Effect of Surface Modification on Sawdust Reinforced High Density Polyethylene Composites Under a Wide Range of Strain Rates

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In this study, the alkali treatment of sawdust (SD) using different concentration (1%, 3%, 5%, and 7%) of sodium hydroxide (NaOH) was performed. The phases change due to alkali treatment on sawdust particles was examined using Fourier Transform Infrared (FTIR) spectroscopy and Field Emission Scanning Electron Microscopy (FESEM). Result shows that the treatment with 5% NaOH on sawdust particles improved the surface roughness of the filler with 21.1% diameter reduction. Both treated and untreated sawdust particles were reinforced in HDPE matrix using an extrusion method. For comparison purpose, both treated and untreated high density polyethylene/sawdust composites were tested under static and dynamic loading up to 1100 s⁻¹ using the universal testing machine and the split Hopkinson pressure bar apparatus, respectively. Results indicate that the treated high density polyethylene/sawdust composites with better filler/matrix interlocking characteristic shows better mechanical performances as compared to untreated high density polyethylene/sawdust composites under a wide range of strain rate investigated. Apart from that, the mechanical properties of both treated and untreated polyethylene/sawdust composites also show great dependency on the strain rate applied where yield stress, compression modulus and ultimate compressive strength were steadily increased with increasing strain rate. Unfortunately, the yield strain shows the contrary trend. While for the fractographic analysis under dynamic loading, the untreated composite specimens had undergone a severe catastrophic deformation and damages than that of treated composite specimens.

Keywords: natural filler, alkaline treatment, strain rates, split Hopkinson pressure bar

Lately, the use of natural filler as a sustainable reinforcement in composite materials is progressively increasing and had gained a major research interest over a decade, probably due to biodegradability, low cost and abundance. Most commonly agro-wastes and agro-forest (e.g. Sawdust, pulp-mill wood residue, bark, nut shells, bagasse, straw, corn cobs, bamboo, etc.) used as the addition to plastics for the production of new materials has been undertaken [1-4]. In particular, sawdust is mainly used in the field of construction (wood decks, window frames, bathroom interiors, etc.) and the automotive industry (dashboards, etc.) [5]. Sawdust is a by-product of sawmills, where it is produced from the cutting of wood. In spite of the application and utilization of sawdust filled composites are increasing, their performance are still limited and restricted owing to their hydrophilic characteristic nature of the wood that gives negative impact and bring problems in obtaining good dispersion of wood particles and poor reinforcement between sawdust and polymer [6]. Previous literatures indicate that the alkaline treatment attained good filler-matrix adhesion and mechanical properties of composites and was commonly used for sawdust particles [7-9]. As the properties of these composites are affected due to the less of surface roughness of sawdust, thus, the aims of the present work are to improve the surface roughness and the adhesion between filler and matrices using alkali treatment for further characterization under static and dynamic conditions, which never been reported in the past.

Since the implementation of Wood Polymer Composites (WPCs) have been extended from conventional to more crucial applications like aerospace, leisure, construction, sport and automotive industries [10], it is essential to investigate its dynamic behaviours in order to prevent any unexpected failure and damage during services. Although there are many previous studies have been reported on the mechanical properties of WPCs, but a few of them were focused on the dynamic mechanical behaviour of this composites. Moreover, the effect of surface treatment on dynamic mechanical properties of WPCs has never been reported before. Based on this concern, an experiment reported here was purposefully designed to fulfil the lack of information in this specific area. As to achieve the goals, sawdust particles were initially treated using an alkaline treatment approach with different concentrations (1, 3, 5, and 7%) of sodium hydroxide (NaOH). Meanwhile, the effectiveness of the alkaline treatment was characterised using Fourier Transforms Infrared (FT-IR) and Field Emission Scanning Electron Microscopy (FESEM). For mechanical analysis, an experimental technique, based on the compression Split Hopkinson Pressure Bar (SHPB), was introduced to perform high strain rate testing; whereas a conventional universal testing machine was used to perform static compression testing on both untreated and

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treated sawdust reinforced high density polyethylene (HDPE/SD) composites [11-15]. For comparison purpose, both untreated and treated HDPE/SD composites response were characterised in terms of their yield behaviour, rigidity and strength properties. Furthermore, a correlation between the applied strain rate and sawdust loading with rate sensitivity and thermal activation volume up to a certain deformation (0.025 of strain), was also clarify. Post damage analysis was also performed to further identify the failure mechanism experienced by both treated and untreated composite specimens under dynamic loadings up to 1100 s⁻¹.

Experimental part

Materials and methods

HDPE was obtained from ADV System Technology at 2.0 g/10 min melt flow index (2.16 Kg/190°C) with the density of 0.9537 g/cm³. Sawdust that obtained from a furniture supplier at Kangar, Perlis, Malaysia was ground and sieved to obtain powder size of approximately 125 µm. NaOH pellets were also purchased from ADV System Technology.

Alkali treatment of sawdust particles

Sawdust was washed thoroughly to remove surface dust and dried at 65°C. Dried substrate was soaked in NaOH solution with different concentrations which are 1, 3, 5 and 7% at room temperature for 2 h. After that, filler was washed several times with distilled water to remove any excessive NaOH solution on the filler’s surface. To neutralize the filler, it was soaked and stirred in dilute acetic acid solution for 5 min and washed again with distilled water. Finally, sawdust particles were dried in oven at 70 °C for 72 h (3 days) before proceed to the fabrication stage of composites.

Fabrication of composites

In this study, the HDPE/SD composites were prepared by an extrusion method. In this extrusion method, HDPE pellets and sawdust particles (15 wt.%) were combined in twin screw extruder. The HDPE/SD granule from the extrusion end was taken and compressed by hot compression moulding using a cylinder mould. The cylindrical shape sample was then taken out and cut into specific slenderness ratio (height/diameter) for compression specimen.

Characterization of alkaline treatment

Fourier Transform Infrared spectroscopy (FTIR)

The confirmation of the new formation of chemical reaction cellulose compound by the chemical reaction with NaOH solution was done for both untreated and treated sawdust using the FTIR spectroscopic analysis. The infrared spectra of the raw sawdust and treated sawdust specimens were recorded on a Shimadzu Fourier Transform Infrared Spectroscopy (FTIR) 81001. The sawdust particles were mixed with KBr and pressed into a small disc approximately 1 mm thick. The mixture was pelletized by using a hydraulic press (Specac-1) at 8 ton pressure and then scans for 32 times. The scanning of the FTIR spectrometer was carried out in the range of wave length of 4000 - 400 cm⁻¹ with 4 cm⁻¹ resolution.

Scanning electron microscopy

The dynamic fracture of the untreated and treated HDPE/SD composites was examined using a Field Emission Scanning Electron Microscope (FESEM) (ZEISS SUPRA 35 VP). The samples were prepared by a cross section of fracture surfaces. The test specimens were attached to an aluminium mount with carbon double-sided tape and sputter with Au/Pd by using Palaron SC 515 sputter coater to eliminate the electron charging effect.

Mechanical tests

Static compression test

For static testing, HDPE/SD composites were tested under constant crosshead speeds of 1.08 mm/min, 10.8 mm/min, and 108 mm/min which corresponded to the strain rates of 0.001 s⁻¹, 0.01 s⁻¹, and 0.1 s⁻¹, respectively using an Axial-Torsion Universal Testing Machine. To reduce frictional effects during the test, a thin film lubricant (petroleum jelly) was applied to both of the specimen’s surfaces. Five measurements were taken for each different loading to compute the average behaviour of tested HDPE/SD composites.

Dynamic Compression Test

The dynamic test was done using the compression split Hopkinson pressure bar (SHPB) apparatus as shown in figure 1. The system comprised principally of a gun barrel, a 152 mm striker bar, a 1500 mm input bar and a 1500 mm output bar, which maintained elastic during the tests. In this study, HDPE/SD composites were tested under high strain rate of 650 s⁻¹, 900 s⁻¹, and 1100 s⁻¹, respectively.

Results and discussions

Confirmation of alkaline treatment

F-FTIR analysis

Fourier Transform Infra Red spectroscopy (FT-IR) has wide applicability in structure interpretation, which are either synthesized chemically or of natural origin [16]. The formation of new chemical reaction cellulose compound by the chemical reaction with NaOH solution was confirmed by the FTIR spectroscopic analysis of the untreated and treated sawdust, as shown in figure 2. Peak
The absorption band at 2916 cm⁻¹ also shifted going through alkaline treatment using sodium hydroxide. The strong C-O band at 1034 cm⁻¹ is specific to the lignin materials, as has been reported previously [20, 21]. The characteristic of the alkaline treatment of lignocellulosic materials is due to the chemical treatment [6]. Similarly, the peak located at 1651 cm⁻¹ is characteristic of carbonyl group stretching in aldehydes and ketones. After treatment, one new peak of functional group appears in the band of 1595 cm⁻¹ that belongs to the aromatic Nitro compound. This band in the spectrum indicates the possible involvement of that functional group on the surface of sawdust in NaOH adsorption process [8].

In the spectrum of untreated sawdust, a band appears at 1736 cm⁻¹ that belongs to the carbonyl vibration in ester groups disappears after treatment in NaOH because the ester carbonyl bonds present in hemicelluloses was break due to the chemical treatment [6]. Similarly, the peak located at 1651 cm⁻¹ is characteristic of carbonyl group stretching in aldehydes and ketones. After treatment, one new peak of functional group appears in the band of 1595 cm⁻¹ that belongs to the aromatic Nitro compound. This band in the spectrum indicates the possible involvement of that functional group on the surface of sawdust in NaOH adsorption process [8].

In the spectrum of untreated sawdust, a band appears at 1237 cm⁻¹ and assigned to the C-O bond of the acetyl group in xylan. After treatment with NaOH, the band splits into two, one at 1269 cm⁻¹ and the other at 1231 cm⁻¹. The first band was cause by vibrations in the structure of the guaiacyl structure of the lignin and the second one is due to the vibrations of the syringyl structure. This band split is characteristic of the alkaline treatment of lignocellulosic materials, as has been reported previously [20, 21]. The strong C-O band at 1034 cm⁻¹ is specific to the lignin component from sawdust. Bands at 898 cm⁻¹ and 897 cm⁻¹ indicated the bonded C-C group present in sawdust. Based on the FT-IR spectrum portrayed in figure 2, it is convenient to say that the implementation of alkaline treatment in this study is successful and therefore, ready for further investigation.

**SEM analysis**

Each unit of sawdust particle mainly consists of crystalline cellulose surrounded and cemented together with hemicelluloses and lignin. These ultimate cells extend longitudinally overlapping each other and form the cellular structure [22]. The alkali reaction between sawdust fiber and NaOH is shown as following:

\[
\text{Sawdust} + \text{OH}^- + \text{Na}^+ + \text{H}_2\text{O} \rightarrow \text{Raw sawdust} + \text{O}^- \text{Na}^+ + \text{H}_2\text{O} \tag{1}
\]

**Mechanical properties**

**Yield behaviour**

Yield behaviour has become the most common material property reported for structural materials due to the ease and relative accuracy of its measurement. Therefore, to further clarify the strengthening effect of sawdust particles treatment under a wide range of strain rates, the yield stress and strain values were pointed out and illustrated in figure 4. For the line graph in figure 4, it can be seen that all...
specimens show positive increments in terms of yield stress values as the strain rate increase. Whereas, the yield strain values show contrary trend. This decrement pattern was attributed to the shear process during the yielding phenomenon, where at high strain rate loading, the motion of the lamellar is restricted and therefore, the HDPE polymer chains did not have sufficient time to reorder amongst themselves [27]. Subsequently, the yield deformation (strain) of the HDPE/SD specimens decreased as the strain rates increased.

For alkaline treatment point of view, it can be pre-concluded that the alkali treatment was successful since the treated HDPE/SD composites show better yield behaviour as compared to its counterpart (untreated specimen). From four different concentrations of NaOH solution, HDPE/SD composites with 5% NaOH recorded the highest yield stress and yield strain values for both static and dynamic loading. It is reported that alkaline treatment has two effects on the treated filler: (1) it increases surface roughness resulting in better mechanical interlocking with the matrix; and (2) it increases the amount of cellulose exposed on the filler surface, thus increasing the number of possible reaction sites [28]. The mechanical interlocking is very important as it is the key that gave rise to an increase of the inter-laminar shear strength of composite. At dynamic loading, this interlocking eventually will provide a continuous stress distribution between filler and matrix that make the composite strong enough to withstand high shear process during the yielding phenomenon.

Strength properties

From the bar graph in figure 6, it can be seen that the ultimate compression strength (UCS) values of both treated and untreated specimens increased steadily with increasing strain rate. The results are in line with the increment of flow stresses in yield characteristic. Related to this issue, Omar and his co-workers [29] had experimentally proved that the viscoelastic properties of polymer based composites had changed from a rubbery-like behaviour at a static loading (0.0001 s\(^{-1}\)) to a glassy-like behaviour at dynamic loading (1000 s\(^{-1}\)) using dynamic mechanical analysis (DMA). This transition (i.e. from static to dynamic condition) alters the intermolecular interaction in the amorphous domains of the polymer matrix and makes composite become stronger.

Apart from that, the treated HDPE/SD composites recorded higher UCS values as compared to its counterpart (untreated specimen) under both static and dynamic loading. Without any surface modification, difficulty in mixing arise due to the poor wetting between SD particles and HDPE matrix which indirectly leads to agglomeration problem [30]. As the state of agglomeration increased, it becomes a stress concentrator causing the voids between matrix and filler to increase, thus, resulting in low compression strength [31, 32]. At high strain rate condition, this agglomeration will make the SD particles incapable to endure the high stress transmission efficiently which consequently give low result of ultimate compression strength.

Strain Rate Sensitivity and Thermal Activation Volume

From the results shown in table I, it can be seen that the magnitude of the strain rate sensitivity of both treated and untreated HDPE/SD composites increased significantly with an increase in strain rates. Theoretically, at high strain rate, higher stress is required to perform deformation since the mobility of the polymer chains was restricted [33, 34]. This increment of flow stresses (i.e. for a given strain) will consistently increase the rate sensitivity of material. Interestingly, the thermal activation volume shows contrary trend with an increasing strain rate. White [35] speculated that the thermal activation volume of polymeric is referred to the free volume between polymer chains structures which influenced by the localised motions of segment or possibly side group of polymer chains. Since the mobility of the molecular chains is restricted at high strain rate, it will therefore attribute to the lower thermal
activation volume of both tested HDPE/SD composites. At low strain rate, the entanglement of the polymer chains has increased, and therefore increasing the thermal activation volume.

On the other hand, based on the results reported in table 1, it can be pre-concluded that the treatment of SD particles do not give any significant relationship with the rate sensitivity as well as thermal activation volume under a wide range of strain rates investigated. Statistically, untreated HDPE/SD composites show the highest reliance towards applied strain rates under static region. However, in quasi-static (static to dynamic) and dynamic regions, HDPE/SD composites treated with 1% NaOH solution recorded the highest sensitivity values compared to others. In this case, although the HDPE/SD composites had been successfully alkaline treated but it still recorded a lower magnitude of the strain rate sensitivity compared to others. The area that experienced agglomeration within the composite tends to be pulled-out more (i.e. debonded) under a dynamic loading, due to them being poorly bonded; and thus enhanced the formation of holes and voids.

**Fractographic Analysis**

Figure 7 (a-e) shows the SEM micrograph of the dynamic compression fracture at a dynamic loading of 1100 s⁻¹ of strain for both untreated and treated composites. From fractographic analysis, it was observed that there are some multi-mechanisms of damage, such as matrix cracking, delamination, filler fracture and filler/matrix debonding [38].

![Fig. 6. The ultimate compression strength value of untreated and treated HDPE/SD composites under a wide range of strain rate loadings](image)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Range of strain rates (s)</th>
<th>Classification</th>
<th>( \beta = \frac{\sigma - \sigma_0}{\ln(\varepsilon_1/\varepsilon_0)} )</th>
<th>( V = kT \left[ \frac{n\beta}{c_0} \right] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated HDPE/SD</td>
<td>0.001 to 0.01</td>
<td>Static</td>
<td>0.342</td>
<td>8.6765 \times 10⁻⁷</td>
</tr>
<tr>
<td>HDPE/SD</td>
<td>0.001 to 0.01</td>
<td>Static</td>
<td>1.174</td>
<td>3.2123 \times 10⁻⁷</td>
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<tr>
<td>0.1 to 600</td>
<td>Static-Dynamic</td>
<td>2.665</td>
<td>1.146</td>
<td>2.4786 \times 10⁻⁷</td>
</tr>
<tr>
<td>600 to 1100</td>
<td>Dynamic</td>
<td>15.21</td>
<td></td>
<td>2.606 \times 10⁻⁷</td>
</tr>
<tr>
<td>Treated with 1% NaOH</td>
<td>0.001 to 0.01</td>
<td>Static</td>
<td>0.308</td>
<td>4.3347 \times 10⁻⁷</td>
</tr>
<tr>
<td>HDPE/SD</td>
<td>0.001 to 0.01</td>
<td>Static-Dynamic</td>
<td>2.017</td>
<td>4.7378 \times 10⁻⁷</td>
</tr>
<tr>
<td>0.1 to 600</td>
<td>Static-Dynamic</td>
<td>2.606</td>
<td>1.216</td>
<td>2.4786 \times 10⁻⁷</td>
</tr>
<tr>
<td>600 to 1100</td>
<td>Dynamic</td>
<td>15.21</td>
<td></td>
<td>2.606 \times 10⁻⁷</td>
</tr>
<tr>
<td>Treated with 3% NaOH</td>
<td>0.001 to 0.01</td>
<td>Static</td>
<td>0.308</td>
<td>5.7960 \times 10⁻⁷</td>
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<td>Static-Dynamic</td>
<td>2.017</td>
<td>4.7378 \times 10⁻⁷</td>
</tr>
<tr>
<td>0.1 to 600</td>
<td>Static-Dynamic</td>
<td>2.606</td>
<td>1.216</td>
<td>2.4786 \times 10⁻⁷</td>
</tr>
<tr>
<td>600 to 1100</td>
<td>Dynamic</td>
<td>15.21</td>
<td></td>
<td>2.606 \times 10⁻⁷</td>
</tr>
<tr>
<td>Treated with 5% NaOH</td>
<td>0.001 to 0.01</td>
<td>Static</td>
<td>0.308</td>
<td>7.6910 \times 10⁻⁷</td>
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<td>HDPE/SD</td>
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<td>2.017</td>
<td>4.7378 \times 10⁻⁷</td>
</tr>
<tr>
<td>0.1 to 600</td>
<td>Static-Dynamic</td>
<td>2.606</td>
<td>1.216</td>
<td>2.4786 \times 10⁻⁷</td>
</tr>
<tr>
<td>600 to 1100</td>
<td>Dynamic</td>
<td>15.21</td>
<td></td>
<td>2.606 \times 10⁻⁷</td>
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<tr>
<td>Treated with 7% NaOH</td>
<td>0.001 to 0.01</td>
<td>Static</td>
<td>0.308</td>
<td>1.4527 \times 10⁻⁷</td>
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<tr>
<td>HDPE/SD</td>
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<td>Static-Dynamic</td>
<td>2.017</td>
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<td>0.1 to 600</td>
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</tr>
<tr>
<td>600 to 1100</td>
<td>Dynamic</td>
<td>15.21</td>
<td></td>
<td>2.606 \times 10⁻⁷</td>
</tr>
</tbody>
</table>

**Table 1**

*The Rate Sensitivity and Thermal Activation Volume of an Untreated HDPE/SD Composites with Alkaline Treated HDPE/SD Composites at Different Strain Rates*

![Fig. 7. The fracture surface of HDPE/SD composites with (a) untreated sawdust (b) treated with 1% NaOH (c) treated with 3% NaOH (d) treated with 5% NaOH (e) treated with 7% NaOH](image)
Theoretically, development of holes and voids disrupt the efficiency of the stress transfer between the matrix and the sawdust, and vice versa. However, those damages did not appear on the fracture surface of the composite with sawdust that has been alkaline treated at optimum concentration of NaOH (5% NaOH solution) as shown in figure 7 (d).

Conclusions

In this study, HDPE/SD composites were developed based on high density polyethylene as a matrix and sawdust as filler. Sawdust particles were treated using alkaline treatment method. For the comparison purpose, static and dynamic compression tests were successfully performed on both treated and untreated HDPE/SD composites up to nearly 1100 s⁻¹ using the universal testing machine and split Hopkinson pressure bar apparatus, respectively. From the results, the following conclusion can be drawn:

- the effectiveness of alkaline treatment on sawdust particles was successfully proven using Fourier Transforms Infrared (FT-IR) and Field Emission Scanning Electron Microscope (FESEM). Alkaline treatment with 5% NaOH concentration was the optimum percentage for the sawdust particles;
- the mechanical properties of both tested HDPE/SD composites show great dependency on the strain rate applied. The yield stress, compression modulus, and ultimate compressive strength were proportionally increased as the strain rate increased. However, the yield strain shows a contradictory pattern where it was gradually decreased with applied strain rate;
- the treatment of sawdust particles had also gave beneficial effect on the mechanical properties of tested HDPE/SD composites. It was found that, treated HDPE/SD composites with better filler/matrix interlocking characteristic exhibit better mechanical performances in terms of yield behaviour, rigidity and strength properties, as compared to HDPE with untreated sawdust particles under a wide range of strain rate investigated;
- the strain rate sensitivity of both tested HDPE/SD composites was significantly increased with increasing strain rate, whereas the thermal activation values show contrary trend;
- ultimately, post damage analysis was successfully determined through fractographic analysis in order to understand the failure mechanism experienced by these composite systems under both static and dynamic loading.

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