INTRODUCTION

Cellulose fibers in the form of microfibrillated cellulose (MFC) or cellulose nanocrystal (CNC) have been studied primarily for application as fillers or reinforcement in composite materials. As “green” issue has become the main concern of many scientists, numerous applications of cellulose fibers in polymer composites such as polypropylene [1], poly(lactic acid) [2,3], poly(vinyl alcohol) [4], polyethylene [5,6], are focusing to produce “green material” with superior properties.

The main obstacle of incorporating cellulose fibers into polymer matrix is incompatibility between those two substances, which may decrease some of composite properties. Cellulose fibers are hydrophilic fibers, meanwhile some of polymer matrices show hydrophobic behavior. Some efforts had been done to overcome this barrier, such as using coupling agent or modifying cellulose fibers through chemical reaction.

Cellulose derivatives with remarkable, distinctive properties superior to the original cellulose achieved by a variety of chemical modifications, such as esterification of the cellulose with various substances: plant triglycerides [7], long chain fatty acids [8], organic acids [9] or more reactive anhydrides [10,11], which are proven to improve the cellulose hydrophobicity.

In 2006, Isogai’s group in University of Tokyo has developed a new method to prepare completely individualized cellulose nanofibers 3-4 nm width and a few microns length from wood cellulose fibers by 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO)-mediated oxidation under moderate aqueous condition [12]. The advantage of TEMPO-mediated oxidation on cellulose fibers is that the original fibrous morphology does not change even after oxidation with sufficient amount of reagents [13,14].

Oxidation of cellulose followed by incorporation with other functionalities is also reported [15-17]. Among these, periodate-mediated oxidation opens wider opportunity to manipulate cellulose. This approach provides a facile and significant strategy as it oxidatively cleaves the C-2 and C-3 glycol bond of the glucose ring to C-2/C-3 dialdehyde product, which is a more reactive intermediate for further derivatization [16,18]. Sirvio et al. [15], Rinaudo [19] and Larsson et al. [20] successfully prepared dialdehyde cellulose adopting this method and further improvement was achieved by Alam et al. [21] in salt-induced acceleration for this process. Several materials derived from this intermediate bearing distinctive properties were successfully afforded as exemplified by highly ductile fibers prepared by subsequent reduction of the aldehyde groups by sodium borohydride [20].

In present work, we present modification of cellulose fibers (CF) isolated from oil palm empty fruit bunch (OPEFB) by regioselective oxidation using sodium metaperiodate...
and utilized it as reinforcement in poly(lactic acid) based composite.

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**EXPERIMENTAL**

Oil palm empty fruit bunch (OPEFB) from Java Island plantation was used as the source of cellulose for chemical treatment. Chemical for cellulose extraction: sodium chlorite 25 % solution, acetic acid glacial 100 %, potassium hydroxide. Chemical for oxidation: sodium chlorite (NaCl), sodium metaperiodate (NaIO₄) and ethylene glycol. Poly(lactic acid) (PLA) semicrystalline, trade name NatureWorks™ 3001D was supplied by Cargill Dow LLC (Minnesota, USA). Glycerol triacetate (Merck) was used as plasticizer for PLA. All chemicals were used as received.

**Isolation of cellulose:** The 40-60 mesh oil palm empty fruit bunch biomass was subjected to a delignification process. As much as 6 g (dry basis) of air-dried OPEFB was suspended in 90 mL distilled water, then 9.6 mL sodium chlorite 25 % solution and 0.48 mL acetic acid glacial were added. The delignification process performed in waterbath at 70 °C for 1 h. After 1 h process, 9.6 mL sodium chlorite 25 % solution and 0.48 mL glacial acetic acid were again added into Erlenmeyer flask and the system was heated at 70 °C for another 1 h. This process was repeated 3 times. At the end of delignification process, the residue was filtered and washed with an excess of cold distilled water and acetone to neutrality. This residue (holocellulose) was then subsequently processed using potassium hydroxide 4 % (w/v) in the water bath at 70 °C for 2 h. The white residue, i.e. the resulting cellulose, was then washed until free from excess KOH and stored at -10 °C. The cellulose was obtained in 35 wt % yield calculated from the original OPEFB biomass in dry basis.

**Preparation of dialdehyde cellulose fibers by oxidation reaction:** Sodium chloride (1 M in overall solution) and NaIO₄ (1.0 mol equivalent per mole of anhydroglucose unit in the cellulose) was added to the water suspension of the cellulose fibre (fibers to water ratio of 1 g:67 mL). The beaker was completely covered with aluminium foil to avoid undesired side reaction. The mixture was stirred at 150 rpm for the desired reaction time (3, 4, 5, or 6 h) at room temperature. On the completion, ethylene glycol was added to the reaction mixture to quench the oxidation and the resulting oxidized cellulose fibers was then washed with distilled water and filtered until free from excess liquid. The oxidized cellulose fibers were then labelled according to the reaction condition, for example, S13 means the oxidation is performed using 100 mol % of NaIO₄ (1.0 eq.) for 3 h.

**Preparation of poly(lactic acid) composite:** For composite preparation, oxidized cellulose fibers in acetone were kept in a sealed container. The solid content of cellulose fibers in acetone was determined and subjected to solvent exchange process with dichloromethane. Then it was ready to be suspended gradually in dissolved PLA. As much as 1 g oxidized cellulose fibers (OCF) was added into dissolved PLA (5 g) and glycerol triacetate (1 mL) and the mixture was stirred until homogeneity for 10 min at the speed of 700 rpm. The OCF-PLA-dichloromethane mixture was spreaded on tray and the solvent was evaporated at room temperature for 12 h followed by oven drying at 60 °C for 24 h providing a sheet.

**Characterization methods:** The Perkin Elmer, Spectrum Two FTIR spectroscopy was used to analyze chemical structure of the oxidized cellulose fibers. The analysis was operated by an attenuated total reflection (ATR) principles, which measured the changes that occur in a totally internally reflected infrared beam when the beam came into contact with the sample. The spectral resolution was 4 cm⁻¹ and the scanning range was from 4000 to 400 cm⁻¹.

DSC measurements were performed on a DSC4000 (Perkin Elmer) in the temperature ranging from 0-200 °C using approximately 5.0 mg of poly(lactic acid)-glycerol triacetate (PLA-GTA). The samples were tested at non-isothermal conditions at the heating rate of 5 °C/min. While the DSC measurement of PLA-oxidized cellulose fibers composites was conducted in the temperature range of 0-200 °C using approximately 5 mg of samples at the same heating and cooling rates of 5 °C/min in two scans: heating and cooling. The thermal properties such as glass transition temperature (Tg), cold crystallization temperature (Tcc), melt temperature (Tm) and enthalpy of melting (ΔHm) were determined from the heating scan and the melt crystallization temperature (Tc) was determined from the cooling scan of the samples. The percentage of crystallinity of each sample was calculated by following equation:

\[
\text{Crystallinity (\%)} = \frac{(\Delta H_{m} - \Delta H_{cc}) \times 100}{\Delta H_{m}^o}
\]

In this equation, the heats of melting (ΔHm) and cold crystallization (ΔHcc) are in terms of J/g. The term ΔHm° is a reference value and represents the heat of melting if the polymer is 100 % crystalline. The theoretically melting enthalpy of 100 % crystalline PLA was taken to be ΔHm° = 93 J/g [22].

Tensile properties of the composite were examined based on ASTM D-882-75b standard test methods for tensile properties of thin plastic sheeting. Five specimens of composites were analyzed using a universal testing machine “Shimadzu” at a cross-head speed of 5 mm/min and a gauge length of 20 mm.

**RESULTS AND DISCUSSION**

In the industry, PLA can be processed in a way similar to polypropylene. However, brittleness of PLA limit the wider applications. Some plasticizer have been applied to improve PLA elongation. However, the addition of plasticizer gave negative influence on mechanical properties. Oksman et al. [23] used glycerol triacetate as plasticizer in compression moulded Flax/PLA composite and the result was glycerol triacetate did not improve the impact properties. Another plasticizer agent, which was poly(ethylene glycol)-PEG, also did not improve the tensile properties of the composites. Okubo [24] experimented with compression moulded bamboo fiber-reinforced PLA, adding micro-fibrillated cellulose (MFC) as an enhancer for the bending characteristics. Three point bending strength was clearly improved. They also found that tangled MFC fibers prevented micro cracks along the interface between bamboo fiber and matrix. In this study, we used glycerol triacetate (GTA) as plasticizer and oxidized cellulose fiber in PLA matrix to produce composite.
Chemical structure of oxidized cellulose: Periodate oxidation of cellulose, initially studied by Fan et al. [25], is a selective oxidation process that converts the 1,2-glycol groups of the glucose residues into two aldehyde groups (Fig. 1). Partial oxidation of cellulose by periodate can lead to the selective cleavage at C-2 and C-3 vicinal hydroxyl groups within glucose to yield dialdehyde units. This process can be carried out at room temperature or slightly elevated temperature [26].

![Chemical structure of oxidized cellulose](image)

Fig. 1. Transformation of cellulose to become dialdehyde cellulose (DAC)

According to Vicini et al. [26], the oxidation leads to the presence of two characteristics bands of dialdehyde cellulose (DAC) in the 1720 and 880 cm$^{-1}$ regions; they increase from a small shoulder to a distinct band increasing the oxidation levels. The broad band at 880 cm$^{-1}$ can be assigned to the hemiacetal and hydrated form of the dialdehyde cellulose; the sharp band at 1740 cm$^{-1}$ is characteristic of carbonyl groups stretching. In addition, Fan et al. [25] reported that the aldehyde IR absorption peak in periodate oxidized cotton is sited in the region 1732–1734 cm$^{-1}$ and may be attributed to the C=O stretching vibration in the free aldehyde.

![FTIR spectra of oxidized cellulose by 3 h reaction (S13), 4 h reaction (S14), 5 h reaction (S15) and 6 h reaction (S16)](image)

Fig. 2. FTIR spectra of oxidized cellulose fibers by 3 h reaction (S13), 4 h reaction (S14), 5 h reaction (S15) and 6 h reaction (S16)

<table>
<thead>
<tr>
<th>Wave-number (cm$^{-1}$)</th>
<th>Absorbance</th>
<th>Wave-number (cm$^{-1}$)</th>
<th>Absorbance</th>
<th>Wave-number (cm$^{-1}$)</th>
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<th>Wave-number (cm$^{-1}$)</th>
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</tr>
</thead>
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<tr>
<td>559</td>
<td>0.09</td>
<td>558</td>
<td>0.10</td>
<td>556</td>
<td>0.11</td>
<td>672</td>
<td>0.03</td>
</tr>
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<td>1020</td>
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<td>1018</td>
<td>0.13</td>
<td>1018</td>
<td>0.16</td>
<td>1015</td>
<td>0.15</td>
</tr>
<tr>
<td>1316</td>
<td>0.03</td>
<td>1315</td>
<td>0.03</td>
<td>1315</td>
<td>0.04</td>
<td>1314</td>
<td>0.01</td>
</tr>
<tr>
<td>1514</td>
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<td>–</td>
</tr>
<tr>
<td>1636</td>
<td>0.01</td>
<td>1628</td>
<td>0.02</td>
<td>1633</td>
<td>0.02</td>
<td>1634</td>
<td>0.01</td>
</tr>
<tr>
<td>2890</td>
<td>0.02</td>
<td>2891</td>
<td>0.02</td>
<td>2890</td>
<td>0.03</td>
<td>2891</td>
<td>0.01</td>
</tr>
<tr>
<td>3329</td>
<td>0.03</td>
<td>3329</td>
<td>0.03</td>
<td>3335</td>
<td>0.04</td>
<td>3318</td>
<td>0.01</td>
</tr>
</tbody>
</table>

**TABLE-1**

**BAND CHARACTERISTICS OF FTIR SPECTRA**

According to Vicini et al. [26], the oxidation leads to the presence of two characteristics bands of dialdehyde cellulose (DAC) in the 1720 and 880 cm$^{-1}$ regions; they increase from a small shoulder to a distinct band increasing the oxidation levels. The broad band at 880 cm$^{-1}$ can be assigned to the hemiacetal and hydrated form of the dialdehyde cellulose; the sharp band at 1740 cm$^{-1}$ is characteristic of carbonyl groups stretching. In addition, Fan et al. [25] reported that the aldehyde IR absorption peak in periodate oxidized cotton is sited in the region 1732–1734 cm$^{-1}$ and may be attributed to the C=O stretching vibration in the free aldehyde.

<table>
<thead>
<tr>
<th>Assignment</th>
<th>S13</th>
<th>S14</th>
<th>S15</th>
<th>S16</th>
</tr>
</thead>
<tbody>
<tr>
<td>γCO at C-3, γ*C-C</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>δCOH out of plane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γCH in cellulose</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lignin aromatic Skeleton vibration</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CO (carbonyl bond)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γCH strech off CO (aldehyde group)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Streching (γ) OH (hydrogen bond)</td>
<td></td>
<td></td>
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<td></td>
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</tbody>
</table>
peaks appear during the transition period [28]. Poly(lactic acid) is a slower-crystallizing material. The fastest rates of crystallization for pure PLA are found in the temperature ranges 110-130 °C, which yield spherulitic crystallization morphology [29].

As seen in Fig. 3, DSC thermogram of neat PLA 3001D showed three apparent transitions upon heating, which included PLA glass transition temperature ($T_g$) at 60 °C, cold crystallization temperature ($T_{cc}$) at 110 °C and melt temperature ($T_m$) at 167 °C [30]. While the DSC thermogram of PLA-GTA (Fig. 4) showed that glass transition and cold crystallization peaks were not emerged, indicating that PLA in this study was fully crystallized due to the addition of plasticizer (GTA) and heating procedure during composite production. The melting peak of PLA-GTA was shifted to lower temperature (153 °C), represented that PLA started to melt sooner than PLA. This information, will be an advantage in processing PLA-oxidized cellulose fiber composite with extruder or laboplastomill. Lower melting point indicates that less energy is required for composite processing that leads to the efficient composite cost production.

The similar pattern was appeared on DSC thermogram of PLA + GTA and its composites (Fig. 5). The heating scan, showed glass transition temperature ($T_g$) and melting temperature ($T_m$), without the peak of cold crystallization. Glass transition temperature ($T_g$) is influenced by amorphous structure of the sample and/or macromolecular translation motion relative to adjacent molecules. The size of the glass transition is linearly proportional to the amount of amorphous structure in the sample [31]. Amorphous and semi-crystalline polymers undergo a phase change from a glassy to rubbery stage at a glass transition temperature ($T_g$). At $T_g$, the segmental mobility of molecular chains increases and a polymer is more elastic and flexible [32].

Glass transition temperature ($T_g$) of PLA + GTA + S13 and PLA + GTA + S14 was similar to $T_g$ of PLA 3001D (60 °C), which were 59.58 and 58.02 °C, respectively. This phenomenon explained that the mobility of molecular chains in S13, S14 and PLA increased at the similar temperature, and hence altered their phase from glassy to rubbery stage. Afterward, the DSC thermogram of PLA + GTA + S15 and PLA + GTA + S16 showed that the composite’s glass transition temperature was slightly higher than that of PLA. Therefore, when oxidized cellulose fibers (oxidized for 5 or 6 h) were introduced into PLA, the composites need higher temperature to change from the glassy stage to rubbery stage (Table-2).

For polymers, the glass transition is typically broader and becomes hard to measure as the crystalline content increases [31]. The temperature of glass transition ($T_g$) can increase or decrease with the degree of crystallinity depending on the relative density of the amorphous and crystalline states. Most often the more orderly crystalline state has the higher density at $T_g$ and the noncrystalline molecular chains are constrained by being anchored to the immobile crystallites and $T_g$ increases [33].
### TABLE-2
EFFECT OF OXIDIZING TIME ON PLA-CELLULOSE COMPOSITE CRYSTALLIZATION

<table>
<thead>
<tr>
<th>Samples</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J g$^{-1}$)</th>
<th>$X_c$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PLA + GTA</td>
<td>–</td>
<td>153.48</td>
<td>31.624</td>
<td>34.00</td>
</tr>
<tr>
<td>PLA + GTA + S13</td>
<td>59.58</td>
<td>145.29</td>
<td>40.073</td>
<td>43.09</td>
</tr>
<tr>
<td>PLA + GTA + S14</td>
<td>58.02</td>
<td>144.88</td>
<td>39.015</td>
<td>41.95</td>
</tr>
<tr>
<td>PLA + GTA + S15</td>
<td>74.39</td>
<td>143.37</td>
<td>51.209</td>
<td>55.06</td>
</tr>
<tr>
<td>PLA + GTA + S16</td>
<td>69.19</td>
<td>141.38</td>
<td>57.123</td>
<td>61.42</td>
</tr>
</tbody>
</table>

In this study, cold crystallization peak was not appeared in DSC curves of all composites, indicating that PLA was fully crystallized due to the addition of cellulose fibers and heating procedure during composite production. Therefore to calculate composite crystallinity, the melting enthalpy of composite ($\Delta H_m$) was divided by the melting enthalpy of 100% crystalline PLA (93 J/g). The addition of oxidized cellulose fibers into PLA could increase PLA crystallinity. Cellulose fibers which oxidized for 3 or 4 h produced similar composite crystallinity, 43.09 and 41.95 %, respectively. Moreover, cellulose fibers which oxidized for 5 or 6 h produced higher composite crystallinity, 55.06 and 61.42 %, respectively.

The oxidation modifies the cellulose characterization, which become more stiff and brittle. By increasing the concentration of the oxidizing agent, degree of polymerization decreases faster; therefore the methaperiodate involves a strong depolymerization of cellulose [26]. The depolymerization reaction of cellulose could disturb amorphous part of cellulose and therefore cellulose fibers become more crystalline, afterward increased the composite crystallinity.

From the DSC thermogram at cooling scan of PLA + GTA + S13 or S14 or S15 or S16 (Fig. 6), melt crystallization peaks appeared at 110.15, 104.48, 98.22, 93.90 °C, respectively. The cooling phase after melting stage, produced crystalline in all composite in this study. The higher the composite crystallinity, the lower the melt crystallization temperature.

**Composite tensile properties:** Representative of stress-strain curves for the composite and pure PLA are shown in Fig. 7. The addition of cellulose which were oxidized for 5 h and 6 h (S15 and S16) turned PLA composite more brittle as compared to the pure PLA as shown by the considerable decrease in the strain to failure of the composites. The strain to failure decreased from 13.5 % for the pure PLA to 9.4 % for the PLA + S15 composite and 5.6 % for the PLA+S16 composite. Meanwhile the addition of cellulose which was oxidized for 3 h and 4 h (S13 and S14) did not give significant influence to the PLA strain.

The strain to failure of the PLA + S13 and PLA S14 was higher than that of the PLA + S15 and PLA + S16, implying greater toughness. Moreover, the tensile strength of PLA + S14 (Fig. 8) was the highest among those of other composites in this study. This superior mechanical properties were probably as a result of the more compact composite structure, so that the stress could be transferred equally to all composite element.

Bulota et al. [34] used Raman spectroscopy to investigate deformation mechanism of TEMPO-oxidizedfibrillated celu-
lose (TOFC)-reinforced composite, finding that stress transfer became dominated by the network mechanics at 30 wt % loading of TOFC.

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