

# Thermal Properties of Polyethylene Grafted Maleic Anhydride Compatibilised High Density Polyethylene/ Thermoplastic Soya Spent Powder Blends

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**Abstract**—The influence of the thermal properties of thermoplastic soya spent powder (TSSP) blends of high-density polyethylene (HDPE) at various compositions was investigated. The difference of thermal properties the blends with and without polyethylene-grafted-maleic anhydride (PE-g-MA) were investigated too. The compatibilizing efficiency of copolymers containing glycerol plasticized soya spent powder (SSP) were prepared by using heated two roll mills. Besides that, for the composition without compatibilizer TSSP was blended with HDPE by using twin screw extruder at 180°C. Thermogravimetric analysis (TGA) reveals that the thermal decomposition temperature reduced with the addition of TSSF. However, the thermal stability of the blends was improved by the incorporation of PE-g-MA. Crystallinity of the blends was significantly dropped with increasing TSSP content and further reduced with the presence of PE-g-MA

**Keywords**—High Density Polyethylene, Thermoplastic Soya Spent Powder, Soya Spent Powder, Polyethylene Grafted-(Maleic Anhydride).

## I. INTRODUCTION

In the last few decades, plastic industry has expanded very quickly, in order to meet the growing demand by the consumers. This phenomenal growth has subsequently increased the volume of domestic and industrial waste plastics. Several negative environmental impacts associated with careless plastic disposal have been reported elsewhere [1]. These include loss of natural resources, land and water pollution, and the reduction of landfill space. An increasing awareness and stringent environmental standards to ensure safe disposal is, therefore, necessary to curb the issue and handle the menace without necessarily creating more secondary problems [2]. However, the awareness and compliance to environmental legislations in the developing countries is very poor and the waste disposal methods are still

not in conformity with the environmental regulations. To avoid the situation from further aggravation, there is a need of safe disposal through reuse, energy recovery and recycling. Among the several safe disposal measures [3], [4] and [5], conversion in to useful products has been the focus of attention in recent years [6] and [7].

Usually native starch contains about 30% amylose, 70% amylopectin and less than 1% lipids and proteins from plant. Physical gels and dispersions from native, purified amylose or amylopectin starches showed differences in properties such as phase separation, physical gelation, aggregation and crystallization [8], [9]. Starch has been processed in various ways to produce starch plastics. Alternatively, polymer blends and composites containing natural polymers as biodegradable additives (such as starch, cellulose and their derivatives) were developed [10]. These composites are easily extrudable and commercialized. The major disadvantage of incorporating natural polymer into synthetic polymer is their compatibility. Natural polymers are hydrophilic while synthetic polymers are hydrophobic in nature. The resultant blend of these two types of polymers is almost immiscible. The poor interaction between matrix and filler interphase causes weaker mechanical properties [11].

PE-g-MA was used as a compatibiliser to improve the interfacial adhesion between HDPE and TSSF. The compatibilisation effect of PE-g-MA has been proven in our previous study [12]. The changes of the TSSF blends with HDPE were studied by investigating the mechanical properties from thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

## II. EXPERIMENTAL

### A. Materials

HDPE grade TITANZEX was supplied by Titan Group. The density is 0.956 g/cm<sup>3</sup> and the melt flow index is 0.45g/10 min. SSF was purchased from Hasrat Bestari Sdn. Bhd. The granular size of SSF is 18µm with 55.5% protein content. The plasticizer that used in preparing TSSF is glycerol. The glycerol that obtained from Sigma Aldrich Inc. contains 11% water. PE-g-MA with 3% grafting level was also supplied by Sigma Aldrich, Inc.

### B. Compounding

In this study, twin screw extruder was used to mix the HDPE, TSSF and PE-g-MA. Then, 30% of PE-g-MA based on SSP was added into the mixture. Twin screw extruder was used extensively for mixing, compounding, or reacting polymeric materials. The twin screw extruder was run at a speed of 50 rpm and temperature of 180 °C. The samples produced were in pellet form.

The product was compression molded at 180°C. The preheating process was around 7 minutes, press heating for 3 minutes and cooling for 3 minutes. Then, the samples were cut into dumbbell shape according to ASTM D638. Table 1 shows the composition of HDPE/SSF blends.

Table 1: Composition of HDPE/SSF blends.

| HDPE (wt%) | SSF blends (wt%) |
|------------|------------------|
| 100        | 0                |
| 99         | 1                |
| 98         | 2                |
| 95         | 5                |
| 90         | 10               |
| 85         | 15               |

### C. Thermogravimetric analysis (TGA)

TGA Analyzer (Perkin Elmer Pyris) provided information on the temperature changes between T<sub>-5%</sub> and T<sub>-30%</sub>. The samples were tested within temperature range from 50°C to 600°C at heating rate of 20°C/min under a flow of nitrogen. 10 to 15 mg of samples was used for this analysis.

### D. Differential Scanning Calorimetry (DSC)

The test was carried out by using a Perkin-Elmer DSC 7 instrument with heating temperature of 10°C/min. Each 4-mg-average sample was encapsulated in a hermetically sealed aluminum pan. The sample was first heated up from room temperature to 200°C at 10°C/min and held at this temperature for 5 min to remove the thermal history. Consequently, the sample was cooled to room temperature at 10°C/min and then

reheated to 200°C at 10°C/min. The analysis was carried out under a nitrogen atmosphere.

The melting temperature (T<sub>m</sub>) and crystallization temperature (T<sub>c</sub>) were obtained from the maximum peak, whereas the heat of fusion (ΔH<sub>f</sub><sup>\*</sup>) was obtained from the area under the peak. The percentage of crystallinity of the LDPE phase was calculated by using the following equation:

$$\% \text{ crystallinity} = \frac{\Delta H_f^*}{\Delta H_f^0} \times 100$$

Where ΔH<sub>f</sub><sup>0</sup> is heat of fusion for 100% crystalline polyethylene (276 J/g) [13] and ΔH<sub>f</sub><sup>\*</sup> is heat of fusion for the semicrystalline LDPE.

## III. RESULTS AND DISCUSSION

### A. Thermogravimetric analysis (TGA) Properties

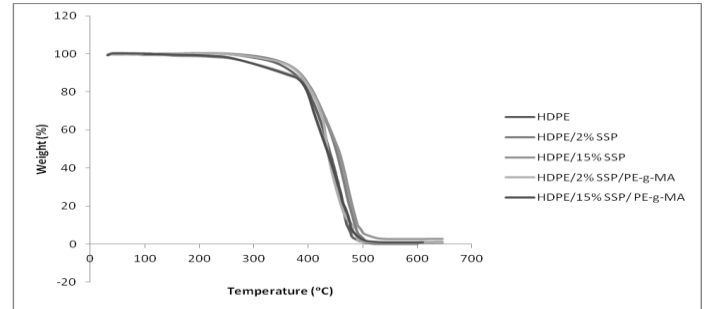


Fig. 1: TGA thermogram of HDPE, HDPE/SSF blends, and HDPE/SSF blends/ PE-g-MA.

Fig. 1 shows the TGA analysis which involved weight loss of the blends HDPE/SSF. The thermal stability of the mixture was measured by TGA. From the TGA thermogram Fig. 1 pure HDPE showed higher thermal stability than the compatibility. The addition of the SSP had reduced the thermal stability of the blends. Table 2 summarises the degradation temperatures of pure HDPE, uncompatibilised HDPE/SSF blends, and PE-g-MA compatibilised HDPE/SSF blends. The T<sub>-5%</sub> and T<sub>-30%</sub> values represent initial degradation at 5 wt% sample weight loss and middle degradation at 30 wt% sample weight loss, respectively.

Table 2: Temperature analysis of the blends sample.

| Formulation          | T <sub>-5%</sub> | T <sub>-30%</sub> |
|----------------------|------------------|-------------------|
| HDPE                 | 64.46            | 205.74            |
| HDPE/2% SSP          | 62.51            | 204.09            |
| HDPE/15% SSP         | 61.82            | 203.38            |
| HDPE/2% SSP/PE-g-MA  | 63.17            | 205.64            |
| HDPE/15% SSP/PE-g-MA | 62.33            | 204.76            |

As shown in Table 2, the thermal stability of HDPE/SSP blends decreased with increased blends content. A significant drop in  $T_{-5\%}$  can be observed from 2 to 15 wt% blends in HDPE. This reduction might be due to the naturally low thermal stability of blends. SSP is a lignocellulosic fibre [14] and it is less thermally resistant than petroleum based polymers. The addition of compatibiliser PE-g-MA, slightly improved the thermal stability of the mixture. For HDPE/2% SSP blends, the changes in  $T_{-5\%}$  and  $T_{-30\%}$  were not obvious.

However, the HDPE/2% SSP blends/PE-g-MA mixture showed a remarkable enhancement in thermal stability, as  $T_{-5\%}$  increased from 62.51 to 63.17°C with the addition of PE-g-MA. The increment was due to the improved interfacial adhesion between HDPE and blends. At higher degradation temperature, the interaction between HDPE and SSP blends was reduced. Therefore, the change in  $T_{-30\%}$  was not obvious. The thermal stability decreased with the addition of SSP but improved after the addition of PE-g-MA. The crosslinking formed between the hydrophilic SSP and hydrophobic HDPE [15] by the addition of PE-g-MA had increased the decomposition temperature compared to the blends without PE-g-MA.

#### B. Differential Scanning Calorimetry (DSC) Properties

Fig. 2 and Fig. 3 illustrate the DSC thermograms of HDPE, HDPE/SSP blends, and HDPE/SSP blends/ PE-g-MA for the second heating and cooling cycle. From the thermograms, the changes in  $T_m$  and  $T_c$  of the mixture were not obvious. The HDPE/SSP blends and HDPE/SSP blends/ PE-g-MA were not miscible, although there was only one endothermic peak for the blends.

This endothermic peak was attributed solely to HDPE, because SSP blend has no melting temperature but has gelatinization and degradation temperatures [13]. The changes in  $T_m$ ,  $T_c$ , and crystallinity of pure HDPE and its blends are summarised in Table 3. There was a slight decrease in crystallinity with the addition of SSP because the incorporation of SSP hindered the molecular motion of HDPE in the super-cooling melt during cooling [16]. In addition, the presence of SSP might hinder the nuclear migration of HDPE. The  $T_m$  of the mixture increased slightly with increasing SSP blends content. Therefore, the SSP affected not only the crystallinity of the mixture but also their melting behavior.

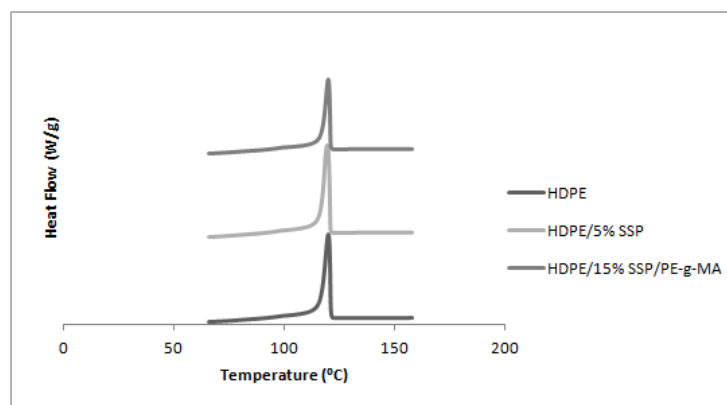


Fig. 2: DSC Melting thermograms of HDPE, HDPE/15% SSP blends, and HDPE/15% SSP blends/PE-g-MA.

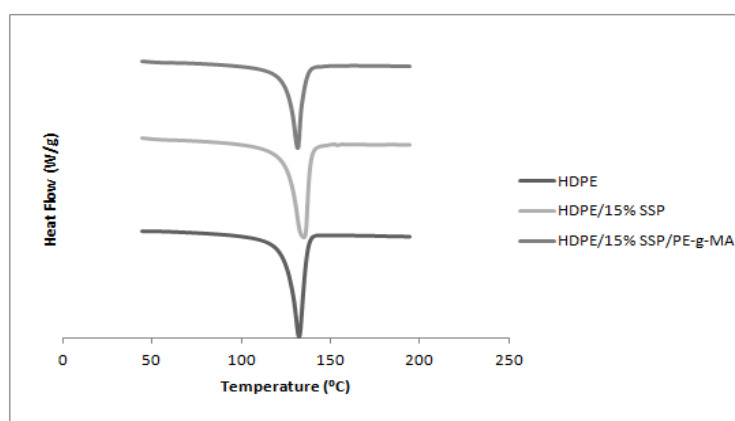


Fig. 3 : DSC crystallization thermograms of HDPE, HDPE/15% SSP blends, and HDPE/15% SSP blends/PE-g-MA.

Table 3 shows the incorporation of PE-g-MA reduced the melting temperature and crystallinity of the HDPE/SSP blends respectively, an observation which suggests that the better interfacial adhesion between HDPE and SSP blends impeded the movement and the molecular arrangement of HDPE [17]. Consequently, the crystallinity was reduced owing to the better mixing of the HDPE/SSP blends.

Table 3: Thermal properties analysis for HDPE/SSP and HDPE/SSP/PE-g-MA.

| Sample                   | $T_m$ (°C) | $\Delta H_f^*$ | Crystallinity (%) |
|--------------------------|------------|----------------|-------------------|
| HDPE                     | 120.13     | 229.7          | 83.2              |
| HDPE / 2% SSP            | 119.97     | 202.8          | 73.5              |
| HDPE / 15% SSP           | 120.15     | 179.0          | 64.9              |
| HDPE / 2% SSP / PE-g-MA  | 119.71     | 154.6          | 56.01             |
| HDPE / 15% SSP / PE-g-MA | 120.10     | 139.2          | 50.4              |

#### IV. CONCLUSION

From the study, the SSP can be blended into HDPE with the presence of PE-g-MA as a compatibiliser. The degradable temperature was reduced with increasing SSP content based on TGA study. However, the PE-g-MA had improved the thermal stability. The  $T_m$  was reduced with the addition of SSP and therefore the processing temperature of the blends can be reduced or consequently beneficial in producing energy saving sample.

#### ACKNOWLEDGMENT

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