High Density Polyethylene Composites Reinforced with BMIMCl- and CTAB- treated Sawdust: Structural and Mechanical Properties.

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Abstract

The successful interactions between the sawdust and matrix are among the significant factors determining the strength and durability of wood-plastic composites (WPCs). This work aims to evaluate the structural and mechanical properties of high-density polyethylene (HDPE) composites reinforced with sawdust pretreated with ionic liquids 1-butyl-3-methylimidazolium chloride (BMIMCl) followed surface modification by cationic surfactant, n-hexadecyl trimethylammonium bromide ($C_{16}H_{33}N(CH_3)_3Br$, (CTAB). The chemical and structural properties of raw and pretreated sawdust were analysed using Fourier transform infrared (FTIR) spectroscopy, X-ray diffraction (XRD). The morphology of the sawdust was observed using field emission scanning electron microscopy (FESEM). After sawdust analysis, the raw and pretreated sawdust was mixed into the HDPE, in a proportion of 30/70 wt% using a single screw extruder followed by injection moulding. Furthermore, the specimens for tensile and flexural testing was prepared to evaluate the mechanical properties. The fractured surface of the composites was also analysed using FESEM. The results showed that the pretreatment with BMIMCl and CTAB had improved the crystallinity and functionalisation of CTAB into sawdust structure. The mechanical results showed that the composites reinforced with BMIMC- and CTAB- treated sawdust showed only an improvement in elongation but did not improve tensile and flexural strength.

Keywords: ionic liquid pretreatment, cationic surfactant, surface modification and wood plastic composite

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Introduction

Plastic composites (WPCs) seems to be the most promising sector for composite, wood and plastic industries. Wood WPCs were produced by combining the wood in particles or fibres with thermoplastic materials. Sometimes additive are added to improve the quality of the composite. WPCs offer several advantages: low cost, abundant natural fibre resources, and less concern about environmental issues. Regardless of the advantages mentioned above, WPCs suffer from poor interfacial strength and mechanical properties essential for high load applications [1]. Natural fibres such as wood sawdust consist of cellulose consisting of numerous hydroxyl groups that can interact with moisture via hydrogen bonding. The hydrophilicity characteristic of the cellulosic components created the polarity discrepancy between sawdust fibres and the hydrophobic matrix, which subsequently caused a poor interfacial adhesion between these two materials. Functionalisation of the hydroxyl group with the hydrophobic group via surface treatment can somewhat overcome this drawback by enhancing sawdust and matrix compatibility. To have effective functionalisation during the surface treatment, sawdust commonly undergoes chemical pretreatment [2]. Studies have shown that natural fibre-reinforced polymer composite has better physical and mechanical properties when suitable pretreatment and surface modification of the fibre is introduced before the composite fabrication [3–5].

In this study, BMIMCl will be used as a pretreatment solvent before surface modification with CTAB. BMIMCl has been used widely as the new type of green solvent pretreatments used in the lignocellulosic field [6-7]. Compared to the other pretreatment, such as acid or base that used strong alkaline, pretreatment with ILs are more environmentally friendly and less energy demand. Ionic liquids have been proved to dissolve cellulose [8] and other types of carbohydrates [9] and extensively used in the field of cellulose technology [10]. The treatment of sawdust with ionic liquid prior to surface modification is expected to improve functionalisation of the hydrophobic group of CTAB to sawdust during chemical modification. Efficient functionalisation of hydrophobicity group to sawdust will then improves the sawdust-matrix interfacial adhesion. This paper investigates the effect of using BMIMCl to pretreat sawdust before the surface modification with CTAB.

Materials and Methods

Materials

Sawdust was collected from The Sawmill Station in Jeli. The cleaned sawdust was oven-dried at 110°C for 24 hours. Then the sawdust was sieved at 350 µm. High-density polyethylene (HDPE) was purchased from Sigma-Aldrich (St. Louis, MO, USA).

Pretreatment and surface modification of sawdust

20 wt% of sawdust was mixed with 80 wt% of BMIMCl in an oil bath with continuously stirring at 80°C for 24 hours. After 24 hours of the heating process, the mixture was cooled at room temperature. Then the sawdust was washed thoroughly with distilled water to remove all BMIMCl. The BMIMCl-treated sawdust was then chemically modified with CTAB. Sawdust was immersed in 10 % of CTAB aqueous solution for 30 minutes at 40°C. After washing with distilled water, the sawdust was oven-dried at 110°C for 24 hours.

Analysis of sawdust

The sawdust was characterised using FTIR Spectroscopy, XRD and SEM to evaluate the physical, chemical, and morphological properties of sawdust. FESEM micrographs were obtained through Extreme High-Resolution Field Emission Scanning Electron Microscope (XHR-FESEM) Model FEI Verios 460L (The Thermo Fisher, USA). The FTIR spectra of sawdust were recorded from 4000-400 cm^{-1} with a resolution of 4 cm^{-1} using Nicolet iZ10 FT-IR Microscope (The Thermo Fisher Scientific, USA). The crystallinity of the samples was studied using D2-Phaser Bruker XRD (Bruker, USA) equipped with a monochromatic CuKα radiation source. The samples were scanned in the range of 5 º to 60 º with a step of 0.01 º and a rate of 1 º min^{-1}. The Crystallinity index (CrI) of the sample was determined based based on the reflected intensity data using method of Segal *et al*. [11]:

$$CrI(\%) = 100\ x\ (I_{002} - I_{am})/I_{002} \quad (1)$$

where I_{002} is the maximum intensity for the crystalline portion in samples (i.e., cellulose) at about 2θ = 22º and I_{am} is the intensity attributed to the amorphous portion of the samples (i.e., hemicellulose and lignin) at 2θ = 18º.

Fabrication of composites

A 30 wt% sawdust content HDPE–sawdust composite was processed to evaluate the effect of the surface treatments of the sawdust on its tensile and flexural properties. The sawdust was mixed with HDPE pellets using a single screw extruder machine and granulator machine (Brabender GMBH & CO.KG, D-47055 Duisburg, Germany). The speed of the screw extruder was set at 45 rpm and the temperature was set at 180°C, 220°C, and 210°C for feed zone, metering and compression zone and die zone respectively. The samples for tensile and flexural testing were prepared using injection moulding.

Mechanical tests

The specimens of the composites were analysed using Universal Testing Machine Electro-Mechanical 50kN. Five specimens of composites were prepared for tensile tests and were analysed according to the ASTM D 638 standard at 5 mm min^{-1} crosshead speed. For the flexural test, five specimens were prepared and analysed according to the ASTM D 790 standard. The tests were carried out using the 3-points method with a crosshead motion rate at 1.2 mm $min^{-1.}$ The fractured sample of tensile was evaluated using field emission scanning electron microscopy (FESEM).

Results and Discussion

Fibre Analysis

FTIR spectra for sawdust and BMIMCl- and CTAB- treated sawdust used in this work are shown in Figure 1. The wide band between 3600 and 3050 cm^{-1} assigned to O–H stretching vibration of hydroxyl groups involved in hydrogen bonds while 2970–2800 cm^{-1} to

C–H stretching vibration indicated the characteristic peaks of cellulose, hemicellulose and lignin. From Figure 1, It can be seen that the sawdust that undergoes CTAB pretreatment showed intense peaks in the range of 2850 cm^{-1} to 2970 cm^{-1}. These peaks are assigned to the CH_2 asymmetric and symmetric stretching vibration of the alkyl chain of the cationic surfactant, CTAB that was indicating the incorporation of CTAB into the sawdust structure. Figure 1 (see the insert) shows that the intensity of O-H bonds in the region 3500 cm-1 and 3100 cm-1 slightly decreased for the sawdust treated with BMIMCl and CTAB. This might be due to the hydrophilicity of sawdust that has decreased and adsorption of CTAB molecules onto the surface of sawdust after treatment and surface modification process. It was also observed that the FTIR spectra of BMIMCl- and CTAB- pretreated sawdust showed a small peak at ~1474 cm^{-1} attributed to the trimethyl groups of the quaternary ammonium and peak at frequencies around 1464 cm^{-1} indicated a reduction of side-by-side chain interactions of CH_2 [12]. The intense peak at ~1027 cm^{-1} correspond to the C-O vibration of cellulose, hemicellulose and lignin molecules in sawdust and peak at ~897 cm^{-1} correspond to C-O-C vibration at -glycosidic linkage. The peak at ~897 cm^{-1} is more intense for BMIMCl- and CTAB- pretreated sawdust indicating the transformation of cellulose I o cellulose II in the lignocellulosic materials after pretreatment [13].

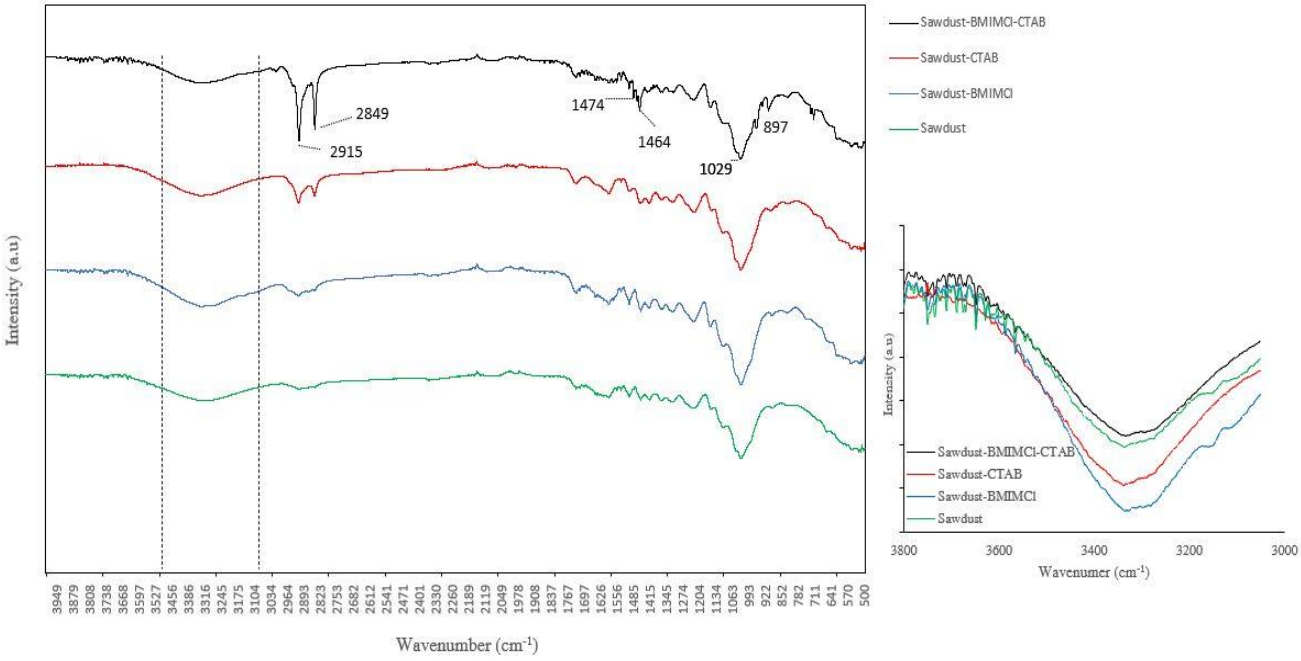

Figure 1: FTIR spectra of treated and untreated sawdust.

From the FTIR result, it is also fascinating to deduce the crystallinity index (CrI_{FTIR}) of sawdust. In this study, the crystallinity index (CrI_{FTIR}) of sawdust was calculated based on the height ratio of the bands at 1371 and 2900 cm^{-1} (H_{1371}/H_{2900}) [9, 10]. It was found that the CrI_{FTIR} is higher for the sawdust that has pretreated with both BMIMCl and CTAB. This result is further supported by the CrI calculated using the XRD result from Figure 2.

Figure 2 shows the XRD diffractogram for the untreated sawdust and BMIMCl- and CTAB- treated sawdust; the sawdust has features of semi-crystalline material. A significant diffraction peak between 22° and 23° attributed to the cellulose crystallographic planes (0 0 2) was observed. As shown in Figure 2, there is a slight difference in the spectra after pretreatment with CTAB. The crystallinity of the sawdust is increased after underwent both BMIMCl and CTAB treatment. The presents of CTAB in the treatment has shifted the peak to 2θ~24°. It is worth noting that the combination of both BMIMCl and CTAB treatment has increased the intensity of the peak. The crystallinity index (%) of all samples has been tabulated in Table 1. As shown in Table 1, the crystallinity index (Crl) is increased after underwent pretreatment with BMIMCl and CTAB. The use of CTAB has reduced the amorphous percentage and increase the percentage of crystallinity. Sawdust pretreated with CTAB shows 54.0 % amorphous and 46.0 % of crystallinity, while sawdust that has been pretreated with both BMIMCl and CTAB shows 57.9 % amorphous and 42.1 % of crystallinity. The higher Crl for the BMIMCl- and CTAB- treated sawdust can be attributed to the rearrangement of the more ordered and crystalline structure of cellulose [13] and removal of the amorphous component during the pretreatment process [16].

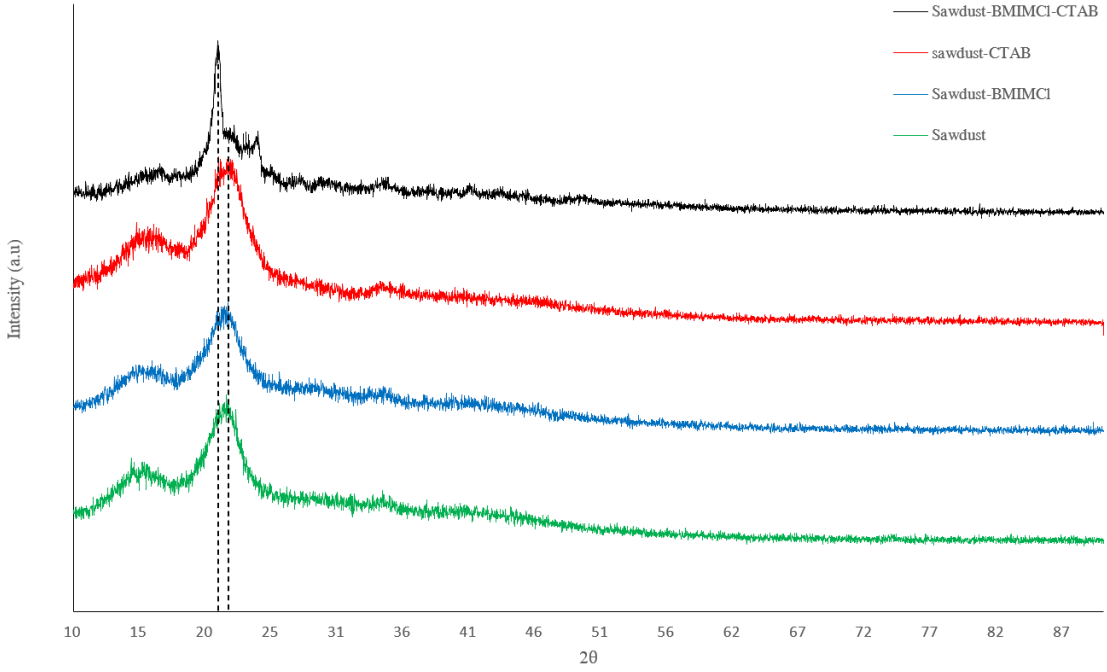

Figure 2: XRD spectra of the treated and untreated sawdust.

Table 1: XRD and FTIR Crystallinity Index (Crl)

Samples	CrI_{XRD} (%)	Crl_{FTIR}
Untreated Sawdust	35.1	0.96
Sawdust - BMIMCl	34.4	0.95
Sawdust - CTAB	46.0	0.97
Sawdust - BMIMCL - CTAB	42.1	1.02

Mechanical Properties of the Composites.

To observe the effect of the sawdust surface treatments on the composites behaviour, tensile testing results for a (70:30 wt%) composite (HDPE–sawdust) are shown in Table 2. The composite reinforced with the CTAB treated sawdust and a previous BMIMCl treatment shows an increase in elongation at break from 2.98 to 10.2 % with respect to the composite made with the untreated sawdust. The sawdust treated with CTAB and BMIMCl does not seem to improve the strength of the composite material. The tensile strength is slightly decreased with the use of BMIMCl and CTAB treated sawdust. This is possibly due to the degradation of the lignocellulosic component during the pretreatment process that required heat use. The degradation of the lignocellulosic component, such as lignin content [17-18], cause a poor stress transfer in the samples.

Table 2: Mechanical properties of the composite materials

Sample	Elongation at break (%)	Tensile Strength (MPa)	Tensile Modulus (MPa)	Flexural Strength (MPa)
Sawdust/PE	2.89 ± 0.4	18.4 ± 0.10	2280 ± 64	32.6 ± 0.56
Sawdust/CTAB/PE	9.98 ± 1.7	15.4 ± 0.17	2080 ± 80	26.1 ± 0.40
Sawdust/IL/CTAB/PE	10.2 ± 0.8	15.8 ± 0.15	1810 ± 54	26.4 ± 0.30

A similar pattern has been observed for the flexural strength which the result is slightly decreased with the use of BMIMCl and CTAB treated sawdust. This is supported by a previous study which suggested that though there is no improvement in tensile strength was observed, but the elongation of the fibre was improved almost double upon chemical treatment [19].

Figure 3 shows FESEM micrographs of BMIMCl-treated sawdust, CTAB-treated sawdust and BMIMCl- CTAB- treated sawdust. The results showed that surface modification of CTAB has increased the number of pores in sawdust. This is agreed with the previous study which depicted that the number of pores in natural fiber increase after surface modification with CTAB [20]. The rise in the number of the pore in sawdust could contribute to the slightly reduction of tensile and flexural strength of the composite due to the poor stress transfer in composite.

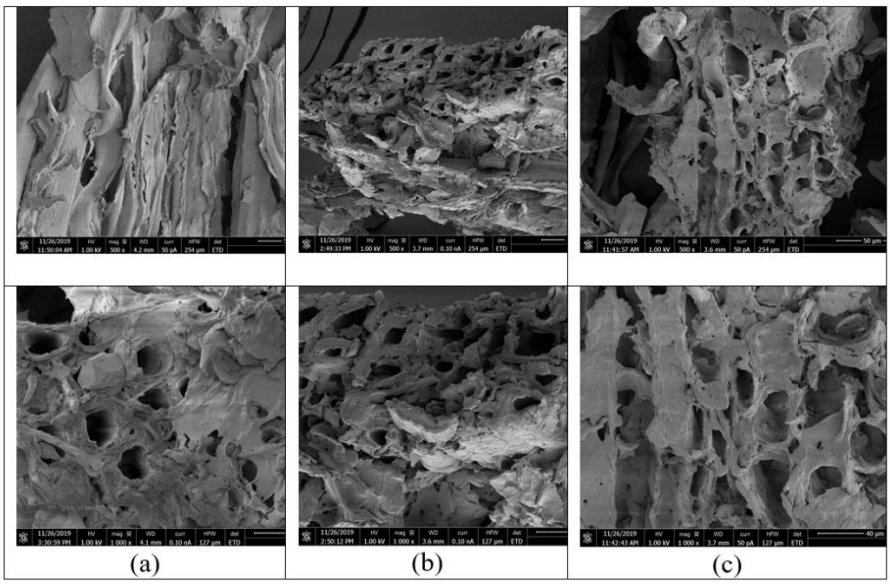

Figure 3 : FESEM micrographs of (a) BMIMCl-treated sawdust, (b) CTAB-treated sawdust and (c) BMIMCl- CTAB- treated sawdust at 500x magnification (top) and 1000x magnification (bottom) images.

Figure 4 shows FESEM micrographs of the tensile fracture surface of the sample for sawdust/PE, sawdust/CTAB/PE, sawdust/BMIMCl/CTAB/PE composites. It is shown that for the treated sawdust/PE composites, there is the substantial elongation of the PE matrix before it breaks. The elongation is more significant in sawdust/BMIMCl/CTAB/PE composites. This shows that the interfacial adhesion between PE and sawdust is stronger than that of the untreated sawdust. This is supported by our previous result that showed elongation at break is improved with the treated sawdust. The improvement of the interfacial adhesion can be explained as follows; due to the capability of BMIMCl to break up cellulose polymer chain in sawdust, the more hydroxyl groups will be accessible for surface modification CTAB. This will result in the better functionalisation of the hydroxyl group with surfactant group and minimising the polarity discrepancy between sawdust and HDPE, which subsequently facilitates better interfacial adhesion of the sawdust in the HDPE matrix.

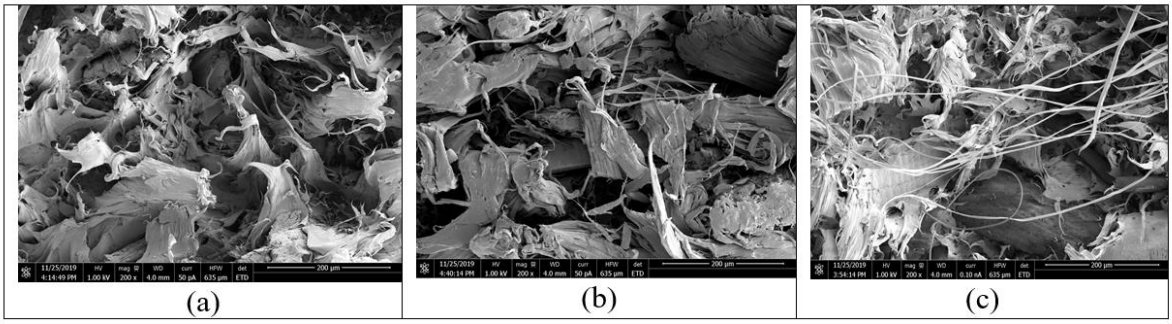

Figure 4: FESEM micrographs of tensile fracture sample for (a) sawdust/PE, (b) sawdust/CTAB/PE, (c) sawdust/BMIMCl/CTAB/PE

Conclusion

Pretreatment of sawdust using BMIMCl and chemical modification with CTAB was found to improve the crystallinity of the sawdust. The analyses of CTAB-modified sawdust using FTIR shows the presence of its functional group on sawdust which subsequently improves the compatibility and adhesion between sawdust and the matrix. This is supported by the improvement of the elongation at break and the FESEM image of the tensile fracture. However, analyses of surface morphology by FESEM shows that the sawdust has higher porosity. This leads to the slight reduction of tensile and flexural properties of the fabricated composite.

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Author Contributions

All authors contributed toward data analysis, drafting and critically revising the paper and agree to be accountable for all aspects of the work

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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