

# Thermal and Mechanical Properties of Potato Starch and Low Density Polyethylene Bio-Composite; Melt-Reactive Blending

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**Abstract:-** In the present research, biocomposite of thermoplastic starch (TPS) and Low density polyethylene have been prepared by melt extrusion reactive blending using maleic anhydride grafted low density polyethylene (LD-g-MA) as compatibilizer. The blends were melt compounded on co-rotated twin screw extruder. The thermal properties, FTIR, tensile strength, % strain, and morphology of fractured samples were studied. The percentage of TPS in the composite were 15%, 20%, and 25% and. The chemical structure was studied by FTIR. The thermal properties were investigated by DSC and TGA. It was found that the tensile strength increased by 13% for blend with 20% starch, while % strain values decreases approximately 35% with increasing starch content in the blend. The scanning electron micrograph (SEM) and melt flow index supports the finding as it shows uniform distribution and proper adhesion of starch particle in the matrix. **Keywords:** Thermoplastic Starch (TPS), Polyethylene, Thermal properties, Mechanical properties, FTIR, SEM, MFI

## 1. INTRODUCTION

Low density polyethylene (LDPE) belongs to a family of commodity polymers, mainly consumed in packaging industry. The polyethylene have replaced paper and other cellulose based products in packaging sector because of better physical and chemical properties like high strength, low density, and resistance to water and barrier to gases. The non degradable nature, low density, and bright color i.e. visibility in litter, LDPE have attracted more public and media attention than any other component of the solid waste stream. Many other factors like limitations and uncertainty in supplies of fossil fuels, environmental consideration also encourages researcher to develop the biodegradable and bio-based polymers. Hence, biodegradable polymers opened the way for new consideration and accelerated the advancement of biodegradable (bio-based) polymers and products [1-2, 15]. The natural polymeric material, like starch may

contribute towards the development of such biodegradable polymers because, their properties are quite similar to the petrochemical based polymers except few problems like poor mechanical strength and moisture absorption. Starch is an important material of choice as approximately 75% of all organic material on earth is present in the form of polysaccharides. The most of the starch crops are very productive, like potato accumulates 75% of the dry wt and corn seeds consists of 65-80% starch by weight. Hence it is inexpensive, sustainable and renewable natural material having good potential for development of biodegradable plastics [3-5].

There, we have selected potato starch, LDPE and LD-g-MA to prepare bio-composite of LDPE and starch with comparable and better properties to replace LDPE. In present research work 15 to 25% of potato starch treated with glycerol and water as plasticizer, have been melt extruded in co-rotating twin screw extruder. The blended granule so obtained was evaluated for DSC, TGA, FTIR, and tensile strength. The fractured surfaces of the blend were investigated by scanning electron microscope (SEM), which provides information for the interfacial adhesion of starch and LDPE in bio-composites. The melt flow index (MFI) gives information about melt characteristics.

## 2. EXPERIMENTAL

### 2.1 Materials

Low density polyethylene (Grade 22FA002, MFI 0.2 g/10 min at 190 °C and 2.16 Kg load) was procured from M/s Reliance Industries. The native potato starch (M.W. 162.14) was procured from M/s Loba Chemie, Mumbai (India). The glycerol was obtained from M/s Fisher Scientific. The LDPE grafted with maleic anhydride (LD-g-MA) grade OPTIM E-126, 0.5% grafted was procured from M/s Pluss Polymers, Delhi (India).

| SAMPLE | LDPE (22FA002) | Starch (TPS) | LD-g-MA (OPTIM E-126) |
|--------|----------------|--------------|-----------------------|
| LDPE   | 100 %          | 0 %          | 0 %                   |
| LDST-A | 75 %           | 15 %         | 10 %                  |
| LDST-B | 70 %           | 20 %         | 10 %                  |
| LDST-C | 65 %           | 25 %         | 10 %                  |

Table 1. Formulation of LDPE/Starch biocomposite

**2.2 Preparation of LDPE/Starch bio-composite** The dry starch was mixed with 25% glycerol (by weight) and left for overnight for swelling action. Thereafter, suspension have been mix thoroughly in high speed mixer till it turn into powder form. The thermoplastic starch (TPS) so obtained was mixed with LDPE and LD-g-MA as experimental formulation listed in Table no. 1.

All above ingredient were mixed homogeneously in high speed mixed for 2 min and biocomposite were prepared by melt blending using co-rotating intermeshing twin screw extruder of L/D 40:1 and screw diameter 25mm. The melt profile of extruder was between 100 to 140 °C, at the screw speed of 250rpm. The melt pressure during extrusion was about 30 MPa.

### 3. CHARACTERIZATION

#### 3.1 Fourier Transmission Infrared Spectroscopy

FTIR spectra of biocomposite has been recorded by employing M/s Agilent Technologies model carry 630. The injection moulded samples have been scanned in frequency region 4000 to 600 cm<sup>-1</sup> with resolution 4 cm<sup>-1</sup> in transmittance mode.

#### 3.2 Thermal Properties

##### Differential Scanning Calorimeter (DSC)

For DSC analysis, 5 mg average weight samples, encapsulated in sealed aluminium pan have been prepared for each sample. The DSC tests performed under nitrogen atmosphere in temperature range from 50 to 180 °C at heating rate of 10°C/min. Melting temperature T<sub>m</sub>, crystallization temperature T<sub>c</sub> has been obtained from the maximum peak and heat of fusion, enthalpy has been obtained from the area under the peak.

The degree of crystallinity calculated via the total enthalpy method, according to equation 1 [6].

$$\%X_c = \Delta H / \Delta H^+ * 100 \quad (1)$$

Where X<sub>c</sub> is the degree of crystallinity, Δ H<sup>+</sup> is the specific melting enthalpy for 100 % crystalline LDPE. Here, the value of Δ H<sup>+</sup> for LDPE has been taken as 276 J/g [7].

##### Thermo Gravimetric Analysis (TGA)

The TGA of the bio-composite so obtained from melt extrusion have been evaluated using Thermo Gravimetric Analyzer (M/s Perkin Elmer). TGA has been carried out

under nitrogen atmosphere at a heating rate of 10 °C/min from room 50 to 650 °C. The onset of the degradation temperature T<sub>d</sub> has been recorded for each sample.

#### 3.3 Mechanical Properties

The tensile properties for the bio-composite have been conducted using Instron universal testing machine model 3369 according to ASTM D 638. The specimen was prepared by injection molding and dimensions were according to ASTM standard. The cross-head speed of 50 mm/min at 23 °C. The samples were conditioned at 23°C temperature and 50% RH for 24 hours. Five specimens were used to obtain the average value of the tensile properties.

#### 3.4 Melt Flow Index

The Melt Flow Index for the blends has been conducted according to ASTM D 1238. The test conducted at 190 °C at 5 kg load. The five tests were used to obtain the average value of the melt.

#### 3.5 Morphological Test

An S-3700N scanning electron microscopy (SEM) (Hitachi) was used to evaluate the sample microstructure. The samples have been first dried in an oven to remove the moisture and then sputter coated with a thin layer of gold to avoid electrical charging.

### 4. RESULTS AND DISCUSSION

#### 4.1 Fourier Transform Infrared Spectroscopy

Figure 1 shows the FTIR spectra of pure LDPE and LDST-A, B, and C- biocomposite. In Figure 1, all the characteristic peaks of LDPE at 2915, 2848, 1462 and 721 cm<sup>-1</sup> appears in all spectrums of prepared injection moulded samples [8,9]. A hump like peak has been observed between 3600 and 3000 cm<sup>-1</sup>, due to O-H bond stretching and at 1530 cm<sup>-1</sup> O-H bond bending. The FTIR spectrum of biocomposite i.e. LDST-A, B, and C shows new peaks at 1740 cm<sup>-1</sup>, which is assigned to the ester carbonyl stretching vibration. The peak observed in this region support the presence of anhydride group in the backbone of LDPE pendant chain [10]. The peaks of starch appearing at 1140, 1100 and 1020 cm<sup>-1</sup> assigned to C-O stretching of alcohol and ether bonds, which state that C-O in C-O-H stretching occurring mainly (peak positions) in the range of 1200-1000 cm<sup>-1</sup> [11].

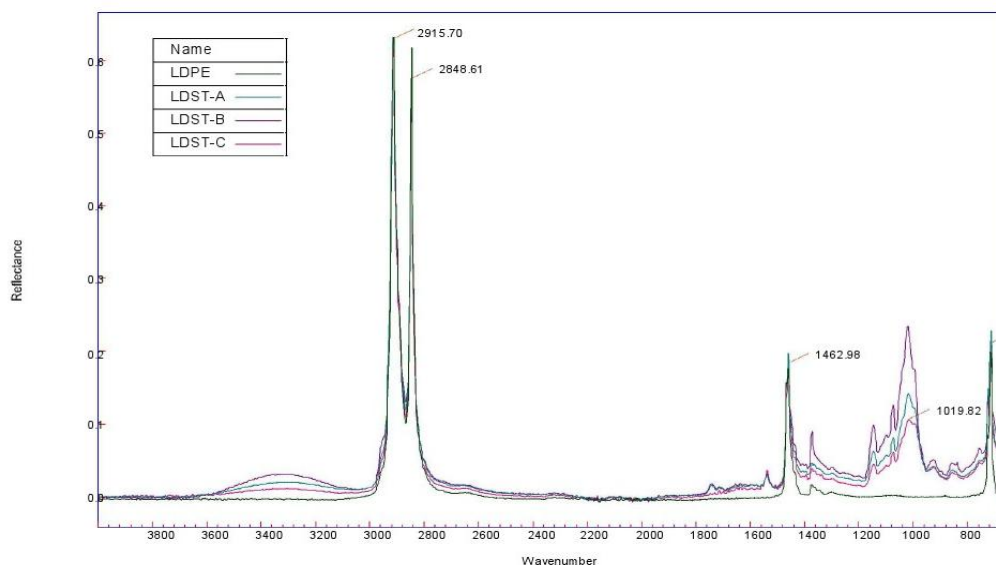


Figure 1 FTIR of LDPE and Biocomposite LDST-A, LDST-B and LDST-C.

#### 4.2 Thermal Analysis

**4.2.1 Differential Scanning Calorimeter (DSC)** DSC was used to study the thermal properties of the polymer/blends. DSC heating thermograms of pure LDPE, LDST-A (15% starch), LDST-B (20% starch) and LDST-C (25% starch) biocomposite are given in Figure 2 (A-D). Table 2 shows the melting, heat of fusion and degree of crystallinity analysed through DSC. It is clear from the table that, as starch contents increases the heat of fusion and crystallinity decrease and melting temperature decrease. The % crystallinity has reduced up to 41.7%. This decrease is due

to the interaction between LD-g-MA/LDPE and Starch, which hinders the close packing of LDPE chain [12]. DSC of biocomposite shows two new endothermic peaks at 135 and 162 °C due to presence of thermoplastic starch (TPS) in the blend, which results from the higher interaction between starch and glycerol leads to increase in the activation energy of the melting of the starch crystallinities [13].

| SAMPLE | $T_m$ (°C) | $\Delta H$ (J/g) | $X_c$ (%) |
|--------|------------|------------------|-----------|
| LDPE   | 114.08     | 72.19            | 26.15     |
| LDST-A | 112.95     | 43.29            | 15.68     |
| LDST-B | 109.52     | 42.07            | 15.24     |
| LDST-C | 111.56     | 45.06            | 16.32     |

Table 2  $T_m$ ,  $\Delta H$ , Crystallinity of Biocomposite with various contents of potato starch.

#### 4.2.2 Thermo Gravimetric Analysis (TGA)

The thermal degradation behaviour of LDPE and biocomposites are displayed in Figure 3. The first decomposition has been observed around 100°C, which leads to the loss of moisture in the samples because of the hydrophilic nature of starch. The second decomposition occurs around 200°C attributed to the evaporation of

volatile substance like glycerol. The third and major decomposition has been observed around 330 to 440°C, which attributed to the thermal degradation of starch and final decomposition occurs after 450 °C, which results from the thermal degradation of LDPE. The Figure 3 clearly shows that the addition of starch decreases the thermal stability of the biocomposite.

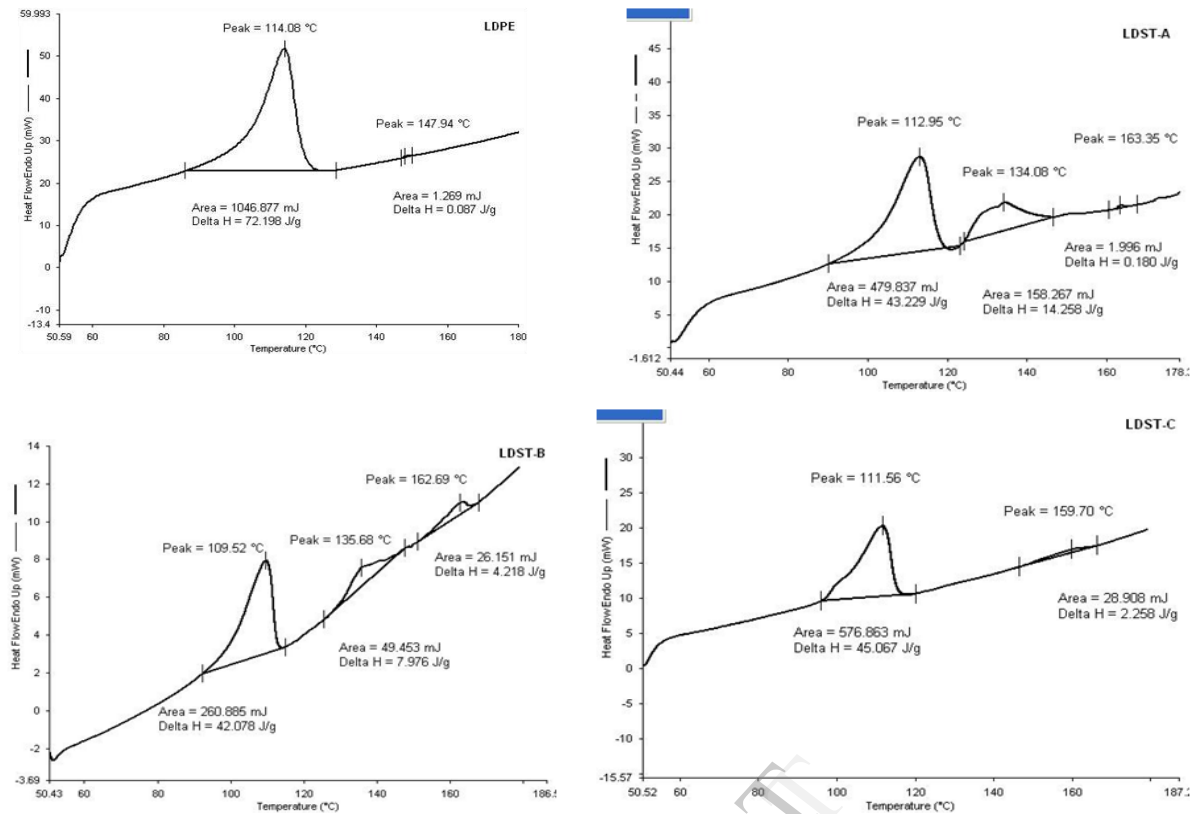


Figure 2 DSC curves of LDPE and Biocomposite LDST-A, LDST-B and LDST-C.

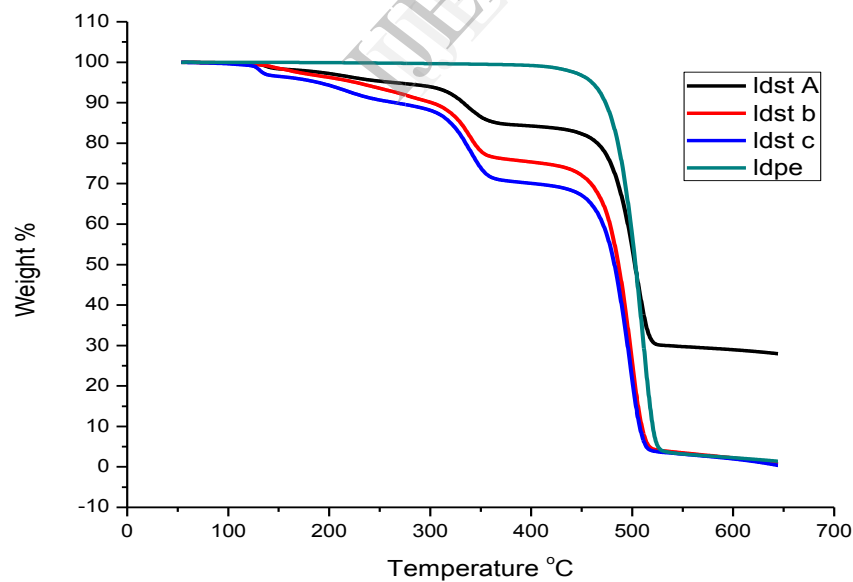


Figure 3 TGA curves of LDPE and biocomposite LDST-A, LDST-B and LDST-C.

#### 4.3 Mechanical Properties

As the interfacial bonding is greatly improved because of the presence of LD-g-MA and plasticization of starch, a considerable enhancement in the mechanical properties of the biocomposite is expected, which could be evident from the test result shown in Figure 4. The addition of starch improved the tensile strength but % strain decrease as the

content of starch increase in the biocomposite. It is evident from the mechanical properties strongly depended on the dispersion and phase size of reinforcement (i.e. starch) in the polymer matrix. As the size of the dispersion phase become smaller, an increase in the mechanical properties, especially in the tensile strength has been observed [15].

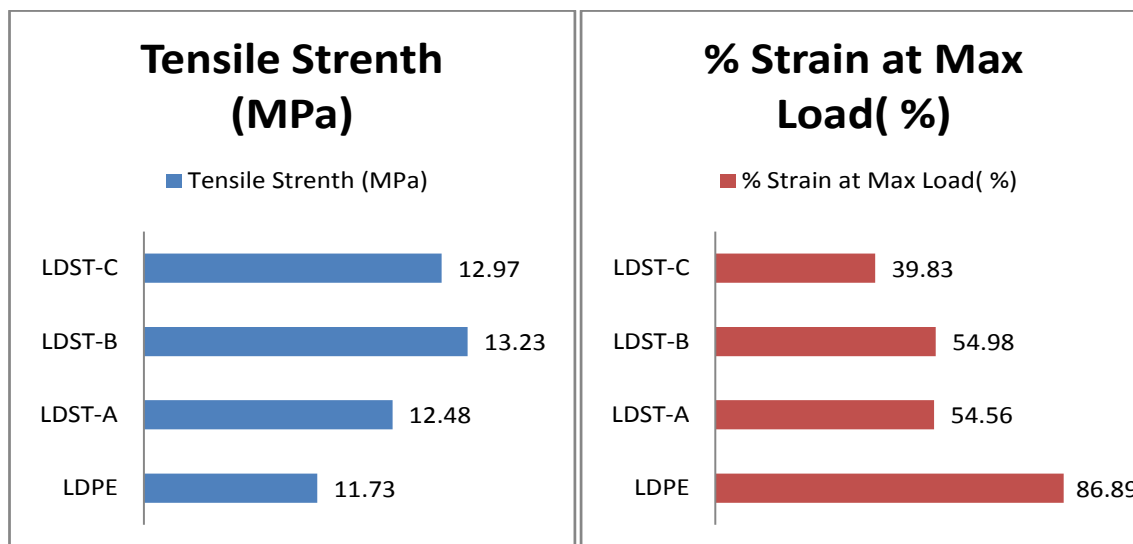


Figure 4 The tensile strength and % strain of LDPE and LDST-A, LDST-B and LDST-C.

#### 4.4 Melt Flow Index (MFI)

The melt flow index is used as a means of measuring of uniformity of the flow rate of the thermoplastic material and blends. It is most accepted and widely used practical method to relate the molecular weight and viscosity of the polymer in industry. The MFI value of the biocomposite indicates the uniform distribution of starch in the

biocomposite. It is further, indicates the grain size of starch in the system. The MFI value in Figure 5 clearly and strongly supports the finding of mechanical test and morphology that starch in LDST-B (20% content) has lowest grain size and uniformly distributed in polymer matrix and has maximum adhesion to the backbone of LDPE.

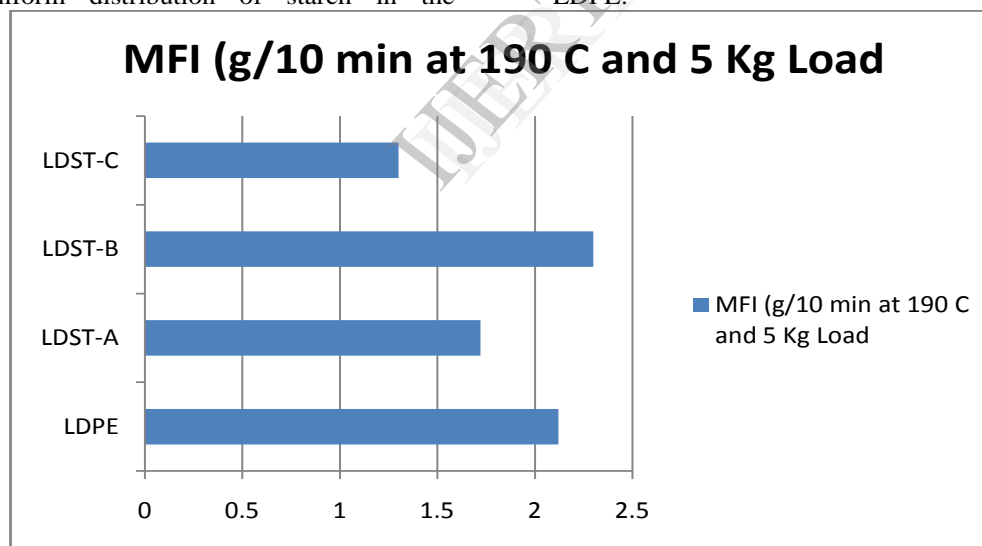


Figure 5 Melt Flow Index of LDPE and LDST-A, LDST-B and LDST-C

#### 4.5 Morphological Test (SEM)

The SEM micrographs of LDPE and biocomposite of various compositions has been presented in Figure 6. The micrographs revealed that the thermoplastic starch granules are being continuously and uniformly dispersed throughout the LDPE matrix and form a homogeneous phase. It is

evident from the SEM that presence of polar group enhances adhesion between two phases (hydroxyl group of starch and polar group of LDPE). Hence, the LD-g-MA played a vital role in reducing the interfacial energy and promoting the interfacial adhesion between the potato starch and LDPE matrix.



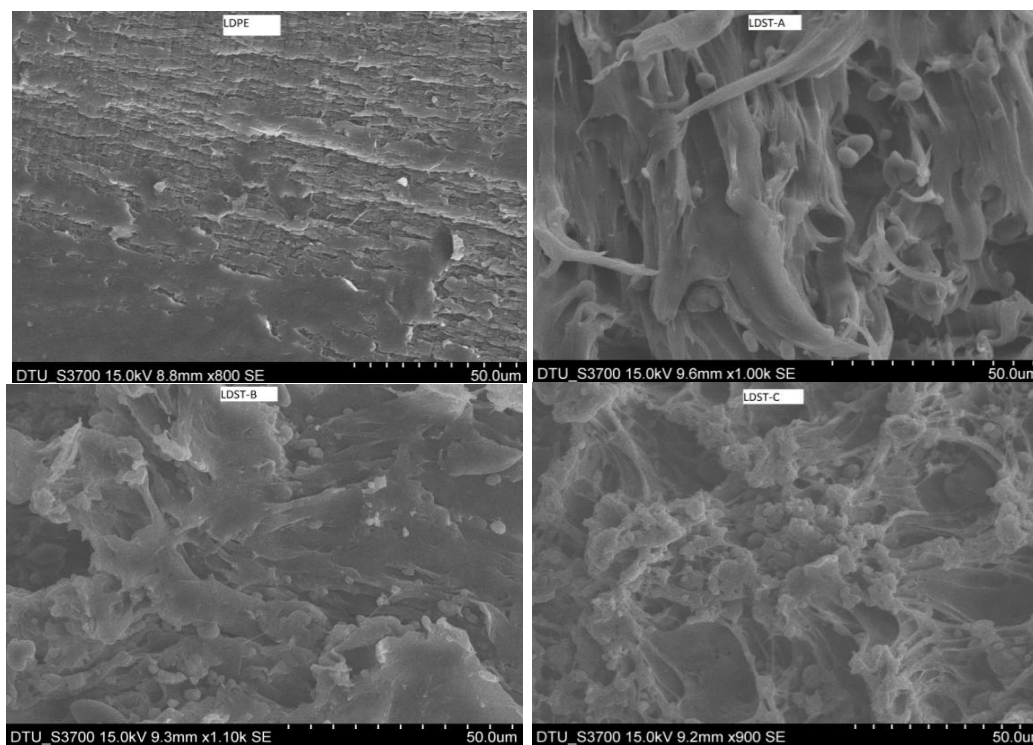


Figure 6 SEM images of the fractured surface of LDPE, LDST-A, LDST-B and LDST-C at magnification with a scale of 50 $\mu$ .

## 5. CONCLUSION

The biocomposite of LDPE and Starch using LD-g-MA as the compatibilizer has significantly improved thermal and mechanical properties. The FTIR characterization shows that an ester carbonyl bond has been formed between –OH group of starch and polymer matrix, which is directly responsible for the improved adhesion between starch and LDPE. When biocomposite has been compare with LDPE, DSC tests showed that the decrements of  $T_m$  and  $\Delta H$  both as the content of starch increase. The morphology and MFI values show that the starch phase size (around 1-2  $\mu$ ) and

distribution has been uniform and homogeneous. The distribution is perfectly uniform in LDST-B and its mechanical value, %crystallinity, MFI and other thermal properties reflects the same. Finally we can conclude that the biocomposite of starch and LDPE prepared from melt extrusion using LD-g-MA having better properties than pure LDPE. This development may prove a milestone towards developing bio-based polymeric material in future in high end application.

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