Exploring Ionic Liquid Assisted Pretreatment of Lignocellulosic Biomass for Fabrication of Green Composite

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Ionic liquids (ILs) pretreatment has emerged as the promising technology toward environmentally benign conversion of lignocellulosic residues into high value cellulosic fiber as sustainable raw material for biocomposite manufacturing. In this work, the impact of an ionic liquid (IL) 1-ethyl-3-methylimidazolium diethylphosphate ([emim] [dep]) pretreatment of oil palm frond (OPF) on the flexural properties of the composite board has been reported. Ionic liquid pretreatment of OPF fiber under high solids loading (IL/biomass ratio = 1.0) was conducted prior to compounding with thermoplastic starch which was used as binder polymer. Effect of IL pretreatment on OPF fiber was assessed by employing Fourier Transform Infrared Spectroscopy technique. IL treated composite board was found to exhibit superior flexural properties than that of untreated board. Flexural strength was increased from 10 MPa for untreated composite to 12.75 MPa for composites fabricated from IL treated OPF particles. The obtained results evidenced that the IL pretreatment could be a promising, cost-efficient and benign approach for conversion of agricultural waste into high value engineered composite panels. The study plainly demonstrates that IL based pretreatment could be a green technology for effective utilization of lignocellulosic waste biomass in the biocomposite manufacturing.

Key Words

Ionic liquid pretreatment, Biocomposite, Oil palm fiber, Thermal-compression

1. Introduction

Composites based on synthetic fiber reinforcements such as glass, carbon or aramid fibers have been utilized in a wide spectrum of applications including structural, automotive, building and construction, furniture and packaging etc.\(^\text{1,2}\).

However, depletion of petroleum reserves at an alarming rate, concepts of sustainability, increasing global environmental sensibility and strict environmental legislations have concurrently provoked the search for novel processes and products which are compatible with our planet’s fragile environmental conditions. Consequently, the plant-based lignocellulosic materials have become a potential alternative to petroleum based synthetic fibers due to their renewability, biodegradability, low price, nonabrasive nature to processing equipment, lesser density, remarkable toughness, sufficient specific strength, enhanced energy recovery and CO\(_2\) neutrality during burning\(^\text{3,4}\).

During the manufacturing of lignocellulosic composites, fiber-binder interfacial conglutination is the most critical factor which identifies the mechanical properties of the composites. However, the presence of non-cellulosic impurities on the fiber surface such as lignin, pectin and waxy substances etc. cause poor fiber-polymer interfacial bonding and render weak mechanical properties to the resulting composite\(^\text{5,6}\). To resolve this issue, various pretreatment methods for lignocellulosic materials have been utilized such as alkali treatment\(^\text{7}\), ammonia fiber explosion (“AFEX”)\(^\text{8}\), carbon dioxide explosion, steam explosion or hot water treatment\(^\text{9}\) etc. Most of these technologies need extreme temperature and pressure conditions as well as highly concentrated chemicals for the fiber cooking process. Sulfite and sulfates pulping methods provoke severe environmental hazards. Therefore, the
development for a novel, efficient and benign pretreatment method is still a challenging task for efficient utilization of biomass waste materials for composite manufacturing.

ILs are classified as new a class of solvents with high polarities, broad liquid range, negligible vapor pressure and usually melt below 100 °C. Many ILs have been used for lignocellulosic biomass dissolution under mild conditions and regenerated material relatively richer in cellulose contents with enhanced thermal stability could readily be separated by the addition of a variety of precipitating anti-solvents. Recently, the concept of high solids loading for lignocellulosic biomass pretreatment has gained significant attraction with the potential advantages over lower solids loading such as improved process efficiency, reduction in capital cost, lower energy consumption and more environmentally friendly as lesser waste water will be generated during washing out residual IL from pretreated material. Konda et al. studied the principal cost drivers and economic potentials and explained that biomass loading as high as 50% was essential for IL based pretreatment to be competitive at industrial level. Further, Cruz et al. investigated the impact of high solids loading pretreatment and observed that IL pretreatment was certainly effective even at 50% solids loading to decrease the recalcitrance of lignocellulosic material and enhance the cellulose accessibility. It has been reported that IL cation with imidazolium based backbone structure along with alkyl-phosphate group as side chain is the most promising candidate for dissolution of lignocellulose in ILs. Also, phosphate based ILs are reported to possess relatively lower viscosity which is a highly desirable characteristic. Thus, the objective of the present study was to explore the effect of IL [emim][dep] pretreatment of oil palm lignocellulosic waste under high IL/biomass ratio on the mechanical properties of fabricated biocomposites by using thermoplastic starch as polymer binder.

2. Procedures

2.1 Fabrication of biocomposite samples

Oil palm frond (OPF) feedstock samples were obtained from plantation area around Universiti Teknologi PETRONAS, Seri Iskandar, Perak, Malaysia. Commercial corn starch and glycerol (99+ %) were received from R & M Marketing, Essex, U.K. IL [emim][dep] (1-ethyl-3-methylimidazolium diethyl phosphate) was purchased from Sigma-Aldrich, Germany.

OPF samples were cut, grinded and subsequently subjected to sieve analysis to ensure particle size below 250 μm. The material was dried in an air-circulation oven at 80 °C for 10 h before IL pretreatment. During pretreatment, a specific quantity of IL [emim][dep] was mixed with an equal quantity of dried OPF in a paddle-type stainless steel reactor fitted with a variable speed stirrer and an electrically heating jacket, at 90 °C for 3 h and 500 rpm. Following this, an equal volume of acetone/water mixture was immediately poured into pretreated material as anti-solvent and stirred vigorously. Ultimately, the regenerated material was precipitated out and washed with distilled water to get complete removal of the IL. Biopolymer thermoplastic starch (TPS) was used as a binder material in our composite product to preserve the sustainability of the product. Commercial corn starch was converted into thermoplastic material by adding and mixing with 30 wt% glycerol and 20 wt% water at the temperature of 80 °C. The polymeric material was then stored in sealed plastic bags. OPF fiber was then added into the polymer emulsion with a fiber/binder ratio 1:1. The compounded mixture was homogenized and dried in an oven at 100 °C to remove surplus water. Finally, composite plated were

Fig. 1 Photographs of some molded composite board (a) and mild steel mold filled with fiber-binder compounded mixture (b)
thermally pressed into 10 cm x 10 cm x 0.2 cm dimensions by using Carver Laboratory compression molding machine (CARVER, INC. USA) at 140 °C and 25 MPa. Fig. 1 shows some samples of fabricated composite board.

2.2 Characterization

In order to investigate the effect on IL pretreatment on lignocellulosic material, Fourier Transform Infrared Spectroscopy (FTIR) technique was utilized in the wavenumber range of 400-4000 cm⁻¹ by employing Perkin Elmer Spectrum One FTIR Spectrometer at a resolution of 4 cm⁻¹. Furthermore, the flexural testing of both untreated and IL treated samples was carried out according to ASTM D 1037 standard with minor modifications with gauge length of 32 mm and cross head speed of 2 mm/min (Zwick-Roel Amsler HA-50 Universal Testing Machine).

3. Results and Discussion

3.1 Effect of IL pretreatment on surface composition of OPF fiber

Ionic liquid [emim][dep] pretreatment under high IL/biomass ratio of 1:1 somewhat changed the color of the fiber from brown to dark brown which may indicate that some expected changes (removal of wax, pectin, surface lignin) in the original OPF particles have been achieved. The FTIR spectra of untreated and IL [emim][dep] treated OPF materials are provided in Fig. 2. Typically, the peaks around 3,465 cm⁻¹ and 2,950 cm⁻¹ are attributed to aliphatic moieties in the lignocellulosic structure. One prominent band is of C=O stretching at 1,742 cm⁻¹. In fact, this band represents the carbonyl groups of amorphous hemicellulose, but at the same time these carbonyl functional groups may also originate from other polymer fractions in lignocellulosic structure. Besides, the peak at 1270 cm⁻¹ attributed to C-O-H vibration of phenolic group and at 1,650 cm⁻¹ represents characteristic peaks of lignin in the lignocellulosic materials. FTIR analysis suggests that IL pretreatment under high solids loading did not significantly change the chemical composition of the OPF fiber.

3.2 Effect of IL pretreatment on flexural properties of the composite board

Flexural properties (strength and modulus) of the composite panels made from untreated and [emim][dep] treated particles by using thermoplastic starch binder are provided in Table 1. The flexural strength of the untreated composite panel was found to be 10 MPa which was enhanced to 12.76 MPa as a result of IL [emim][dep] pretreatment of fiber. In addition, [emim][dep] treatment improved the flexural modulus to 1239 MPa as compared to the value of 929 MPa for untreated composite panel. It is well known that mechanical properties are strongly dependent on the interfacial adhesion between fiber and biopolymer binder. Higher flexural properties of the biocomposites made from IL treated OPF fiber may be due to the fact that in untreated fiber, cellulose microfibrils are entrapped by a complex heterogeneous matrix of hemicellulose, lignin and pectin. Lignin is intimately integrated and acts as a protective layer around the cellulose microfibrils. This firm association between cellulose and other components in untreated fiber could be the main reason for weak fiber-binder interfacial adhesion and restrains the accessible cellulose surface area. It has been reported that IL pretreatment partially removed the non-cellulosic impurities from the lignocellulose surface and exposed more active sites for binder interaction. Thus the better mechanical properties of the IL treated

<table>
<thead>
<tr>
<th>Biocomposite</th>
<th>Flexural strength ± STD (MPa)</th>
<th>Flexural modulus ± STD (MPa)</th>
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<tbody>
<tr>
<td>Untreated</td>
<td>10 ± 1.8</td>
<td>929 ± 39</td>
</tr>
<tr>
<td>[emim][dep] treated</td>
<td>12.76 ± 2.1</td>
<td>1239 ± 5.6</td>
</tr>
</tbody>
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![Table 1] Flexural properties of untreated and IL treated composite boards

Fig. 2 FTIR spectra of untreated (a) and IL [emim][dep] treated (b) OPF fibers
composite panels may be due to the increased wettability of lignocellulosic material and good fiber-binder interfacial adhesion which provoked proficient stress transfer between fiber and polymer during molding process.

4. Conclusion

Effect of pretreatment of an efficient IL [emim][dep] on the flexural properties oil palm frond based biocomposites was evaluated. A biodegradable thermoplastic starch polymer was successfully employed as binder material in composite manufacturing. IL pretreatment improved the flexural strength and modulus of the composite panels as compared to those of untreated composite. The present work demonstrates that IL pretreatment under high biomass loading and mild process conditions could be a proficient, cost-effective and environmentally benign pretreatment technology for the conversion of agricultural based solid waste into high value engineered composite products.

References