EFFECT OF ECO-DEGRADANT ON PROPERTIES OF LOW DENSITY POLYETHYLENE/CORN STALK ECO-COMPOSITES

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Abstract
The eco-composites were prepared from corn stalk (CS) and low density polyethylene (LDPE) using Brabender internal mixer. An eco-degradant was used as degradable additive in LDPE/CS eco-composites. This study was focused on the effect of filler loading and eco-degradant on tensile, thermal, morphological and water absorption properties of LDPE/CS eco-composites. The incorporation of CS deteriorated the tensile strength and elongation at break of LDPE/CS eco-composites, but increased the Young’s modulus of eco-composites. The water absorption of LDPE/CS eco-composites also increased with increases of CS content. However, the addition of CS has contributed to increase of the crystallinity of LDPE matrix which due to nucleating effect of filler. The addition of eco-degradant has increased the tensile strength and elongation at break in average of 17.4% and 78.6%, respectively. However, the Young’s modulus was decreased. The present of eco-degradant also improved the water resistivity and crystallinity of eco-composites. The increase of crystallinity in LDPE/CS eco-composites causes the increase in melting temperature. The filler dispersion and filler-matrix adhesion of LDPE/CS eco-composites were improved due to addition of eco-degradant which evidenced by scanning electron microscope.

Keywords: Corn stalk, Low density polyethylene, Eco-degradant, Eco-composites.

1. Introduction
Corn or called as Maize (Zea mays) is globally cultivated crops. Corn stover (containing corn leaves and stalk) is the most abundant agricultural residue [1-2].
Nomenclatures

\begin{align*}
M_t & \quad \text{Percentage of water absorption} \\
W_d & \quad \text{Dried weight} \\
W_{f/LDPE} & \quad \text{Weight fraction of LDPE matrix.} \\
W_n & \quad \text{Weight after immersion} \\
X_c & \quad \text{Degree of crystallinity of composites} \\
X_{LDPE} & \quad \text{Crystallinity of LDPE matrix}
\end{align*}

Greek Symbols

\begin{align*}
\Delta H_f & \quad \text{Heat fusion of the composites} \\
\Delta H_f^0 & \quad \text{Heat of fusion for 100\% crystalline LDPE}
\end{align*}

Abbreviations

\begin{align*}
\text{CS} & \quad \text{Corn Stalk} \\
\text{LDPE} & \quad \text{Low Density Polyethylene} \\
\text{php} & \quad \text{Part per Hundred Polymer}
\end{align*}

Glassner et al. [3] estimated that the availability of corn stover is about 200 million dry tonnes per year. This means the corn waste is readily abundant and widely available. Corn stalk (CS) is part of corn stover and it mainly consists of cellulose, hemicellulose and lignin [4]. Therefore, the CS has potential use as natural filler in production eco-composites. The incorporation of CS as filler given many advantages in plastic materials, such cost reduction and it provides certainly of biodegradability. Moreover, the utilization of CS reduced the waste material in corn field. In present, the eco-composites made from agriculture waste materials and thermoplastic (either, biodegradable plastic or conventional plastic) have great interest among the industries and academic researchers due to the ecological concerns and legislations [5-8]. There are many benefits using agricultural waste in producing eco-composites, since it is low cost, readily abundant, widely available and sustainable [7-11]. The eco-composites have wide range of applications from household products to automotive parts. For examples, tableware [8], packaging tray [9, 12], and car panelling [13].

Currently, the development of CS filled low density polyethylene (LDPE) eco-composites has been underway and this material is suitable for short life span applications, such as eco-friendly utensil and packaging product. However, the eco-composites using LDPE as matrix only can be partially biodegrade, it is because of LDPE is a non-biodegradable plastic. To overcome this issue, a degradant additive called eco-degradant can be introduced to LDPE/CS eco-composites to have better biodegradability. Eco-degradant is a plastic master batch essentially incorporated with P-life degradable additive which provided biodegradability to plastic materials [14]. In addition, the P-life additive is formulated compound which containing transition metal (as pro-oxidant), metal salt of fatty acid and lubricant. The plastic materials containing eco-degradant would progressively degrade to lower molecular weight once they exposed to natural environment after their service lifetime. Recently, some literature studies found the eco-degradant was used in recycled polyethylene/chitosan [14] and high density polyethylene/alpinia galangal [15] eco-composites. However, the research study on addition of eco-degradant on LDPE/CS eco-composites was not found.
This research was focused on the effect of filler loading and addition of eco-degradant on tensile, thermal and water absorption properties of LDPE/CS eco-composites.

2. Experimental

2.1. Materials

Low density polyethylene (grade LDF200YZ, density 0.922 g/cm³) used in this research was supplied Titan Chemical Sdn Bhd. The eco-degradant masterbatch (type PD 04) was supplied by Behn Meyer Polymer Sdn. Bhd. The eco-degradant consists 3% of eco-degradant PD 04, 77% of high density polyethylene, and 20% of LDPE.

2.2. Preparation of corn stalk

The CS waste was collected from corn plantation located at Kodiang (Kedah, Malaysia). First, the collected CS was dried at 80°C for 24 hours at circulated air oven. Then, the dried CS was crushed and ground into fine powder using miniature grinder. The fine CS powder was sieved to obtain in average particle size of 30 μm (measured using Malvern Particle Size Analyzer Instrument Mastersizer 2000).

2.3. Mixing and moulding procedures

The LDPE/CS eco-composites with and without eco-degradant were prepared using Brabender Plastograph mixer Model EC PLUS at 160°C and rotor speed of 50 rpm. The formulation of LDPE/CS eco-composites was listed in Table 1. The amount of eco-degradant used in this experimental was referred to Azieyanti and Salmah [14].

<table>
<thead>
<tr>
<th>Materials</th>
<th>LDPE (php)</th>
<th>CS (php)</th>
<th>Eco-degradant (php)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDPE/CS eco-composites</td>
<td></td>
<td></td>
<td>-</td>
</tr>
<tr>
<td>(without eco-degradant)</td>
<td>100</td>
<td>0, 10, 20, 30, 40</td>
<td>-</td>
</tr>
<tr>
<td>LDPE/CS eco-composites</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(with eco-degradant)</td>
<td>100</td>
<td>10, 20, 30, 40</td>
<td>3*</td>
</tr>
</tbody>
</table>

*3 php based on weight of LDPE.

The mixing process of LDPE/CS eco-composites as following: i) Pre-mixing of LDPE and eco-degradant pellets and transferred into compounding chamber for 2 minutes until it completely melted; ii) added the CS powder into melted LDPE and mixed for 6 minutes. The total mixing time involved was 8 minutes. All the LDPE/CS compounds was compressed into 1 mm thickness sheet using
compression moulding machine (model GT 714A). The compression procedure started with four minutes for the preheating at 160°C then 1 minute for compressing and 5 minutes cooling under pressure of 9.81 MPa. The LDPE/CS eco-composite sheets were cut into tensile bar using dumbbell cutter with dimension following to ASTM D638 type IV [16].

2.4. Testing and characterization

Test testing on LDPE/CS eco-composites was carried out using an Instron universal testing machine model 5569 according to ASTM D 638 [16]. A cross head speed of 30 mm/min at was selected and the testing condition at 23±2°C. For formulated eco-composites, five identical specimens have been measured and average values of tensile strength, elongation at break and Young’s modulus were obtained.

The water absorption of LDPE/CS eco-composites was measured regarding to ASTM D570 [17]. The specimens were prepared with dimension of 25 mm x 20 mm x 1 mm. All specimens were dried at 80°C for 24 hours. Then, the specimens immersed in distilled water at room temperature and water absorption was measured by weighting the specimens at regular intervals with Mettler balance; model AX 200, Shimadzu (Japan, precision of ± 1 mg). The percentage of water absorption, \( M_t \), was calculated by the formula below: Where \( W_d \) and \( W_n \) are original dried weight and weight after immersion, respectively.

\[
M_t = \frac{W_n - W_d}{W_d} \times 100
\]

Differential Scanning Calorimetry (DSC) analysis was carried out using DSC Q10, TA Instrument. A specimen (weight of 7 ± 2 mg) was placed in close aluminium pan and heated from 30°C to 270°C with a heating rate of 10°C/min under nitrogen atmosphere. The nitrogen gas flow rate was 50 ml/min. The degree of crystallinity of composites (\( X_c \)) can be calculated from DSC data by using the following equation 2. Where \( \Delta H_f \) was the heat fusion of the LDPE composites, and \( \Delta H_f^0 \) was the heat of fusion for 100% crystalline LDPE (\( \Delta H_f^0 = 285 \text{ J/g} \)).

\[
X_c = \left( \frac{\Delta H_f}{\Delta H_f^0} \right) \times 100
\]

The crystallinity of LDPE matrix (\( X_{LDPE} \)) was calculated using following equation:

\[
X_{LDPE} = \frac{X_c}{W_{LDPE}}
\]

where \( W_{LDPE} \) is the weight fraction of LDPE matrix.

The tensile fracture surface of specimens was examined for morphological study by using a scanning electron microscopy (SEM, model JOEL, JSM-6460LA). The specimens were mounted on aluminium stubs and sputter-coated with a thin layer of palladium for conductive purpose. The SEM analysis performed under an accelerating voltage of 5kV.

3. Results and Discussion

3.1. Tensile properties

The tensile strength of LDPE/CS eco-composites with and without eco-degradant are shown in Fig. 1. The increases of CS loading decreased the tensile strength of
both eco-composites. This is because the CS was particulate filler and low aspect ratio. Thus, the ability of particles filler to carrying stress is poor. In addition, the incorporation of particulate filler usually acts as stress concentrator in composites and it initially failure the composites when stress was applied. The presence of filler agglomeration also increased the stress concentration effect on composites and assigned to the decreases of tensile strength. The poor interfacial adhesion between hydrophilic filler and hydrophobic matrix also a critical reason caused the poor stress transfer at the interface region. Hence, the tensile strength of LDPE/CS eco-composites reduced at higher CS loading. Many researchers also found the addition of more particulate natural decreased the tensile strength of composites [7-9, 18-20]. In contrast, the incorporation of eco-degradant improved the tensile strength of LDPE/CS eco-composites.

As mentioned before, the eco-degradant masterbatch contains metal salt of fatty acid and lubricant. The presence of lubricant might promote the fusion process between LDPE and CS, which can improved the filler dispersion and further increased the tensile strength of composites. Chun et al. [7] also reported that the present of fatty acid will promote the dispersion of natural filler and further improve the tensile strength of composites. In addition, the present of metal salt fatty acid will attached on the filler surface, and naturally provided the filler surface organophilic properties. For this reason, the filler-matrix adhesion was improved and it contributed to improvement of tensile strength. Mustapha et al. [15] also reported that the addition of eco-degradant improved the dispersion of alpinia galangal filler and increased the tensile strength of HDPE eco-composites.

Figure 1 illustrates the elongation at break of LDPE/CS eco-composites with and without eco-degradant. The elongation at break of LDPE/CS eco-composites decreased with increasing of CS loading. The CS is rigid particulate filler and it have undergoes less plastic deformation. Thus, the addition of CS decreased the
ductility of LDPE matrix. Moreover, the presence of filler agglomeration will cause the premature failure of composites at lower elongation at break [21]. Therefore, the presence of filler agglomeration decreased the flexibility of LDPE matrix. The similar phenomenon also reported by other researchers [7, 9, 12]. On the other hand, the LDPE/CS eco-composites with eco-degradant exhibited a higher elongation at break compared to LDPE/CS eco-composites. This is because the lubricant from eco-degradant improved the flexibility of LDPE matrix. Furthermore, this might due to the addition of eco-degradant enhanced the process ability and improve the filler dispersion in composites. Hence, the filler agglomeration reduced and it cause the elongation at break increased. Some researchers also found that the addition of lubricant has positive effect of elongation at break of composites containing natural filler [22-23].

![Fig. 2. The elongation at break of LDPE/CS eco-composites with and without eco-degradant.](image)

The Young’s modulus of LDPE/CS eco-composites with and without eco-degradant were displayed in Fig. 3. The result indicated the Young’s modulus of both eco-composites increased at higher CS loading. The incorporation of CS increased the relative stiffness of LDPE/CS eco-composites. The increase of Young’s modulus is related to few factors, such as amount of filler used, the orientation of filler, filler-matrix adhesion and the ratio filler to matrix [24]. Usually, the modulus of filler is higher than matrix. As results, the addition of more CS will increase the stiffness of LDPE/CS eco-composites. In addition, the presence of CS also cause the flexibility of polymer chain in LDPE matrix reduced. This also might contribute to the stiffness of LDPE/CS eco-composites. However, the incorporation of eco-degradant decreased the Young’s modulus of eco-composites due to the lubricant action from eco-degradant. Suryadiansyah et al. applied a fatty acid amine in polypropylene/ waste paper composites and they also found the lubricating effect of additive reduced the modulus of the composites [22].
3.2. Morphological properties

Figure 4 shows the SEM micrograph of CS. The CS used in this experiment was irregular in shape and particle form. The SEM micrograph on tensile fracture surface of LDPE/CS eco-composites without eco-degradant (at 20 and 40 php filler loading) were illustrated in Figs. 5(a) and (b). The SEM micrographs found a detached CS particle on LDPE/CS eco-composites. This evidenced the poor adhesion between CS and LDPE matrix. From Fig. 5(b) showed that the filler agglomeration found in LDPE/CS eco-composites at 40 php of filler loading. This indicated the CS form agglomeration at higher filler loading.
Fig. 5. SEM micrographs of tensile fracture surface of LDPE/CS without eco-degradant at (a) 20 php and (b) 40 php of filler loading.

Figures 6(a) and (b) show the SEM micrograph on tensile fracture surface on LDPE/CS eco-composites with eco-degradant at 20 and 40 php of filler loading. It can be seen that better filler dispersion found in LDPE/CS eco-composites with eco-degradant. The CS particles also embedded in LDPE matrix. This indicated that the adhesion between CS and LDPE matrix improved after presence of eco-degradant. The SEM micrograph of LDPE/CS with eco-composites with eco-degradant also show ductile fracture surface, which evidenced the addition of eco-degradant improved the ductility of LDPE/CS eco-composites.

Fig. 6. SEM micrographs of tensile fracture surface of LDPE/CS with eco-degradant at (a) 20 php and (b) 40 php of filler loading.

3.3 Water absorption

Figure 7 exhibits the water absorption against time curves of neat LDPE, LDPE/CS eco-composites with and without eco-degradant. Figure 8 shows the equilibrium of water absorption of LDPE/CS eco-composites with and without eco-degradant. The increase of filler loading and immersion times increased the water absorption of both eco-composites. The CS consists of hemicellulose, cellulose and lignin in structure which causes a hydrophilic behaviour on CS. Therefore, the addition of hydrophilic CS in eco-composites will absorb certain amount of water and the increase of CS loading also raised the water absorption of eco-composites. A similar observation also found by other researchers [25, 26].

Regarding to Fig. 8, the water absorption of LDPE/CS eco-composites with eco-degradant was lower compared to LDPE/CS eco-composites without eco-degradant. This is assigned to the presence of metal salt of fatty acid from eco-
degradant reacted with CS and form a fatty acid layer on the filler surface. The fatty acid layer blocked the CS from forming hydrogen bonding with CS. Thus, the water absorption of LDPE/CS eco-composites reduced after addition of eco-degradant. In other previous studies found that the addition of fatty acid based additives improved the water resistivity of eco-composites [23, 27-28].

![Graph showing water absorption of LDPE/CS eco-composites with and without eco-degradant at selected filler loading.]

**Fig. 7.** The water absorption of LDPE/CS eco-composites with and without eco-degradant at selected filler loading.

![Graph showing percentage of equilibrium water absorption of LDPE/CS eco-composites with and without eco-degradant at selected filler loading.]

**Fig. 8.** The percentage of equilibrium water absorption of LDPE/CS eco-composites with and without eco-degradant at selected filler loading.

### 3.4. Thermal properties

The DSC thermograms of neat LDPE and LDPE/CS eco-composites with and without eco-degradant at selected filler loading were displays in Fig. 9. Table 2 shows the DSC data obtained from DSC thermograms. The $\Delta H$ and $X_c$ of LDPE/CS eco-composites slightly reduced at higher filler loading. By considering the fraction of LDPE matrix, the increase of filler loading also increased the $X_{LDPE}$. This is due to the nucleating effect of CS. Ndiaye and Tidjani [29] and Chun et al. [23] also reported the incorporation of natural filler induced nucleating effect on polymer
matrix and it increased the crystallinity of composites. From Table 2, the addition of eco-degradant increased the $\Delta H$, $X_c$, and $X_{LDPE}$ of LDPE/CS eco-composites. This revealed the presence of eco-degradant enhance the nucleating effect of CS filler. In our previous studies found that the addition of fatty acid compound increased filler dispersion and filler-matrix interaction, which further improved the nucleating effect on composites containing natural filler [23]. Azieyanti et al. [14] also reported that the presence of eco-degradant increased the enthalpy and crystallinity of recycled polyethylene/chitosan eco-composites. The $T_m$ of LDPE/CS eco-composites did not significantly change with the increase of filler loading. However, the presence of eco-degradant cause the $T_m$ of LDPE/CS eco-composites shifted to higher temperature. This probably due to the addition of eco-degradant enhanced the filler-matrix interaction. Thus, the filler-matrix interaction restricted the chain mobility and cause the melting temperature increased.

![Fig. 9. DSC thermograms of neat LDPE, LDPE/CS eco-composites with and without eco-degradant at selected filler loading.](image)

<table>
<thead>
<tr>
<th>Materials</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$\Delta H$ (J/g)</th>
<th>$X_c$ (%)</th>
<th>$X_{LDPE}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Neat LDPE</td>
<td>116.40</td>
<td>78.46</td>
<td>27.50</td>
<td>27.50</td>
</tr>
<tr>
<td>LDPE/CS:100/20</td>
<td>116.96</td>
<td>88.15</td>
<td>30.93</td>
<td>37.12</td>
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<tr>
<td>(without eco-degradant)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE/CS:100/40</td>
<td>115.84</td>
<td>84.90</td>
<td>29.79</td>
<td>41.71</td>
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<td>(without eco-degradant)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LDPE/CS:100/20</td>
<td>126.68</td>
<td>104.4</td>
<td>36.60</td>
<td>43.92</td>
</tr>
<tr>
<td>(with eco-degradant)</td>
<td></td>
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<td></td>
</tr>
<tr>
<td>LDPE/CS:100/40</td>
<td>124.23</td>
<td>99.40</td>
<td>34.88</td>
<td>48.83</td>
</tr>
<tr>
<td>(with eco-degradant)</td>
<td></td>
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</tbody>
</table>
4. Conclusion

The results show the increase of CS loading decreased the tensile strength and elongation at break of LDPE/CS eco-composites, but the Young’s modulus, water absorption and crystallinity were increased. The SEM results evidenced the CS is poorly dispersed and weak adhesion with LDPE matrix. The addition of eco-degradant had significantly improved the tensile strength, elongation at break, and crystallinity of LDPE/CS eco-composites. The tensile strength and elongation at break of composites increased by average of 17.4% and 78.6%, respectively, after the addition of eco-degradant. However, the presence of eco-degradant reduced the Young’s modulus and water absorption of LDPE/CS eco-composites. The improvement of LDPE/CS eco-composites with eco-degradant was due to the better interfacial adhesion between CS and LDPE matrix. The SEM micrographs show the good adhesion between CS and LDPE after addition eco-degradant.

References


