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On The Crystallinity of Eco Bioplastics Packaging Using DSC Techniques

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ABSTRACT

The aim of this study is to examine Eco Bioplastics Packaging containing LDPE/CS. Effects content concentration of corn stalk and inclusion compatibilizer on the crystallinity and morphology of Eco Bioplastics Packaging biocomposites. It was found that the by using similar filler loading, compatibilized Eco Bioplastics Packaging has revealed higher enthalpy and crystallinity of Eco Bioplastics Packaging with MAPE. Additionally, the addition of MAPE improved the interfacial interaction between corn stalk and LDPE biocomposites, as confirmed by SEM analysis.

Keywords: Corn Stalk Powder (CSP), Maleic Anhydride Polyethylene (MAPE), Light Density Polyethylene (LDPE)

1. INTRODUCTION

Biocomposites are materials made by combining a resin matrix with natural fibers, which are usually derived from plants or cellulose. Previous studies have referred to composites that consist of a plastic matrix and natural fibers as biocomposites [1]. Mohanty et al. (2000) defined biocomposites as materials that consist of a biodegradable polymer as the matrix material, with natural fibers acting as the reinforcement [2]. According to Joshi et al. (2004), natural fiber composites may be more environmentally friendly compared to alternatives that use glass fibers [3]. Sherely et al. (2008) further expanded the definition of biocomposite materials to include the incorporation of natural fillers in the form of fibers or particles, which are processed with polymers to achieve desired thermal, mechanical, and electrical properties [4].

According to this study, plastic matrices, particularly those derived from polyethylene thermoplastics, have found extensive use in daily life. Polyethylene (PE), the most widely used plastic in packaging, poses significant challenges as it is highly resistant to biodegradation. While starch has been investigated as a filler in plastics for approximately 40 years, it wasn't until the mid-1970s that degradable starch-plastic composites with satisfactory mechanical properties were developed [5]. However, environmentalists have expressed serious concerns about the degradation of these composites due to the slow biodegradation of polyethylene. Consequently, starch has been incorporated to facilitate biodegradation, and biodegradation aids such as photooxidants have been utilized to accelerate the process. Nevertheless, the molecular weight of PE only decreases over an extended period [6].

Agriculture plays a crucial role in the Malaysian economy. In the past, agricultural materials were either transported for processing or discarded after harvesting. However, to promote economic stability and expansion, it is necessary to diversify this sector. One way to achieve this is through value-added processing. Currently, there is indiscriminate disposal of various industrial and waste materials, including agricultural biomaterials. These biomaterials make up a significant portion of the universal waste generated from industrial processing and related operations. They can be found in different processed forms, such as pulp sludge from paper manufacturing (commonly known as clarifier sludge), as well as wood, sugar cane, bagasse pith, grasses, sisal, pineapple, coir, and jute [7].

Corn Stalk (CS), the focal point of this investigation, is a byproduct of corn cultivation. Consequently, corn stalks can be obtained for industrial purposes without incurring additional expenses. Presently, waste corn stalks are commonly utilized as animal feed. Furthermore, the pulp and paper industry also incorporate corn stalks. Utilizing corn stalks enables the harnessing of waste material. Thus, this study opts to utilize corn stalks as a natural filler in biocomposites, indirectly enhancing the value of corn stalk waste [8]. This approach addresses environmental concerns and leverages agricultural waste to mitigate production costs.

The main challenge with these composites is the adhesion between the natural reinforcing filler and the matrix polymers. The issue arises from the contrasting nature of polyolefin, which is non-polar and hydrophobic, and the natural polymer, which is polar and contains cellulose with -OH groups. This difference leads to poor adhesion, which reduces the effectiveness of the reinforcing filler in the composite. Improving the compatibility between these materials is essential to unlock the desired properties of these composites. To address these challenges, researchers have focused on modifying the filler's surface or treating it with compatibilizing agents or coupling agents to reduce its hydrophilicity [9].

This study aims to investigate the impact of filler loading of corn stalk (CS) and Maleic Anhydride Polyethylene (MAPE) as a compatibilizer into LDPE/CS biocomposites on crystallinity and morphology.

II. EXPERIMENTAL

2.1 Materials

The Light Density Polyethylene grade LDF200YZ, typically utilized for general-purpose film extrusion, was supplied by Titan Chemicals Corp. Bhd. Corn stalks sourced from Kodiang Plantations in Kedah underwent manual cleaning before being crushed and ground into a powder. This resulting powder, referred to as corn stalk powder (CSP), was subsequently dried at 80°C for 24 hours. Using the Malvern Particle Size Analyzer Instrument, the average particle size of the CSP was determined to be 29.96µm. Maleic Anhydride Polyethylene (MAPE) was obtained from Aldrich.

2.2. Preparation of Eco Bioplastics Packaging

The LDPE/CS biocomposites were prepared using the Brabender Plastograph mixer Model EC PLUS. The mixer was set at a temperature of 160°C and a rotor speed of 50 rpm. LDPE and MAPE were added to the mixing chamber and melted completely for two minutes. After that, CS powder was introduced and the mixing process continued for an additional six minutes, resulting in a total mixing time of eight minutes. The biocomposites were then molded into tensile bars using a compression molding machine model GT 7014A. These tensile bars followed the ASTM D638 tensile bar type IV specifications, with a thickness of 1mm. The compression process involved preheating at 160°C for 4 minutes, followed by compression for 1 minute, and then cooling under pressure for five minutes. A similar procedure was followed for PLA/CS with MAPE. The formulation details of uncompatibilized and compatibilized Eco Bioplastics Packaging biocomposites with varying filler loading can be found in Table 1.

Table 1 Formulation of Eco Bioplastics Packaging

Materials	**Eco Bioplastics Packaging uncompatibilized**	**Eco Bioplastics Packaging compatibilized**
LDPE(php)	100	100
CS (php)	0,10,20,30,40	0,10,20,30,40
MAPE(php)*	-	3

*3php from weight LDPE.

2.3. Differential Scanning Calorimetry (DSC)

An analyzer called the Perkin Elmer DSC-7 was utilized to conduct Differential Scanning Calorimetry (DSC) analysis. The samples, weighing approximately 10-25 mg, were heated from 20 to 250°C at a rate of 20°C/min, with a nitrogen airflow of 50 ml/min. The melting and crystallization properties of specific composites were evaluated using the same Perkin Elmer DSC-7 instrument. The crystallinity (Xbiocom) of the composites was calculated using the following equation:

$$X_{biocom} \text{ (\% crystallinity)} = \triangle H_f \;/\; \triangle H^o_f \times 100$$

H_f represents the enthalpy of fusion of the system, while H_f^0 denotes the enthalpy of fusion of perfectly crystalline LDPE. The enthalpy of fusion of 100% crystalline LDPE homopolymer, which is 285 J/g, was used for the latter purpose.

2.4. Morphology Analysis

The distribution of corn stalks within the LDPE matrix was analyzed using a Scanning Electron Microscope (SEM) model JEOL JSM-6460LA. To reduce electrostatic charging during examination, the fractured ends of the specimen were mounted on an aluminum stub and coated with thin layers of palladium.

III. RESULTS

Figure 1.0 depicts the DSC curves of uncompatibilized and compatibilized Eco Bioplastics Packaging biocomposites at CS loadings of 0 and 20 php. The DSC measurements are outlined in Table 2.0. The findings in Table 2.0 indicate that compatibilized Eco Bioplastics Packaging biocomposites exhibit higher enthalpy and crystallinity compared to uncompatibilized Eco Bioplastics Packaging biocomposites with the same filler loading. This increase in enthalpy and crystallinity suggests enhanced compatibility between CS and LDPE, along with improved filler nucleation activity.

Youseff et al. (2008) noted that adding lignocellulosic fibers to the LDPE matrix leads to a slight increase in the degree of crystallinity [10]. They examined four types of lignocellulosic fibers—cotton stalk, bagasse, rice straw, and banana plant waste—using DSC. The cotton stalk-LDPE composites exhibited higher crystallinity compared to the other fiber types. This observation could be attributed to the significant presence of lignin and hemicelluloses in cotton stalk fibers, which demonstrate strong molecular interactions with the compatibilizer.

Similarly, Araujo et al. (2008) documented an increase in crystallinity in HDPE/curaua fiber composites treated with maleic anhydride [11]. This observation can be explained by the heightened crystallinity provided by the fibers, acting as nucleating agents due to the trans crystallinity effect facilitated by the strong interaction between the curaua fiber and the matrix in the presence of PE-g-MA as a coupling agent.

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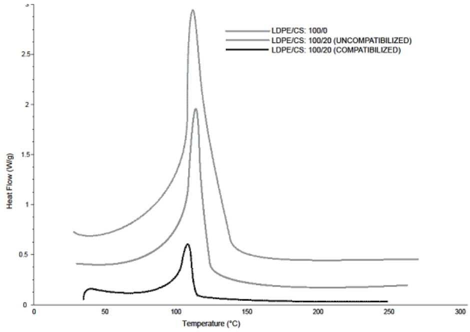

Figure 1: Differential scanning calorimetric (DSC) curve of uncompatibilized and compatibilized Eco Bioplastics Packaging biocomposites at different filler loading

Table 2.0: Parameter DSC analysis of uncompatibilized and compatibilized Eco Bioplastics Packaging biocomposites at different filler loading.

Biocomposites	T_m (°C)	ΔH_f (J/g)	X_c (% crystallinity)
LDPE/CS: 100/0	116.40	78.46	27.50
LDPE/CS: 100/20 uncompatibilized	115.96	88.15	30.93
LDPE/CS : 100/40 uncompatibilized	115.84	84.9	29.80
LDPE/CS :100/20 compatibilized	117.02	90.04	31.59
LDPE/CS: 100/40 compatibilized	115	88.03	30.89

3.4. Morphology Study

Figures 2 and 3 display micrographs of the tensile fracture surface of uncompatibilized Eco Bioplastics Packaging biocomposites at 20 and 40 php, respectively. These micrographs indicate that the corn stalk is not sufficiently wetted within the LDPE matrix in the uncompatibilized biocomposites. It is evident that the bonding at the interface of CS and LDPE matrix is weak, as the CS is pulled away from the LDPE surface, illustrating poor adhesion between CS and LDPE matrix. In contrast, Figures 4 and 5 illustrate that compatibilized biocomposites demonstrate improved interfacial adhesion between the filler and matrix, with less CS pullout from the matrix.

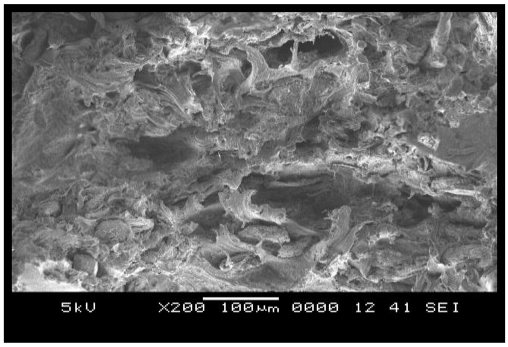

Figure 2: SEM micrograph of tensile fracture surface of uncompatibilized Eco Bioplastics Packaging biocomposites with MAPE (20php) at magnification 200X.

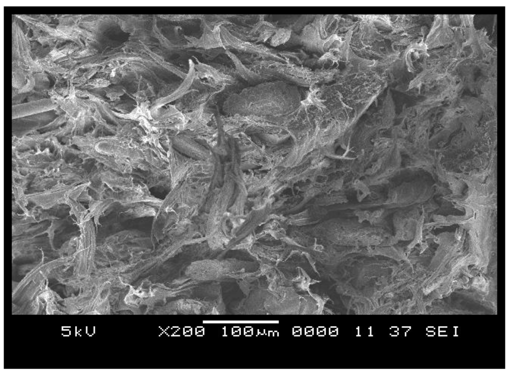

Figure 3: SEM micrograph at 200X magnification depicting the tensile fracture surface of Eco Bioplastics Packaging biocomposites compatibilized with MAPE

(20phr).

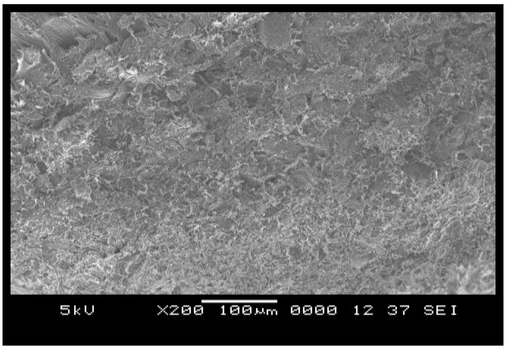

Figure 4: SEM micrograph of the tensile

fracture surface of compatibilized Eco Bioplastics Packaging biocomposites with MAPE (20php) at a magnification of 200X

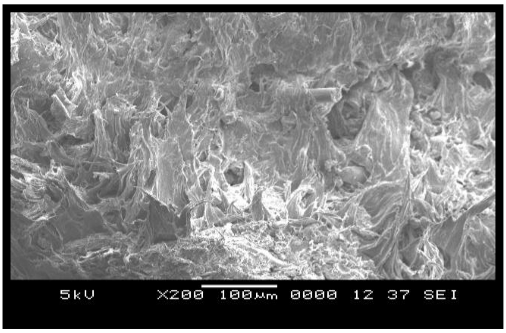

Figure 5: SEM micrograph at 200X magnification of the tensile

fracture surface of Eco Bioplastics Packaging biocomposites, which have been compatibilized with MAPE (40php).

IV. CONCLUSION

The inclusion of MAPE as a compatibilizer has improved the compatibility between corn stalk (CS) and the LDPE matrix. This improvement is clearly seen in the enhanced crystallinity observed in DSC tests. Additionally, SEM studies show that the presence of MAPE strengthens the adhesion between CS and the LDPE matrix.

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