lignocellulosic residue in every part of the world has, in part, fuelled their use for fabrication of biocompatible and biodegradable materials in the past few years. Only in Malaysia, the palm oil industry generates an average of 53 Mt of lignocellulosic residues every year (Juliana et al., 2012). In comparison with synthetic fibres, lignocellulosic fibres have more advantages, such as low cost, light weight, abundant availability and wide distribution, versatility, competitive specific mechanical strength, carbon dioxide sequestration, recyclability, biodegradability, sustainability and safe working environment (Zhang and Hu, 2014). However, lignocellulosic fibres are not a problem-free alternative and they exhibit certain shortfall in properties. Typically, the structural heterogeneity and

complexity of the cell-wall microfibrils in lignocellulosic biomass are the biggest challenges for their effective utilization for biocomposite material fabrication. The highly recalcitrant 3-D network structure and presence of hemicellulose, lignin, pectin and waxy substances allow poor fibre-matrix interfacial bonding and causes inefficient stress transfer throughout interface of composite material and consequently impart weak mechanical properties (Abdelmouleh et al., 2007) Presently, chemical (e.g., alkaline hydrolysis, acid hydrolysis and oxidative delignification), physical (e.g., pyrolysis and mechanical disruption), physico-chemical (e.g., ammonia fibre explosion and steam explosion) and biological methods have been investigated for pretreatment of lignocellulosic biomass at laboratory and pilot-plant scales (Moniruzzaman and Ono, 2012). But most of these methods require severe temperatures and pressures conditions as well as highly concentrated chemicals for the cooking process. Sulphite and sulphates pulping processes bear serious environmental hazards. In addition, high temperature-based cooking processes result in the production of degraded byproducts and inhibitory chemicals. To address such issues, development of novel, cost-effective and environmentally compatible pretreatment technologies are urgently needed for efficient application of lignocellulosic biomass in composite materials field. One highly promising alternative could be the ionic liquids (ILs).

ILs, a potentially attractive “green” alternative to environmentally harmful classical organic solvents, have been extensively exploited as solvents and/or reagents and/or (co)solvents in a broad range of applications including lignocellulosic biomass pretreatment. ILs are salts consist entirely of ions and melt below 100 °C and are recyclable. The high solvating capabilities of ILs have been studied for the dissolution of different lignocellulosic biomass and wood (Zavrel et al., 2009). After pretreatment with IL, a variety of precipitating solvents can be added to readily separate cellulose-rich biomaterial from lignin and hemicellulose. Nguyen et al. (2010) successfully carried out the IL pretreatment of rice straw and concluded that IL-facilitated pretreatment was an economical and eco-friendly method as compared to the conventional pretreatment technologies.

In summary, the objective of the present contribution was to analyze the effect of environmentally benign IL-assisted pretreatment of lignocellulosic OPF fiber on the mechanical properties of biocomposite board fabricated by compression moulding technique with biopolymer thermoplastic starch as binder. Thermal properties of the untreated and IL-treated fiber particles were also studied. The imidazolium-based ILs with chloride and phosphate anions which are known to have dissolution capabilities for lignocellulosic biomass and can easily be produced on industrial scale in high yield (Zavrel et al., 2009), have been selected for pretreatment of OPF fiber in the present work.

## **2. Methods**

### **2.1 Materials and reagents**

Oil palm frond (OPF) biomass samples in form of 80 - 90 cm long strands were obtained from nearby plantation around Universiti Teknologi PETRONAS, Seri Iskandar, Perak, Malaysia. Commercial corn starch (moisture contents 12 %) and plastifying agent glycerol (99+ %) were purchased from R & M Marketing, Essex, U.K. ILs 1-butyl-3-methylimidazolium chloride [Bmim][Cl], 1-ethyl-3-methylimidazolium diethyl phosphate [Emim][DEP] and co-solvent diethyl dimethyl sulfoxide (DMSO) were received from Sigma-Aldrich, Germany. All the chemicals were of analytical grade and used as received.

### **2.2 Fiber preparation**

OPF sample were cut by a knife into smaller chips in the range of 2-3 cm strand and then grinded by using Retch SM 100 series grinder. The grinded biomaterial was subjected to sieve analysis to ensure fibre size below 250 µm.

### **2.3 Ionic Liquid pretreatment of OPF fiber**

In a typical experiment, IL [Bmim][Cl] or [Emim][DEP] and co-solvent DMSO were poured into a 200 mL beaker in ratio 1:1 and thoroughly mixed at 90 °C for 30 min to form a homogeneous solution. Dried OPF fiber was added into IL/DMSO solution to adjust a 15 % biomass loading. Pretreatment conditions were controlled at 90 °C under magnetic stirring of 600 rpm for 1 h.

After pretreatment an anti-solvent comprising of an equal volume acetone/water solution (Moniruzzaman et al., 2012) was immediately added into pretreated mixture and stirred vigorously. The regenerated fiber was precipitated and washed out with distilled water several times to ensure complete removal of residual IL. The wet fibre was dried in air-circulating oven at 105 °C for 12 h.

### **2.4 Binder preparation**

Commercial corn starch was mixed with 30 wt% glycerol and 20 wt% distilled water in the temperature range of 70-80 °C. Adding 20 % water to corn starch gives the optimum tensile stain at break without appreciable change in the tensile strength. Addition of glycerol increases processability and reduces

embrittlement by blocking retrogradation phenomenon after processing (Ibrahim et al., 2014). Thermoplastic starch (TPS) was then stored in air-tight container overnight to enhance its flow properties.

## 2.5 Composite board fabrication

TPS pellets were emulsified with distilled water in ratio of (TPS:water) 1:2. Fiber was then added into the emulsion so that fiber/binder ratio 1:1 was achieved. After homogenization, the compounded mixture was dried in an oven at 105 °C to remove excess water. The dried material was again grinded and put into stainless steel mold having inner dimensions of 10 x 10 cm for a target density of 0.9 g/cm<sup>3</sup>. The mold was thermal-pressed in 30 t Carver Laboratory compression moulding machine (CARVER, INC. USA) at 170 °C and 25 MPa for 10 min and then allowed to cool down to the room temperature under pressure. Non-stick Teflon paper sheet was used as mould-releasing agent. The composite plates fabricated from treated and untreated fibers were conditioned in a conditioning room at room temperature before further characterization.

## 2.6 Characterization of treated and untreated fiber

### 2.6.1. Fourier transform infrared spectroscopy (FTIR)

The chemical functional groups of untreated and IL-pretreated fibres were studied by Fourier transform infrared spectroscopy (FTIR) technique. The analysis was conducted on Perkin-Elmer Spectrum One FTIR Spectrometer in the wavelength range 400-4,000 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup>.

### 2.6.2. Thermal characterization

Thermogravimetric analysis (TGA) of untreated and IL-pretreated OPF fibre was conducted. The test was performed on Perkin Elmer STA 600 model from 50 °C to 800 °C under nitrogen gas atmosphere with flow rate 20 mL/min. The heating rate was 20 °C/min.

## 2.7 Composite board characterization

### 2.7.1. Flexural testing

Three-point bending test was carried out according to ASTM D 790 at a cross-head speed of 2 mm/min with a support span of 40 mm by using Zwick-Roel Amsler HA-50 UTM (Universal Testing Machine) to measure flexural strength and modulus.

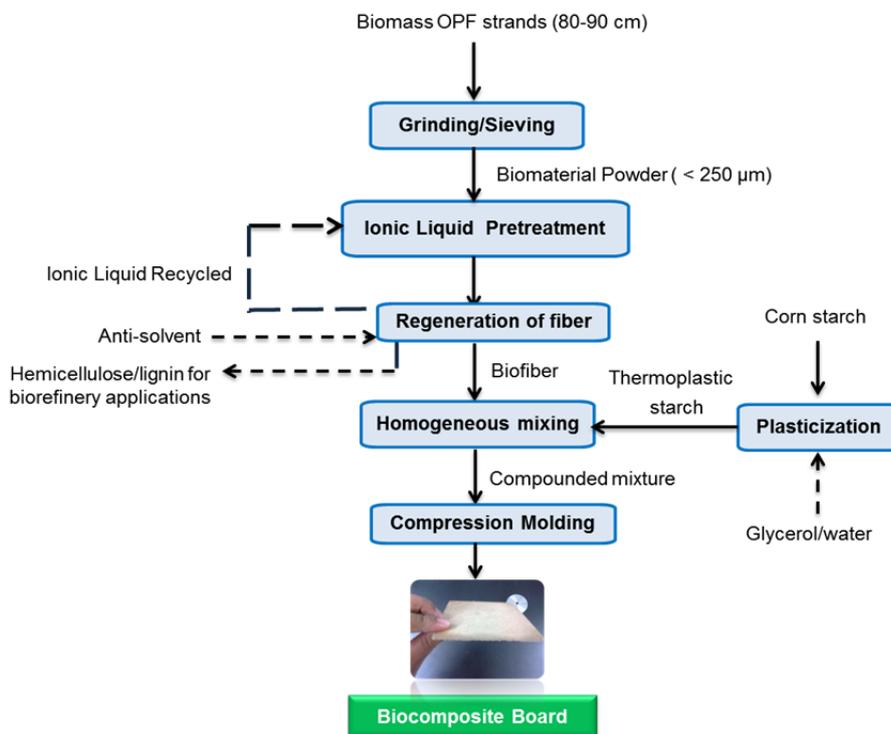


Figure 1: Schematics of the processing steps in the present work

### 3. Results and discussions

#### 3.1 Effect of IL treatment on chemical functional group and thermal stability of OPF fiber

IL pretreatment slightly changed the colour of the fibre from brown to light brown which shows that expected modification (removal of wax, fatty substance, partially hemicellulose and lignin) might have been achieved. The FTIR spectra of untreated, [Bmim][Cl] treated and [Emim][DEP] treated fiber are shown in Figure 2. The broader peaks at  $3,465\text{ cm}^{-1}$  and  $2,950\text{ cm}^{-1}$  represent aliphatic moieties. One important band is C=O stretching around  $1,742\text{ cm}^{-1}$ ; its intensity decreased in [Bmim][Cl] and [Emim][DEP] treated fiber. This band characterizes the carbonyl groups of hemicellulose, but these carbonyl groups can also be present in other polymer components of lignocellulose. The band at  $1,270\text{ cm}^{-1}$  assigned to C-O-H of phenolic group vibration and at  $1,650\text{ cm}^{-1}$  are characteristic bands of lignin in the wood (Moniruzzaman and Ono, 2012).

It is extremely important to study the thermal properties of lignocellulosic fibres to gauge their suitability for biocomposite processing in which the processing temperature for certain thermoplastic polymers rises above  $200\text{ }^{\circ}\text{C}$ . Figure 3 shows the results obtained after thermogravimetric analysis for untreated and different IL-treated OPF fibers and are summarized in Table 1. These results indicate that the thermal stability of the biofibre increased after IL pretreatment. In particular, decomposition profiles of the treated and untreated OPF fibres are characterized by three prominent peaks (Nguyen et al. (2010)). The first one corresponds to the evaporation of water from biomass and occurs between room temperature and  $140\text{ }^{\circ}\text{C}$ . The second and third step corresponding to hemicellulose and cellulose degradation starts after  $200\text{ }^{\circ}\text{C}$  and  $290\text{ }^{\circ}\text{C}$ . However, lignin degradation occurs over a broad temperature range of  $280$  to  $500\text{ }^{\circ}\text{C}$  and overlaps partially with hemicellulose.

IL-facilitated pretreatment had a significant effect on the thermal degradation behaviour of the OPF fibers, promoting an increase in the temperatures at which the thermal degradation started. This increase can be explained in terms of removal of some easily hydrolyzed components, which decompose earlier than the main components, cellulose and lignin, leading to higher thermal stability of the second step of decomposition which had also been reported earlier (Moniruzzaman et al., 2010). It can also be observed from Figure 3 that fibre residue remained in all treated and untreated samples after temperature of  $550\text{ }^{\circ}\text{C}$ . However, the amount of the fibre residues left were different in all cases presumably due to partial removal of hemicelluloses and lignin from the fibres.

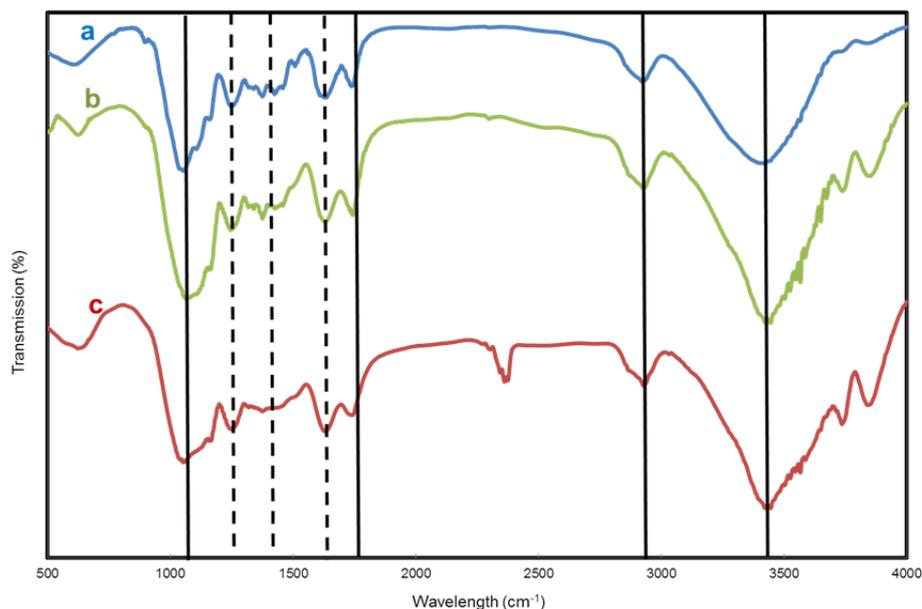


Figure 2: FTIR spectra of (a) untreated, (b) [Emim][DEP] treated and (c) [Bmim][Cl] treated OPF fibre. Vertical solid lines represent cellulose and hemicellulose characteristic peaks whereas vertical dashed lines represent lignin

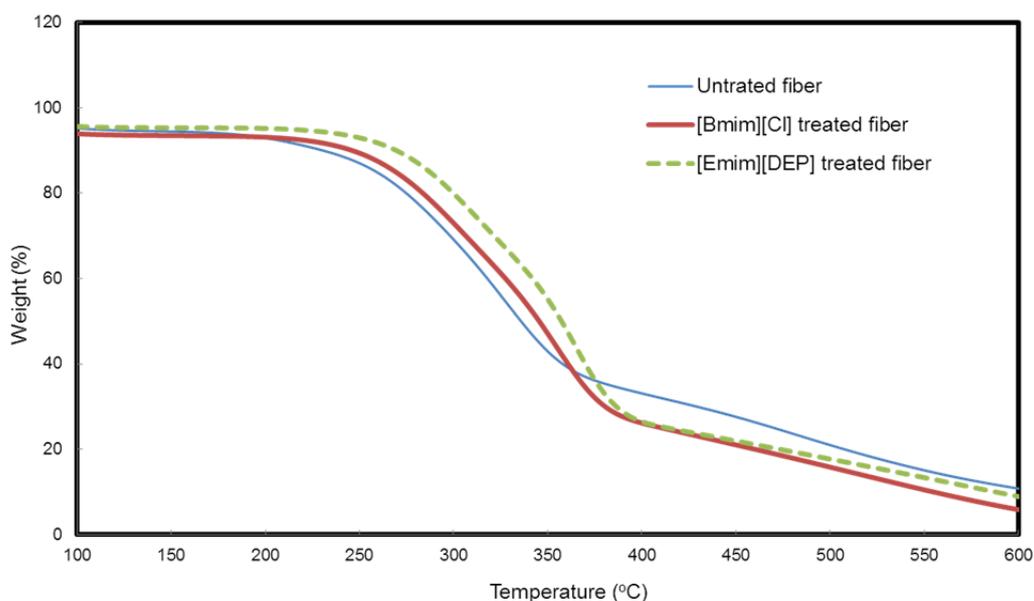


Figure 3: TG curves for untreated and IL-treated OPF fibre

### 3.2 Effect of IL treatment on the mechanical properties of composite board

Figure 4 shows the mechanical properties (flexural strength and flexural modulus) of the biocomposite panels thermo-moulded from untreated and IL pretreated OPF fibres. Flexural properties were highly influenced by interfacial adhesion between fibre and biopolymer binder. Pretreatment of OPF particles with ILs [Bmim][Cl] and [Emim][DEP] had significant effect on the flexural strength and modulus, producing composite panels with superior flexural properties. The flexural strength (modulus of rupture) of untreated OPF fibre-composite board was 5 MPa which was improved to 9 MPa and 8.5 MPa after carrying out the pretreatment of fiber with ILs [Bmim][Cl] and [Emim][DEP] respectively. Moreover, the flexural modulus (modulus of elasticity) followed the same trend and increased from 529 MPa for untreated composite to 1,325 MPa for [Bmim][Cl] treatment and 1,025 MPa for [Emim][DEP] treated composite board. The overall sequence in the flexural properties can be summarized in the order as: [Bmim][Cl] treated composite > [Emim][DEP] treated composite > untreated composite. The improvement in the mechanical properties of the biocomposite board after IL pretreatment may be attributed due to the better wettability of fibre and good fibre-matrix adhesion which caused efficient stress transfer between biopolymer matrix and fibre. Improvement in the mechanical properties of biodegradable matrix based composite materials reinforced by lignocellulosic fibres after chemical pretreatment has also been reported earlier (Ibrahim et al., 2014).

Table 1: Thermogravimetric results for untreated and IL treated OPF fiber

OPF fiber	Transition temperature range (°C)	Temperature of maximum rate of weight loss (°C)	Weight loss (%)
Untreated	50-135	63	3
	135-298	291	27
	298-500	330	47
[Bmim][Cl] treated	50-140	64	4
	140-320	306	30
	320-500	359	59
[Emim][DEP] treated	50-140	64	3
	140-330	312	26
	330-500	368	59

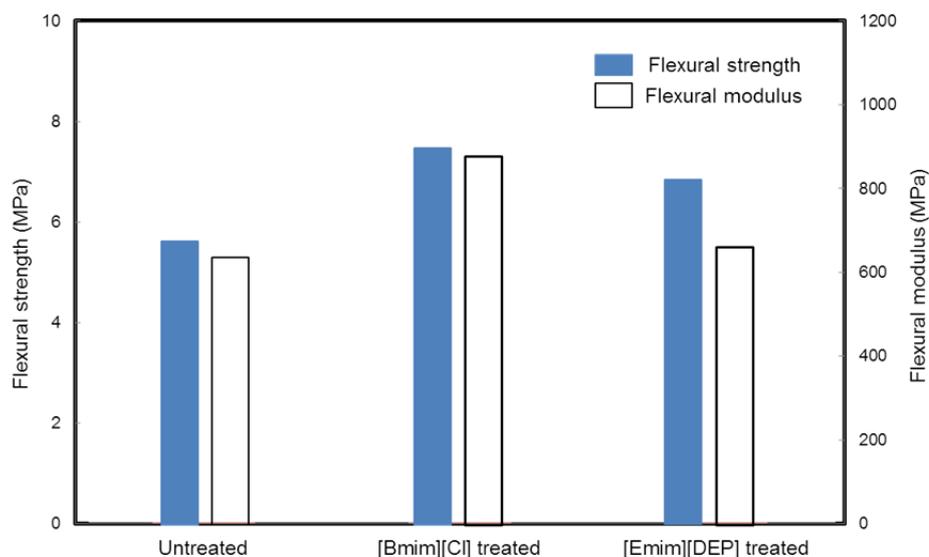


Figure 4: Flexural properties of untreated and IL treated composite board; filled columns represent flexural strength and unfilled columns represent flexural modulus

Actually biomass particle diameter reduces as a result of IL-assisted pretreatment with [Bmim][Cl] and [Emim][DEP] by partial dissolution and removal of hemicellulose and cementing material from the fiber surface and thereby increases the aspect ratio and improving the mechanical characteristics of the composites (Zhang and Hu, 2014). Higher values of flexural strength and flexural modulus of the composite panels achieved by IL-assisted pretreatment of OPF fiber have great importance in several major applications such as structural materials.

#### 4. Conclusions

Some of the properties of biocomposite board fabricated from untreated and IL pretreated lignocellulosic OPF fiber were measured. The influence of the IL pretreatment on the thermal stability of OPF fiber was also analyzed. Thermal stability of the IL-treated fibers and the flexural properties of the biocomposite board fabricated from these fibers were significantly improved as compared to those of untreated fiber. The study demonstrates the feasibility of using highly effective and clean IL-assisted pretreatment technology of lignocellulosic fiber for fabrication thermo-moulded biocomposite panels.

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