# Effect of Calcium Carbonate Incorporation on the Properties of Low Linear Density Polyethylene/Thermoplastic Starch Blends

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Abstract: The characterisation of low linear density polyethylene/thermoplastic starch (LLDPE/TPS) composite with calcium carbonate (CaCO<sub>3</sub>) filler was investigated. LLDPE/ TPS composite with different CaCO<sub>3</sub> loadings were prepared using HAAKE internal mixer at 145°C and rotor speed of 50 rpm. The first step includes the preparation of TPS using heated two roll mill at temperature of 150°C. All composites were characterised by Instron machine, scanning electron microscopy (SEM), thermogravimetry analysis (TGA), and Fourier transform infrared (FTIR) spectroscopy. The result indicated that LLDPE/TPS blends with incorporation of CaCO<sub>3</sub> gave higher value of tensile properties as compared to LLDPE/TPS blend. However, at higher  $CaCO_3$  (30%) loading, the particles tend to form the agglomeration within the matrix. The agglomeration formation decreases the mechanical properties of LLDPE/TPS composite by weakening the interfacial interaction between the matrix and the filler particle as shown in morphological study. The incorporation of  $CaCO_3$  particles also improve the thermal stability of LLDPE/TPS blends as shown in thermogravimetric curve.

Keywords: LLDPE, thermoplastic starch, CaCO<sub>3</sub>, mechanical properties, thermal properties

#### 1. INTRODUCTION

Interest in bio-degradable polymers has continued to increase due to the problems associated with the plastics disposal and effects on the environment. Biodegradable plastic is a plastic designed to undergo a significant change in its chemical structure under specific environmental condition, resulting in a loss of some properties. The change in chemical structure are result from the action of naturally occurring microorganism. Starch are widely used as a viable alternative to making biodegradable plastic. Starch is cheap, renewable, and biodegradable, but it lacks in strength, low water resistance, and processability. To improve the targeted properties, starch is often blended with other biodegradable polymers such as poly (ɛ-caprolactone) (PCL), polylactic acid (PLA), and polyvinyl alcohol (PVA),<sup>1-5</sup> or with conventional petroleum-based plastic, such as polyethylene (PE) and polypropylene (PP).<sup>6-11</sup> PE is regarded as an inert bulk polymer and slowly degradable compared to PLA and PVA, in which PE takes longer time to degrade.<sup>12-14</sup> On the other hand, lack in mechanical properties and weak moisture resistance of starch can be overcome by blending it with low linear density polyethylene (LLDPE), which has high strength, flexible, and high mechanical properties. Starches are incorporated during producing plastic films, will enhance the accessibility of the PE plastic to oxygen and microorganism attack and leads to chain breakdown. Thermoplastic starch (TPS) as opposed to native starch, which is capable to flow and can be processed with conventional plastic equipment.<sup>15</sup> TPS is obtained from plasticised starch, in the presence of glycerol as the plasticiser. TPS has been melt blended with synthetic polymers to produce partially biodegradable materials, which shows high ductility similar to certain commercial plastics.<sup>16</sup> In this study, calcium carbonate (CaCO<sub>3</sub>) was used as reinforcing filler in LLDPE/ TPS matrix to compensate the deterioration of blends properties due to the presence of TPS. The effect of CaCO<sub>3</sub> as reinforcing filler on the mechanical, morphology, and thermal properties were focused in this study.

#### 2. EXPERIMENTAL

#### 2.1 Materials

LLDPE was purchased from Lotte Chemical Titan (Johor, Malaysia) with density of 0.920 g cm<sup>-3</sup>. Food grade cassava starch was used to prepare TPS. CaCO<sub>3</sub> in odourless and fine white powder was purchased from Sigma Aldrich Chemical Company (St Louis, Missouri, USA) with density of 2.83 g cm<sup>-3</sup>. Glycerol used as plasticiser was also supplied by Sigma Aldrich Chemical Company (St. Louis, Missouri, USA).

#### 2.2 LLDPE/TPS/CaCO<sub>3</sub> Composites Preparation

TPS was prepared using 65% of cassava starch and premixed with 35% of glycerol.<sup>17</sup> The mixtures were stored in room temperature for 24 h after the preparation. This is to allow the plasticiser to permeate inside the starch granule. Then, the mixtures were mixed by using hot two roll mill at temperature of 150°C for 10 min. For LLDPE/TPS/CaCO<sub>3</sub> composites, the LLDPE/TPS matrix were compounded with different CaCO<sub>3</sub> loadings, which varied from 5% to 30%. The compounding process was done using HAAKE internal mixer (Thermo Fischer Scientific, Massachusetts, USA) at temperature of 135°C for 15 min. Then, the compounding was moulded into 1 mm sheets using a hot press machine.

## **3.** CHARACTERISATION

#### **3.1** Tensile Testing

Instron Tensile Test Machine 3366 was used to analyse the mechanical properties of the blends. The specimens were cut into a rectangular shape, with the dimension of 100 mm total length, 50 mm gauge length, 30 mm width, and 1 mm thickness for the tensile test under ISO 527-3.<sup>17</sup> The cross-head speed was set at 50 mm min<sup>-1</sup> under an ambient temperature. An average value was taken out of five samples to get an accurate value of tensile strength, modulus of elasticity, and elongation at break.

### 3.2 Morphology Study

The morphological studies were carried out on the tensile fracture surface using the analytical scanning electron microscopy (SEM) (model JEOL JSM-6460LA, Tokyo, Japan) with the supply of accelerating voltage at 10 kV. The tensile fracture sample was coated with palladium layer at about 1.5–3.0 nm thickness with aid of utilising the auto fine coater (model JEOL JFC 1600, Tokyo, Japan) to prevent the charging effect on the surface morphology.

### 3.3 Structural Analysis

Fourier transform infrared spectroscopy (FTIR) (model Perkin Elmer spectrometer 2000, Massachusetts, USA) was used to inspect structural changes at a resolution of 4 cm<sup>-1</sup> and in the range of 4,000–650 cm<sup>-1</sup>. The samples were scanned for 32 times for a good resolution on the reading.

#### 3.4 Thermal Stability

The thermogravimetric analysis (TGA) (model Pyris Diamond, Perkin-Elmer, Massachusetts, USA) was used to measure the amount and rate of change in weight of material as function of temperature and time in a controlled atmosphere. The sample was heated from the 20°C to 700°C at 10°C min<sup>-1</sup> under nitrogen atmosphere.

### 4. **RESULTS AND DISCUSSION**

#### 4.1 Tensile Properties of LLDPE/TPS Blends

Effect of TPS content towards properties of LLDPE has been identified by blending both materials at different TPS loadings. Blending of TPS with LLDPE affect the properties of the LLDPE, which it tends to reduce the tensile properties. Based on Figures 1 and 2, the tensile strength of LLDPE/TPS decrease with increase of TPS content. The tensile strength of the LLDPE, which was 20.1 MPa decreased as the TPS loading increased until 4.9 MPa at 50 wt. %. However, to optimise the biodegradable properties, LLDPE/TPS with blend ratio of 70:30 was chosen due to acceptable tensile properties than other compositions. The tensile strength for LLDPE/TPS (70/30) was 7.9 MPa with 467% of elongation at break value. In Figure 3, the tensile strength of LLDPE/TPS blend improved as CaCO<sub>3</sub> was initially added. The tensile strength increased from 7.9 to 12.1 MPa at 5%



Figure 1: Effect of TPS content on tensile strength of LLDPE/TPS blend.

filler loading. The initial increase in strength of the composite is due to good fillermatrix interaction.<sup>18</sup> It enables more stress to be transferred from the matrix to the filler when external forces is applied. However, further increase in CaCO<sub>3</sub> loading will influence the tensile strength value. The decrement in tensile strength value at 20% and 30% TPS loading was attributed to the formation of filler aggregates. The aggregates are easily detached from the LLDPE/TPS matrix and resulted in decrease of the strength of the composite.



Figure 2: Effect of TPS content on elongation at break (%) of LLDPE/TPS blend.



Figure 3: Effect of filler loading on tensile strength of LLDPE/TPS blend.

### 4.2 SEM Morphology of LLDPE/TPS and LLDPE/TPS/CaCO<sub>3</sub> Composites

To study the interfacial adhesion between the matrix and the dispersed phase, SEM micrographs of fracture surface were observed at 300× magnification (as shown in Figure 4). Based on Figure 4(a), SEM micrograph at 10% of TPS loading shown that the blend exhibited smooth fracture surface compared to another blend. SEM micrograph for TPS-40% gave rougher surface than SEM micrograph TPS-30% (as shown in Figures 4[c] and [d]), which it clearly showed less homogeneity and interfacial adhesion. The starch particles were completely disrupted and some of them were pull-out from the surface of the blend, thus, leaving several cavities in the fracture surface. Immiscibility of TPS effect the mechanical properties of the blending, which it decreased tensile properties. However, it gives better degradability characteristic on the blends. The increase in TPS content will increase the surface areas for the microbes to consume, and thus create pores on the LLDPE/TPS surface. Effects of CaCO<sub>3</sub> loading on the LLDPE/TPS matrix can be observed from the SEM micrographs (as shown in Figure 5). Figure 5(a) show good dispersion of CaCO<sub>3</sub> in the LLDPE/TPS matrix. With increase of CaCO<sub>3</sub>, the particle tends to attract each other and group together forming the agglomerations. Besides, the detachment of CaCO<sub>3</sub> from LLDPE/TPS matrix causes voids, which can lead to the crack formation in the blends.

#### 4.3 Structural Analysis

Based on Figure 6, there were two characteristic peaks of LLDPE between 2,915 and 2,846 cm<sup>-1</sup>, which attributed to C–H stretch of alkanes. The peaks at 1,467 and 717 cm<sup>-1</sup> were attributed to C–H<sub>2</sub> bending<sup>19</sup> and two peaks from 1,151 and 1,020 cm<sup>-1</sup> were attributed to C–O–C bond bending while peak at 3,245 cm<sup>-1</sup> attributed to O–H bond stretching, which it characterise TPS functional group.<sup>20</sup> In addition, the characterisation peaks for O–H bond and C–O–C bond show obvious spectrum peaks, indicating the possible interaction of the starch with glycerol. The presence of CaCO<sub>3</sub> was identified by the existence of O–C–O bond in LLDPE/TPS composite. Spectrum peaks of 927 and 926 cm<sup>-1</sup> for LLDPE/TPS-10% CaCO<sub>3</sub> and LLDPE/TPS-30% CaCO<sub>3</sub>, respectively, attributed to O–C–O bending band. Band spectrum for O–C–O at 926 cm<sup>-1</sup> is wider than band spectrum at 927 cm<sup>-1</sup> due to the amount of CaCO<sub>3</sub> used in LLDPE/TPS matrix.



Figure 4: SEM micrograph for LLDPE/TPS blend: (a) TPS-10%, (b) TPS-20%, (c) TPS-30%, and (d) TPS-40% at 300× magnification.



Figure 5: SEM micrograph of LLDPE/TPS blend: (a) LLDPE/TPS-10% CaCO<sub>3</sub> and (b) LLDPE/TPS-30% CaCO<sub>3</sub> at 500× magnification.



Figure 6: FTIR spectrum of LLDPE/TPS, LLDPE/TPS-10% CaCO<sub>3</sub>, and LLDPE/ TPS-30% CaCO<sub>3</sub> composites.

## 4.4 Thermal Stability of LLDPE/TPS/CaCCO<sub>3</sub> Composites

Figure 7 shows the TGA thermogram for LLDPE/TPS composite at different CaCO<sub>3</sub> loadings. TG curves for all compounds exhibit three stages of decomposition. First stage of decomposition start at temperature between 90°C to 200°C, which involve the evaporation and elimination of water and glycerol in the TPS phase.<sup>21</sup> The second stage, at temperature between 250°C to 350°C, is attributed to decomposition of TPS in the composite.<sup>22</sup> The last stage, ranging from 380°C to 480°C is attributed to LLDPE decomposition curve.<sup>23</sup> The remaining weight above the 500°C is attributed to CaCO<sub>3</sub> because the decomposition temperature for CaCO<sub>3</sub> is between 850°C–900°C.<sup>22</sup> Besides that, the decomposition temperatures curves of the blends increase to higher temperature showing increased stability when CaCO<sub>3</sub> is added.



Figure 7: TGA thermograms of LLDPE/TPS, LLDPE/TPS-10% CaCO<sub>3</sub>, and LLDPE/ TPS-30% CaCO<sub>3</sub> composites.

#### 5. CONCLUSION

Optimum LLDPE/TPS blend chosen was 70/30 due to acceptable tensile properties along with partial biodegradable properties. From SEM micrograph, increased weight percentage of TPS tends to form agglomeration and reflect in reduction for tensile strength. In order to give better properties of LLDPE/TPS blend, addition of CaCO<sub>3</sub> filler was performed at different weight percentages, ranging from 5% to 30%. The tensile strength increased up to 12.0 MPa for 10% CaCO<sub>3</sub> loading and further CaCO<sub>3</sub> incorporation tends to decrease the tensile value. Among the LLDPE/TPS composites, LLDPE/TPS composite at 70:30 composition with 10% of CaCO<sub>3</sub> showed the best tensile strength and thermal stability.

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