Physico-mechanical properties of bio-composites fabricated from polylactic acid and rice husk treated with alkali and ionic liquid

Md. Sakinul Islam¹, Mohamed Rashid Ahmed-Haras¹, Nhol Kao¹,*, Rahul Gupta¹, Sati Bhattacharya¹, Md. Nazrul Islam²

¹ Department of Chemical and Environmental Engineering, School of Engineering, RMIT University, Melbourne, VIC 3000, Australia.
² Department of Chemistry, Bangladesh University of Engineering & Technology, Dhaka 1000, Bangladesh

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ABSTRACT

In the present work, chemically treated rice husk (TRH) and untreated rice husk (UTRH) reinforced polylactic acid (PLA) bio-composites were produced using Haake rheomixer and compression moulding processes. Alkali (NaOH) and ionic liquid (IL: 1-ethyl-3-methylimidazolium acetate) treated rice husk samples are TRHN4 and TRHILN4 respectively. Using UTRH, TRHN4 and TRHILN4 the fabricated bio-composites are UTRH-PLA, TRHN4-PLA and TRHILN4-PLA respectively. The tensile strength (TS), tensile modulus (TM), impact strength (IS) and hardness values of TRHN4-PLA and TRHILN4-PLA were found to be much higher than the corresponding values of the UTRH-PLA bio-composites. The tensile fracture surface morphological features of TRHN4-PLA and TRHILN4-PLA composites, observed by scanning electron microscopy (SEM), revealed less micro voids and fibre agglomerates, which indicates that better filler-matrix interfacial adhesion occurred in the case of chemical treated RH compared to UTRH when blended with PLA. However, composites TRHN4-PLA and TRHILN4-PLA showed lower water uptake capacity compared to UTRH-PLA. From the FTIR spectra of UTRH, TRHN4 and TRHILN4 together with water absorption behaviour of the composite specimens, it appeared that chemical modifications significantly reduced the hydrophilic nature of RH, resulting in improved fibre-matrix interfacial adhesion. The overall physico-mechanical properties of fabricated bio-composites were found to follow this order: TRHILN4-PLA>TRHN4-PLA>UTRH-PLA.

*Corresponding author: Nhol Kao, Department of Chemical and Environmental Engineering, School of Engineering, RMIT University, Melbourne, VIC 3001, Australia, E-mail: nhol.kao@rmit.edu.au Phone No.: +61 3 9925 3257, Fax No.: +61 3 9639 0138

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Nomenclature

\[ A \] Area of tensile test
\[ E_{\text{av}} \] Averaged energy
\[ E_M \] Elasticity Modulus
\[ F \] Load
\[ I_{002} \] Intensity of the (002) lattice diffraction
\[ I_{\text{am}} \] Intensity scattered by the amorphous phase
\[ L \] Length
\[ \Delta L \] Length of object change
\[ \sigma_T \] Tensile strength
\[ W \] Nominal width
\[ W_i \] Initial weight
\[ W_f \] Final weight
\[ Y \] Pendulum energy (joule)

1. Introduction

Due to growing concern over environmental and food safety issues, green technology has attracted the attention of the scientific community through the development of renewable source-based bio-composites (Ismail, Dhakal, Popov, & Beagrand, 2016). A bio-composite is a material which is formed from a matrix (resin) and a biodegradable filler. Biodegradable filler is compatible with environment and it is added with matrix for reinforcement to enhance the physico-mechanical properties. Biodegradable polymers can be potential alternatives for food packaging materials to solve serious environmental problems caused by petrochemical-based polymers (Burgos, Martino, & Jiménez, 2013). The rising awareness towards environmental, health and safety issues have enormously encouraged researchers towards the interest about natural fibres reinforced bio-composites (Rasidi, Husseinsyah, & Leng, 2015). Agricultural waste biomass has been utilized to produce bio-composites in the recent years due to their several advantages over mineral fibres. For instance, agro-waste biomass are low cost, lightweight, renewable, biodegradable and environmentally friendly. Different types of natural fibres such as kenaf (Lee, Kim, Lee, Kim, & Dorgan, 2009), jute (Adhikari et al., 2017), graphite (Sathees Kumar & Kanagaraj, 2016), rice husk (Battagazzore, Bocchini, Alongi, Frache, & Marino, 2014) and wood dust (Islam & Islam, 2015), are extensively used to improve the mechanical properties of the natural fibre reinforced thermoplastic composites (Ndiaye, Gueye, & Diop, 2013; Satyanarayana, Arizaiga, & Wypych, 2009). Generally, thermoplastic polymers such as polyethylene (PE), polypropylene (PP), polystyrene (PS) and polyvinyl chloride (PVC) are applied in composite industry (10). Most of the petrochemical based plastics are not environmentally friendly due to their non-degradable nature. Hence, they can cause enormous environmental and ecological problems. Polyactic acid (PLA) is a biodegradable polymer which is suitable in producing bio-composites using agro-waste biomass as a filler material (Raquez, Habibi, Murariu, & Dubois, 2013; Södergård & Stolt, 2002; Wan, Yang, Du, & Zhang, 2015). PLA can also be mixed with nano-fillers such as nanocrystalline cellulose, nanographene, and carbon nanotube for the fabrication of nanocomposites (Muntha, Siddiq, Kausar, & Khan, 2018; Wei, Huang, Dong, Qi, & Fu, 2018). PLA has played a major role for replacing polyolefins in “green” packaging applications, due to its good mechanical properties, moderate barrier properties, processability (Lostocco & Huang, 1998; Ngo, Nguyen, Nguyen, & Tran, 2016), and transparency (Rasal, Janokar, & Hirt, 2010; Siracusa, Rocculi, Romani, & Rosa, 2008). To further improve the physico-mechanical properties of PLA, many studies focus on blending and grafting with other biodegradable polymers such as thermoplastic starch (Yeul Jang, Young Shin, Jin Lee, & Narayan, 2007), poly(ethylene oxide) (Rashkov, Manolova, Li, Espartero, & Vert, 1996; Tew, Sanabria-DeLong, Agrawal, & Bhatia, 2005), poly(E-caprolactone) (Bastami & Salehi, 2016; Garkhal, Verma, Jonnalagadda, & Kumar, 2007), poly(vinyl acetate) (Gajria, Davé, Gross, & McCarthy, 1996), poly(hydroxyl butyrate) (Focarete, Scandola, Dobrynski, & Kowalczuk, 2002; Vogel & Siesler, 2008), cellulose (Petersson, Kvien, & Oksman, 2007), and poly(butylene succinate) (Bhatia, Gupta, Bhattacharya, & Choi, 2007; Harada et al., 2007). Blending and grafting of PLA with other polymers for improving mechanical properties is cost and energy effective. Therefore, to improve the mechanical strength of PLA economically is the major concern for the fabrication of bio-composites from PLA. Recently, rice husk (RH) biomass, a lignocellulosic waste, has attracted a lot of research interest due to its high cellulose content, annually renewable, easily available almost everywhere in the world and very low cost (Dimzoski et al., 2013). It has been reported that agro waste biomass can be used as a filler material because it can significantly improve the mechanical strength of polymer matrix (Battegazzore et al., 2014; Islam & Islam, 2015). However, the main problem in producing PLA-RH bio-composites is the bacterial infection due to of cellulose. The hydrophilic nature can be substantially reduced by chemical modification of RH biomass. Chemical modification of lignocellulosic biomass significantly improves the physico-mechanical properties of composites by improving the interfacial cross linking between filler and matrix materials. This also improves the dispersion of filler materials into the matrix as well. Therefore, chemical modification is a key factor for improving physico-mechanical properties of composites. In the open literature, a significant number of reports have already been published on the chemical modifications of natural fibre (M. M. Haque, Islam, & Islam, 2012; Islam & Islam, 2015; Satyanarayana et al., 2009). Nevertheless, chemical modification of lignocellulosic biomass by ionic liquid (IL) is still ongoing research; so many unknowns need to be explored in order to bridge the gap (Ang, Ngoh, Chua, & Lee, 2012).

In this work, a detailed investigation has been conducted to find out how physico-mechanical properties are affected by the addition of IL in producing raw and chemically treated RH reinforced PLA bio-composites.

In essence, this is a utilization of acid, alkali and ionic liquids to chemically treat the RH biomass for the fabrication of bio-composites with PLA.
2. Methodology

2.1 Overview of Methodology

For the fabrication of PLA-TRH/UTRH bio-composites, raw rice husk biomass (R-RHB) was converted to powder form and processed for chemical treatment. The chemical treatment was performed to enhance crosslinking between fibres and matrix with removing lignin and other non-cellulosic components from R-RHB. The chemical treatment of powdered RH was performed using alkali and alkali-ionic liquid blends, separately. The bio-composites were then fabricated using PLA mixed with untreated rice husk (UTRH) and chemically modified RH samples TRHN4 and TRHILN4. The produced bio-composites were named according to chemical modification as involved in this research. Finally, the bio-composites were characterized by physical, mechanical and morphological analyses to investigate the effect of chemical treatment. A schematic diagram of this work is shown in Fig. 1.

![Schematic diagram of bio-composites production from RH biomass and PLA](image1)

**Figure 1**: Schematic diagram of bio-composites production from RH biomass and PLA

2.2 Materials and Chemicals

Polylactic acid (PLA) grade 4032D, produced by Natureworks, has been procured from Seeplas Pty. Ltd. and required chemicals - sodium hydroxide (NaOH), hydrochloric acid (HCl) and 1-Ethyl-3-methylimidazolium acetate (EMIMAc) used were purchased from Science Supply Australia, and Sigma Aldrich. RH has been provided by Downes Rice Hulls Pty. Ltd.

2.3 Chemical Treatment of Rice Husk (RH)

Prior to chemical treatment, RH biomass was washed by deionized distilled water (DDW) and dried at 80°C in an electric oven until it reached a constant weight. The dried and cleaned RH biomass was then grinded using a Rockwell ring machine to convert into powder form. The average particle size of RH powder ranges from 75-700 µm. The processing of R-RHB is shown in Figure 2.

The chemical modification of RH biomass was conducted in a 1L reaction vessel under predetermined experimental parameters. Chemical modifications of RH biomass was performed by acid (1), alkali (2) and alkali-ionic liquid (3) reagents as shown in Table 1.

At the beginning of the chemical treatment, pre-modification of RH biomass was conducted by 0.1M HCl, followed by post treatment with NaOH and IL (EMIMAc). The post treatment of acid treated rice husk (ATRH) biomass was conducted in 1L reaction vessel by alkali and IL reagents as shown in the Table 1. Finally, untreated and treated RH biomass samples (TRHN4, TRHILN4) were dried at 60°C for 24 hours and analysed by FTIR to observe the chemical change.

![Grinding and processing of raw rice husk biomass](image2)

**Figure 2**: Grinding and processing of raw rice husk biomass
2.4 Fabrication of Bio-composites

Untreated and treated RH reinforced PLA bio-composites and specimens for mechanical testing were prepared by using the Haake rheomixer and compression moulding machine, respectively. For composites preparation, RH sample was initially mixed thoroughly with PLA pellets at 1/99, 3/97, 5/95, 7/93 and 9/91 wt% mixing ratios. About 60 g mixture of each composite was introduced into the Haake rheomixer according to the formulation given in Table 2. The composite preparations were carried out at 50rpm at 180°C for 15 minutes. The various specimens for physico-mechanical characterisation were particularly prepared for tensile, impact, hardness and water absorption tests. For each test and type of the composites, five specimens were tested and the average values were presented. The prepared composite specimens are shown in Table 2. The variation of the values for the five specimens tested was found to be within 5%. The fabrication and characterisation of bio-composites were conducted according to the reported work by Islam et. al. and his co-workers (Ang et al., 2012; M. Haque et al., 2010; Islam & Islam, 2011).

2.5 Characterization of Composites and RH

FT-IR spectra of both untreated and treated RH biomass by acid (1), alkali (2) and alkali-ionic liquid (3) reagents were recorded by using a Shimadzu FT-IR 81001 spectrophotometer in the wavenumber range of 800cm⁻¹ to 4,000cm⁻¹. An Instron 4467 Universal Testing Machine was used to measure tensile properties of composites according to ASTM D638-08 standard. For hardness measurement durometer (type D) was used according to standard ASTM D2240 standard. For impact strength measurement, notch impact tester machine was used according to ASTM D6118-08 standard. Cold water absorption test was conducted according to the ASTM D570-98 standard for 72 hours. Surface morphology of UTRH, TRH and composite’s fractured surface was analysed by FEI Quanta 200 SEM instrument in the RMIT Microscopy and Microanalysis Facility Laboratory at RMIT. The standard ASTM methods were used to determine the physico-mechanical properties of bio-composites according to the following equations:

\[
\text{Water absorption (\%)} = \frac{W_f - W_i}{W_i} \times 100 \quad (2.1)
\]

\[
\text{Impact Strength} = \frac{12.7eVY_i}{10W} \times 100 \quad (2.2)
\]

\[
\sigma_t = \frac{P}{A_t} \quad (2.3)
\]

\[
E_H = \frac{P}{A_{LL}} \quad (2.4)
\]

Table 1: Chemical modification of RH biomass by acid (1), alkali (2) and alkali-ionic liquid (3) reagents

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Treated Samples</th>
<th>Reagent &amp; Concentration</th>
<th>Temperature (°C)</th>
<th>RPM</th>
<th>Time (hrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>ATRH</td>
<td>HCl [0.1 M]</td>
<td>80</td>
<td>800</td>
<td>1</td>
</tr>
<tr>
<td>(2)</td>
<td>TRHN4</td>
<td>NaOH [4M]</td>
<td>80</td>
<td>800</td>
<td>4</td>
</tr>
<tr>
<td>(3)</td>
<td>TRHILN4</td>
<td>EMIMAc/NaOH [0.02M</td>
<td>4M</td>
<td>80</td>
<td>4</td>
</tr>
</tbody>
</table>

Note:
- ATRH: Acid treated rice husk
- TRHN4: Treated rice husk by 4M sodium hydroxide
- TRHN4: Treated rice husk by 4M sodium hydroxide and 0.02M ionic liquid (IL)
- IL: 1-ethyl-3-methylimidazolium acetate (EMIMAc)

Table 2: Formulation of untreated rice husk (UTRH) and treated rice husk (TRH) reinforced PLA bio-composites

<table>
<thead>
<tr>
<th>Filler ID</th>
<th>Matrix</th>
<th>Composite ID</th>
<th>Composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[a] UTRH</td>
<td>PLA</td>
<td>UTRH-01</td>
<td>UTRH 1% + PLA 99%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UTRH-02</td>
<td>UTRH 3% + PLA 97%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UTRH-03</td>
<td>UTRH 5% + PLA 95%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UTRH-04</td>
<td>UTRH 7% + PLA 93%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>UTRH-05</td>
<td>UTRH 9% + PLA 91%</td>
</tr>
<tr>
<td>[b] TRHN4</td>
<td>PLA</td>
<td>TRHN4-01</td>
<td>TRHN4 1% + PLA 99%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TRHN4-02</td>
<td>TRHN4 3% + PLA 97%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TRHN4-03</td>
<td>TRHN4 5% + PLA 95%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TRHN4-04</td>
<td>TRHN4 7% + PLA 93%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TRHN4-05</td>
<td>TRHN4 9% + PLA 91%</td>
</tr>
<tr>
<td>[c] TRHILN4</td>
<td>PLA</td>
<td>TRHILN4-01</td>
<td>TRHILN4 1% + PLA 99%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TRHILN4-02</td>
<td>TRHILN4 3% + PLA 97%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TRHILN4-03</td>
<td>TRHILN4 5% + PLA 95%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TRHILN4-04</td>
<td>TRHILN4 7% + PLA 93%</td>
</tr>
<tr>
<td></td>
<td></td>
<td>TRHILN4-05</td>
<td>TRHILN4 9% + PLA 91%</td>
</tr>
</tbody>
</table>
In equation (2.1), \( W_i \) and \( W_f \) are the specimen weight before and after the water absorption, respectively. In equation (2.2), \( E_{av} \) is the measured average energy from impact test and \( Y \) is the pendulum energy (Joule). \( W \) is the nominal width of specimen for impact test. In equations (2.3) and (2.4), \( \sigma_T \) is the tensile strength, \( F \) is the maximum load, \( E_M \) is the elasticity modulus, \( A \) is the area of tensile test specimen (width \( \times \) thickness), \( L \) is the original length of specimen and \( \Delta L \) is the length of the object changes.

The crystallinity of UTRH, TRHN4 and TRHILN4 samples were determined by the Bruker AXS D8 ADVANCE wide angle X-ray diffraction instrument using the following model equation (2.5) proposed by Segal and co-workers.

\[
\text{CrI}(\%) = \left( \frac{I_{002} - I_{am}}{I_{002}} \right) \times 100 \tag{2.5}
\]

Where, \( I_{002} \) is the maximum intensity of the (002) lattice diffraction peak and \( I_{am} \) is the intensity scattered by the amorphous phase of the sample. The diffraction peak for plane (002) is located at a diffraction angle around \( 2\theta = 22^\circ \) and the intensity scattered by the amorphous part is measured as the lowest intensity at a diffraction angle around \( 2\theta = 18^\circ \).

3. Results and Discussion

This section describes the results of various experimental analyses of fabricated bio-composites as shown in Table 2. The analyses are FT-IR, XRD, water absorption, hardness, impact strength, tensile properties and surface morphology.

3.1 Chemical Treatment of RH

Chemical modification significantly changed the physical structure and colour of R-RHB due to chemical reaction between hydroxyl groups exist in the cellulose at 2 and 6 positions and chemical reagents (alkali and IL). The chromophoric and auxochromic groups exist in RH biomass were broken due to chemical modification, which significantly changed the straw colour of R-RHB to light yellow as shown in Figure 3(c) and Figure 3(d). The raw and grinded rice husk biomass are shown in the Figure 3(a) and Figure 3(b) respectively and both are untreated. Grinded RH biomass was mainly used as a UTRH for bio-composites fabrication in this research.

There are three hydroxyl groups exist in a cellulose anhydroglucose unit. One is a primary hydroxyl group at C6 and the other two are secondary hydroxyl groups present at C2 and C3 (Kord, 2013). Although the primary hydroxyl group is more reactive than the secondary groups, the alkali treatment breaks the \(-\text{OH}\) group of carbon at 6 and carbon 2 positions during the reaction. This converts the two hydroxyl groups into \(-\text{ONa}/-\text{OIL}\) group which has been reported by many researchers (M. Haque et al., 2010; Hristov, Lach, & Grellmann, 2004). It may be due to steric effect as NaOH cannot form a bond with O atom at C3 position. The reaction between cellulose and sodium hydroxide is shown in Figure 4.
3.2 FTIR Analysis of Raw and Treated RH

The FT-IR spectra of UTRH, TRHN4 and TRHILN4 samples upon various modifications are shown in Figure 5, which explores the absorption band and region for various functional groups. The absorption band position and respective peak assignments are shown in Table 3. The absorption bands at 800 cm\(^{-1}\)-900 cm\(^{-1}\) region were observed for all samples due to the presence of C-O vibration (Alam, Arifuzzaman Khan, & Abdur Razzaque, 2009). The spectrum (a) of UTRH clearly shows the presence of the characteristic band of the -NO group in the region of 1,600 cm\(^{-1}\)-1,700 cm\(^{-1}\). In this spectrum the absorption band at the region near 1,700 cm\(^{-1}\) may be due to the carbonyl group of acetyl ester in cellulose and the carboxyl aldehyde in lignin (Hristov et al., 2004). This band is not apparent in the case of TRHN4 (b) and TRHILN4 (c). This means the chemical modification has significantly removed lignin from raw RH biomass. The broad absorption band with peaks located from 3300 cm\(^{-1}\) to 3,400 cm\(^{-1}\) is due to stretching of \(-\text{OH}\) groups and the other one near 2,900 cm\(^{-1}\) is related to the C-H stretching vibrations. The intensity of \(-\text{OH}\) group in TRHN4 and TRHILN4 has decreased due to conversion of \(-\text{OH}\) to \(-\text{ONa}\) and \(-\text{OIL}\).

Table 3: FT-IR spectral peak assignments of untreated (UTRH), alkali treated (TRHN4) and alkali-IL treated (TRHILN4) rice husk biomass.

<table>
<thead>
<tr>
<th>Band position (cm(^{-1}))</th>
<th>UTRH</th>
<th>TRHN4</th>
<th>TRHILN4</th>
<th>Band Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000-1100</td>
<td>1000-1100</td>
<td>1000-1100</td>
<td>C-O-C stretching vibration for amorphous and crystalline cellulose</td>
<td></td>
</tr>
<tr>
<td>1100-1300</td>
<td>1100-1300</td>
<td>1100-1300</td>
<td>C-O stretching vibration for cellulose or hemicellulose</td>
<td></td>
</tr>
<tr>
<td>1600-1700</td>
<td>1600-1700</td>
<td>1600-1700</td>
<td>C=C stretching for lignin and aromatic ring</td>
<td></td>
</tr>
<tr>
<td>2900-3000</td>
<td>2900-3000</td>
<td>2900-3000</td>
<td>C-H stretching vibration</td>
<td></td>
</tr>
<tr>
<td>3300-3400</td>
<td>3300-3400</td>
<td>3300-3400</td>
<td>-OH stretching vibration</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5: FT-IR spectrum of (a) untreated (UTRH), (b) alkali treated (TRHILN4), and (c) alkali-IL treated (TRHN4) rice husk samples

3.3 Crystallinity of untreated and treated RH samples

Crystallinity of UTRH, TRHN4 and TRHILN4 were measured by XRD analysis. From the XRD analysis it is found that, TRHILN4 has higher crystallinity than UTRH and TRHN4. On the other hand, TRHN4 has higher crystallinity than UTRH. The crystallinity of treated and untreated samples is shown in the following Figure 6.

R-RHB consists of amorphous and crystalline components. The amorphous components of RH are lignin, hemicellulose, silica and other extractives. On the other hand, the crystalline component of RH is cellulose. To remove these amorphous components from R-RHB chemical modification is extensively used (Battegazzore et al., 2014; Islam & Islam, 2015). Chemical medications remove amorphous components and separate cellulose fibres from raw biomass which also significantly increase the crystallinity of cellulose as well (Battegazzore et al., 2014). In this analysis it has been reported that, alkali-IL treatment increases the crystallinity of raw biomass 34.5 to 56.6, whereas alkali treatment increases 34.5 to 51.5. From this analysis it can also be concluded that, alkali-IL removes impurities from R-RHB than only alkali treatment. From the surface morphology of raw and treated samples it can be understood properly whether the cellulose is fibrillated with clean surface or not.
### 3.4 Surface morphology of untreated and treated RH samples

The surface morphology of treated and untreated rice husk samples was investigated by SEM analysis to identify the performance of chemical treatment. Chemical treatments subsequently remove white amorphous materials such as lignin, hemicellulose, silica and other organic extractives from R-RHB and increase the crystallinity of extracted micro-fibres. The white waxy layer on the raw or untreated rice husk biomass was indicated by red arrow and the extracted cellulose fibres are shown by the red circle in the following Figure 7. The white colour chunks are gradually reducing from UTRH by successive chemical treatments and these are very less in TRHILN4 (c) with compare to TRHN4 (b). From this observation it can be concluded that, TRHILN4 contains less impurities due to alkali-IL treatment and which would be greater crystallinity than TRHN4 and UTRH. XRD analysis strongly supports this result. In addition, the chemical modification is also produced micro-fibres separation from RH biomass which is crystalline in structure. The production of micro-fibres from R-RHB is significantly increasing due to chemical modification and this is clearly appearing in the Figure 7. Chemically treated RH samples contain less impurities and huge crystalline micro-fibrils which make crosslinking with polymer matrix during the fabrication of composites. The strong mechanical cross linking and bond formation between fillers and matrix significantly increase the physico-mechanical properties of composites (Islam & Islam, 2015). The physico-mechanical properties of UTRH-PLA, TRHN4-PLA and TRHILN4-PLA were discussed in the following description in order to investigate the performance of chemical modification.

![Figure 7: Surface morphology of untreated and treated RH samples: (a) UTRH, (b) TRHN4 and (c) TRHILN4](image)

### 3.5 Water Absorption

Cold water absorption test was performed for 24 hours and 72 hours durations at room temperature under normal atmospheric conditions. In the case of 72 hours absorption test, most of the bio-composites developed cracks and absorbed more water. The similar kind of findings have been reported in case of natural fibre reinforced polypropylene and polyethylene composites.
Due to high moisture absorption many cracks were apparent on the composite surface and original composite’s colour became fade (Figure 8). These cracks were clearly visible in the morphological profiles and the colour change was observed optically.

Cold water absorption behaviours of the composites as a function of filler concentration are shown in Figure 9(a) and Figure 9(b) for 24 hours and 72 hours, respectively. It is evident that, water absorption (%) increases with the increment of filler loading in composites for both absorption periods (24 and 72 hours). The water uptake tendency of all composites increases with increasing filler content and time duration. Water absorption significantly decreased the mechanical properties of composites by breaking the filler–matrix bonding and therefore surface cracking was observed. This phenomenon of water absorption proves that fabricated composites are 100 % biodegradable and eco-friendly. It has been reported that natural fibre reinforced polymer composites without compatibiliser shows remarkable water absorption due to the presence of micro voids in the fibre-matrix interfacial region which originates due to weak fibre-matrix interfacial adhesion (Islam & Islam, 2015; Thakur & Singha, 2010). Alkali-IL treated filler reinforced bio-composites (TRHILN4-PLA) were found to show comparatively less hydrophilic nature than their corresponding counterparts prepared from UTRH. This observation implies that the hydrophilic nature of RH has substantially reduced due to the introduction of hydrophobic alkyl chain in the cellulose upon treatment with alkali and IL.

![Figure 8: Water absorption properties of fabricated bio-composites: UTRH-PLA, TRHN4-PLA and TRHILN4-PLA](image)
3.6 Impact Strength and Hardness

Impact strength (IS) of a material provides information regarding the ability of the material to resist a sudden impact. The notched IS values of both untreated and treated RH-PLA composites at different filler loading are shown in Fig. 10 (a). The IS values of the composites decreased as the filler content increased. Higher IS values at lower RH content may be attributed to the capacity of the matrix to absorb more energy for crack initiation. Poor interfacial bonding between the filler and the matrix causes micro cracks to occur at the point of impact, which causes micro cracks to propagate easily in the composite. The IS values of the composites are found to follow this order TRHILN4-PLA > TRHN4-PLA > UTRH-PLA. A similar trend has been observed for coir fibre reinforced PP composites as reported by M. Haque et al., 2010 and M. M. Haque et al., 2012.

Hardness is the measure of resistance of a composite to localized deformation that depends on the distribution of the fibre into the matrix. The hardness properties of untreated and treated RH reinforced PLA bio-composites are shown in Fig. 10 (b). Incorporation of untreated and treated RH into the PLA matrix has reduced the flexibility of the matrix resulting in more rigid composites. The hardness values of the bio-composites are found to exhibit this order TRHILN4-PLA > TRHN4-PLA > UTRH-PLA. This is attributed to the improvement in the fibre-matrix interfacial adhesion and better dispersion of the fibre into the matrix, which led to an increase in the efficiency of stress transfer from the matrix to the fibre.
3.7. Tensile Properties

The tensile properties of fabricated biocomposites are also found to follow the same order i.e. TRHILN4-PLA > TRHN4-PLA > UTRH-PLA. Tensile strength and modulus of bio-composites are shown in Figure 11(a) and Figure 11(b), respectively. The high tensile strength values could be attributed to the cross linking between the filler and the matrix. In this case, the treated RH can build strong interfacial bond with PLA, which significantly increases tensile properties of the composite. The tensile modulus of fabricated biocomposite was found to increase with filler concentration, whereas the Alkali-IL treated filler reinforced composites TRHILN4-PLA shows high value of modulus. Alkali-IL treated RH reinforced bio-composites show high magnitude of tensile modulus due to the strong cross linking with matrix PLA. Chemically treated fillers are highly dispersed in the PLA matrix during the composites fabrication and significantly increases the mechanical properties (M. Haque et al., 2010; Islam & Islam, 2011). In this study IL and alkali were found to significantly reduce the hydrophilic nature of RH and increased the affinity to make strong bond with matrix PLA. IL, being more active than alkali, can readily remove lignin and gives more...
crystalline RH pulp. Due to high crystallinity, TRHILN4 treated PLA composite possesses high tensile properties. Untreated RH shows low tensile strength and modulus. This is probably due to the weak interfacial bond between PLA and RH. The other possible reason could be poor dispersion and the tendency of the filler to agglomerate in the matrix. Untreated RH surface not functionalized at all the UTRH-PLA bio-composites were found to have lower tensile properties than TRHILN4-PLA and TRHN4-PLA.

Figure 11: Variation of tensile strength (a) and tensile modulus (b) of untreated (UTRH-PLA), alkali treated (TRHN4-PLA) and Alkali-IL treated (TRHILN4-PLA) bio-composites.

3.8 SEM Analysis
SEM images of the fractured surface of the impact specimens as shown in Figure 12 (a, b, c). It is evident from Figure 12(a), that for the UTRH-PLA bio-composite possesses, fibre-matrix interfacial micro voids, indicating weak interfacial adhesion between PLA and RH fibrils. Besides, there are some signs of fibre agglomeration and micro hole, which results from preferential fibre-fibre interactions or impurities of UTRH. There is a big chunk of fibre agglomeration due to non-cellulosic components of UTRH appears in Figure 12(a) as indicated by red circle. However this type of agglomeration is absent in Figure 12(a) and Figure 12(b). On the other hand, for TRHN4-PLA and TRHILN4-PLA composites, the fibre-matrix interfacial voids were found to have significantly minimised as shown in the Figure 12(b) and Figure 12(c), respectively. Due to
the change in the property of RH biomass upon treatment with alkali, as well as adsorption of IL molecules onto the RH surface, the polarity gap between the fibre and the matrix has largely minimized, thus facilitating better dispersion of RH in the PLA matrix. As a result, the micro holes between the fibre and matrix has significantly minimized with fibre-matrix crosslinking as indicated by red arrow in the images. This is further corroborate the mechanical properties of the chemically treated RH reinforced composites with PLA. Similar investigations and results were reported in the case of chemically treated jute fibre, coir fibre and wood flour reinforced polymer composites (Adhikari et al., 2017; M. Haque et al., 2010; Islam & Islam, 2011).

**Figure 12:** SEM images of fractured surface of (a) untreated (UTRH + PLA), (b) alkali treated (TRHN4 + PLA) and (c) Alkali-IL treated (TRHILN4 + PLA) bio-composites.

4. Conclusions

From this study, it has been shown that RH biomass, a low cost annually renewable agricultural waste material, can be used for the fabrication of bio-composites for potential engineering applications. Here, the effects of surface modification of RH by alkali and IL, as well as the effect of fibre content on the mechanical properties of the treated and untreated RH reinforced PLA bio-composites have been presented. The study reveals that upon treatment with IL and alkali, the hydrophilic nature of RH can be significantly reduced as observed from water absorption behaviour of the fabricated composites. The reduced intensity of IR absorption band for the -OH group indicates that the hydrophilic nature of RH has significantly decreased upon chemical treatment. This is reflected also in the SEM images where fibre agglomerates and fibre pull-out traces in the TRHN4-PLA and TRHILN4-PLA composite were reduced compared to those of the UTRH-PLA bio-composites. It is important to note here that the tensile strength, impact strength, and hardness values of TRHN4-PLA and TRHILN4-PLA were found to be higher than the corresponding values of UTRH-PLA. This suggested that upon treatment with IL and alkali, better dispersion of RH in the PLA matrix could be achieved. At the same time, it can be emphasized that better interfacial adhesion as well as reduction of micro voids at the fibre-matrix interface has occurred upon chemical treatment of the RH, resulting in better mechanical properties and lower water absorption uptake capacity of TRHN4-PLA and TRHILN4-PLA bio-composites.

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